Synthetic and Structural Studies of Low Coordinate Group 13 Ligand Systems

by

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B.Sc. (Hons)

This thesis is presented for the degree of Doctor of Philosophy to the Faculty of Science,
Cardiff University, October 2005.

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Acknowledgements

I would firstly like to express my special thanks to Dr. Simon Aldridge for his outstanding supervision, trust, guidance and unfaltering enthusiasm. It has truly been a pleasure to work for him over the past three years.

Furthermore I would like to acknowledge Prof. Cameron Jones, Dr. Li –ling Ooi, and Jo Day for X-ray crystallography; Dr. David Willock, Andrea and Mini Coombs for theoretical calculations; Rob Jenkins for constantly maintaining the NMR machine; Ricky and Alan for repairs; and all other technical staff who supported my time in the laboratory.

Many thanks also go to members of labs 1.124 and 1.125 (past and present) especially Debbie, Bres, Andrea, Mini C, Jo, Amal, Neha, Cerys, Tom, Ruth, Becky, Anne, Graham, Dan, Despina, Geraint and to the other fellow members of the inorganic chemistry department, for all of their support and for making the last three years such an enjoyable and unforgettable time!

Thanks also to my former house-mates, Kath, Cerys, Neha, Kerin and Hayley for their continuous support, friendship and for the many enjoyable nights (and meals) out.

I would also like to say a big heartfelt thank-you to my beloved parents for their immeasurable love and support, without which this would not have been possible. Thanks for always believing in me!

Finally, I would like to thank Marc for his tireless help and support and for all the love and happiness that we share. X

Dedicated to my beloved Nan, Dorothy Legge,

who was truly an inspiration to us all and is deeply missed.

***20.4.1922 † 23.6.2005**

Abstract

The work presented in this thesis describes the synthesis, structure and characterisation of a range of transition metal complexes of gallium and indium. The underlying theme is the synthesis of low coordinate unsaturated group 13 complexes *via* halide abstraction methodology. The work upon this subject is divided into five chapters.

Chapter 1 provides a general introduction to the low oxidation state group 13 halide chemistry and to the general structural types of transition metal complexes of gallium. The history, synthesis, reactivity and spectroscopic aspects of gallyl and diyl complexes is explored in detail.

Chapter 2 details the use of standard Schlenk and high vacuum line techniques for the manipulation of air and moisture sensitive compounds. Details of the purification and preparation of essential solvents, reagents and precursors are also given.

Chapter 3 discusses the synthesis of essential transition metal complexes containing three coordinate halo-gallium ligands suitable for subsequent halide abstraction chemistry. The synthesis of a number of such precursors *via* a convenient one-pot salt elimination methodology utilising organometallic anions is explored. This has led to the preparation and characterisation of a number of monomeric trigonal planar gallyl complexes of the type $\mathrm{L_nM{-}Ga(Aryl)X}$ and halodiyl systems of the type $\mathrm{(L_nM)_2GaX}$. Furthermore, the crucial role of steric factors in preventing halide bridged oligomerisation is illustrated. The possibility of subsituting the carbonyl ligands of $[\{\mathrm{Cp^*Fe(CO)_2}\}_2\mathrm{GaCl}]$ with stronger σ donor, weaker π acceptor phosphine ligands is also explored.

Chapter 4 investigates the preparation of transition metal complexes containing three coordinate halo-gallium ligands by a two-stage approach involving insertion chemistry followed, where necessary, by halide substitution. A series of halide bridged dimeric transition metal complexes of gallium have been synthesised and characterised, *e.g.* $[\mathrm{CpFe(CO)_2Ga(I)Br}]_2$ and $[\mathrm{Cp^*Fe(CO)_2GaI_2}]_2$, whose subsequent gallium centred substitution has also been investigated. Desired monomeric three coordinate systems such as $[\mathrm{Cp^*Fe(CO)_2}]_2\mathrm{GaI}$ and $[\mathrm{Cp^*Fe(CO)_2Ga(Mes^*)I}]$ have been prepared from the reaction between $[\mathrm{Cp^*Fe(CO)_2GaI_2}]_2$ and $\mathrm{Li[Mes^*]}$ and $\mathrm{Na[Cp^*Fe(CO)_2]}$, respectively. Salts of the composition, $[\mathrm{CpFe(CO)_2GaX_3}]^-[\mathrm{RH_n}]^+$, were however often found to be the undesirable products of such reactions.

Chapter 5 explores the use of halide abstraction chemistry as a viable synthetic route to cationic two-coordinate derivatives featuring gallium as the donor atom. This has led to the preparation and structural characterisation of a number of cationic gallium-containing systems. Thus, the linear trimetallic species $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}Ga)]^+$ featuring a naked bridging gallium atoms can be synthesized by the reaction of the corresponding chloro-substituted bridging diyl complexes with $Na[BAr^f_4]$. Structural, spectroscopic and computational studies performed for $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}Ga)]^+$ are consistent with appreciable Fe—Ga π bonding character. The fundamental reactivity of $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}Ga)]^+$ is also explored. Analogous reactions utilising super-mesityl substituted gallyl precursors, such as $[(\eta^5\text{-}C_5R_5)Fe(CO)_2Ga(Mes^*)Cl]$ (R= H, Me) led to the synthesis of halide-bridged species of the type $[\{(\eta^5\text{-}C_5R_5)Fe(CO)_2Ga(Mes^*)\}_2(\mu\text{-}X)]^+$. The mechanism for this reaction presumably occurs *via* trapping the highly electrophilic putative cationic diyl complex $[(\eta^5\text{-}C_5R_5)Fe(CO)_2Ga(Mes^*)]^+$.

Table of Contents

Chapter One
General Introduction

Chapter Two

Experimental Techniques

Chapter Three

Synthesis of Gallyl Precursors *via* Salt Elimination Methodology

Chapter Four

Synthesis of Precursors *via* Insertion/Substitution Methodology

Chapter Five

Synthesis and Reactivity of Cationic Gallium Containing Systems

Abbreviations

Å	Angstrom, 1 x 10^{-10} metre
Ar, Ar*	A general aryl substituent
Ar^{f}	3,5-$(CF_3)_2C_6H_3$
BHT	2,6-di-tert-butyl-4-methylphenoxo
bipy	2,2'-bipyridine
br	Broad
^{t}Bu	Tertiary butyl
^{n}Bu	Normal butyl
cat	Catechol
cm^{-1}	Wavenumber, unit of frequency (= ν/c)
Cod	Cyclooctadiene
Cp	Cyclopentadienyl, cyclopentadiene
Cp*	Pentamethylcyclopentadiene
Cp'	Methylcyclopentadienide
CVD	Chemical Vapour Deposition
δ	Chemical shift in NMR (ppm)
d	Doublet
DAB	Diazabutadiene
DFT	Density Functional Theory
Dppe	1,2-bis(diphenylphosphino)ethane
dvds	1,3-divinyl-1,1,3,3-tetramethyldisiloxane
E	Group 13 element
EI	Electron impact
ES	Electrospray
Et	Ethyl
Et_2O	Diethyl ether
FT	Fourier Transform
FTIR	Fourier Transform Infra-Red spectroscopy
Fp	Cyclopentadienyliron dicarbonyl
Fp'	Methylcyclopentadienyliron dicarbonyl
Fp*	Pentamethylcyclopentadienyliron dicarbonyl

GGA	Generalised Gradient Approximation
h	Hour
HOMO	Highest Occupied Molecular Orbital
Hz	Hertz, s^{-1}
IR	Infrared
L	A general ligand
LUMO	Lowest Unoccupied Molecular Orbital
M	A general metal or Molar (mol dm^{-3})
M^+	Molecular ion
Me	Methyl
m/z	Mass / charge ratio
Mes	Mesityl (2,4,6-trimethylphenyl)
Mes*	Super-mesityl (2,4,6-tri-*tert*-butylphenyl)
MOCVD	Metal Organic CVD
MS(EI)	Electron Ionisation Mass Spectrometry
m	Multiplet, medium or meta-substituent
NHC	N-heterocyclic carbene
NMR	Nuclear Magnetic Resonance spectroscopy
OTf	Triflate
Ph	Phenyl
Pic	Picoline
Pin	$1,2\text{-}O_2\text{-}Me_2CH\text{-}CHMe_2$
^{i}Pr	Isopropyl
ppm	Parts per million
PPN	Bis(triphenylphosphoranylidene)ammonium
py	Pyridine
q	Quartet
R	General organic substituent
s	Singlet
sh	Sharp
st	Strong
tert	Tertiary
THF	Tetrahydrofuran

TMEDA	N,N,N',N'-tetramethylethane-1,2-diamine
Tmpa	$Me_2NCH_2CH_2CH_2NMe_2$
Tmp	2,2,6,6-tetramethylpiperidine
Trip	2,4,6-triisopropylphenyl
t	Triplet
μ	Bridging mode of coordination
ν	Frequency in Hz
X	A general halide

Chapter One

General Introduction

1.1 History of Transition Metal Group 13 Complexes

Complexes which contain M—E bonds between transition metals (M) and group 13 metals (E) have a long history.[1] However, since 1950 it is the chemistry of organoaluminium compounds, which has dominated the literature. This development was triggered by the crucial discovery of alkene insertion reactions by Ziegler, which led to the use of alkyl aluminium compounds as co-catalysts for the polymerisation of ethane to polyethene.[2] Although less studied than their Al analogues, Ga and In organyls do find use as doping agents in the manufacture of semiconductors.[3]

The chemistry of low coordinate or multiply-bonded group 13 ligand systems is currently a very topical area of main group chemistry from a fundamental structure and bonding viewpoint. This area has attracted considerable research effort,[4-6] and in some cases significant controversy.[7,8] A systematic appraisal of both structural and reaction chemistry for diyl systems, $L_nM(EX)$ (E = B, Al, Ga, In), lags behind that of analogous group 14 systems (such as carbenes and silylenes). Therefore one of the primary aims of this project was to examine the use of halide abstraction chemistry to generate cationic derivatives of the heavier group 13 elements in an attempt to broaden the scope of synthetic methodologies available for unsaturated group 13 systems.

1.2 Group 13 Low Oxidation State Complexes

Whereas the +1 oxidation state in group 13 metal compounds is most common for indium and thallium, most modern inorganic textbooks still describe the +III oxidation state as being the dominant oxidation state of aluminium and gallium. The reason for this lies partly with the general assumption that compounds containing gallium in lower oxidation states, although accessible, are inherently unstable and only 'chemical curiosities'. Whereas the monohalides of indium and thallium, which are both commercially available and thermally stable and find use as useful synthetic precursors to indium(I) and thallium(I) alkyls, aryls, and amides, it has only been in the past 15 years that the chemistry of low valent compounds of the lighter group 13 elements has made rapid progress. Pioneering work by

Schnöckel on the isolation and characterization of gallium (I) species[9] and Schmidbaur on mixed-valence arene complexes[10] has changed the situation dramatically.

There has been a great deal of interest in the chemistry of metastable aluminium(I) and gallium(I) halide complexes, $[\{MX(L)\}_n]$, M = Al or Ga; X = halide; L = Lewis base, which are turning out to be very useful as precursors to a wide range of novel alkyl, silyl and amido low-oxidation state metal complexes and cluster compounds. Schnöckel has prepared such complexes by the co-condensation of the M(I)-halide with a donor solvent using a specially designed reactor; several have been crystallographically characterised, for example $[Al_4Br_4(NEt_3)_4]$.[11,12]

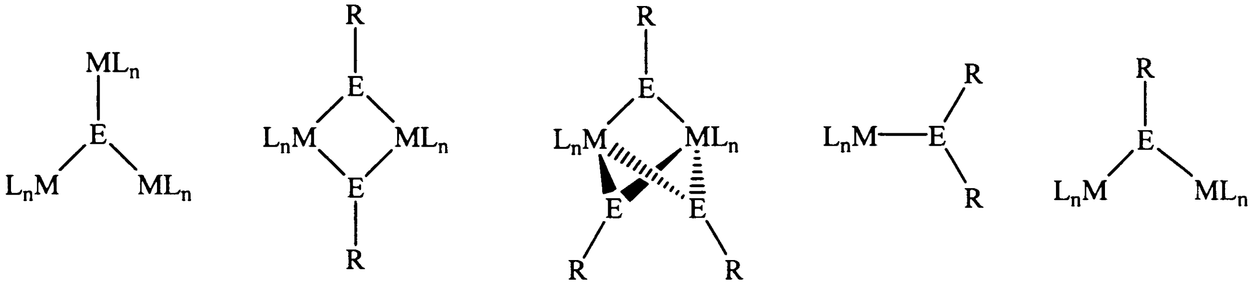
A much more convenient starting material for many low-valent gallium species is Ga_2Cl_4, which exists as a salt, $Ga^+GaCl_4^-$, in the solid as well as in the molten state.[13] By addition of arenes, a series of Ga^+-arene compounds with interesting Ga—π interactions have been prepared.[12] On the other hand genuine gallium(II) species with Ga—Ga bonds can be formed by addition of certain donor compounds. $Ga_2Cl_4{\cdot}2$dioxane[14] was the first prominent example, which was followed by the analogous bromide and by two other examples of donor-stabilized Ga_2I_4 compounds.[15] However, monomeric paramagnetic species containing M^{II} have only transient existence under normal conditions.[16]

1.3 General Structural Types

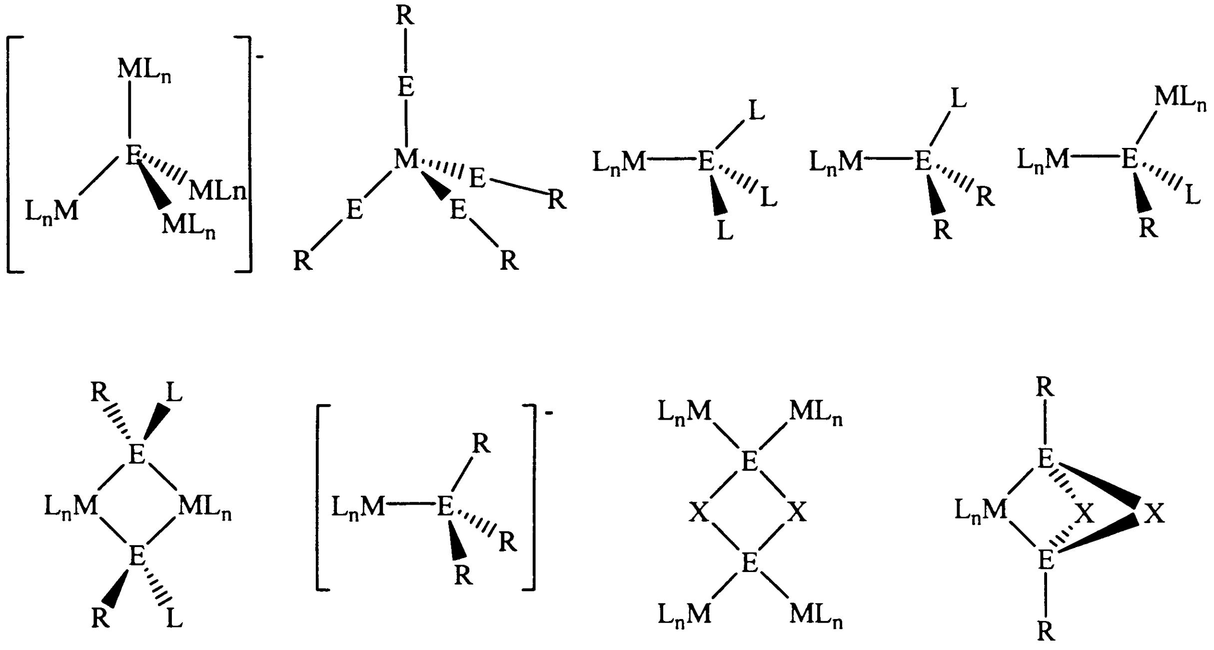
In the +III oxidation state of gallium and indium, these elements show well established coordination numbers of three, four, five or six dependent on the nature of element, the ligand, and in the case of certain anionic complexes, the balancing cation. Aggregation is a distinctive feature of the chemistry of the group 13 metals, reflecting the electrophilicity of the metal centre in relation to its ligands. It can be curbed by the coordinating action of suitable donor species or by the steric bulk of appropriate ligands.[17] A comprehensive survey of known structures of M—E complexes is given in Figure 1.[18]

$L_nM—E—ML_n$ $L_nM—ER$

2 coordinate complexes



3 coordinate complexes



4 coordinate complexes

Figure 1: Structural variety of M—E complexes

1.4 Gallyl Complexes

There are a number of structural types of transition metal complex featuring a two-centre two-electron interaction between a gallium atom and a metal centre. Transition metal gallyl complexes ($L_nM—GaX_2$) represent one of these structural classes and typically feature a three-coordinate gallium centre. Some base-stabilised derivates, of the type $L_nM—GaX_2.D$ are also known.

1.4.1 History of gallyl complexes

Whereas transition metal boryl complexes ($L_nM—BX_2$) have been the subject of considerable recent research effort[19] and a large number (> 100) of structurally authenticated boryl complexes have been reported,[20] examples of analogous three coordinate aluminyl, gallyl, and indyl complexes are relatively rare. The first structurally characterised transition metal gallyl complex, $[Cp(CO)_3WGa(CH_3)_3]$, **1.1**,[21] appeared in 1977 being prepared by the reaction of $[CpW(CO)_3H]$ with $[GaMe_3]$. In 1997, Nöth reported the first example of a tricoordinated alanyl group bonded to a transition metal, $[CpFe(CO)_2Al(tmp)_2]$, **1.2**.[22] However, very few structurally authenticated transition metal gallyl complexes have been reported since and consequently little of the chemistry of such species is known.

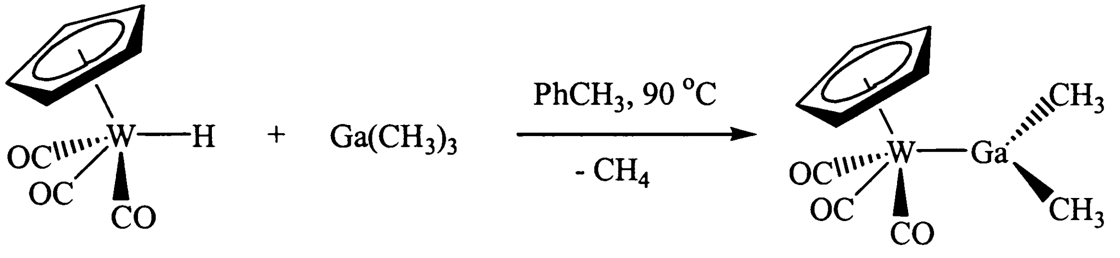
1.4.2 Synthesis of gallyl complexes

Aggregation is a distinctive feature in the chemistry of the Group 13 metals. As a result of the increase in atomic radius upon descending the group, the formation of three coordinate systems is more favourable for boron, whereas aggregation is more common for gallium and indium. This is also due to the higher bond polarity of Al, Ga, and In compared to boron causing a greater $\delta+$ on the group 13 metal centre. Such complexes are also susceptible to disproportionation and decomposition unless the metal centre is protected, either sterically or by base stabilisation. Therefore in order to synthesise three coordinate gallyl complexes, the choice of a suitable steric hindered alkyl or aryl group is vital. For example, Power *et al.*, reported the synthesis of the transition metal complex, $[Cp(CO)_2FeGa(^tBu)_2]$, **1.3**, whereas formation of analogous complexes with greater steric hindrance, *e.g.* 2,4,6-$^iPr_3C_6H_2$, was not possible. Typically, however, with less bulky substituents, *e.g.* Me, unstable methylgallyl derivatives were formed.[23]

Although there are several methods for synthesising transition metal gallyl complexes, salt elimination approaches, typically in coordinating solvents, are most common. This can be contrasted with the synthesis of analogous boryl complexes where the presence of coordinating solvents leads to decomposition.

i) Synthesis of gallyl complexes by alkane elimination

St. Denis *et al.*, used the elegant strategy of alkane elimination to synthesise the first example of a transition metal gallyl complex.[21] Reaction between [Cp(CO)$_3$WH] and [Ga(CH$_3$)$_3$], at elevated temperatures (90 °C) with photoactivation, results in the formation of [Cp(CO)$_3$WGa(CH$_3$)$_3$], **1.1**, and the elimination of a single equivalent of methane. The reaction presumably proceeds *via* a radical mechanism (Scheme 1). Corresponding reactions are known for indium and thallium. Selective reactions of this type are rare, and restricted to reactive M—H functions and simple sterically unhindered organometallic complexes.

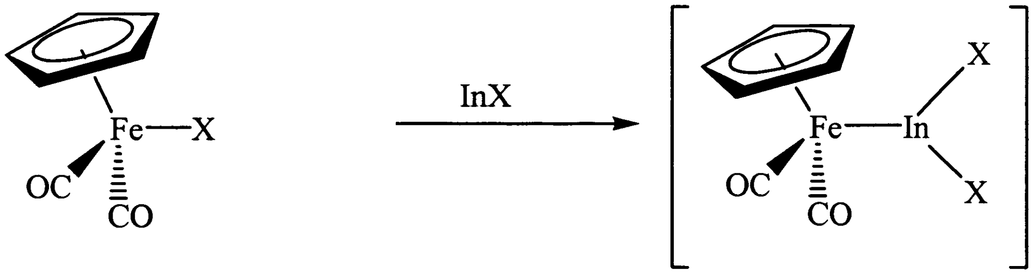


(1.1)

Scheme 1

ii) Synthesis of gallyls by insertion of metal(I) halides

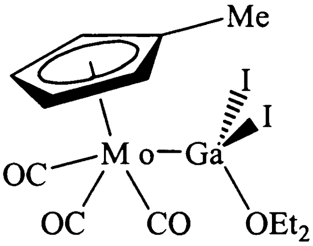
Insertion of a metal(I) halide (EX) into a metal—metal bond or metal—halide bond is another possible route to the generation of gallyl and indyl complexes. Early work by Hsieh and Mays *et al.*, demonstrated the insertion of indium (I) chloride into the Fe—Fe bond of [Cp$_2$Fe$_2$(CO)$_4$], which afforded the diiron-indium-chloride complex [{Fe(CO)$_2$Cp}$_2$InCl], **1.4**, although no structural data was obtained. Analogous insertion of InX, (X = halide), into iron—halogen bonds yielded the monoiron complexes [{Fe(CO)$_2$Cp}InX$_2$], **1.5** (Scheme 2), and [{Fe(CO)$_2$Cp}InBr$_2$(THF)], **1.6**.[24] Norman and co-workers later structurally characterised the dimeric diiron indium halide complex, [{Fe(CO)$_2$Cp}$_2$ InCl], **1.4**.[25]



(1.5)

Scheme 2

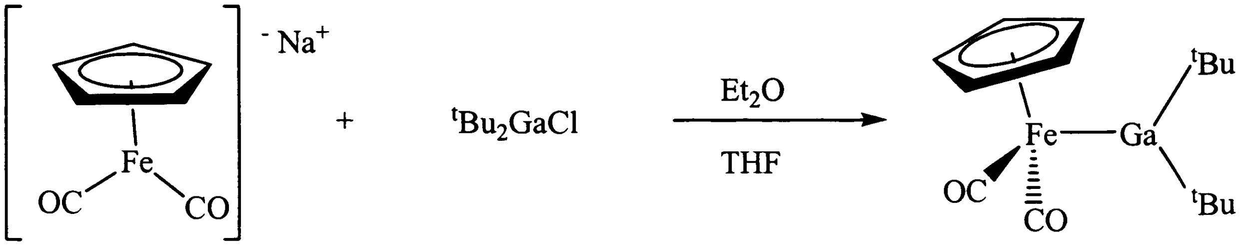
The same year, Green *et al.*, reported a new convenient synthesis of 'GaI' which is simply formed by the ultrasonic irradiation of gallium metal with 0.5 equivalents of I_2 in toluene. Although not a homogeneous material, this highly reactive pale green powder behaves as a monovalent gallium system, and a number of compounds with transition metal—gallium bonds have been made as a result of a formal insertion 'GaI' into metal—halogen bonds. For example, Green investigated whether 'GaI' would undergo insertion reactions with metal—iodine bonds. The reaction between $[Cp(CO)_2FeI]$ and 'GaI' followed by recrystallisation from ether yielded $[Cp(CO)_2FeGaI_2.(Et_2O)]$, **1.7**. Analogously, the reactions between 'GaI' and $[(\eta\text{-}C_7H_7)(CO)_2MoI]$ and a heated reaction with $[(CO)_3(\eta\text{-}C_5H_4Me)MoI]$ gave similar complexes, $[(\eta\text{-}C_7H_7)(CO)_2MoGaI_2.(THF)]$, **1.8,** and $[(\eta\text{-}C_5H_4Me)\ (CO)_3MoGaI_2.Et_2O]$, **1.9**, respectively.[26]



(1.9)

iii) Synthesis of gallyls by salt elimination

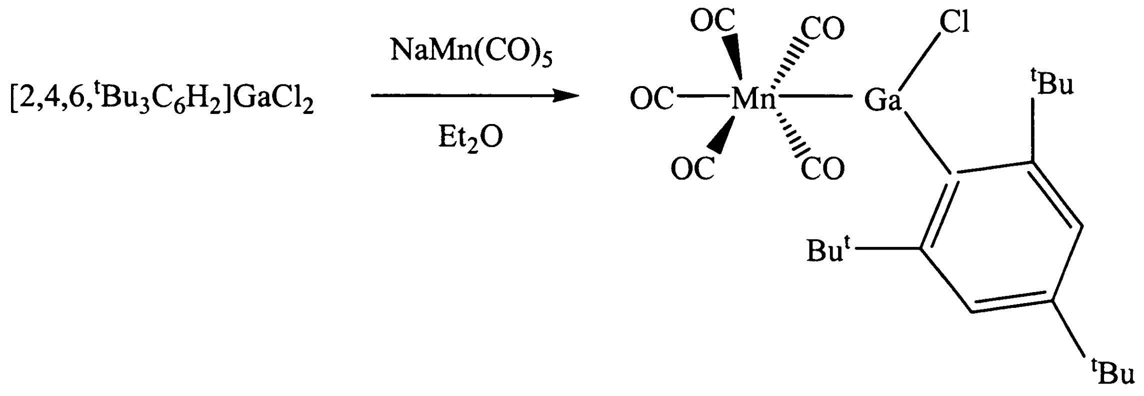
In 1993, Power *et al.*, used a salt elimination methodology to prepare several new tricoordinate organogallium-iron complexes featuring terminal alkyl gallyl groups, *e.g.* [Cp(CO)$_2$FeGa^{t}Bu$_2$], **1.3**, (Scheme 3), [{Cp(CO)$_2$Fe}$_2$Ga^{t}Bu], **1.10**, and [Cp(CO)$_2$FeGa^{t}Bu$_2$.{Cp(CO)$_2$Fe}$_2$], **1.11**. All compounds were synthesised in good yields by a simple salt elimination reaction between Na[FeCp(CO)$_2$] and [^{t}Bu$_2$GaCl] or [^{t}BuGaCl$_2$], in THF.[23]



(1.3)

Scheme 3

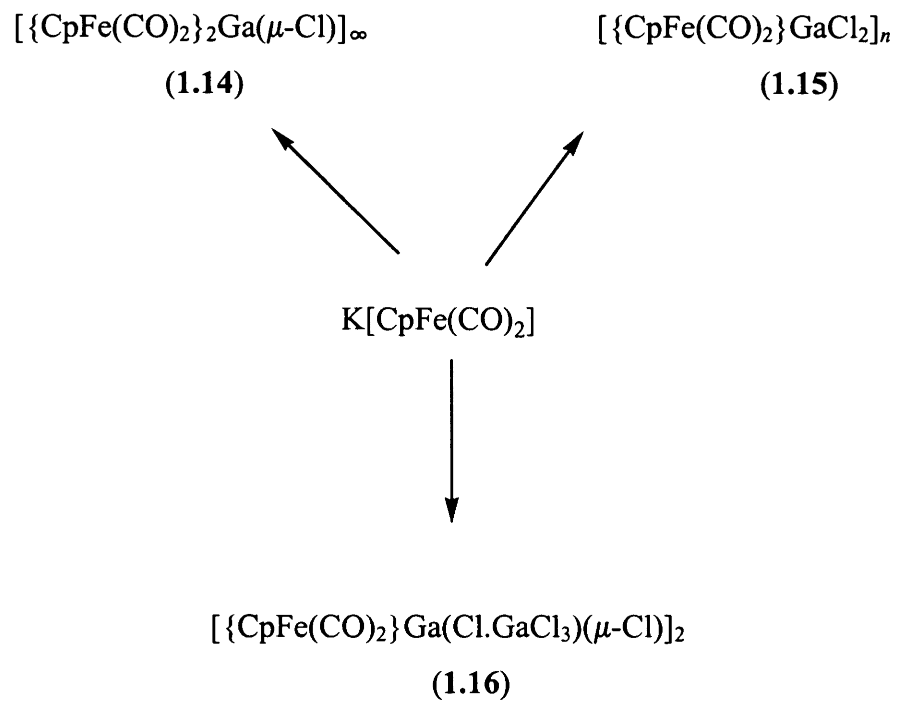
Subsequently Cowley *et al.*, reported the synthesis of a compound featuring a gallium—manganese bond, [{Mn(CO)$_5$}Ga(Mes*)Cl], **1.12**, by the treatment of [(2,4,6, ^{t}Bu$_3$C$_6$H$_2$)GaCl$_2$] with Na[Mn(CO)$_5$] in diethyl ether (Scheme 4). In contrast, the analogous reaction with Na[Co(CO)$_4$]$^-$ led to the formation of [{Co(CO)$_4$}$_2$Ga(Mes*)], **1.13**, presumably due to the smaller steric demand of the cobalt tetracarbonyl fragment.[27]



(1.12)

Scheme 4

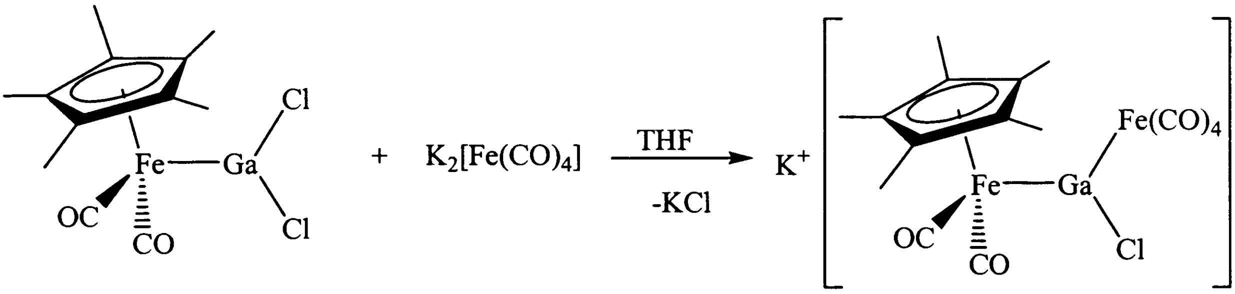
Barron *et al.*, have shown that the metathesis reaction between K[CpFe(CO)$_2$] and GaCl$_3$ is dependent on the stoichiometry. Reaction of 0.5 equivalents of GaCl$_3$ with K[CpFe(CO)$_2$] yielded [{CpFe(CO)$_2$}$_2$Ga(μ-Cl)]$_\infty$, **1.14**, which is polymeric in the solid state and features bridging chlorides and pendant [CpFe(CO)$_2$] units. Reaction of 1.0 equivalents of GaCl$_3$ yielded [{CpFe(CO)$_2$}GaCl$_2$]$_n$, **1.15**, although this was not structurally characterised. Whereas reaction with excess GaCl$_3$ gave the compound [{CpFe(CO)$_2$}Ga(Cl·GaCl$_3$)(μ-Cl)]$_2$, **1.16**, (Scheme 5).[28]



Scheme 5

This work was subsequently extended to the reaction between [CpMo(CO)$_3$H] and E^{t}Bu$_3$ which yielded the monomeric compound, [CpMo(CO)$_3$E^{t}Bu$_2$] (E = Ga (**1.17**) or Al (**1.18**)). The analogous reaction of [CpMo(CO)$_3$H] with [(BHT)$_2$AlH(Et$_2$O)] gave the sterically hindered aryloxide derivative, [{CpMo(CO)$_3$}Al(BHT)$_2$], **1.19**.[28]

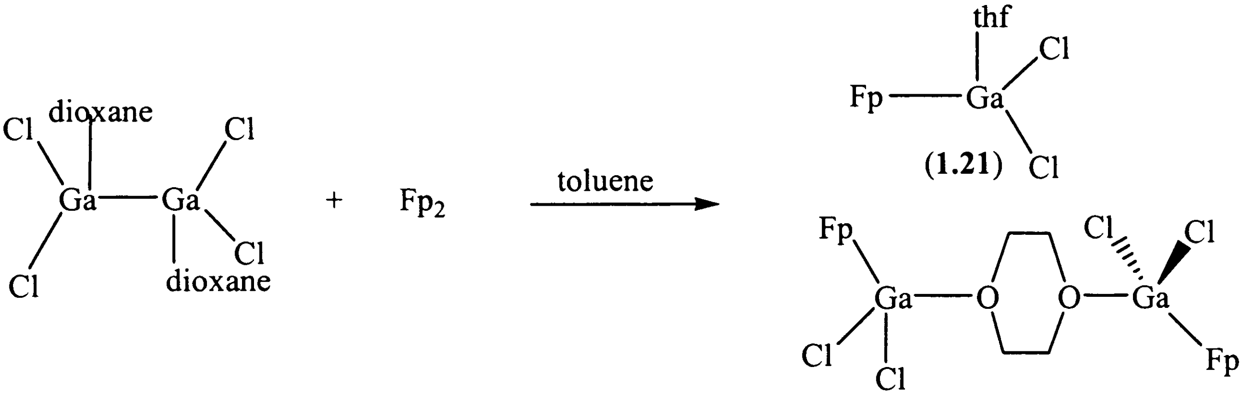
Recently Ogino *et al.*, reported the synthesis of the unstable anionic complex, K[{Cp*(CO)$_2$Fe}(μ-GaCl){Fe(CO)$_4$}], **1.20**, *via* the salt elimination reaction between [Cp*(CO)$_2$FeGaCl$_2$] and K$_2$[Fe(CO)$_4$] in THF (Scheme 6). Subsequently, **1.20**, was further derivatized to incorporate a chelating phosphine ligand, dppe, instead of carbonyl functionalities.[29]



(1.20)

Scheme 6

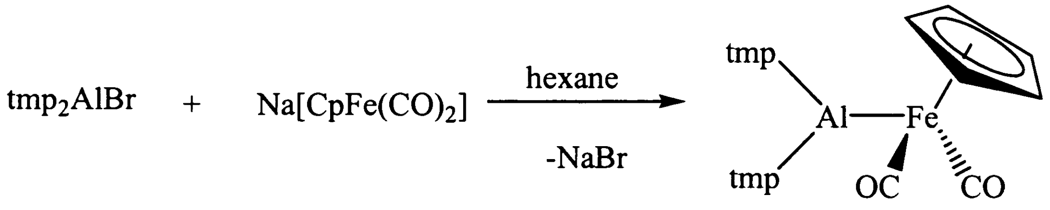
An alternative method to salt elimination reactions is the metathesis reaction between compounds with Ga—Ga and Fe—Fe bonds. Linti *et al.*, explored the reactions between gallium subhalides, *e.g.* Ga_2Cl_4·2dioxane and 'GaI', with $K[Cp(CO)_2Fe]$ and $[Cp(CO)_2Fe]_2$, respectively. In all cases, it is proposed that gallium(I) and gallium(II) compounds are formed *via* disproportionation involving the formation of elemental gallium and gallium(III) halides. Several novel complexes containing tetracoordinated gallium centres of the types $[Cp(CO)_2FeGaX_2(L)]$, **1.21**, (L = THF, dioxane, $[FeCp(C_7H_8)]^+I^-$; (X = Cl, I), and $[Cp(CO)_2Fe]_2GaCl(L)$ (L = THF, 0.5 KCl), **1.22**, were synthesised (Scheme 7).[30]



(1.22)

Scheme 7

In 1997, Nöth *et al.*, reported the first example of a tricoordinated aluminyl group bonded to a transition metal, **1.2**, *via* the salt elimination reaction of Na[CpFe(CO)$_2$] with [(tmp)$_2$AlBr] (Scheme 8).[22]



(1.2)

Scheme 8

iv) Synthesis of gallyls by dehalosilylation

Recently, Ogino *et al.*, have shown that Fp'GaCl$_2$, **1.23,** first reported by Barron *et al.*, can alternatively be prepared purer and in almost quantitative yields, *via* the dehalosilylation reaction between FpSiMe$_3$ or Fp*SiMe$_3$ and GaCl$_3$ in either toluene or hexane respectively (Scheme 9).[31]

$$GaCl_3 \quad + \quad Fp'SiMe_3 \xrightarrow[\text{Hexane} \\ \text{-Me}_3\text{SiCl}]{\text{RT}} Fp'GaCl_2$$

(1.23)

Where Fp'= Fp or Fp*

Scheme 9

1.4.3 Spectroscopic and Structural Aspects of Gallyl Complexes

i) Bonding in gallyl complexes

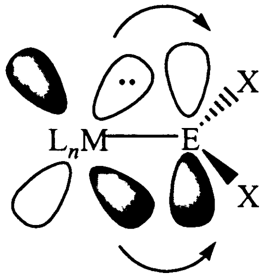


Figure 2

A simplified model of the bonding in gallyl transition metal complexes ($L_nM—GaX_2$) involves the sp^2 hybridised gallium centre forming σ bonds with an empty metal based orbital of σ symmetry and with the gallyl substituents X (Figure 2). In addition there is the possibility of supplementing bond order formally by π donation from a metal based frontier orbital of the appropriate symmetry into the empty gallium p orbital, which is in competition with π donation from filled non-bonding orbitals of the substituents (X). Hence the degree of back bonding is dependent on the nature of the metal (M), the metal substituents (L) and the gallium based substituents (X). The extent of which can be probed by study of the metal gallium bond lengths, the relative orientation of metal and gallyl fragments, and the IR stretching frequencies of ancillary carbonyl ligands.[32] However, in practice, the degree of back bonding in gallyl complexes is minimal. This is because the p orbital of π symmetry at gallium is too high in energy.

A 'competitive π-bonding' model has been proposed for analogous boryl transition metal complexes ($L_nM—BX_2$),[20] comparable to that suggested for Fischer carbene complexes.[33] The extent of the σ and π contributions to M—B bonding has been the subject of several theoretical studies.[32,34] The π component of the covalent interaction between the metal and the boron centres was found to be minimised by strongly π donating substituents at boron, *e.g.* F, however even in the case of weaker π donors such as H this never exceeded 20%.[20,35] Thus, it was concluded that although modification of the boryl substituents can exert some influence on the extent of the metal to boron π bonding, π interactions represent a relatively minor contribution to the overall bonding. This is not surprising, given that the boron-based acceptor orbital is calculated to lie too high in energy with respect to the corresponding filled metal orbital for significant π back bonding.[35] This orbital would be expected to lie even higher in energy for gallium than for boron. In addition such compounds typically contain strongly π donating boryl substituents, *e.g.* cat, and π acceptor spectator ligands, *e.g.* CO.

ii) Spectroscopic features of gallyl complexes

IR stretching frequencies of CO ligands are very sensitive to the effects of other ligands at the metal centre. Tolman, for example, has shown that the replacement of a CO with PMe_3 ligand (a better σ donor but a poorer π acceptor than CO) results in a shift of the ν(CO) bands to a lower frequency, *i.e.* $Ni(CO)_4$ (2094 cm^{-1}), $Ni(CO)_3PMe_3$ (2064, 1982 cm^{-1}), $Ni(CO)_2(PMe_3)_2$ (1990, 1926 cm^{-1}) and $Ni(CO)(PMe_3)_3$ (1900 cm^{-1}).[36] This can be explained by considering the situation when a poorer π acceptor but better σ donor ligand is attached to the metal centre. This causes the metal centre to be more electron rich and increases the π donation into the π^* orbital on CO, leading to a lower C—O bond order and lower accompanying stretching frequencies in the IR spectrum. However, if the ligand attached to the metal centre is also a good π acceptor, competition arises, which leads to a reduction in the electron density at the metal centre and hence higher CO stretching frequencies. Therefore, by examination of the stretching frequencies of the ancillary carbonyl ligands in a complex, the nature of the M—Ga bond can be probed. For example, in the IR spectra of $[Cp(CO)_2FeGa^tBu_2]$, **1.3**, two very strong absorptions can be observed at 1980 and 1928 cm^{-1}. These bands are at a significantly lower frequency than those observed for $[Cp(CO)_2Fe]$-methyl compounds,[23] which show bands at 2010, and 1960 cm^{-1}. These lower frequencies maybe due to increased electron density (and increased back-donation into the π^*-CO orbitals) caused by the electropositive nature of the Ga^tBu_2 ligand. This behaviour can be contrasted with the boryl species, $[CpFe(CO)_2Bcat]$, **1.24**, in which the carbonyl stretching frequencies are higher than the analogous methyl complex, $[Cp(CO)_2FeCH_3]$, **1.25**, indicating the presence of a M—B interaction.[32,34] Typically gallyl complexes are worse π acceptors and better σ donors than corresponding boryl complexes.

iii) Structural features of gallyl complexes

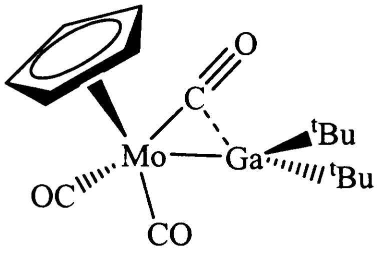
The highly air sensitive compound, $[Cp(CO)_3WGa(CH_3)_2]$, **1.1**, has a trigonal planar geometry with all angles around the gallium centre near 120° and an W—Ga distance of 2.71 Å.[21] This bond length is approximately equal to the sum of the covalent radii of tungsten and gallium (2.72 Å), indicating that there is minimal π back-bonding in this complex.

The trigonal planar organogallium-iron complex, $[Cp(CO)_2FeGa^tBu_2]$, **1.3**, features a Fe—Ga distance of 2.417 Å. The dihedral angles between the Cp(centroid)—Fe—Ga and C—Ga—C planes are 90.2 and 88.2°, which suggests that π-interactions between the iron and gallium fragments are quite weak.[23] Such an observation is supported by a theoretical study by Hoffman,[37] which considered the orbital interactions of the $[Cp(CO)_2Fe]^+$ fragment and concluded that the most efficient π-overlap with ligands, such as related carbenes, involves the a" orbital at iron. Since this orbital is orientated parallel to the Cp ring plane, maximum π-overlap with the carbene (or gallium) p-orbital is observed when the plane of the ligand is perpendicular to the Cp ring which corresponds to a zero dihedral angle between the Cp(centroid)—Fe—Ga and C—Ga—C planes. For $[Cp(CO)_2FeGa^tBu_2]$, **1.3**, the sterically demanding ^{t}Bu substituents may effectively prevent an orientation that would maximise π-bonding.

$[\{Mn(CO)_5\}Ga(Mes^*)Cl]$, **1.12**, represents a rare example of a tricoordinate gallium compound bearing three different substituents. Again the geometry around gallium is trigonal planar, with a Ga—Mn bond length of 2.495(4) Å. The large C—Ga—Mn bond angle (140.9(6)°) can be attributed to a large steric interaction between the aryl and $Mn(CO)_5$ groups.[27]

By contrast, $[\{CpFe(CO)_2\}_2Ga(\mu\text{-}Cl)]$, **1.14**, is polymeric in the solid state and features an infinite chain of bridging chlorides and two pendent $[CpFe(CO)_2]$ units per gallium. The chloride bridges are near linear (171.9(7)°) and symmetrical with the $CpFe(CO)_2$ groups positioned both above and below the plane defined by the Ga—Cl···Ga—Cl chain, orientated to provide C_2 symmetry about the gallium. The short Ga—Fe bond distance of 2.3654(7) Å is somewhat surprising given the four coordinate nature of the gallium centre.[28]

The molecular structure of monomeric $[CpMo(CO)_3]Ga^tBu_2]$, **1.17**, is similar to that reported for $[Cp(CO)_3WGa(CH_3)_3]$, **1.1**, with the gallium alkyl groups orientated in the Ga—Mo—Cp centroid plane. Interestingly however, the geometry of the Mo and Ga features a distinct asymmetry to the Ga^tBu_2 moiety and one of the carbonyl carbon atoms is positioned very close to the Ga. This is probably due to the presence of an unusual weakly bridging carbonyl interaction as a consequence of the electron-deficient nature of gallium.[28]

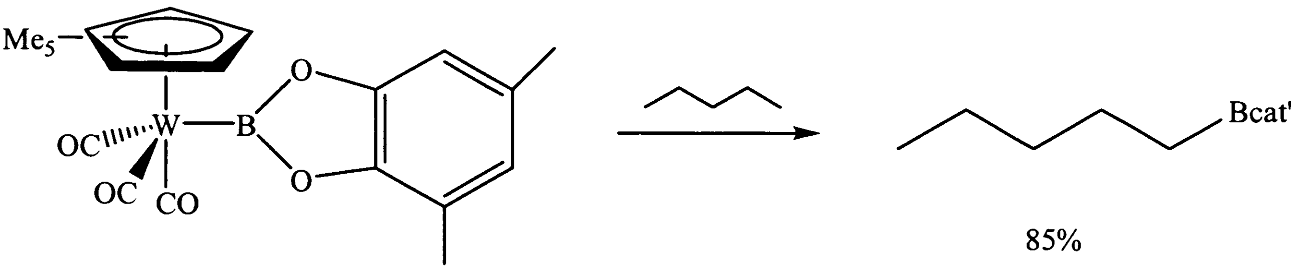


(1.17)

The molecular structure of [CpFe(CO)$_2$GaCl$_2$·THF], **1.21**, exhibits a tetrahedrally coordinated gallium atom with the bonding parameters of the Cp(CO)$_2$Fe fragment in the normal range with a Ga—Fe bond length of 2.317 Å.[30]

1.4.4 Reactivity of gallyl complexes

The reactivity of transition metal boryl complexes has been heavily studied, partly because of their involvement in organic transformations such as the hydroboration and diboration of carbon—carbon multiple bonds and the highly selective stoichiometric C—H functionalisation of alkanes and arenes. Hartwig and others have demonstrated the functionalization of a number of alkanes by cyclopentadienyl transition metal boryl complexes under photolytic conditions, with good selectivity for the terminal position (Scheme 10).[38] In addition, a photolytic [Cp*Re(CO)$_3$] catalysed process, in which a 1-pentylboronate ester is formed *via* the functionalisation of pentane in the terminal position using B$_2$Pin$_2$ has also been reported.[39]



Scheme 10

By comparison transition metal gallyl complexes are relatively rare and their chemistry has been sparsely investigated. In general, such complexes are air- and moisture-sensitive to varying degrees and reaction chemistry which proceeds with retention of the metal—gallium bond is uncommon. Reactivity studies have principally been confined to adduct formation. Green *et al.*, have shown that the adducts [Cp(CO)$_2$FeGaI$_2$.(Et$_2$O)$_n$], **1.6**, and [(η^5-C$_5$H$_4$Me)Mo(CO)$_3$GaI$_2$.Et$_2$O], **1.9**, readily undergo displacement reactions of ether to form 1:1 adducts with pyridine.[26]

Barron *et al* briefly investigated the reactivity of a series of cyclopentadienyliron- and cyclopentadienylmolybdenum—gallium compounds. Reaction of [CpFe(CO)$_2$GaCl$_2$]$_n$, **1.14**, with MeCN and NMe$_3$ results in the formation of [CpFe(CO)$_2$GaCl$_2$(MeCN)], **1.26**, and [CpFe(CO)$_2$GaCl$_2$(NMe$_3$)], **1.27**, respectively. On the other hand, attempted reduction of [{CpFe(CO)$_2$}$_2$Ga(μ-Cl)]$_\infty$, **1.14**, with potassium in ether has been reported to yield gallium metal and [{CpFe(CO)$_2$}$_3$Ga], **1.28**.[28]

1.5 Group 13 Diyls

1.5.1 History of group 13 diyl complexes

The last decade, in particular, has seen a dramatic development in the chemistry of low oxidation state compounds of the heavier group 13 elements. Whereas the +1 oxidation state in organometallic compounds has been known for many years for thallium and indium, it was virtually unknown for gallium. However pioneering work by Schnöckel and Uhl has dramatically changed this situation, opening the door to novel low oxidation state group 13 metal species.

For the heavier group 13 elements it is possible to isolate stable discrete monovalent ligands of the type $R^{I}E$ (E = Al, Ga, In; R = suitable sterically demanding substituent such as Cp*) in solution. Such monomeric compounds are remarkable as they contain coordinatively and electronically highly unsaturated group 13 metal atoms, of interest from both a fundamental structure/bonding viewpoint and as potential single-source precursor molecules in MOCVD.[3,40]

Recently Power *et al.*, have investigated the reaction of bulky terphenyllithium reagent LiAr* (Ar* = C_6H_3-2,6-$Trip_2$; Trip = C_6H_2-2,4,6-$^{i}Pr_3$) with the monohalides of gallium in an attempt to synthesise the neutral dimer Ar*GaGaAr* [41,42] However, depending on the nature of the aryl group employed, monomers of the type, GaAr* were isolated instead. Presumably this reflects the weakness of the Ga—Ga bond and can be primarily attributed to the large energy difference between the frontier lone pair and p-orbitals of the GaAr monomers. This was of particular interest due to the information it might provide on the controversial nature of the gallium—gallium bond in Na_2(Ar*GaGaAr*), **1.29**.[43]

1.5.2 Synthesis of group 13 diyls

There are two main synthetic strategies for the synthesis of diyls (RE): dehalogenation of REX_2 and salt elimination approaches.

i) Synthesis of diyls by dehalogenation

The simplest and most common method to prepare diyls is by dehalogenation. Trivalent aluminium and gallium compounds are reduced with common reducing agents such as alkali metals, Riecke magnesium and $NaSi^{t}Bu_3$ (Scheme 11).

$$REX_2 + 4M \longrightarrow 4MX + (RE)_n$$

E = Al, Ga; X = Halide; M = alkali metal

Scheme 11

Such a methodology was used by Paetzold and co-workers to synthesise the organo B(I) cluster [(B^{t}Bu)$_4$], **1.30**, by the reductive dehalogenation of ^{t}BuBF$_2$ with Na/K alloy.[44] Roesky *et al.* also prepared [AlCp*]$_4$, **1.31**, in high yield by the reaction of [Cp*AlCl$_2$] with potassium in toluene.[45] Analogously, Jutzi *et al.* synthesised the compound, [GaCp*]$_6$, **1.32**, by the reductive dehalogenation of [Cp*GaI$_2$] with potassium metal[46] and [{AlC(SiMe$_3$)$_3$}$_4$], **1.33**, was recently prepared by the reduction of [(Me$_3$Si)$_3$CAlI$_2$.THF] by Na/K alloy.[47]

ii) Synthesis of diyls by salt elimination

Low valent gallium and aluminium compounds can also be synthesised by salt elimination approaches. Such a synthetic strategy typically involves a group 13 monohalide dissolved in a stabilising solvent. Examples include the preparation of [InCp*], **1.34,** from the reaction of InCl and LiC$_5$Me$_5$ in diethyl ether,[48] or the synthesis of [InC(SiMe$_3$)$_3$]$_4$, **1.35**, from the metathetical reaction between LiC(SiMe$_3$)$_3$ with InCl (Scheme 12).[49]

$$EX + MR \longrightarrow MX + (RE)_n$$

$$InCl + LiCp^* \longrightarrow \underset{\textbf{(1.34)}}{InCp^*} + LiBr$$

Scheme 12

Schnöckel *et al.*, demonstrated a more intricate variation of this methodology synthesising the first organo Al(I) compound [AlCp*]$_4$, **1.31**, from metastable AlCl [50] (and later the analogous GaCp* compound, **1.32**).[51] Using a specially designed reactor, $AlCl_3$ gas was passed over aluminium metal at high temperature (1000 °C) and low pressure (10^{-2} mbar), then co-condensed with a donor solvent to give a metastable solution of nearly pure AlCl. Addition of bis(cyclopentadienyl) magnesium to the metastable AlCl solution then yielded [AlCp*]$_4$, **1.31**, (Scheme 13).[50]

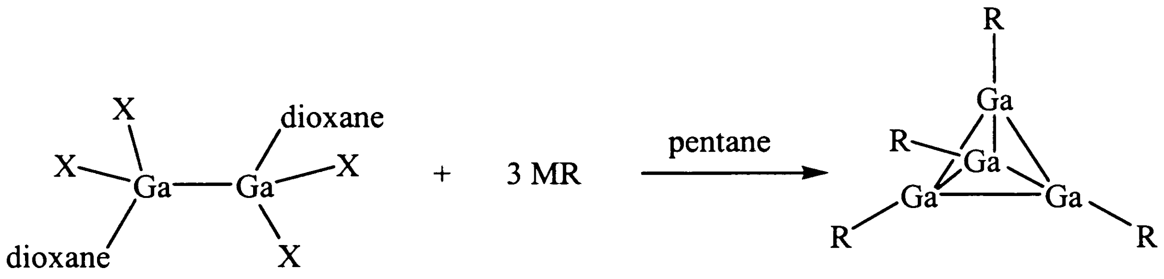
$$2Al_{(l)} \quad + \quad AlCl_{3(g)} \xrightarrow[10^{-2}\ \text{mbar}]{1000\ ^{0}C} 3AlCl_{(g)}$$

$$4AlCl \quad + \quad 2Cp_2Mg \longrightarrow [AlCp^*]_4$$

(1.31)

Scheme 13

Diyls can also be synthesised by salt elimination reactions from the subhalides of gallium and aluminium compounds. Uhl *et al.*, originally prepared [{Ga(C(SiMe$_3$)$_3$}$_4$], **1.36**, in low yield, from the metathesis reaction between $Ga_2X_4{\cdot}$2dioxane and $LiC(SiMe_3)_3$ in pentane (Scheme 14).[52]



X = Cl, Br

(1.36)

MR = $LiC(SiMe_3)_3$

Scheme 14

Synthetic routes to diyls which utilise ‘GaI’ often represent a more viable option to reduction reactions which tend to be low yielding or technically challenging. Jutzi *et al.*, have shown that GaCp*, **1.32**, can alternatively be formed in both large-scale quantities and high yields, by the treatment of ‘GaI’ with the potassium salt of a substituted cyclopentadienyl ligand (Scheme 15).[53] Several other Ga(I) alkyls or aryls, such as [{$GaC(SiMe_3)_3$}$_4$], **1.36**, have also been synthesised by reactions with ‘GaI’.[6,7,54]

$$\text{Ga} + 0.5\ \text{I}_2 \xrightarrow[\text{sonication}]{\text{benzene}} \text{'GaI'} \xrightarrow[\text{-KI}]{\text{Cp*K} \atop \text{benzene}} \text{Cp*Ga}$$

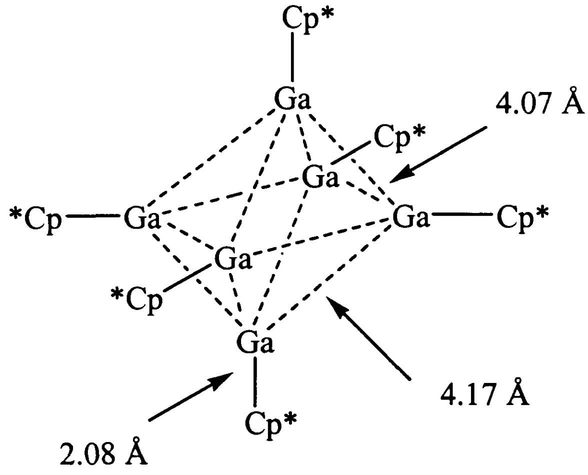
(1.32)

Scheme 15

1.5.3 Structure/bonding of group 13 diyl complexes

For the stabilisation of low oxidation state species of the type ER, it is vital that substituents R with appropriate steric demands and electronic properties are used. Typically such ER fragments are monomeric in solution and in the gas phase but demonstrate interesting aggregation properties in the solid state unless R is extremely sterically demanding. For example [(AlCp*)$_4$], **1.31**,[50] [{$Al(Si^tBu_3)_4$}], **1.37**,[55] and [{$GaC(SiMe_3)_3$}$_4$][47,49,52,56], **1.36**, are tetrameric whereas [MCp*]$_6$ (M = Ga, **1.32**, and In, **1.38**) are hexameric.[51,57] Monocoordination can be forced by the larger packing requirements of sterically demanding terphenyl ligands such as 2,6-$C_6H_3Trip_2$.

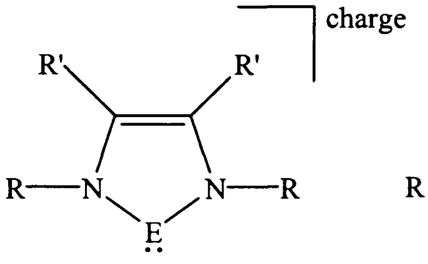
The complex GaCp*, **1.32**, prepared by Schnöckel *et al.*, for example,[51] is hexameric in the solid state, and is made up of two distinct Ga_3 units. The Ga···Ga distances in these subunits however are only weak and very long, only weakly influencing the aggregation. Clusters of this type are probably primarily formed as a result of the van der Waals interactions between the Cp* ligands and not the metal—metal bonds. In fact, the metal—metal bond lengths in [GaCp*]$_6$ are actually slightly longer than those of the isomorphous [InCp*]$_6$ cluster, **1.38**, presumably due to ligand packing requirements.[58] The aggregates are however unstable in comparison with the monomers, and theoretical calculations on both $[(AlCp)_4]$, **1.39**, and $[(AlCp^*)_4]$, **1.31**, have suggested that Cp→ Al π backbonding is the primary reason for this.[59]



(1.32)

1.6 Related Amido Group 13 Systems

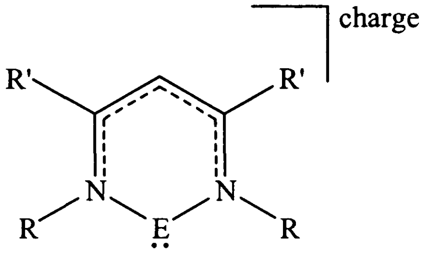
The isolation of stable carbenes based on imidazolium heterocycles (N-heterocyclic carbenes, NHCs) has attracted much attention over the last decades. Like group 13 diyls, the NHC class of ligand, **1.40**, E = C, possess a singlet lone pair and act as strong σ-donors towards a wide range of s, p and d-block metal fragments.[60] In NHC-transition metal complexes, the *p*-orbital at the carbene centre is not thought to engage in π-bonding with filled metal *d*-orbitals to any great extent. This arises from a significant overlap of the nitrogen *p*-orbital lone pairs with the carbene *p*-orbital. The electronic and steric properties of NHCs have lent them to a variety of applications in synthesis and catalysis where they are often thought of as phosphine mimics. There has been considerable attention paid to the heavier group 14 analogues of NHCs, E = Si, Ge or Sn, and valence isoelectronic cationic phosphorous and arsenic analogues of NHCs, E = P or As, **1.41**.[61] However, anionic group 13 heterocycles have only recently been synthesised. Related neutral 6-membered aluminium, gallium and indium heterocycles have also been reported, **1.42**.



(1.41)

E = group 13 element, charge = -1
E = group 14 element, charge = 0
E = group 15 element, charge = +1

R and R' = alkyl, aryl or H

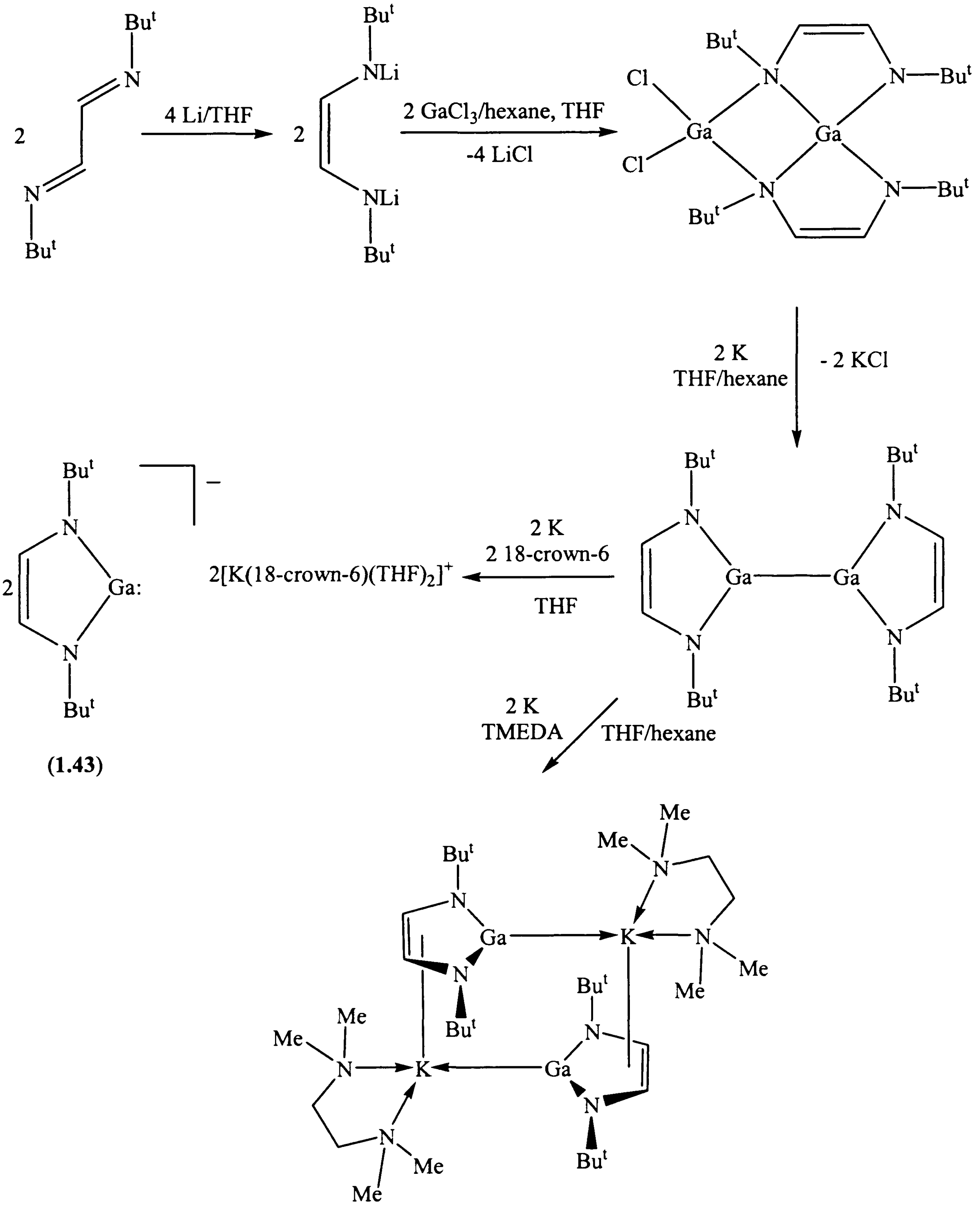


(1.42)

E = Al, Ga, In, charge = 0
E = Ge, charge = +1

1.6.1 Synthesis of anionic 5-membered group 13(I) heterocycles

In 1999, Schmidbaur and co-workers reported the first synthesis of an anionic gallium carbene analogue. The synthesis of which is depicted in Scheme 16.[62]



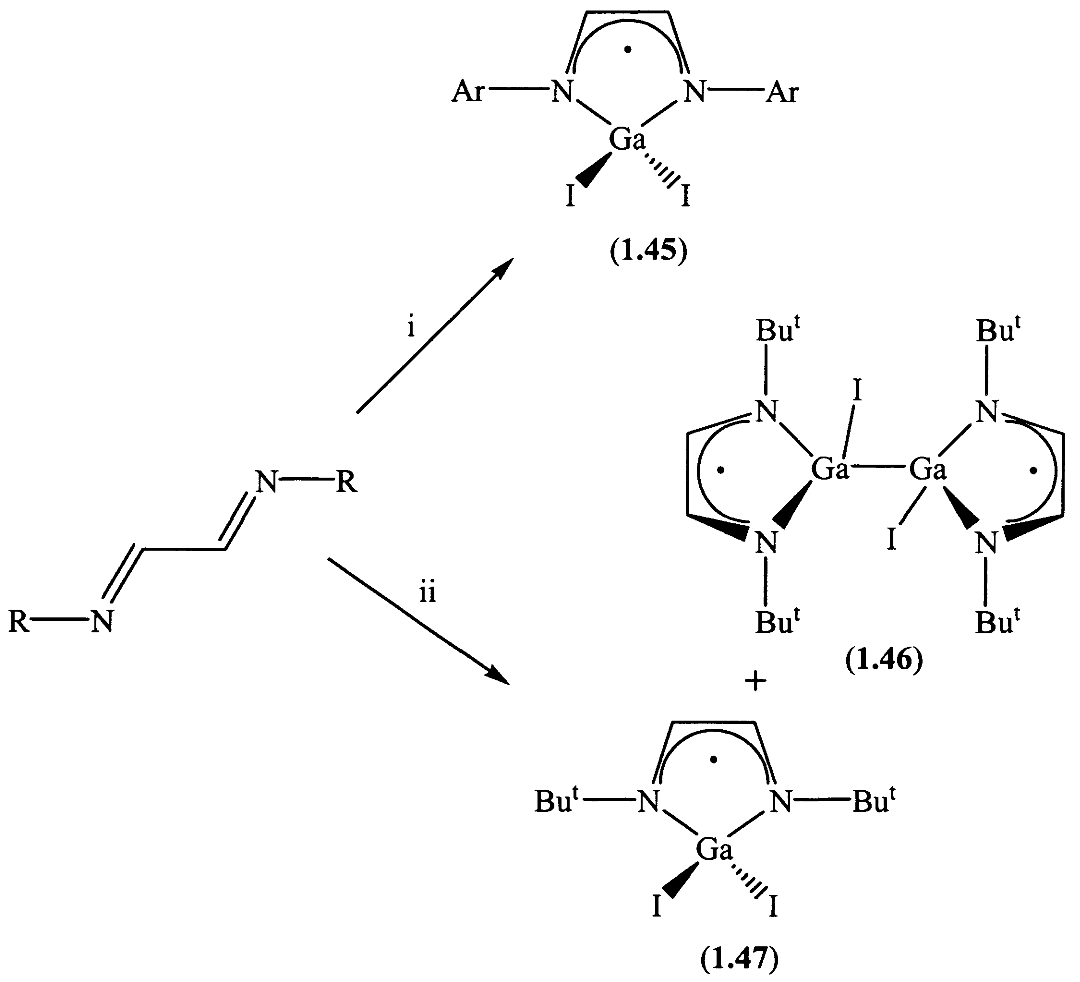
(1.43)

(1.44)

Scheme 16

Treatment of the dilithiated diazabutadiene ligand with $GaCl_3$ gives a chlorogalla-imidazole which can be reduced stepwise over 5 days with potassium and a crown ether to give the anionic heterocycle **1.43** in poor yield (3 %). If the reduction is carried out in the presence of TMEDA as a chelating agent, complex **1.44** can be isolated in 18 % yield after 14 days.[62] Both compounds were structurally characterised and compound **1.43** shows no cation-anion contacts, *i.e.* it contains a discrete 2 co-ordinate gallium centre where the oxidation state of the metal is +1. Complex **1.44** was shown to be dimeric in the solid state and can be considered as consisting of monomeric units which comprise a gallium 'carbene' heterocycle η^5-co-ordinated to a K(TMEDA) fragment. An intermolecular interaction of the gallium lone pairs with two potassiums aggregates these monomeric units into centrosymmetric dimers.

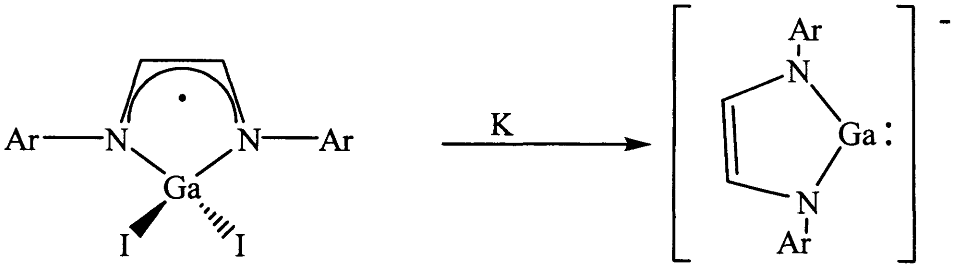
In related work, Jones *et al*, later examined the reactions of diazabutadienes, $\{RN=C(H)\}_2$ (DAB) with 'GaI' which yielded either Ga(II) or Ga(III) complexes, **1.45-1.47**, depending on the nature of the DAB N-substituents (Scheme 17). The mechanism of formation of **1.45** was proposed to involve a combination of one electron DAB reduction and disproportionation reactions.[63]



Ar = $2,6\text{-}\mathrm{Pr}^i{}_2\mathrm{C}_6\mathrm{H}_3$

Scheme 17

Reduction of **1.45**, with potassium metal gives the anionic Ga(I) heterocycle, **1.48**, which is valence isoelectronic with the important N-heterocyclic carbene class of ligand (Scheme 18). This anion possesses a singlet lone pair at the gallium centre and as a result its coordination chemistry has been extensively examined. These studies have proved to show close analogies to NHCs, particularly with regard to its strongly nucleophilic nature and stabilising properties.[64]



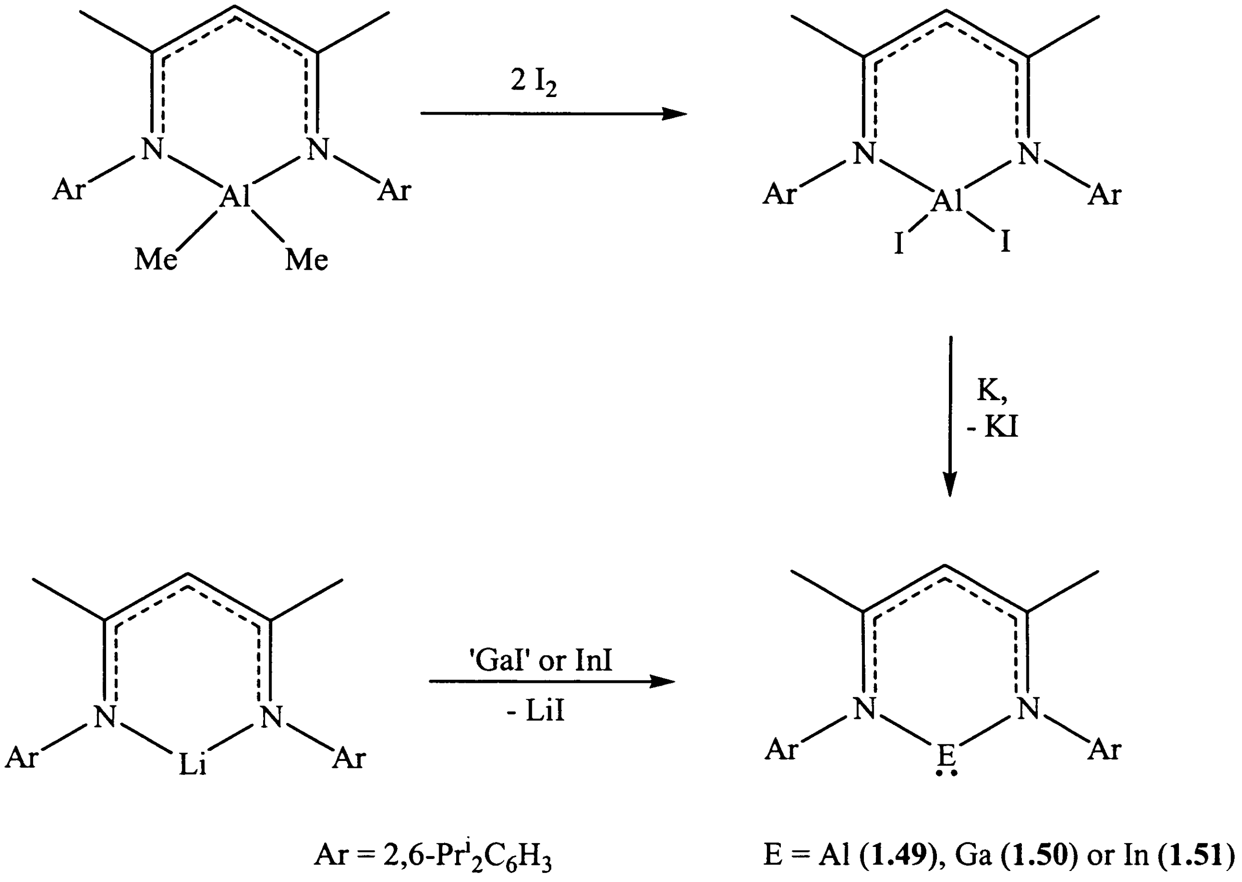
(1.45)

(1.48)

Scheme 18

1.6.2 Synthesis of neutral 6-membered group 13(I) heterocycles

The synthesis of related neutral 6-membered aluminium(I)[65], gallium(I)[66] and indium(I)[67] heterocycles derived from the β-diketiminate ligand $HC(CMeNAr)_2^-$ (Ar = 2,6-diisopropylphenyl) have also been reported and their syntheses are shown in Scheme 19.



Scheme 19

Reaction of [{HC(CMeNAr)$_2$}AlMe$_2$] with I$_2$ gives the corresponding diiodide in good yield. This can be reduced with potassium over 3 days to give **1.49** in 21% yield. A crystal structure determination shows well-separated monomeric units with the first example of a two co-ordinate aluminium centre. Analysis of the Laplacian of electronic density in the plane of the ligand shows clearly the presence of a lone pair localised on the metal and outside the heterocycle in a quasi-trigonal-planar geometry. The authors argue that the electrons originating from an s^2 configuration of the Al^{I} centre are stereochemically active, leading to an *sp*-like hybrid. The aluminium atom can be considered as acting as both a Lewis acid in its interaction with the nitrogen atoms of the ligand and potentially as a Lewis base with its lone pair of electrons.

The synthesis of both the gallium, **1.50**, and the indium, **1.51**, ring systems involve salt elimination reactions between the β-diketiminate anion and the appropriate metal(I) iodide

(Scheme 20). It is noteworthy that a previous attempt to prepare, **1.51**, by this method but using InCl was not successful.[68] The bonding situation of **1.50**, can be considered as a Ga^+ ion chelated by a monoanionic $[(NArCMe)_2CH]^-$ ligand.

1.7 Transition Metal Complexes of Group 13 Diyl Ligands

1.7.1 Introduction to transition metal complexes of group 13 diyl ligands

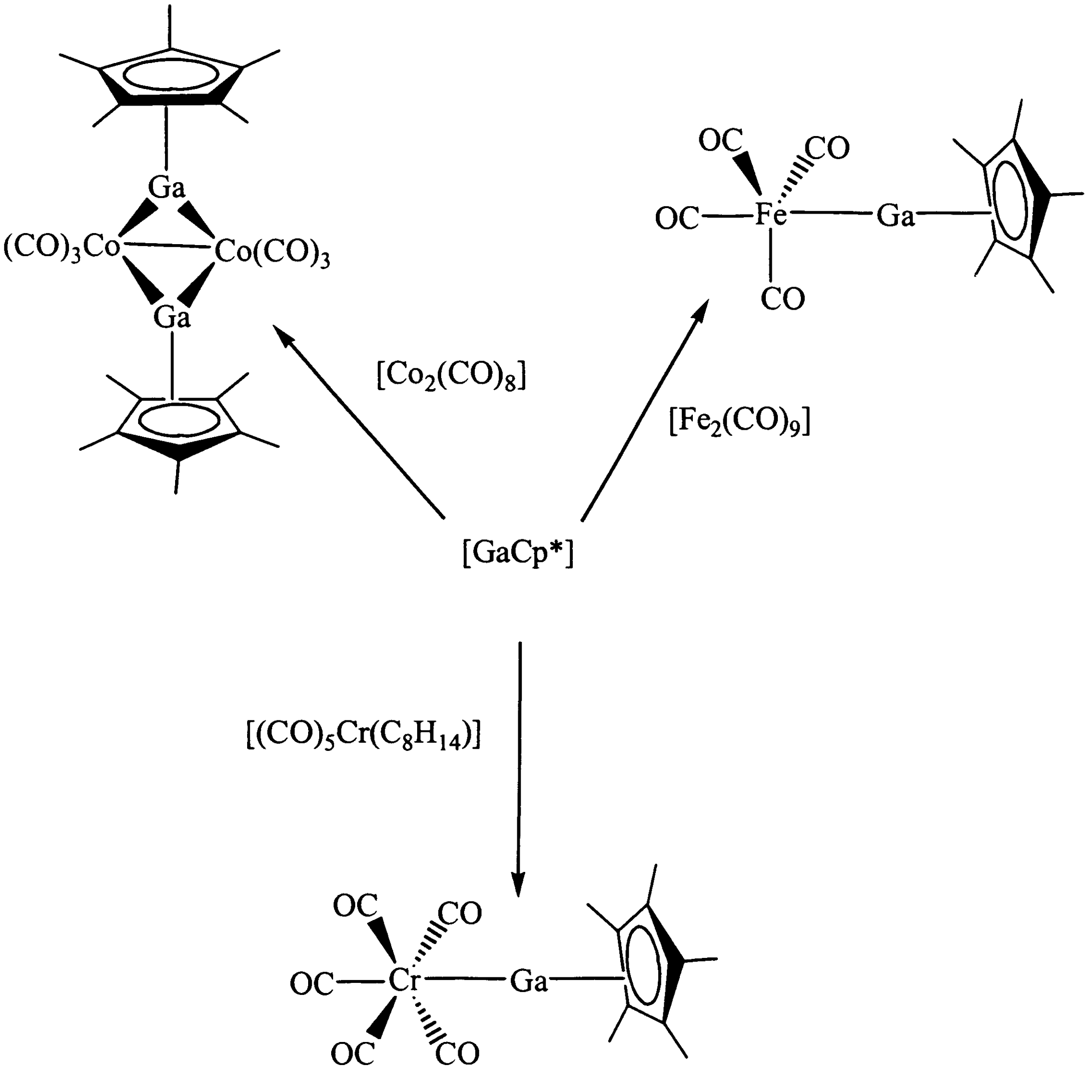
Group 13 fragments of the type ER which contain coordinatively and electronically highly unsaturated group 13 elements are highly reactive. Their ability to function as Lewis bases towards a variety of transition metals make them versatile starting materials for synthesis. Only in the last few years has the coordination chemistry of organo RE fragments become established; numerous examples of transition metal complexes featuring terminal and bridging ER fragments have been reported in the interim.

1.7.2 Synthesis of transition metal complexes of group 13 diyl ligands

Typically synthetic strategies for the preparation of metalladiyls are principally confined to salt elimination reactions between divalent metal carbonylates $[M(CO)_n]^{2-}$ and aluminium or gallium halide derivatives, the substitution of labile ligands by ER, and insertion reactions.

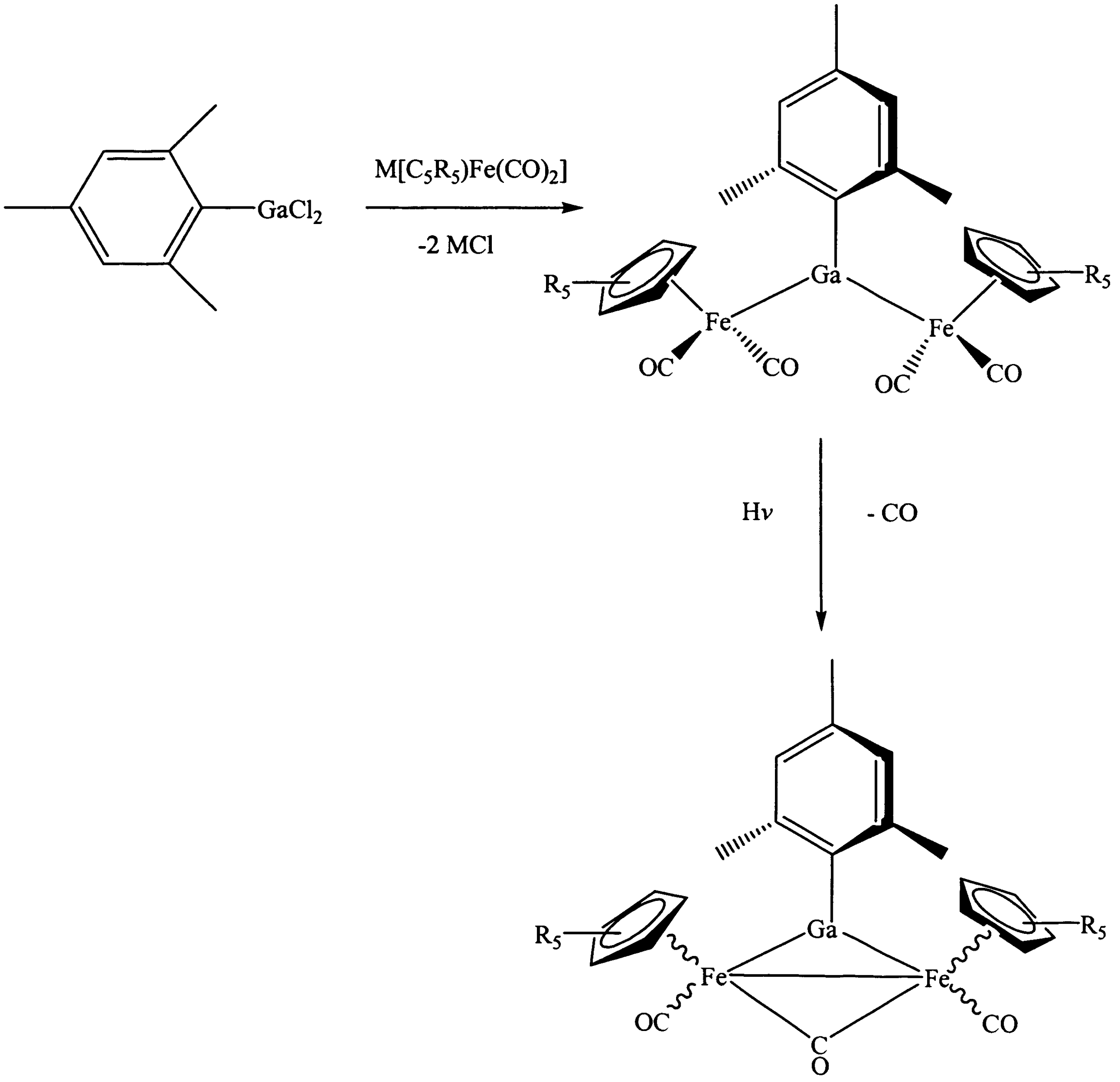
i) Synthesis of transition metal complexes of group 13 diyl ligands by substitution of labile ligands

As a result of the isolobal relationship between ER fragments and CO, labile ligands such as CO and alkenes coordinated to transition metal fragments can be readily substituted by ER fragments giving access to complexes with both terminal and bridging ligands. Numerous examples of transition metal complexes with ER bridged ligands have been synthesised *via* this methodology. In particular, the reaction of ER fragments with homoleptic transition metal carbonyls has been heavily studied. For example, the complexes $[Mn_2(CO)_8(\mu_2\text{-}InC(SiMe_3)_3)_2]$, **1.52**[69] $[Mn_2(CO)_6\{\mu_2\text{-}In\text{-}C\text{-}(SiMe_3)_3)_2]$, **1.53**,[69] and $[Co(CO)_6(\mu_2\text{-}InC(SiMe_3)_3)]$, **1.54**,[21] were isolated from the reaction of the parent carbonyl dimers with ER ligands. Linti and co-workers have synthesised derivatives of $[Fe_2(CO)_9]$, in which some or all of the bridging carbonyls have been replaced with monomeric $Ga[C(SiMe_3)_3]$, **1.36**, *via* the reaction of $[Ga\{C(SiMe_3)_3\}_4]$ with the iron carbonylates $Na_2[Fe(CO)_4]$, $Na_2[Fe_2(CO)_8]$, and $Na_2[Fe_3(CO)_{11}]$.[58] Jutzi *et al.*, used substitution methodology to prepare a variety of first row transition metal carbonyl species with coordinated GaCp* groups in both terminal and bridging positions (Scheme 20).[46]



Scheme 20

Ogino *et al.*, have recently reported the unsupported bridging gallylene complexes [{(η^5-C$_5$R$_5$)Fe(CO)$_2$}$_2$Ga(2,4,6-Me$_3$C$_6$H$_2$)] (R = H, Me), **1.55**, from the reaction of [2,4,6-Me$_3$C$_6$H$_2$GaCl$_2$] with the appropriate anion. The supported bridging gallylene complex was synthesised *via* photolysis of the unsupported complex; for η^5-C$_5$H$_5$ this was formed in a mixture of *cis* and *trans* isomers due to the small steric bulk (Scheme 21).[70] However such a methodology has limited synthetic applicability due to the reliance on a gallylene precursor.

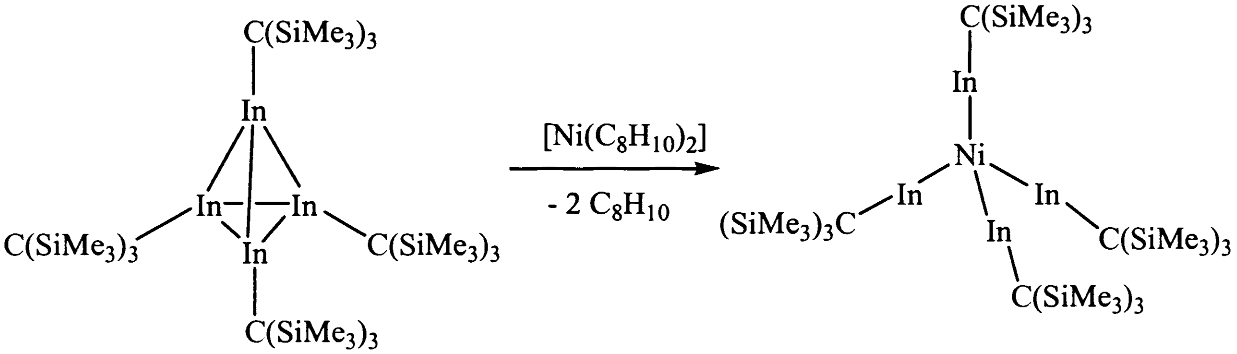


R = Me, *trans* isomer exclusively
R = H, mixture of *cis* and *trans*

(1.55)

Scheme 21

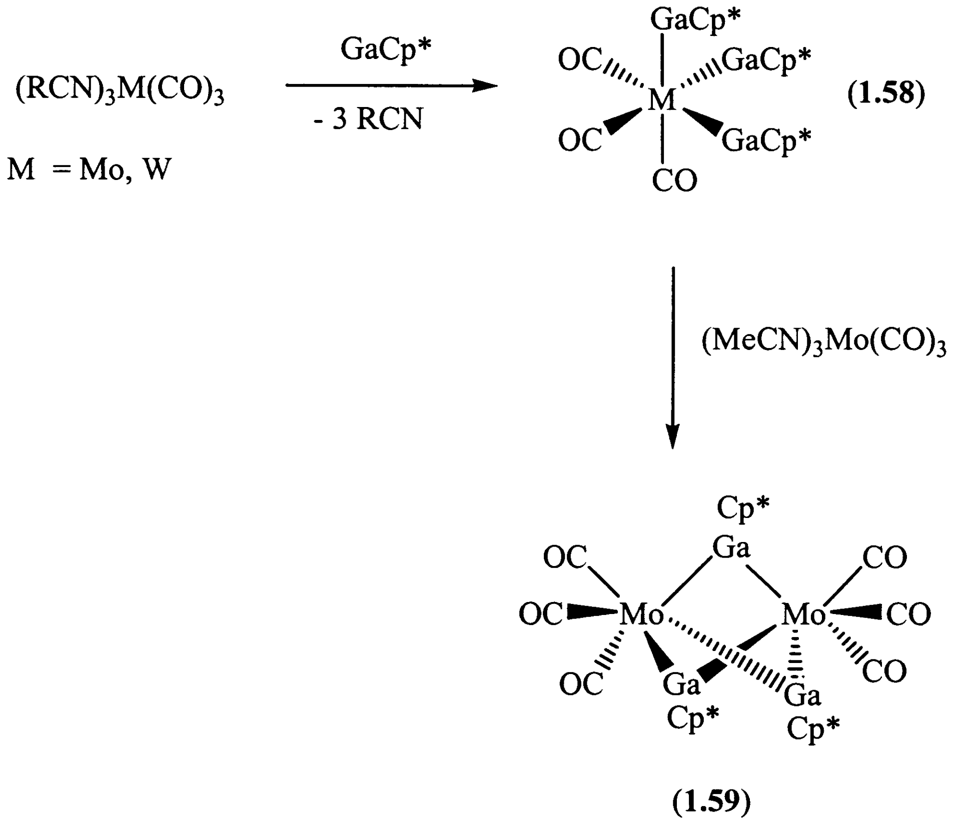
Substitution of other labile ligands by ER is also possible. For example chelating olefin ligands such as norbornadiene,[71] cyclooctatetraene,[72] cycloheptatriene[46] and cyclooctene[73] can be displaced. In 1998 the synthesis of an unusual Ni(0) complex [Ni(In{$C(SiMe_3)_3$}$_4$], **1.56**, was reported by Uhl *et al.* *via* the reaction of [Ni(cod)$_2$] and [In{$C(SiMe_3)_3$}]$_4$. This illustrated the possibility of synthesising complexes with an 'inverted' ratio (E/M>1) via ligand substitution chemistry (Scheme 22).[74] The gallium analogue was reported later.[75]



(1.56)

Scheme 22

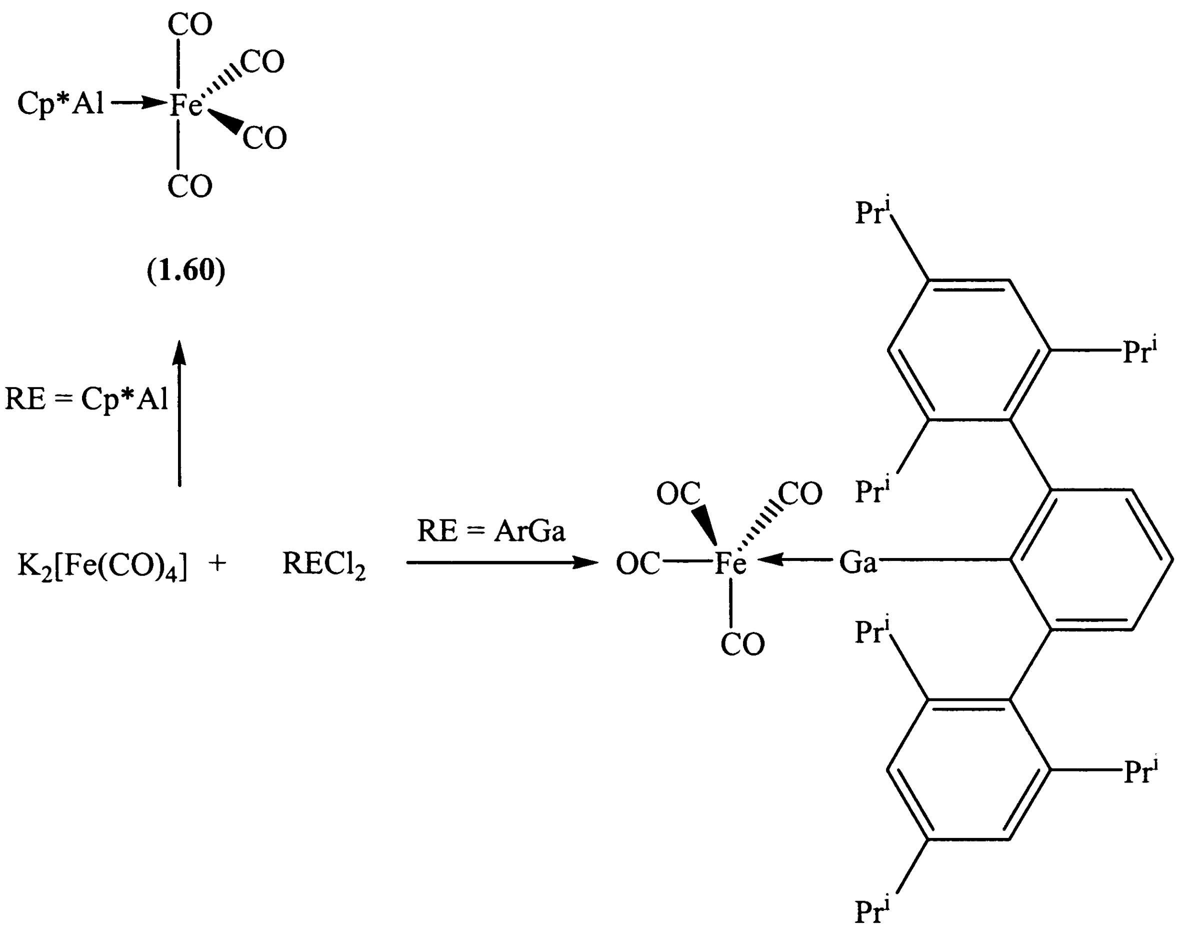
There are also reports of the substitution of heteroatom donor ligands such as THF or MeCN. In 1998, Power *et al.*, synthesised [$Cp(CO)_2MnInC(SiMe_3)_3$], **1.57**, *via* the reaction of In[$C(SiMe_3)_3$] with [$Cp(CO)_2Mn(THF)$].[76] The reaction of GaCp* with [*fac*-$(MeCN)_3M(CO)_3$] to yield monomeric compounds of the type [*fac*-$(GaCp^*)_3M(CO)_3$], **1.58**, has recently been reported. Such species can then act as building blocks for dinuclear complexes, in which the GaCp* ligand adopts a bridging mode of coordination, **1.59** (Scheme 23).[77]



Scheme 23

ii) Synthesis of transition metal complexes of group 13 diyls *via* salt elimination

Transition metal complexes of group 13 diyls can also be synthesised by metathesis reactions between carbonylmetallates $[M(CO)_n]^{2-}$ (M = Fe, n = 4; M = Cr, n = 5), and REX_2 in coordinating solvents, examples of which include $[Fe(CO)_4(AlCp^*)]$, **1.60**,[78] and $[(Ar^*Ga)Fe(CO)_4]$, **1.61**, (Scheme 24).[7]



(1.60)

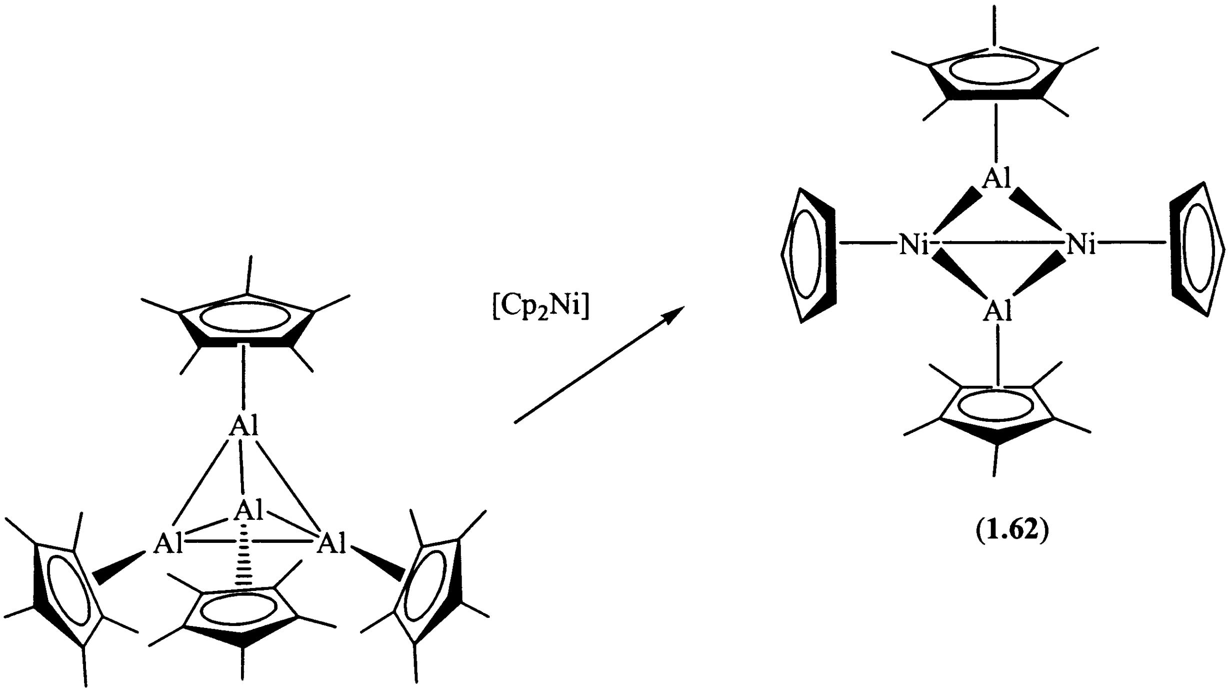
(1.61)

Scheme 24

iii) Synthesis of transtion metal complexes of group 13 diyls *via* EX insertion

Although insertion reactions of EX (X = halide) have a long history, analogous insertions of ER are only a recent development. However, due to the availability of group 13 diyls, insertion reactions of this type represent a readily accessible route into the formation of M—E bonds especially for the synthesis of CO-free systems.

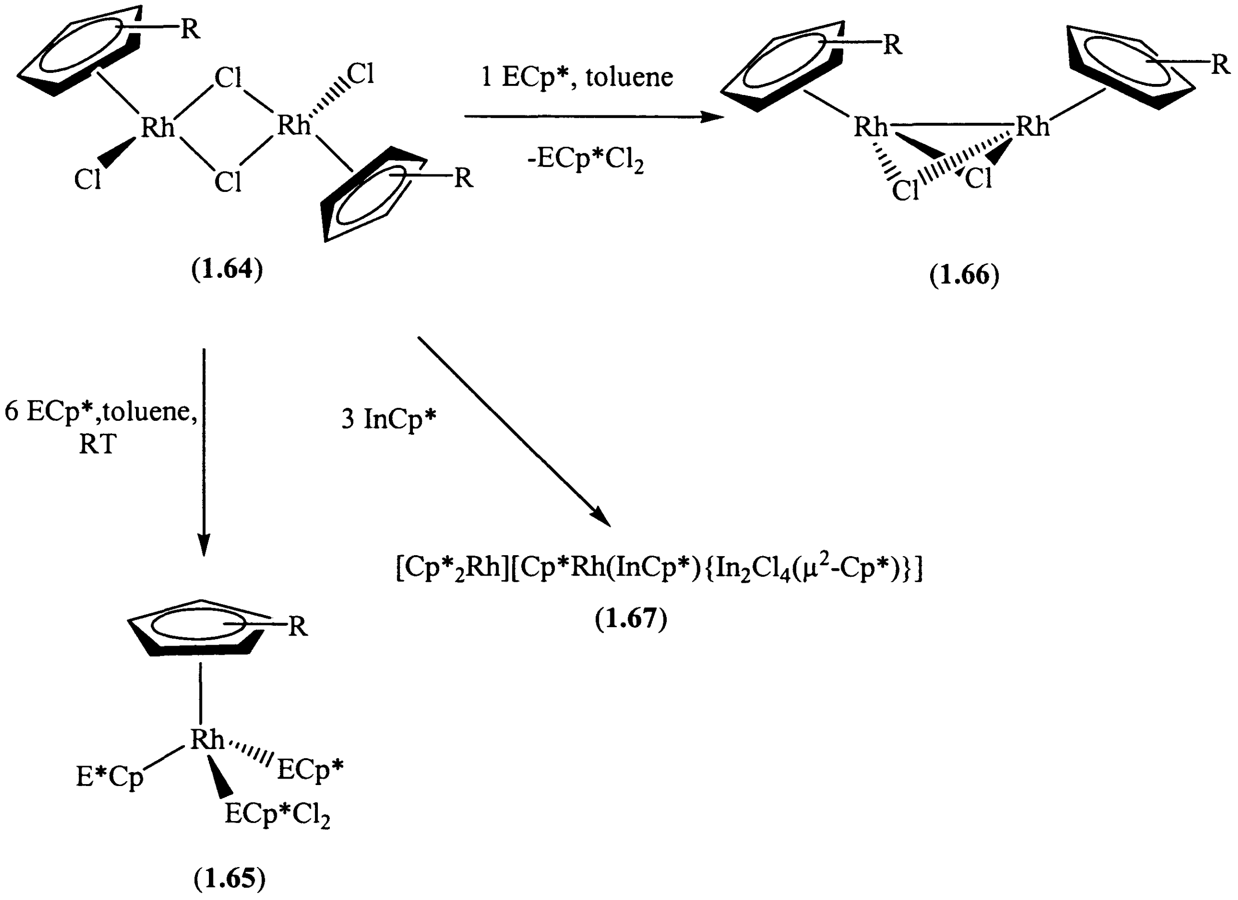
In 1994 Schnöckel *et al.*, reported the compound $[(CpNi)_2(\mu_2\text{-}AlCp^*)_2]$, **1.62**, the first transition metal complex bearing a bridging ER fragment, which was synthesized from the insertion of AlCp* into the Ni—C(Cp) bond of $NiCp_2$ (Scheme 25).[79]



(1.62)

Scheme 25

Jutzi and co-workers have also demonstrated the potential of ER fragments as both reducing and Cp*-transfer reagents, reporting the insertion of GaCp* into the Fe—Cl bonds of $FeCl_2$ to give [Cp*Fe(GaCp*)$_2$(GaCl$_2$.THF)], **1.63**.[80] Typically insertion reactions tend to be highly sensitive to reaction conditions with many different pathways often possible. This is exemplified by the reaction of [{RhCp*Cl$_2$}$_2$], **1.64**, with ECp* (E = Ga, In).[58] Reaction of [{RhCp*Cl$_2$}$_2$] with six equivalents of ER at room temperature in toluene yields the monomeric product [RhCp*(ECp*)$_3$Cl$_2$], **1.65**, whereas reaction with a single equivalent of ECp* gives the Rh(II) dimer [(RhCp*Cl)$_2$], **1.66**. In contrast the salt, [Cp*$_2$Rh][Cp*Rh(InCp*){In$_2$Cl$_4$(μ^2-Cp*)}], **1.67**, is prepared by the reaction of [(Cp*RhCl$_2$)$_2$] with three equivalents of InCp* (Scheme 26).



(1.64) (1.66)

[Cp^*_2Rh][$Cp^*Rh(InCp^*)\{In_2Cl_4(\mu^2\text{-}Cp^*)\}$]

(1.67)

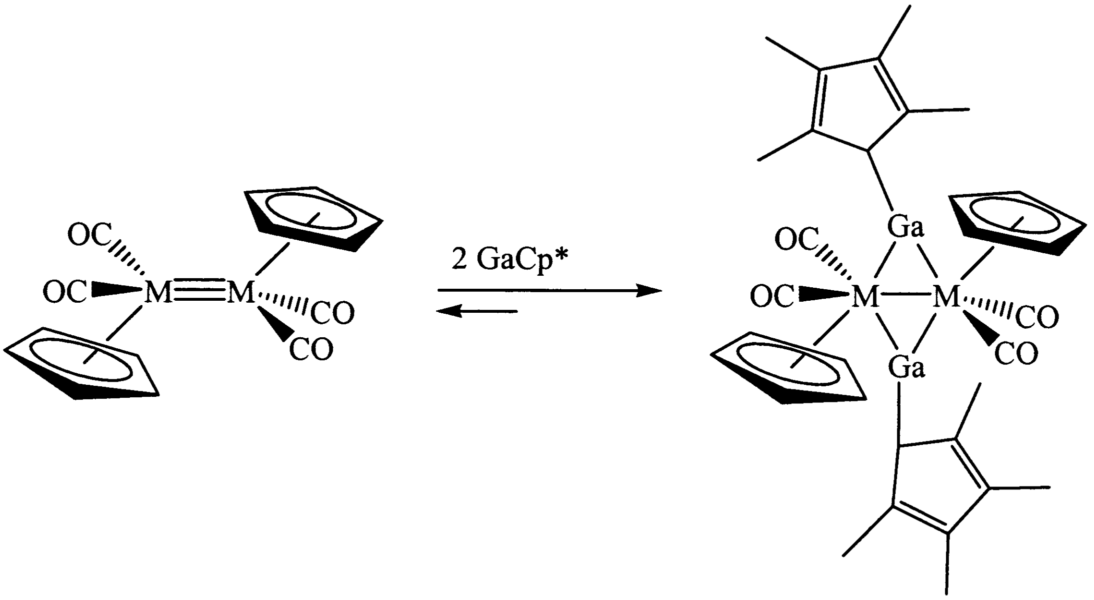
(1.65)

For **1.64** - **1.67**, R = Me_5; E = Ga, In

Scheme 26

Additionally, in related work, Fischer *et al.* have shown that [$(Cp^*RuCl)_4$] reacts with both Cp*Ga and Cp*In to yield monomeric 'piano-stool' complexes of the type, [$Cp^*Ru(ECp^*)_3Cl$] (E = Ga, In), **1.68**, while the complex [$Ru(GaCp^*)_6Cl$], **1.69**, can be prepared by the insertion of Cp*Ga into the ruthenium—halide bonds of [$(Ph_3P)_3RuCl_2$], leading to the complete substitution of PPh_3 ligands.[58]

Reaction of GaCp* with multiple bonded complexes of the type [$\{CpM(CO)_2\}_2$] (M = Mo, W), **1.70**, have been studied in more detail. The coordination of GaCp* is unexpectedly weak and demonstrates a temperature dependent association/dissociation (Scheme 27).[58,77]



M = Mo, W

(1.70)

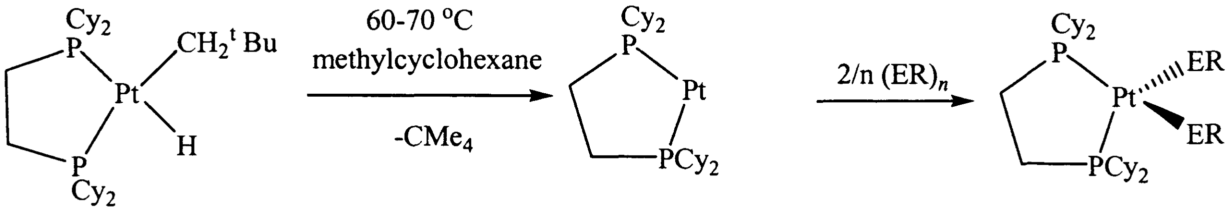
Scheme 27

iv) Synthesis of transition metal complexes of group 13 diyls *via* oxidation of ER

The ease of oxidation of ER provides a less common pathway to the synthesis of metalladiyls. ER fragments can act as *in situ* reducing agents towards higher oxidation state transition metal complexes, $[L_nMX_n]$, giving either insertion products if ER remains coordinated to the transition metal centre or low oxidation state complexes, $[M_a(ER)_b]$, by cleavage of X_2ER.[58]

v) Synthesis of transition metal complexes of group 13 diyls by addition

There are only a few examples of addition reactions of ECp* to coordinatively unsaturated centres. Fischer *et al.*, has shown that it is possible to synthesise bis(phosphine)platinum complexes of the type $[(dcpe)_2Pt(ER)_2]$, **1.71**, by trapping the 14 VE reactive intermediate [(dcpe)Pt] with the low valent diyls. This intermediate is produced by the reductive alkyl elimination from the platinum hydride $[(dcpe)Pt(H)(CH_2{}^tBu)]$, **1.72**, (Scheme 28).[21,77,81]



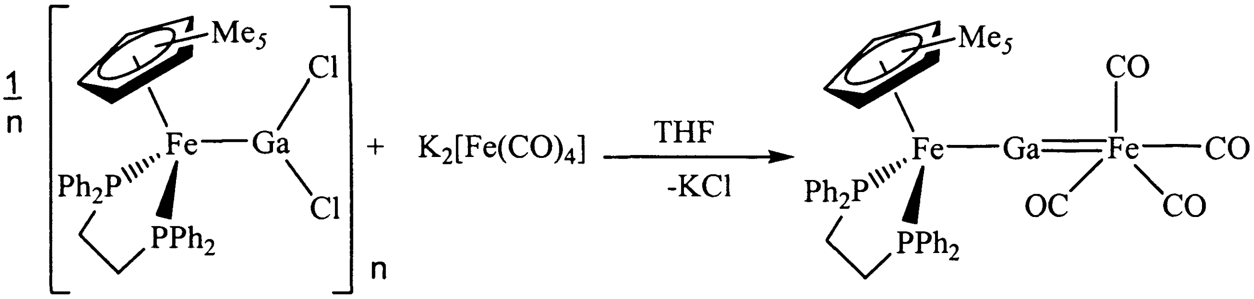
(1.72) **(1.71)**

E = Al, Ga, In; R = Cp*
E = Ga; R = $C(SiMe_3)_3$

Scheme 28

1.7.3 Group 13 metalladiyl and related complexes

In 2003 Ogino *et al.*, reported the first dinuclear complex bridged by a substituent-free 'naked' gallium atom $[Cp^*Fe(dppe)(\mu\text{-}Ga)Fe(CO)_4]$, **1.73**, the bonding in which can be formally be described as a single bond between Cp*(dppe)Fe and Ga and a double bond between Ga and $Fe(CO)_4$ (Scheme 29).[29] In practice, the Fe—Ga bond lengths imply appreciable delocalisation of π bonding over the Fe—Ga—Fe framework. Such a bonding framework can be compared to $[Cp^*Fe(CO)_2(\mu\text{-}B)Fe(CO)_4]$, **1.74**, which contains a substituent free boron centre bridging the transition metal-ligand fragments.[82]



(1.73)

Scheme 29

1.7.4 Aspects of bonding in transition metal complexes of group 13 diyls

i) Bonding in diyl complexes

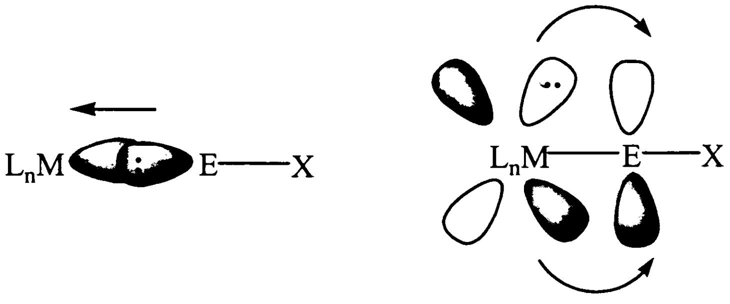


Figure 3

ER compounds typically have a singlet ground state and formally have two empty p orbitals and a lone pair of electrons at the metal. Consequently the frontier orbitals are similar to those of the CO ligand and therefore ER may be regarded as isolobal with CO and PR_3, capable of exhibiting both σ-donation and π-acceptor properties, the relative extents of which are dependent on the nature of the metal and the organic group R (Figure 3).[58] For Cp*, the vacant p-orbitals of the group 13 metal are partially populated by the π-donor orbitals of the Cp* groups thus diminishing the π-acceptor properties of the ligand. Typically ER fragments are very good σ-donors with weak π-acceptor properties. In addition, recent theoretical studies have suggested that the electrostatic attraction between the group 13 metal and transition metal plays a significant role.[83,84]

ii) Structural and spectroscopic aspects of transition metal group 13 diyl complexes

There have been numerous structurally authenticated transition metal group 13 diyl complexes reported to date and only representative examples of structural interest will be discussed here.

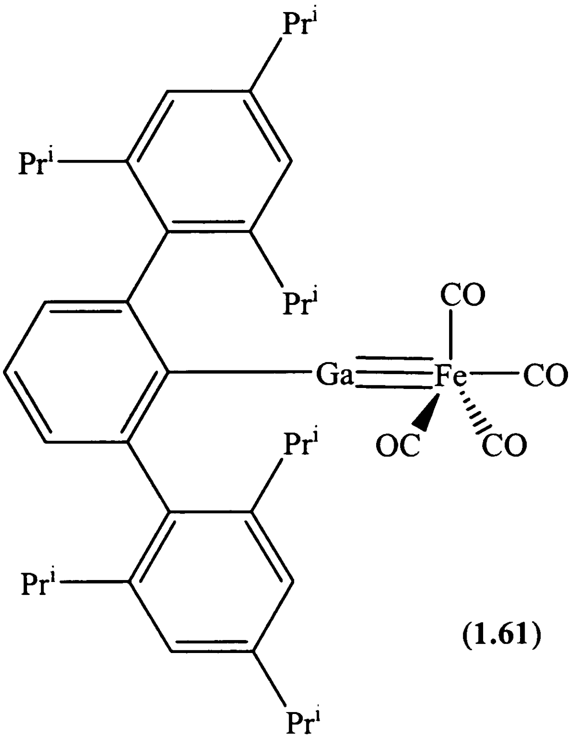
In 1994 Schnöckel *et al.*, reported $[(CpNi)_2(\mu_2\text{-AlCp*})_2]$, **1.62**, the first transition metal complex bearing a bridging ER fragment in a μ_2 coordination mode.[85] Numerous examples of ER bridging ligands have since been reported, for example, $[InC(SiMe_3)_3]$, **1.37**, acts as a bridging ligand in $[Mn_2(CO)_8\{\mu_2\text{-InC(SiMe}_3)_3\}_2]$, **1.52**, and $[Co_2(CO)_7\{\mu_2\text{-InC(SiMe}_3)_3\}]$, **1.54**.[72]

Terminal metalladiyls which contain the ER fragment (ER) bound to one metal centre are relatively few in number compared to bridging metalladiyls. [$Fe(CO)_4AlCp^*$], **1.60**, was the first example of a terminally coordinated Cp*Al ligand and confirmed the isolobal analogy between CO and ER.[78] Other examples include [$Cp^*AlCr(CO)_5$], **1.75**,[86] [$Fe(CO)_4GaCp^*$], **1.76**,[46] and recently Leiner and Scheer have synthesised [$W(CO)_5GaCp^*$], **1.77**.[87] Jutzi *et al.*, have prepared a variety of metal carbonyl clusters containing monomeric GaCp* groups as terminal as well as bridging ligands.[46] Compounds with more than one terminal ER unit, e.g. [*cis*- $Mo(CO)_4(Cp^*Ga)_2$], **1.70**, have also been the focus of research.[71]

Multinuclear homoleptic cluster compounds such as [$Pt_2(GaCp^*)_5$], **1.78**, and [$Pd_3(InCp^*)_8$], **1.79**, with tetra-coordinated metal centres, which have no direct carbonyl or phosphine analogue have also been reported, as have mononuclear heteroleptic carbonyl containing complexes of the type [$M(CO)_a(ER)_b$].[88,89] A series of homoleptic complexes of the type [$M(ER)_4$] synthesised for the nickel group elements, (Ni, Pd, Pt) with E = Ga and In and R = Cp* and $C(SiMe_3)_3$, were recently reported. The unusual and fascinating homoleptic Ni(0) complexes, [$Ni(In\{C(SiMe_3)_3\}_4$], **1.56**, and [$Ni(Ga\{C(SiMe_3)_3\}_4$], **1.80**, represent the first examples of transition metal complexes with the metal exclusively coordinated to terminal ER groups in an undistorted tetrahedral coordination sphere.[75] These enabled direct comparison with [$Ni(CO)_4$] featuring isolobal CO ligands. The Ni—In—C bonds in [$Ni\{InC(SiMe_3)_3\}_4$] are linear with a Ni—In—C bond angle of 180°. The short Ni—In bonds (2.310 Å) are indicative of π-back bonding and quantum chemical calculations confirm that there is significant π-back bonding of electron density from nickel to the empty orbitals at indium. By analogy, the Ni—Ga—C bonds in [$Ni\{GaC(SiMe_3)_3\}_4$], **1.80**, are also linear with a Ni—Ga—C bond angle of 180°. The Ni—Ga bond distances are also very short (2.014 Å), indicating that back bonding can be significant for homoleptic systems with competing π acid ligands.[75]

A degree of controversy however surrounds the degree of back bonding in diyl complexes featuring ancillary carbonyl ligands. This is perhaps best exemplified by the iron—gallium diyl complex, [$Fe(CO)_4(GaAr^*)$], **1.61**, Ar* = 2,6-(2,4,6-$Pr^i{}_3C_6H_2)_2C_6H_3$, reported by Robinson in 1997, which features the shortest reported Fe—Ga bond length (2.2248(7) Å).[7] The X-Ray diffraction data revealed a linear Fe—Ga—C(ipso) arrangement which, together with the short Fe—Ga bond, the authors attributed to a triple Fe—Ga bond. This was later dismissed by Cotton and Feng who proposed a Fe← Ga donor/acceptor bond.

The molecule can be built up, theoretically, by first combining the Ar*Ga unit with the trigonally symmetric $Fe(CO)_4$ to give an 18-electron configuration and a bond order of 1. Any further increase in this bond order can only occur by back-donation of electrons on the iron atom to the empty orbitals on the gallium atom. Therefore to obtain a Ga—Fe triple bond, there would have to be two fully formed Fe→ Ga dative π bonds. However, Cotton and Feng concluded that this degree of back-bonding was unlikely given the charge separation entailed and comparisons with $[Fe(CO)_4Ph_3P]$, **1.81**. For example, the CO stretching frequencies of $[Fe(CO)_4(GaAr^*)]$, **1.61**, are actually significantly lower than those in $[Fe(CO)_4Ph_3P]$, where only a small amount of π back-bonding is thought to occur (2032, 1959, 1941 and 1929 cm^{-1} for **1.61** *vs.*2052, 1979, 1947 cm^{-1} for **1.81**). This implies that there is actually less Fe—Ga π back-bonding than Fe—P back-bonding. In addition the Fe—Ga distance, 2.2248(7) Å, is only slightly shorter than the P—Fe distance, 2.2244(1) Å, in $[Fe(CO)_4Ph_3P]$.[8]



(1.61)

Numerous theoretical studies on this and related complexes have since been carried out and it is now generally accepted that the degree of metal—metal back-bonding is minimal due to the relatively high energy of the group 13 metal p-orbitals.[83]

By contrast the monomeric organoindium(I) compound [InC_6H_3-2,6-$Trip_2$] is thought simply to act as a two-electron donor, displacing THF from [$Cp(CO)_2Mn(THF)$][76] to give [$Cp(CO)_2MnInC_6H_3$-2,6,-$Trip_2$], **1.82**. The X-ray structure showed a near-linear C—In—Mn arrangement (175.39(9)°) and a short In—Mn bond (2.4102(9) Å). Carbonyl stretching frequencies (1940, 1864 cm^{-1}) are comparable to those of [$Cp(CO)_2Mn(THF)$], **1.83**, (1925, 1850 cm^{-1}) and [$Cp(CO)_2MnPPh_3$], **1.84**, (1932, 1869 cm^{-1}) indicating that [InC_6H_3-2,6-$Trip_2$] is a two electron σ donor with weak π acceptor properties. This endorses the view that the In—Mn bond and the analogous Ga—Fe bond in Robinson's compound simply owe their deceptive shortness to the lower coordination number of the group 13 metal atom.

1.7.5 Theory of the bonding in transition metal group 13 diyl complexes

In recent years the progress in synthetic chemistry of transition metal complexes with donor atoms of group 13 (B, Al, Ga, In) has encouraged the parallel development of theoretical tools that can investigate the nature of these M—E bonds.

Although low coordinate diyl complexes (L_nMEX) of group 13 elements are a relatively recent synthetic development, the nature of bonding between group 13 elements and transition metals has spurred considerable recent discussion and a number of thorough computational studies have been reported.[83,84] Two questions that have been heavily debated are the degree of covalent and ionic character of the TM—ER bonds and the extent of the TM→ ER π backbonding contribution to the metal-ligand orbital interactions.[84] Typically, neutral complexes such as [$(CO)_4FeEX$], [$Fe(EX)_5$] and [$Ni(EX)_4$] have been studied and the effect of E, X and ancillary π-acidic carbonyl ligands on the nature of the M—E bond has been investigated.

Four bonding models (A-D) can be considered for the covalent interaction between group 13 (ER) and transition metal (ML_n) fragments (Figure 4).

$RE \longrightarrow ML_n$	$RE \rightleftarrows ML_n$	$RE \equiv ML_n$	$RE = ML_n$
A	B	C	D

Figure 4

Structures A, B, and C imply that the ER ligand coordinates in a singlet state; whereas structure D implies that the RE fragment bonds as a triplet state. Structure A is a purely σ-bonded model with a simple donor-acceptor bond between E and M, while structures B and C feature, respectively, one and two additional back bonding interactions from the transition metal to the group 13 element, thus forming overall double and triple bonds.[90]

Macdonald and Cowley recently investigated the nature of the bonding in diyl complexes such as [$(CO)_4FeER$] (R = Cp, Me or $N(SiH_3)_2$) by DFT, assessing the relative merits of the proposed bonding models. The uncoordinated ER ligands were also studied to establish their ground states, frontier orbitals, and singlet-triplet energy gaps with a view to understanding the coordination behaviour of ER ligands.[91] Generally, the HOMO of ER ligands exhibits distinctly lone pair (σ type) character with the magnitude of the 'lone pair' contribution to the wave functions decreasing with atomic number. The nature of the π-type LUMOs and the highest occupied π-type orbitals are dependent upon the conjugative ability of the R substituent. With MeM ligands, the p_x and p_y orbitals on the group 13 element are essentially vacant. However ER fragments with π-donating substituents such as Cp populate the p_x and/or p_y orbitals on M. Such interactions are most significant for boron as a result of its greater electronegativity and more effective π-bonding capacity. In addition, boron has a smaller atomic radius and its acceptor orbitals are lower in energy.

In general, the DFT calculations indicate that regardless of the substituent R, each ER fragment has a singlet ground state, with the singlet-triplet energy gap, $\Delta E_{S\text{-}T}$, increasing with atomic number. Singlet-triplet gaps are also larger with π-donating substituents. In principle, the RE ligands with non-π-donating R substituents could possess some π-acceptor capability (bonding models B and C) but evidence of such metal-ligand back-bonding was only found in the case of [$MeBFe(CO)_4$] and not for the heavier group 13 analogues. Therefore it was proposed that RE ligands effectively behave as two-electron donors (*i.e.* bonding model A).[91]

Frenking *et al.,* proposed that the TM—E bonds of homoleptic complexes, such as [$Fe(ER)_5$] and [$Ni(ER)_4$], have a stronger ionic character than they have in [$(CO)_4FeER$]. The contribution of the TM→ ER π backdonation to the ΔE_{orb} term is clearly higher in the homoleptic complexes where no other competing π acceptor ligands, such as CO, are present.[84]

Recently Aldridge *et al.,* have sought to characterise the nature of the TM—E interaction in cationic diyl complexes, such as [$Cp^*Fe(CO)_2EMes)]^+$ (E = B, Al, Ga), and assess the relative merits of a simple bonding model for comprising of E→ Fe σ donation, supplemented by Fe→ E π back-bonding. On the evidence of molecular orbital compositions, BDEs and ΔE_{orb} values and σ/π covalent ratios, it was concluded the bonding in the cationic terminal borylene complex, $[Cp^*Fe(CO)_2(BMes)]^+$, **1.85**, is best described as a Fe═B double bond. For the heavier congeners (E = Al, Ga), π back bonding may become significant due to the lowering of the energy of the E-based acceptor orbital for cationic species.[92]

1.7.6 Reactivity of transition metal complexes of group 13 diyls

Despite the widespread interest in the synthetic and structural chemistry of metalladiyls, the fundamental chemical reactivity of such complexes remains virtually unexplored.

i) Substitution /addition reactions of transition metal complexes of group 13 diyls

Transition metal complexes of group 13 diyls feature relatively polar M—E bonds and the large steric demand for ER ligands means that dissociative or associative reactions, at the metal centre, are unlikely. In fact sterically saturated monomeric complexes $[M(ECp^*)_4]$ are kinetically inert. Related cluster complexes $[M_a(ER)_b]$ however react with a variety of ligands, such as CO and phosphines, yielding di- and trinuclear substitution products. Reaction of $[M_2(GaCp^*)_2(\mu^2\text{-}GaCp^*)_3]$, **1.86**, with PPh_3 yields the mono- or disubstituted complexes $[MPt(GaCp^*)(PPh_3)(\mu^2\text{-}GaCp^*)_3]$ (M = Pd, Pt), **1.87**, and $[Pd_2(PPh_3)(\mu^2\text{-}GaCp^*)_3]$, **1.88**, respectively. Heteroleptic complexes, $[M(GaCp^*)_{4x}(L)_x]$ (x = 1-4), are not usually accessible by substitution reactions, however the addition of a chelating diphosphine ligand, such as dppe, to $[M_2(GaCp^*)_2(\mu^2\text{-}GaCp^*)_3]$, **1.89**, leads to the complete substitution of GaCp* units yielding $[M(dppe)_2]$ (M = Pd, Pt), **1.90**, quantitatively.[58]

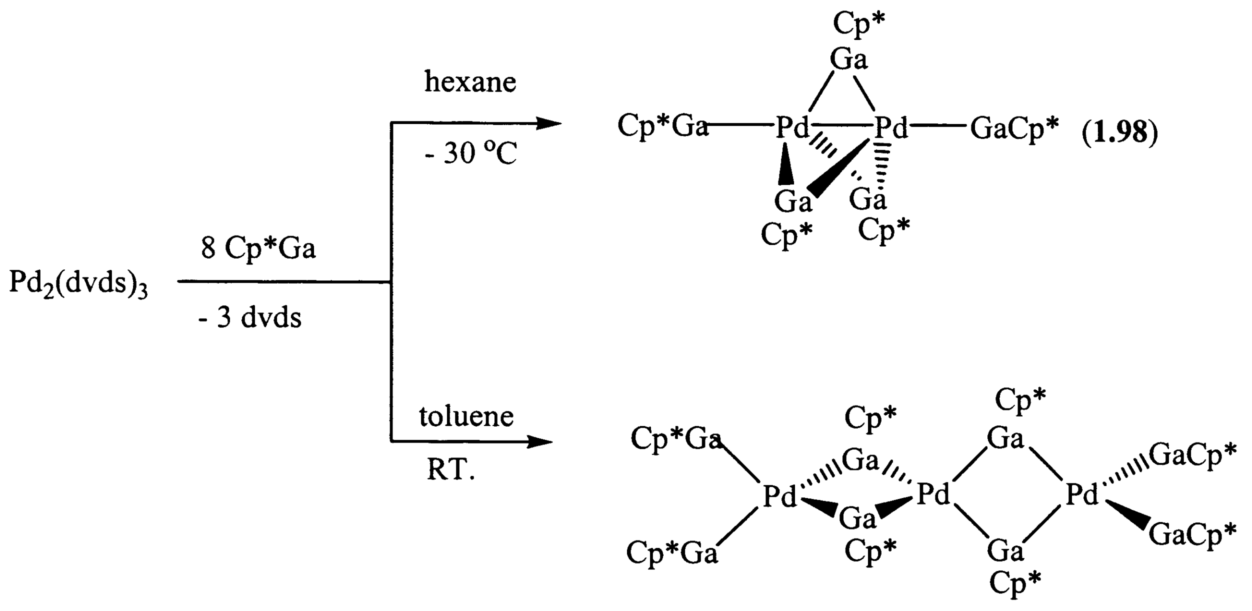
ii) Bond activation reactions of transition metal complexes of group 13 diyls

The strong polar donor/acceptor bond in $[L_nM\leftarrow ECp^*]$ which increases the electron density of the transition metal centre considerably upon coordination is of interest from a classical bond activation viewpoint and might be expected to facilitate oxidative addition reactions. This is because this type of bonding causes the metal centre to become more electron rich and thus more susceptible to oxidation. However, the full potential of ER fragments in such reactions remains to be explored. Reaction of $[Ni(COD)_2]$ with four equivalents of AlCp* in benzene yields the compound $[NiH(AlCp^*)_3(AlCp^*Ph)]$, **1.91**, quantitatively and not $[Ni(AlCp^*)_4]$, **1.92**, as expected. The proposed method of activation involves the formation of the reactive intermediate $[(AlCp^*)_nNi(H)(C_6H_5)]$, migration of the phenyl group, followed by oxidation of the aluminium, formation of a strong Al—C bond and coordination of a fourth equivalent of AlCp*.[73] Another example of C—H bond activation is the reaction of [(η^6-$C_6H_5CH_3$)Fe(η^4-C_4H_8)] with AlCp* which gives the unusual chelating system Cp*Al-CH_2(C_5Me_4)Al-CH_2(C_5Me_4)Al, **1.93**.[58] GaCp* has also been involved in bond activation reactions. Reaction of [Cp*Rh(CH_3)$_2$L] (L = dimethyl sulfoxide, pyridine) with GaCp* gives the zwitterionic rhodium species [Cp*Rh{(η^5-C_5Me_4)Ga(CH_3)$_3$}], **1.94**. The driving force of which is presumably the migration of the phenyl groups to ECp* (E = Al, Ga), oxidation of the group 13 metal and the formation of a strong E—C bond.[93]

iii) Formation of cluster complexes by transition metal complexes of group 13 diyls

In general, diyls such as ECp* can act as suitable stabilising ligands in metal cluster compounds. Neutral homoleptic cluster compounds of the type [M_a(ECp*)$_b$] (M = Pd, Pt; b > a >1) represent a relatively new field in the coordination chemistry of ER fragments. Such compounds can be regarded as the basic building blocks of larger transition metal ECp* clusters such as Schnöckel's elaborate cluster compound [Al_{38}(AlCp*)$_{12}$], **1.95**.[94]

Monomeric compounds of the type [M(GaCp*)$_4$] (M = Pt, Pd), can serve as building blocks for the synthesis of dinuclear cluster complexes [MPt(GaCp*)$_5$] with terminal and bridging GaCp* ligands. For example, the 1:1 reaction of [Pt(COD)$_2$] and [M(GaCp*)$_4$] followed by addition of GaCp* yields [Pt_2(GaCp*)$_2$(μ^2-GaCp*)$_3$], **1.96**, and [PtPd(GaCp*)$_2$(μ^2-GaCp*)$_3$], **1.97**.[58] Homoleptic cluster complexes can also be prepared by direct substitution reactions between ER fragments and transition metal complexes with labile ligands. The subtle kinetic control of cluster formation is probably best exemplified by the reaction between [Pd_2(dvds)$_3$] and GaCp* (dvds = 1,3 divinyl-1,1,3,3-tetramethyldisiloxane). Two different homoleptic clusters are formed depending upon reactions conditions, **1.98** and **1.99** (Scheme 30).[58]



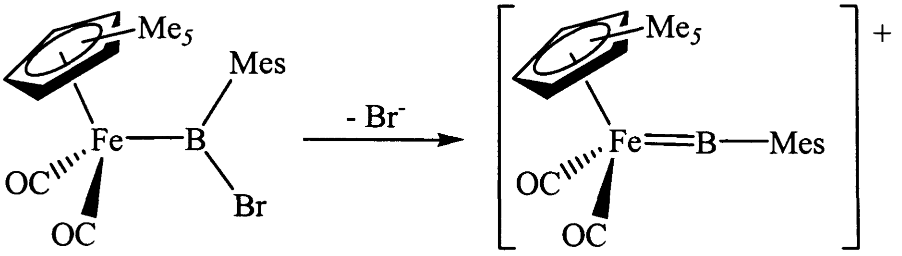
(1.98)

(1.99)

Scheme 30

1.8 Aims of Current Research

The chemistry of low coordinate or multiply-bonded group 13 ligand systems continues to be the focus of considerable research effort,[4,5] and in some cases significant controversy.[7,8] Within this area, a systematic appraisal of both structural and reaction chemistry for diyl systems, $L_nM(EX)$ (E = B, Al, Ga, In), lags behind that of analogous group 14 systems (such as carbenes and silylenes).[95] To a certain extent, this reflects the limited number of structurally authenticated complexes reported so far in the literature which have typically been synthesised *via* salt elimination or ligand substitution methodologies. With a view to expanding the number of synthetic routes available for the preparation of unsaturated group 13 systems, a new synthetic approach to two-coordinate diyl complexes has recently been developed by our research group, using halide abstraction chemistry to generate the Fe=B double bond in $[Cp^*Fe(CO)_2B(Mes)]^+[BAr^f_4]^-$, **1.85**, (Scheme 31).[96]



(1.85)

Scheme 31

Preliminary computational analyses have suggested that the positive charge in cationic terminal diyl species, $[L_nM(EX)]^+$, rests primarily at the group 13 centre {e.g. Mulliken charges of +0.438, +0.680 and +0.309 for $[Cp^*Fe(CO)_2E(Mes)]^+$, E = B, Al, Ga}, and that M→ E back-bonding may contribute appreciably to the overall metal ligand interaction {e.g. a 38 % π contribution to the FeB bonding density in $[Cp^*Fe(CO)_2B(Mes)]^+$}. Hence the Fe=B double bond in $[Cp^*Fe(CO)_2B(Mes)]^+$ can be described simplistically as comprising of B→ Fe σ donor and Fe→ B π acceptor components (Figure 5).[97]

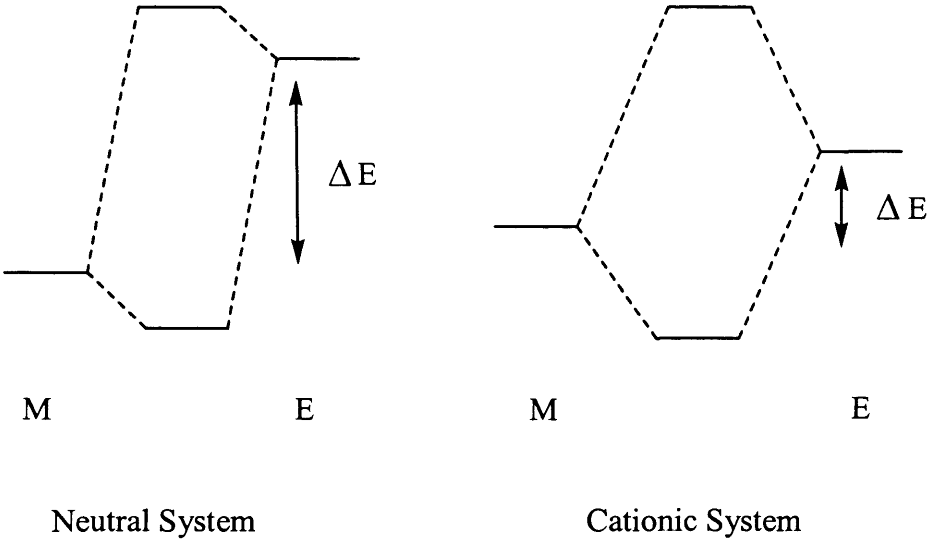


Figure 5

Therefore it is our intention to extend this synthetic approach from boron to the heavier group 13 elements and investigate the use of halide abstraction chemistry to generate cationic derivatives of gallium and indium. However, in view of the small number of reported examples of neutral three-coordinate systems of the type L_nM—E(X)(E'R'$_x$) (E = Ga, In; X = halide), the preparation of these key halogallyl precursors suitable for halide abstraction, is first necessary. These three coordinate gallium systems will be targeted *via* two different synthetic approaches: (i) firstly direct substitution of a gallium—bound halide by an organometallic anion; and (ii) *via* a two step strategy involving insertion of a gallium(I) halide into a metal-halogen (or metal-metal) bond, followed by substitution at the group 13 center by an suitably sterically hindered anionic nucleophile.

The nature of the M—E bond in such cationic systems will then be analysed by comparative spectroscopic, structural and computational studies as a function of the element E, thereby probing the controversial subject of multiple bonding involving the heavier group 13 elements. In addition, preliminary studies of the fundamental reactivity of these novel cationic systems will also be investigated in reference to the cationic terminal borylene complex, **1.85**.

1.9 References

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Chapter Two
Experimental Techniques

2.1 The Manipulation of Air-Sensitive Compounds

Due to the highly sensitive nature of many of the compounds described in this thesis, it was essential to rigorously exclude both air and moisture for their synthesis and manipulation. As a result, standard Schlenk line and high vacuum techniques were routinely utilised and therefore these practices are discussed briefly in this chapter. A more detailed discussion of inert atmosphere techniques can be found in a number of textbooks.[1,2]

2.1.1 Inert atmosphere techniques

One of the most common methods for the manipulation of air-sensitive compounds is by excluding air using an inert atmosphere. The two such methods routinely used during the course of this work were: (i) Schlenk line techniques, which provide an easy and convenient method of manipulating air sensitive materials on the bench top *via* the use of specially designed glassware; and (ii) glove box techniques, which enable the manipulation and storage of solid compounds under an inert atmosphere in a specially designed unit.

For this project, a Schlenk line, the general set-up of which is illustrated in Figure 1, provided the inert atmosphere under which both large and small quantities of solids and liquids could be manipulated. The line was made of a Pyrex glass tube incorporating ground glass joints and featured a number of two-way stopcocks, which enabled the internal atmosphere to easily be switched between vacuum and an inert gas, which in this case was argon. The ground-glass stopcocks were lightly lubricated with 'Dow-Corning High Vacuum' grease to minimise leaks. Glass reaction vessels were connected *via* one of the three heavy-walled rubber tubes. Having several ports on the line is convenient because several different flasks or reaction vessels may be used simultaneously.

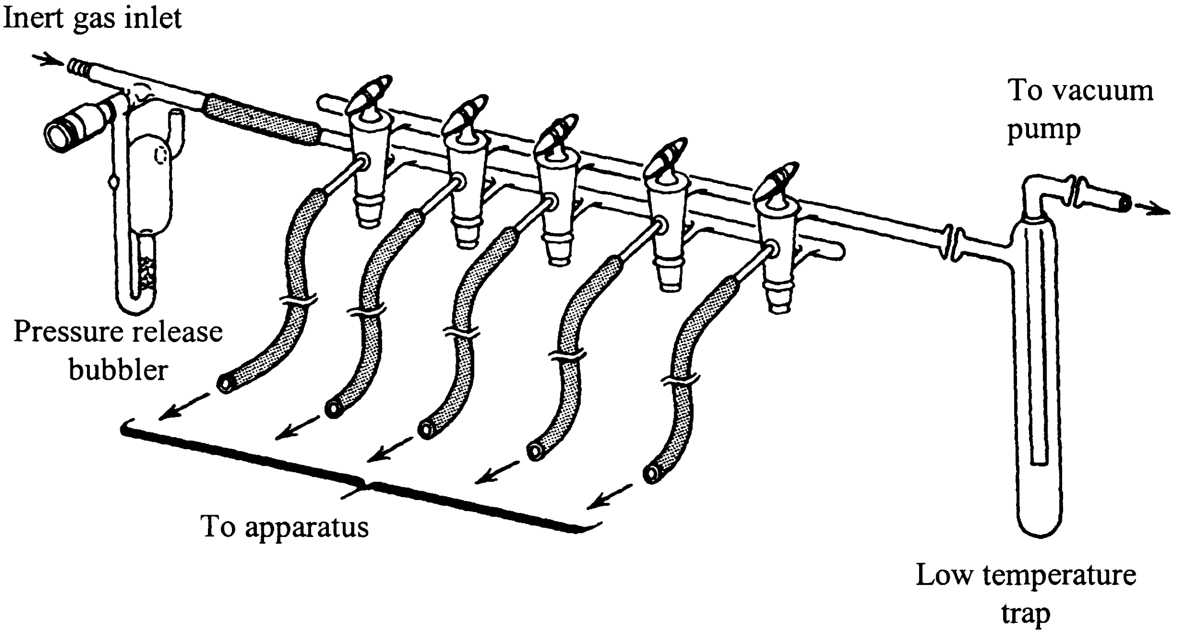

Figure 1: A Schlenk line

Evacuation was achieved by a mechanical vacuum pump; a low temperature liquid nitrogen cooled trap served to collect and thus prevent volatiles contaminating the vacuum pump. This set-up enabled evacuation to a pressure of typically 10^{-2} Torr, which was monitored by a Pirani pressure gauge. The pure inert gas (Argon) was introduced into the apparatus from a cylinder through a scavenger column packed with molecular sieves to remove any traces of moisture and a mercury bubbler prevented any excess pressure. An inert atmosphere was achieved by the 'pump-and-fill' method, a technique which involves the repeated evacuation of glassware followed by its filling with an inert gas. This standard pump-and-purge process was typically repeated at least three times in order to generate an inert atmosphere. Both liquids and solutions were transferred between Schlenk vessels *via* standard cannular and syringe techniques using rubber septa.

Air-sensitive solids used in this work were conveniently manipulated in a 'Saffron Scientific Omega' glove box. This specialist piece of equipment consists of a large sealed stainless steel chamber with a toughened glass viewing panel, which could be accessed *via* two neoprene gloves and an evacuable side-port. An inert atmosphere (nitrogen) was supplied by a gas cylinder, which was re-circulated internally through catalyst, molecular sieve and solvent scrubbing columns to provide an atmosphere with oxygen and moisture levels less than 5 ppm and 10 ppm, respectively.[3]

2.1.2 High vacuum techniques

Procedures such as vacuum sublimation or the removal of trace solvent from compounds where a mechanical pump on a Schlenk line provided insufficient vacuum were performed on a high vacuum line. This system was simply a single-manifold design consisting of a Pyrex glass tube incorporating a number of Young's greaseless stopcocks. Evacuation was achieved by a combination of a mercury diffusion pump and a mechanical pump, which enabled a pressure of *ca.* 10^{-4} Torr to be achieved. This was monitored by the use of a Tesla coil, which produced a high frequency discharge at pressures between 1 and 10^{-3} Torr. An associated low-temperature trap served to prevent contamination of the vacuum pump.

2.2 Physical Measurements

2.2.1 NMR spectroscopy

NMR spectra were recorded on either Bruker AM-400 or Jeol Eclipse 300 Plus FT-NMR spectrometers. Residual signals of solvents were used for ^{1}H and ^{13}C NMR, and a sealed tube containing a solution of $[^{n}Bu_4N][B_3H_8]$ in $CDCl_3$ was used as an external reference for ^{11}B. $CFCl_3$ and an 85% solution of H_3PO_4 were used as the external references for ^{19}F NMR and ^{31}P NMR respectively. Samples were prepared by transferral (*via* cannula) of a sufficient volume (*ca.* 1 cm^3) of the freshly prepared solution into a Young's NMR tube placed in an Schlenk, which had previously been evacuated, purged and flamed.

2.2.2 Infrared spectroscopy

Infrared spectra were measured on a Nicolet 500 FT-IR spectrometer. Disks of air and moisture sensitive samples were either recorded as a solution in dichloromethane or prepared by the compression of a powdered sample in a ten-fold excess of KBr in the glove box. The KBr had previously been heated under high vacuum prior to use.

2.2.3 Mass spectrometry

Mass spectra were recorded at the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea. Perfluorotributylamine and polyethylenimine were used as the standards for high resolution EI and ES mass spectra, respectively.

2.2.4 X-Ray crystallography

Data collection was carried out on an Enraf Nonius Kappa CCD diffractometer (at either the EPSRC Crystallography Service, University of Southampton or at Cardiff University) and structure solution and refinement were carried out by Prof. C. Jones, Dr. L.-L Ooi, or Miss J. Day (Cardiff).

2.2.5 Theoretical calculations

Theoretical calculations were performed by Dr. D. J. Willock, Dr. A. Rossin and Miss N. Coombs (Cardiff University). Calculations were carried out, in part, using ‘Glyndwr’, a Silicon Graphics Multiprocessor Origin 200 machine. A detailed computational methodology can be found in the appendix.

2.3 Purification and Preparation of Essential Solvents and Reagents

Many of the compounds synthesised during the course of this research had precursors that were not readily available. Such starting materials were prepared from commercially available reagents, some of which were further purified before use. A list of commercial sources and purification procedures is given in Table 1.

Table 1: Commercial sources and purification procedures of essential solvents and reagents

Compound	**Source**	**Quoted purity**	**Procedure**
Reagents			
Cyclopentadienyliron-dicarbonyl dimer	Fluorochem	*a*	Used as supplied
$Fe(CO)_5$	Aldrich	99.999%	Used as supplied
^nBuLi (1.6M in hexanes)	Aldrich	*a*	Used as supplied
Magnesium turnings	Avocado	>99%	Activated using iodine in acetone prior to use
HCl	Fisher	37%	Used as supplied
Bromine	Lancaster	>99%	Used as supplied
1,2-Dibromoethane	Aldrich	98%	Used as supplied
Sodium	Lancaster	99%	Used as supplied
3,5-*Bis*(trifluoromethyl)-bromobenzene	Avocado	98%	Used as supplied
1,3,5-tri-*tert*-butylbenzene	Fluka	>97%	Used as supplied
Mercury	Johnson Matthey Chemicals	99.998%	Used as supplied
Methyl iodide	Avocado	99%	Used as supplied
Trimethyl phosphate	Aldrich	97%	Used as supplied
Iodine (Resublimed)	Acros	99.5%	Used as supplied
Gallium	Aldrich	99.999%	Used as supplied
Gallium Trichloride	Aldrich	99.999%	Used as supplied
$dppePtCl_2$	*b*	*a*	Used as supplied
B-bromocatecholborane	*c*	*a*	Used as supplied
Bis(cyclopentadienyl zirconium dichloride)	Aldrich	98+%	Used as supplied

2,2,6,6-Tetramethylpiperidine	Aldrich	99+%	Dried over molecular sieves prior to use
[PPN]Cl	Aldrich	97%	Used as supplied
[^{n}Bu$_4$N]BF$_4$	Fluka	98%	Used as supplied
Solvents			
Toluene	Fisher	>99%	Heated under reflux over sodium followed by distillation.
Hexane	Fisher	>99%	Heated under reflux over potassium followed by distillation.
Dichloromethane	Fisher	>99%	Heated under reflux over CaH_2 followed by distillation.
Diethyl Ether	Fisher	>99%	Heated under reflux over sodium followed by distillation.
THF	Fisher	>99%	Heated under reflux over sodium followed by distillation.
o-Xylene	Aldrich	>99%	Heated under reflux over sodium followed by distillation.

Deuterated solvents			
Benzene-d_6	Gross Scientific Instruments Ltd.	99.6 atom%	Stored under argon over potassium mirror
Chloroform-d	Aldrich	99.8 atom%	Stored under argon over flamed-out molecular sieves
Methylene chloride-d_2	Gross Scientific Instruments Ltd.	99.8 atom%	Stored under argon over flamed-out molecular sieves
Gases			
Argon	B.O.C	*a*	Used as supplied
Nitrogen	B.O.C	*a*	Used as supplied

[a] Information not available. Courtesy of [b] Dr. A. Rossin, [c] Miss N. Coombs; School of Chemistry, Cardiff University, respectively.

2.4 Preparation of Precursors

Many of the compounds synthesised during the course of this research had precursors that were not readily available for this research, and therefore the synthetic routes are described here.

2.4.1 Preparation of transition metal anions

i) Preparation of $[Cp^*Fe(CO)_2]_2$

Cp*H was prepared according to the standard literature procedure of Fendrick, Schertz, Minz and Marks.[4] Typically, Cp*H (10 g, 74 mmol) and $Fe(CO)_5$ (18.5 cm^3, 27.5 g, 140 mmol) were heated under reflux in xylenes (40 cm^3) for 48 h. An additional 9.5 cm^3 of $Fe(CO)_5$ was added after the first 24 h. After cooling to room temperature, the product was filtered, washed with hexane and recrystallised from CH_2Cl_2 to yield $[Cp^*Fe(CO)_2]_2$ in 75%

yield. Characterisation was achieved by comparison of the ^1H, ^{13}C NMR and IR data with that reported in the literature.[5]

ii) Preparation of $Na[Cp^*Fe(CO)_2]$ [6]

Typically, $[Cp^*Fe(CO)_2]_2$ (4.8 g, 9.7 mmol) was dissolved in THF (180 cm^3) and stirred over sodium amalgam (3.7 g, 16 equivalents) for 48 h at room temperature. Filtration and removal of the solvent *in vacuo* gave the sodium salt $Na[Cp^*Fe(CO)_2]$ which was subsequently washed several times with hot toluene (90 °C) and hexane, before being dried by continuous pumping under high vacuum to give $Na[Cp^*Fe(CO)_2]$ in 40 % yield. The clean product was stored in a glove box prior to use.

iii) Preparation of $Na[CpFe(CO)_2]$ [7]

In an analogous manner to the preparation of $Na[Cp^*Fe(CO)_2]$, $[CpFe(CO)_2]_2$ (7 g, 19.8 mmol) was dissolved in THF (80 cm^3) and transferred *via* cannula onto sodium amalgam (1.5 g, 3 equivalents of Na) and stirred for 24 h at room temperature. Filtration and removal of the solvent *in vacuo* gave the sodium salt $Na[CpFe(CO)_2]$. This was subsequently washed several times with hot toluene (90 °C) and hexane, before being dried by continuous pumping under high vacuum to give $Na[CpFe(CO)_2]$ in 50 % yield.

2.4.2 Preparation of $[2,4,6\text{-}^tBu_3C_6H_2GaCl_2]$

i) Preparation of $[2,4,6\text{-}^tBu_3C_6H_2Br]$ [8]

A two-necked round-bottomed flask fitted with a reflux condenser was charged with 1,3,5-tri-*tert*-butylbenzene (10 g, 41 mmol) and trimethyl phosphate (110 cm^3). The temperature of the reaction mixture was raised to 85 °C to dissolve the hydrocarbon then lowered to 70 °C and bromine (8.47 g, 2.7 cm^3, 53 mmol) added. The reaction mixture was then stirred at this temperature for 30 h, before being cooled to room temperature and quenching with iced water (350 cm^3). The product was then filtered, extracted into petroleum ether (40-60) and the organic layer washed with saturated sodium metabisulphite solution. The solution was dried over magnesium sulphate and volatiles were removed *in vacuo.* Recrystallisation from hot ethanol yielded $[2,4,6\text{-}^tBu_3C_6H_2Br]$ as a white powder in 40% yield. Characterisation was achieved by comparison of ^1H NMR data with that reported in the literature.[8]

ii) Preparation of [2,4,6-^{t}Bu$_3$C$_6$H$_2$Li(THF)$_2$] [9]

^{n}BuLi (4.0 cm^3, of a 1.6 M solution, 6.2 mmol) was added to a solution of 2,4,6-^{t}Bu$_3$C$_6$H$_2$Br (2.0 g, 6.2 mmol) in hexane (20 cm^3) and THF (5 cm^3) at –78 ^{0}C. The mixture was stirred at this temperature for 3 h and then at 0 °C for a further 1 h. The supernatant solution was subsequently filtered from the white precipitate, which was washed with hexane and volatiles were removed *in vacuo* to yield [2,4,6-^{t}Bu$_3$C$_6$H$_2$Li(THF)$_2$] as a white solid in 50 % yield. Characterisation was achieved by comparison of ^{1}H NMR data with that reported in the literature.[9]

iii) Preparation of [2,4,6-^{t}Bu$_3$C$_6$H$_2$GaCl$_2$] [10]

A solution of GaCl$_3$ (0.448 g, 2.54 mmol) in hexane (30 cm^3) was added dropwise with stirring to a suspension of [2,4,6-^{t}Bu$_3$C$_6$H$_2$Li(THF)$_2$] (0.643 g, 2.54 mmol) in hexane (100 cm^3) at –78 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 12 h. Filtration and removal of the solvent *in vacuo* yielded [2,4,6-^{t}Bu$_3$C$_6$H$_2$GaCl$_2$] as a white solid in 78 % yield. Characterisation was achieved by comparison of ^{1}H and ^{13}C NMR data with that reported in the literature.[10]

2.4.3 Preparation of transition metal halides

i) Preparation of [CpFe(CO)$_2$Br] [11]

A solution of bromine (2.06 g, 0.66 cm^3, 25.8 mmol) in CHCl$_3$ (60 cm^3) was added dropwise to a solution of [CpFe(CO)$_2$]$_2$ (4.0 g, 11.3 mmol) in CHCl$_3$ (200 cm^3) at 0 °C over 1 h. The reaction mixture was then stirred at room temperature for 3 h, washed with a saturated Na$_2$S$_2$O$_3$ solution (3 x 50 cm^3) and water (100 cm^3), dried over magnesium sulphate and filtered. Concentration followed by the addition of hexane yielded [CpFe(CO)$_2$Br] as a orange crystalline solid in 72 % yield. Characterisation was achieved by comparison of ^{1}H NMR and IR data with that reported in the literature.[11]

ii) Preparation of [CpFe(CO)$_2$I] [12]

A mixture of [CpFe(CO)$_2$]$_2$ (2 g, 5.65 mmol) and iodine (2 g, 7.88 mmol) in CHCl$_3$ (50 cm^3) was heated at reflux for 30 min under an inert atmosphere. The reaction mixture was then cooled, washed with a saturated Na$_2$S$_2$O$_3$ solution (3 x 50 cm^3), the chloroform layer separated, and the solvent removed *in vacuo.* The resulting black crystalline solid washed several times with hexane (40 cm^3) to yield [$CpFe(CO)_2I$] in 75% yield. Characterisation was achieved by comparison of ^{1}H NMR and IR data with that reported in the literature.[12]

iii) Preparation of [$CpRu(PPh_3)_2Cl$] [13]

Triphenylphosphine (21 g, 0.08 mol) was dissolved in degassed ethanol (1000 cm^3) by gentle heating, in a 2000 cm^3 round-bottomed flask equipped with a reflux condenser and a 500 cm^3 dropping funnel. Hydrated ruthenium trichloride (5 g, 0.02 mol) was dissolved in degassed ethanol (100 cm^3), heated to reflux, and gently allowed to cool. To this dark-brown ruthenium trichloride solution, freshly distilled cyclopentadiene (10 cm^3, 0.12 mol) was added. The mixture was then added dropwise to the triphenylphosphine solution over a period of 10 min under reflux. The resulting dark brown reaction mixture was refluxed for an additional 2 h during which time a dark orange solution had formed. The solution was filtered and cooled to – 30 °C. The pale orange liquid was decanted and the orange crystals were washed with cold ethanol (5 x 20 cm^3), 40-60 petrol (5 x 20 cm^3), and dried *in vacuo* to yield [$CpRu(PPh_3)_2Cl$] as a orange crystalline solid in 72 % yield. Characterisation was achieved by comparison of the ^{1}H and ^{31}P NMR data with that reported in the literature.[13]

iv) Preparation of [CpRu(dppe)Cl] [14]

To a 250 cm^3 round-bottomed flask equipped with a reflux condenser under argon, was added dppe (1.24 g, 3.11 mmol) and [$CpRu(PPh_3)_2Cl$] (1.5 g, 2.07 mmol) dissolved in toluene (120 cm^3). The red reaction mixture was then refluxed for 2 h, during which time a bright orange solution formed. The solution was filtered and volatiles removed *in vacuo*. The resulting yellow solid was then washed with degassed hexane (3 x 20 cm^2) and dried *in vacuo* affording [CpRu(dppe)Cl] in 38 % yield. Characterisation was achieved by comparison of ^{1}H and ^{31}P NMR data with that reported in the literature.[14]

2.4.4 Preparation of $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ [15]

A three-necked flask fitted with a reflux condenser and an addition funnel was charged with magnesium (1.0 g, 41.7 mmol), $NaBF_4$ (0.7 g, 6.1 mmol) and diethyl ether (150 cm^3). Dibromoethane (0.5 cm^3, 5.7 mmol) was added and the flask was heated for several minutes to initiate the reaction. A solution of 3,5-*bis*(trifluoromethyl)bromobenzene (10.0 g, 5.9 cm^3, 34.1 mmol) in diethyl ether (50 cm^3) was added over a period of 30 min, the reaction mixture was then refluxed for 30 min and stirred at room temperature overnight. The solution was added to Na_2CO_3 (16 g, 151 mmol) in water and stirred for 30 min, and filtered. The ether layer was then separated and the aqueous layer washed with ether. The combined organic layers were dried over sodium sulfate and treated with decolourising charcoal. Filtration of the solution and removal of volatiles gave rise to an oily solid which was then dissolved in benzene (200 cm^3) and water removed by azeotropic distillation. The solvent volume was reduced and cooled to room temperature; the solution was then filtered from the solid product *via* cannula. The solid was washed with hexane and dried under high vacuum for 12 h affording $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ in 32 % yield. Characterisation was achieved by comparison of ^1H, ^{11}B, ^{13}C and ^{19}F NMR data with that reported in the literature.[15]

2.5 References

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Chapter Three

Synthesis of Gallyl Precursors *via* Salt Elimination Methodology

3.1 Introduction

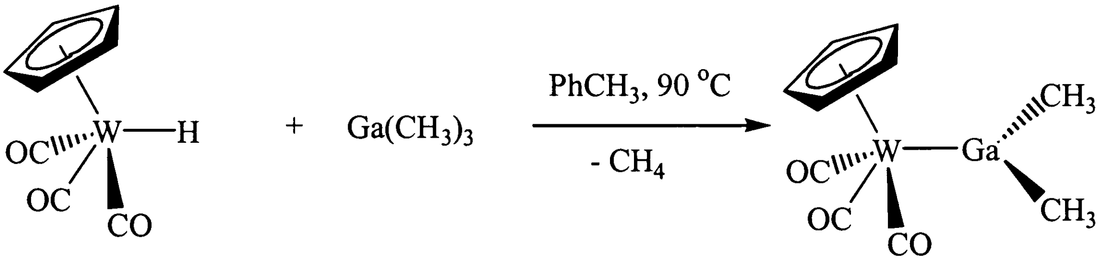
This chapter explores the synthesis of key neutral halogallyl precursors of the types L_nM—Ga(Aryl)X and $(L_nM)_2GaX$ (X = halide) featuring three-coordinate gallium centres suitable for the synthesis of two coordinate cationic systems *via* halide abstraction chemistry.

Transition metal halogallyl precursors have been prepared *via* direct substitution of a gallium-bound halide by an organometallic anion. Enforcement of the required trigonal planar ligand geometry has been achieved by the use of sterically demanding metal fragments, such as $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]$, and/or very bulky gallyl substituents, namely $[(2,4,6,\text{-}^tBu_3C_6H_2)]$.

3.2 Introduction to Transition Metal Gallyl Complexes

Whereas transition metal boryl complexes (L_nM—BX_2) have been the subject of considerable recent research effort and a large number of structurally authenticated boryl complexes have been reported,[1,2] examples of analogous three-coordinate gallyl complexes are relatively rare. This is not surprising given the tendency of halogallium systems in general to increase the coordination number at the group 13 center through bridging halide ligands.[3] Consequently little is known about the chemistry of transition metal gallyl complexes with reactivity studies principally confined to adduct formation.

The first structurally authenticated transition metal gallyl complex was elegantly prepared in 1977, *via* alkane elimination. Reaction between $[Cp(CO)_3WH]$ and $[Ga(CH_3)_3]$, at raised temperatures with photoactivation, resulted in the formation of $[Cp(CO)_3WGa(CH_3)_2]$, **1.1**, and the elimination of a single equivalent of methane (Scheme 1).[4]

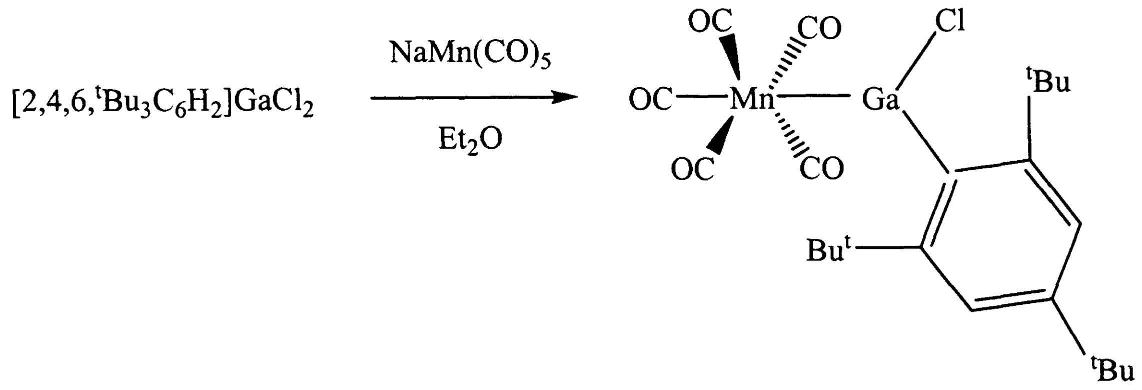


(1.1)

Scheme 1

The development of new synthetic routes for the preparation of transition-metal gallyl complexes has helped to broaden this field. Four routes are currently adopted in the synthesis of gallyl complexes: alkane elimination, insertion of metal(I) halides, dehalosilylation and most commonly, salt elimination. Examples of each route are found in the literature. The preparation of **1.1**, as depicted in Scheme 1, represents an example of a gallyl complex synthesised by alkane elimination.[4] Another possible route to the generation of gallyl complexes is the insertion of a metal(I) halide (EX) into a metal—metal or metal—halide bond. Green *et al.*, have prepared a number of compounds with transition metal—gallium bonds such as [$Mo(CO)_3(\eta$-$C_5H_4Me)GaI_2.Et_2O$], **1.9**, as a result of the formal insertion of 'GaI' into metal—halogen bonds.[5] Recently, Ogino *et al.*, have shown that $FpGaCl_2$ or Fp^*GaCl_2, **1.23,** first reported by Barron *et al.*, can alternatively be prepared in almost quantitative yields *via* the dehalosilylation reaction between $FpSiMe_3$ or Fp^*SiMe_3 and $GaCl_3$ in toluene or hexane respectively.[6] The most popular synthetic route for the generation of gallyl complexes, however, is the reaction between an anionic transition metal fragment and a halogallane precursor. Power *et al.*, successfully used this approach to prepare several tricoordinate organogallium-iron complexes featuring terminal alkyl gallyl groups, *e.g.* [$Cp(CO)_2FeGa(^tBu)_2$], **1.3**, [$\{Cp(CO)_2Fe\}_2Ga(^tBu)$], **1.10**, and [$Cp(CO)_2FeGa(^tBu)_2.\{Cp(CO)_2Fe\}_2$], **1.11**.[7] In 1994, Cowley *et al.* prepared the only structurally authenticated three-coordinate halogallyl system using this salt elimination methodology. The complex [$Mn(CO)_5Ga(Mes^*)Cl$], **1.12**, was synthesised by the treatment of

[(2,4,6,-$^{t}Bu_3C_6H_2$)$GaCl_2$] with [$NaMn(CO)_5$] in diethyl ether (Scheme 2). This compound represents only the third example of a compound featuring a gallium—manganese bond.[8]



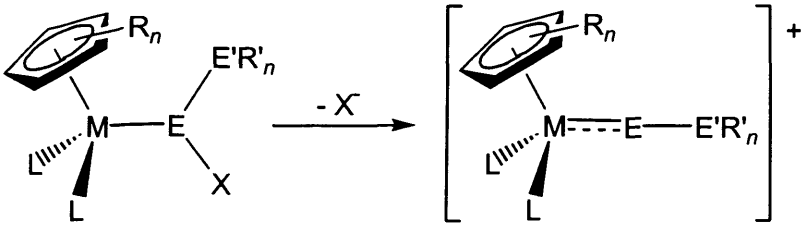
(1.12)

Scheme 2

3.3 Research Proposal

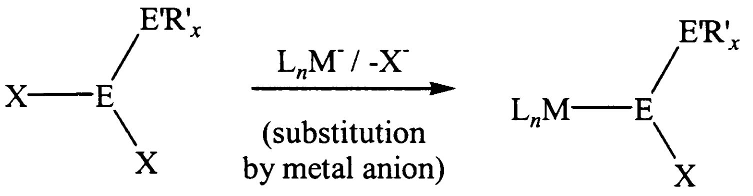
The chemistry of low coordinate or multiply-bonded group 13 ligand systems is currently a very topical area of main group chemistry, attracting considerable research effort,[9,10,11] and in some cases significant controversy.[12,13] Interesting recent examples include Uhl's unusual and fascinating homoleptic Ni(0) complexes, *i.e.* [Ni(E{C(SiMe$_3$)$_3$}$_4$] (E = In, (**1.56**), Ga (**1.80**)),[14] and the iron—gallium diyl complex, [(Ar*Ga)Fe(CO)$_4$], **1.61**, Ar* = 2,6-(2,4,6-Pr$^i_3$C$_6$H$_2$)$_2$C$_6$H$_3$, reported by Robinson in 1997.[12]

Systematic studies to probe the nature of the bonding in two coordinate gallylene complexes, however have been hindered by the scarcity of structural data available on these systems. At present synthetic routes to such species are principally confined to salt elimination and ligand substitution methodologies. One of the primary aims of this project was to attempt to broaden the scope of synthetic methodologies available by examining the use of halide abstraction chemistry to generate cationic derivatives of gallium (Scheme 3).



Scheme 3

However, in view of the small number of reported examples of neutral three-coordinate systems of the type L_nM—E(X)(E'R'$_x$) (E = Ga, In; X = halide),[8,15] the preparation of these key halogallyl precursors suitable for halide abstraction, was first necessary. Therefore it was our intention to synthesise such three coordinate gallium systems *via* direct substitution of a gallium—bound halide in an organodihalogallane by an organometallic anion (Scheme 4).[5] Enforcement of the desired trigonal planar ligand geometry would be achieved by using sterically demanding metal fragments, such as [Cp*Fe(CO)$_2$], and/or very bulky gallyl substituents, namely [(2,4,6,-^{t}Bu$_3$C$_6$H$_2$)].



Scheme 4

3.4 Experimental

[CpFe(CO)$_2$Ga(Mes*)Cl] (3.1)

To a solution of Na[CpFe(CO)$_2$] (0.052 g, 0.26 mmol) in diethyl ether (10 ml) was added a solution of Mes*GaCl$_2$ (0.100 g, 0.26 mmol) in diethyl ether (10 ml), and the reaction mixture stirred at 20 °C for 12 h. Filtration, concentration of the reaction mixture and cooling to –50 °C yielded **3.1** as pale yellow crystals suitable for X-ray diffraction. Yield: 0.040 g, 29 %. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 1.25 (s, 9H, para ^{t}Bu), 1.52 (s, 18H, ortho ^{t}Bu), 4.75 (b s, 5H, Cp), 7.34 (s, 2H, aryl CH). ^{13}C NMR (76 MHz, CD$_2$Cl$_2$): δ 31.0 (CH$_3$ of para ^{t}Bu), 34.0 (CH$_3$ of ortho ^{t}Bu), 34.7 (quaternary of para ^{t}Bu), 38.3 (quaternary of ortho ^{t}Bu), 82.8 (Cp), 119.5 (aryl CH), 142.1 (aryl ipso), 150.1 (aryl para), 154.8 (aryl ortho), 214.6 (CO). IR (KBr): ν(CO) 2004, 1948 cm^{-1}; (C$_6$D$_6$) ν(CO) 1996, 1951; (CD$_2$Cl$_2$) ν(CO) 1999, 1952. Mass spec. (EI): m/z 526.1 (weak) [M]$^+$, correct isotope distribution for 1 Fe, 1 Ga and 1 Cl atoms, significant fragment ion peaks at m/z 498.1 (5 %) [M – CO]$^+$, 470.1 (8 %) [M – 2CO]$^+$; exact mass: calc. For [M]$^+$ 526.0847, exp. 526.0845.

[Cp*Fe(CO)$_2$Ga(Mes*)Cl] (3.2)

To a solution of Na[Cp*Fe(CO)$_2$] (0.248 g, 0.92 mmol) in diethyl ether (10 ml) was added a solution of Mes*GaCl$_2$ (0.354 g, 0.92 mmol) in diethyl ether (10 ml), and the reaction mixture stirred at 20 °C for 12 h. Filtration, concentration of the reaction mixture and cooling to –50 °C yielded **3.2** as pale yellow crystals suitable for X-ray diffraction. Yield: 0.100 g, 30 %. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 1.27 (s, 9H, para ^{t}Bu), 1.53 (s, 18H, ortho ^{t}Bu), 1.74 (s, 15H, CH$_3$ of Cp*), 7.33 (s, 2H, aryl CH). ^{13}C NMR (76 MHz, CD$_2$Cl$_2$): δ 10.0 (CH$_3$ of Cp*), 31.0 (CH$_3$ of para ^{t}Bu), 33.9 (CH$_3$ of ortho ^{t}Bu), 34.7 (quaternary of para ^{t}Bu), 38.6 (quaternary of ortho ^{t}Bu), 94.1 (quaternary of Cp*), 122.6 (aryl CH), 151.0 (aryl para), 154.7 (aryl ortho), 212.9 (CO), ipso carbon of Mes* not observed. IR (KBr): ν(CO) 1983, 1931 cm^{-1}. Mass spec. (EI): m/z 596.1 (3 %) [M]$^+$, correct isotope distribution for 1 Fe, 1 Ga and 1 Cl atoms, significant fragment ion peaks at m/z 568.1 (22 %) [M – CO]$^+$, 540.1 (40 %) [M – 2CO]$^+$; exact mass: calc. For [M]$^+$ 596.1630, exp. 596.1634.

[{CpFe(CO)$_2$}$_2$Ga$_3$Cl$_3$(OSiMe$_2$OSiMe$_2$O)$_2$] (3.9)

A solution of [CpFe(CO)$_2$Ga(Mes*)Cl] (0.310 g, 0.52 mmol) in toluene (5 ml) was cooled to –30 °C over a period of 1 week. Reaction with adventitious grease yielded

$[Cp\text{-}Fe(CO)_2]_2Ga_3Cl_3(OSiMe_2OSiMe_2O)_2$, **3.9**, as colourless blocks in low yield (four or five crystals).

$[\{Cp^*Fe(CO)_2\}_2GaCl]$ (3.11)

To a solution/suspension of $Na[Cp^*Fe(CO)_2]$ (0.500 g, 1.85 mmol) in diethyl ether (30 ml) was added a solution of $GaCl_3$ (0.163 g, 0.93 mmol) in diethyl ether (20 ml) and the reaction mixture stirred at 20 °C for 12 h during which time **3.11** precipitated out of solution as a yellow powder. Filtration, and recrystallization from dichloromethane/hexane at –30 °C led to the isolation of microcrystalline **3.11**.Yield: 0.320 g, 58 %. A lower yield is obtained if toluene is used as the reaction solvent, rather than diethyl ether (0.200 g, 36 %). X-ray quality crystals could be grown by slow diffusion of hexanes into a solution in thf at –50 °C. ^1H NMR (300 MHz, C_6D_6): δ 1.68 (s, 30H, Cp*); (CD_2Cl_2): δ 1.85 (s, 30H, Cp*). ^{13}C NMR (76 MHz, C_6D_6): δ 9.7 (CH_3 of Cp*), 94.4 (quaternary of Cp*), 217.2 (CO). IR (KBr): ν(CO) 1955, 1932, 1919; (CH_2Cl_2) 1960, 1925, 1910. Mass spec. (EI): m/z 598 (5 %) $[M]^+$, correct isotope distribution for 2 Fe, 1 Ga and 1 Cl atoms, significant fragment ions at m/z 570 (35 %) $[M\text{-}CO]^+$, 542 (25 %) $[M\text{-}2CO]^+$; exact mass: calc. for $[M]^+$ 597.9782, exp. 597.9780.

Attempted synthesis of $[\{CpFe(CO)_2\}_2Ga(Mes^*)]$

To a solution/suspension of $Na[CpFe(CO)_2]$ (0.104 g, 0.52 mmol) in diethyl ether (20 ml) was added a solution containing 0.5 equivalents of Mes^*GaCl_2 (0.100 g, 0.26 mmol) in diethyl ether (30 ml). Despite extensive variation of reaction conditions (temperature, solvent *etc*), only mono-substituted **3.1** was formed (as ascertained by ^1H NMR and IR).

Attempted synthesis of $[\{Cp^*Fe(PMe_3)_2\}_2GaCl]$

A solution of PMe_3 (0.150 mmol, 11.4 mg) and $[Cp^*Fe(CO)_2]_2GaCl$ (0.09 g, 0.150 mmol) in toluene (40 ml) was irradiated with a 100 W lamp. Despite extensive variation of reaction conditions (irradiation time, solvent, temperature, concentration and source of irradiation *etc*), only a complex mixture of products was obtained. The reaction was monitored by ^{31}P NMR, which revealed five peaks at δ 21.5, 23.7, 27.1, 28.4 and 35.3 ppm and the complete consumption of starting material at δ – 61.9 ppm.

Attempted synthesis of [{Cp*Fe(dppe)}$_2$GaCl]

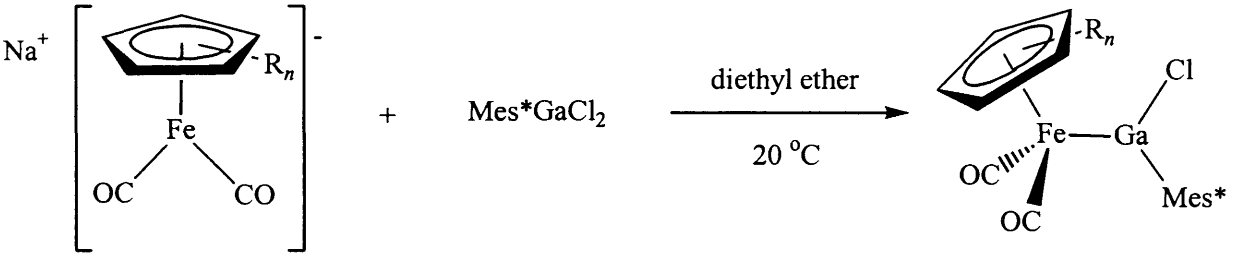
A solution of dppe (0.04 g, 0.100 mmol) in toluene (20 ml) was added to a solution of [Cp*Fe(CO)$_2$]$_2$GaCl (0.06 g, 0.100 mmol) in toluene (40 ml) and the reaction mixture was irradiated with a 100 W lamp at 20 °C for 48 h. Despite extensive variation of reaction conditions (temperature, solvent, irradiation source, concentration etc), only a complex mixture of products was obtained. The reaction was monitored by ^{31}P NMR which revealed peaks at δ 87.2, 87.5, 87.6, 88.2 and 92.1 ppm and unconverted starting material at δ – 12.1 ppm.

3.5 Results and Discussion

Two classes of three-coordinate gallium containing ligand systems, (i) asymmetric halogallyl systems of the type L_nM—Ga(Mes*)Cl; and (ii) bridging halogallanediyl complexes $(L_nM)_2GaCl$, have been synthesised directly from anionic organometallic precursors. In both cases, sterically demanding metal fragments, such as $[Cp^*Fe(CO)_2]$, and/or very bulky gallyl substituents, namely $[(2,4,6,\text{-}^tBu_3C_6H_2)]$ were utilised to enforce a trigonal geometry at the gallium centre by effectively preventing the tendency for aggregation through bridging halide ligands.[3]

3.5.1 Asymmetric halogallyl systems

Reaction between $Na[(\eta^5\text{-}C_5R_5)Fe(CO)_2]$ (R = H, Me) and Mes^*GaCl_2 in diethyl ether at 20 °C (Scheme 5) yields asymmetric halogallyl systems of the type $(\eta^5\text{-}C_5R_5)Fe(CO)_2$—Ga(Mes*)Cl (R = H (**3.1**), Me (**3.2**)) in moderate yields. This can be contrasted with the corresponding aryl(halo)boryl complexes $[(\eta^5\text{-}C_5R_5)Fe(CO)_2B(Aryl)X]$, **3.3** (R = H, Me; Aryl = Ph, Mes, $2,6\text{-}(2,4,6\text{-}^iPr_3C_6H_2)_2C_6H_3$; X = F, Cl, Br, I), which are known to decompose rapidly in the presence of coordinating solvents.[16,17]



R = H (**3.1**), Me (**3.2**)

Scheme 5

For boron based systems, halide abstraction chemistry only leads to isolable cationic diyl derivatives with boryl precursors containing sterically hindered aryl groups.[16,18] Therefore the super-mesityl substituent was incorporated into gallyl complexes **3.1** and **3.2**. Although Mes^*BBr_2 is itself inert to boron-centered substitution chemistry with anions of the type $[(\eta^5\text{-}C_5R_5)Fe(CO)_2]^-$, presumably on steric grounds,[17c] the synthesis of monomeric, three-coordinate group 13 systems featuring the heavier group 13 elements and the super-mesityl substituent are known. For example, [Mes*Ga(Cl)N(SiMe$_3$)$_2$], **3.4**, and [Mn(CO)$_5$Ga(Mes*)Cl], **1.14**,[8,19] are readily synthesised *via* salt elimination reactions from Mes*GaCl$_2$.

Both compounds **3.1** and **3.2** are pale yellow crystalline solids, which have been fully characterised by multinuclear NMR, IR and mass spectrometry. The geometries of species **3.1** and **3.2** were also confirmed crystallographically. All spectroscopic data are consistent with the proposed formulations. For example, for **3.1**, the protons of the Cp ring maybe identified in the ^{1}H NMR and ^{13}C NMR spectra as single resonances at δ 4.75 and 82.8 ppm, respectively. For **3.2**, the CH$_3$ groups of the Cp* ring may be identified in the ^{1}H NMR and ^{13}C NMR spectra as single resonances at δ 1.74 and 10.0 ppm, respectively. Resonances associated with the Mes* group can also be assigned in the ^{1}H and ^{13}C NMR spectra. In addition, the carbonyl carbons may also be identified in the ^{13}C NMR spectra at δ 214.6 and 212.9 ppm for **3.1** and **3.2**, respectively. IR spectroscopy indicates two strong C—O stretches at 2004, 1948 cm^{-1} and 1983, 1931 cm^{-1} for **3.1** and **3.2**, respectively. Mass spectrometry data for **3.1** and **3.2** reveals the correct isotope distribution for 1 Fe, 1 Ga and 1 Cl atom, together with significant fragment ions peaks corresponding to [M - CO]$^+$and [M - 2CO]$^+$. The exact mass of each molecular ion has also been determined, giving satisfactory agreement with theory.

These spectroscopic inferences were subsequently confirmed by the results of an X-ray diffraction study in each case. Cooling of a solution of **3.1** (or **3.2)** in diethyl ether to –50 °C for one week yielded single crystals suitable for X-ray diffraction, the structures of which are depicted in Figures 1 and 2, respectively.

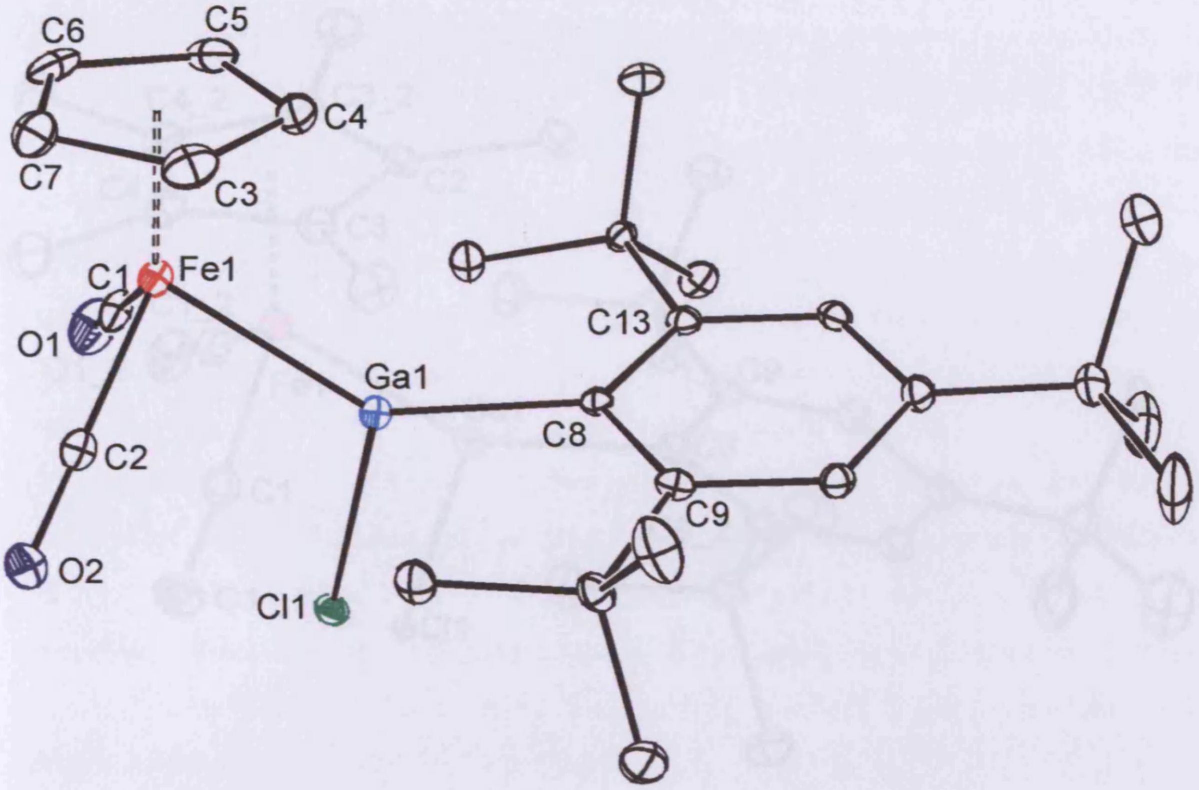


Figure 1: Molecular structure of [CpFe(CO)$_2$Ga(Mes*)Cl] (**3.1**)

Selected bond lengths (Å) and angles (°): Fe(1)—Ga(1) 2.346(1), Fe(1)—Cp centroid 1.713(4), Fe(1)—C(1) 1.758(5), Ga(1)—Cl(1) 2.272(1), Ga(1)—C(8) 1.997(3), Fe(1)—Ga(1)—C(8) 139.18(10), Fe(1)—Ga(1)—Cl(1) 112.62(3), Cl(1)—Ga(1)—C(8) 108.21(10), Cp centroid—Fe(1)—Ga(1)—C(8) 2.40(10), Fe(1)—Ga(1)—C(8)—C(9) 97.51(18).

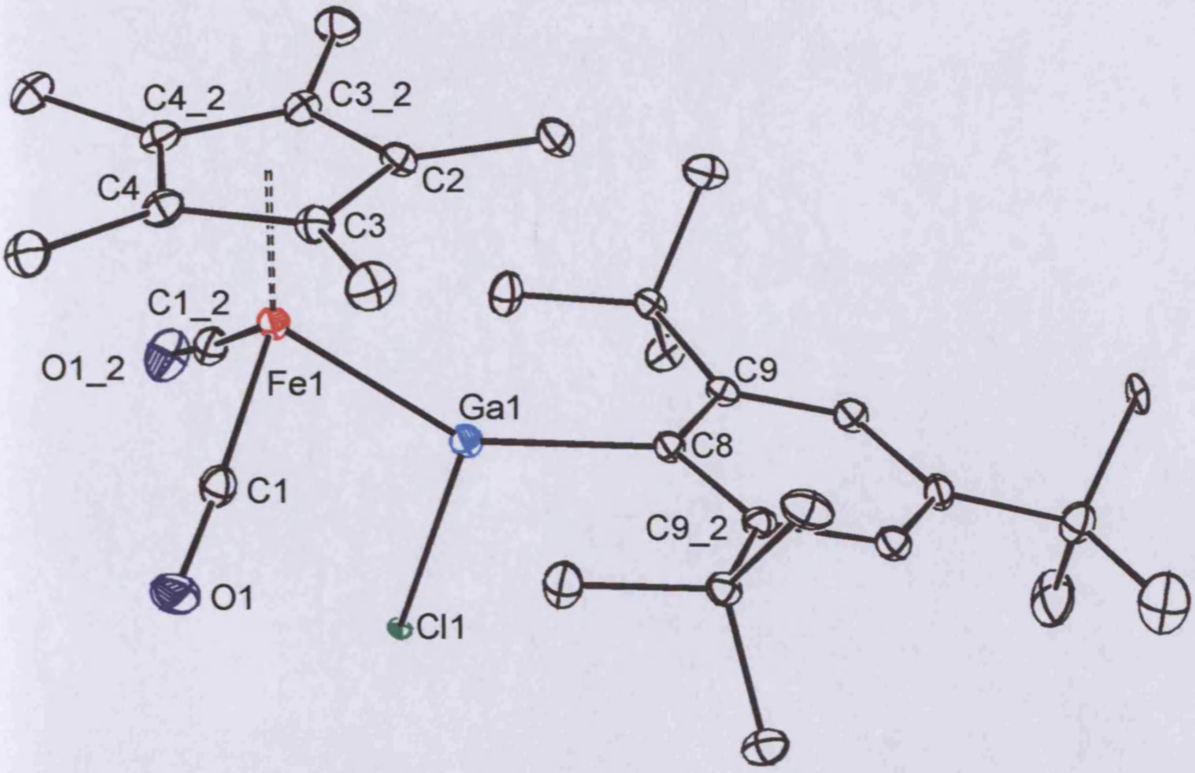


Figure 2: Molecular structure of [Cp*Fe(CO)$_2$Ga(Mes*)Cl] (**3.2**)

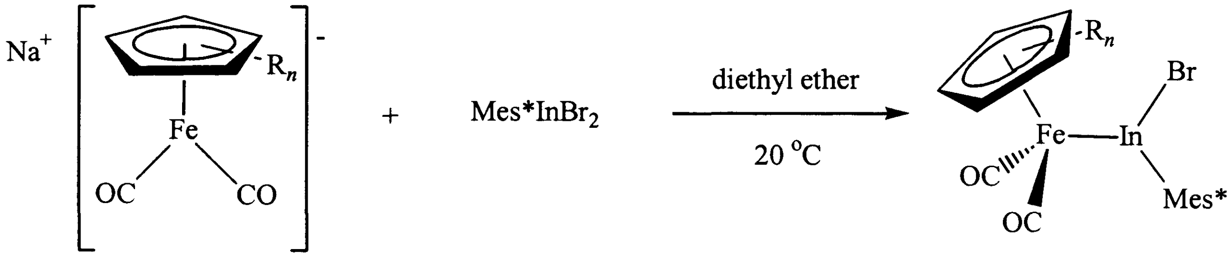
Selected bond lengths (Å) and angles (°): Fe(1)—Ga(1) 2.372(2), Fe(1)—Cp centroid 1.729(7), Fe(1)—C(1) 1.749(7), Ga(1)—Cl(1) 2.358(2), Ga(1)—C(8) 2.025(8), Fe(1)—Ga(1)—C(8) 146.7(2), Fe(1)—Ga(1)—Cl(1) 111.46(6), Cl(1)—Ga(1)—C(8) 101.8(2), Cp centroid—Fe(1)—Ga(1)—C(8) 0.0(1), Fe(1)—Ga(1)—C(8)—C(9) 93.6(3).

Aryl(chloro)gallyl species **3.1** and **3.2** are very rare examples of structurally authenticated three-coordinate halogallyl systems. The only other reported example in the literature, is [Mn(CO)$_5$Ga(Mes*)Cl], **1.12**, prepared by Cowley and co-workers as a co-crystallate with the hydrolysis product [Mn(CO)$_5$Ga(Mes*)]$_2$(μ-O).[8] As expected, the gallium centre in each case is trigonal planar (sum of angles = 360.0(1) and 360.0(6)° for **3.1** and **3.2**, respectively). The orientation of the gallyl ligand is such that it lies essentially co-planar with the Cp centroid—Fe—Ga plane ($\angle$Cp centroid—Fe—Ga—C$_{ipso}$ = 2.40(10) and 0.0(1)°, for **3.1** and **3.2**, respectively, the latter being enforced by a crystallographic mirror plane). This ligand orientation and the near perpendicular alignment of the gallyl and super-mesityl planes ($\angle$Fe—Ga—C_{ipso}—C_{ortho} = 97.5(2) and 93.6(3)°, for **3.1** and **3.2**, respectively) is analogous to that observed for boryl complexes of the type [(η^5-C_5R_5)Fe$(CO)_2$B(Mes)X], **3.5**.[16,17,18b] Presumably this is largely enforced to minimize steric interactions between the (η^5-C_5R_5) and aryl substituents. The relatively long Fe—Ga bonds (2.346(1) and 2.372(2) Å for **3.1** and **3.2**, respectively) are probably due to the large steric effects of the super-mesityl substituent. The Fe—Ga bond of **3.1**, for example, is significantly longer than those reported for [CpFe$(CO)_2$GaCl_2·THF], **1.23**, and [CpFe$(CO)_2$GaCl_2]$_2$·dioxane, **1.24**, (2.317(1) Å for both),[20] despite the reduction in coordination number at gallium from four to three.

Presumably steric influences primarily account for any differences *between* the structures of **3.1** and **3.2.** Both the opening out of the Fe—Ga—C_{ipso} angle (146.7(2) *vs.* 139.2(1)°) and lengthening of the Fe—Ga bond reflect the greater size of the Cp* substituent. Interestingly, there is also a distinct lengthening of the Ga—Cl bond (2.358(2) *vs.* 2.272(1) Å), which with subsequent halide abstraction chemistry planned, is perhaps indicative of a thermodynamically more attractive target bond.

Using a different synthetic approach, which is discussed in more detail in Chapter 4, the analogous aryl(iodo)gallyl complex [Cp*Fe$(CO)_2$Ga(Mes*)I], **3.6**, was synthesized *via* reaction of [Cp*Fe$(CO)_2$GaI_2]$_2$ with Li[Mes*] in diethyl ether in a 33 % isolated yield. Although single crystals of **3.6** could not be obtained, its identity was confirmed by mass spectrometry (including exact mass determination), multinuclear NMR and IR data, which are essentially identical to those for the structurally characterized chloride analogue, **3.2**. For example, both compounds **3.2** and **3.6**, display single resonances corresponding to the CH_3 groups of the Cp* ring at δ_H 1.77 and 1.74 ppm and at δ_C 9.2 and 10.0 ppm, respectively. Resonances associated with the Mes* group can also be identified in the ^{1}H and ^{13}C NMR spectra. A single signal associated with the carbonyl group of **3.6** is visible at δ 211.8 ppm in the ^{13}C NMR spectrum (c.f. 212.9 for **3.2**). Two bands are observed in the IR spectrum at 1983, 1933 cm^{-1} *vs.* 1981 and 1931 cm^{-1} for **3.2** and **3.6**, respectively.

Within our research group, the corresponding indium analogues ([(η^5-C_5R_5)Fe$(CO)_2$In(Mes*)Br], R = H (**3.7**), Me (**3.8**)) have also been prepared using the same methodology (work carried out by Miss N. Coombs) (Scheme 6). For indyl complexes **3.7** and **3.8**, however, the bromide precursor Mes*InBr_2 was used instead of Mes*InCl_2 because of reported problems in obtaining Mes*InCl_2 free from InCl_3.[21]



R = H (**3.7**), Me (**3.8**)

Scheme 6

Both complexes **3.7** and **3.8** have been characterized by multinuclear NMR, IR, and mass spectrometry, including exact mass determination. Spectroscopic data was in accordance with the proposed formulation and in the case of **3.8**, these spectroscopic inferences were subsequently confirmed crystallographically (Figure 3).

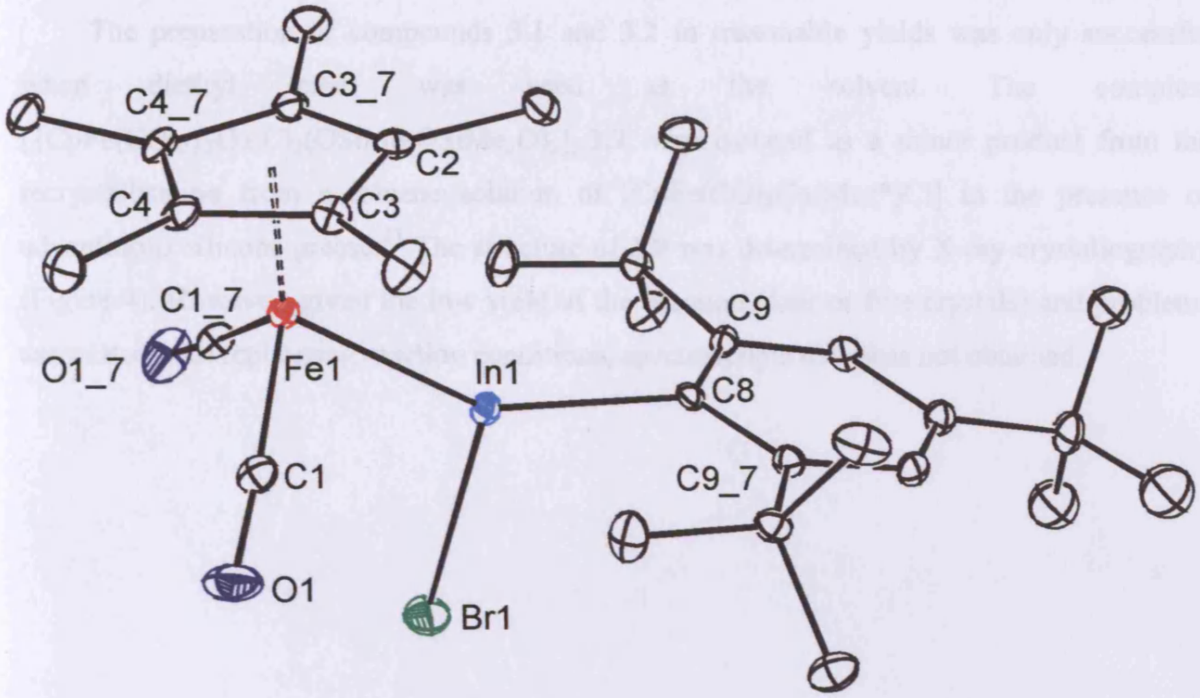


Figure 3: Molecular structure of [Cp*Fe(CO)$_2$In(Mes*)Br] (**3.8**)
(This crystal structure was obtained by Miss N. Coombs)

Selected bond lengths (Å) and angles (°): Fe(1)—In(1) 2.509(11), Fe(1)—Cp centroid 1.719(1), Fe(1)—C(1) 1.747(6), In(1)—Br(1) 2.610(10), In(1)—C (8) 2.178(7), Fe(1)—In(1)—C(8) 148.92(18), Fe(1)—In(1)—Br(1) 110.35(4), Br(1)—In(1)—C(8) 100.73(18), Cp centroid—Fe(1)—In(1)—C(8) 0.0(1), Fe(1)—In(1)—C(8)—C(9) 94.3.

As with gallyl complexes **3.1** and **3.2**, the aryl(bromo)indyl species, **3.8**, is monomeric with a trigonal planar ligand geometry. The orientation of the indyl ligand is such that it lies co-planar with the Cp* centroid—Fe—In plane (∠Cp* centroid—Fe—In—C_{ipso} = 0.0(1)°), and is enforced by a crystallographic mirror plane. As with **3.2**, this ligand orientation and the near perpendicular alignment of the indyl and super-mesityl planes (∠Fe—In—C_{ipso}—C_{ortho} = 94.3°) minimizes steric interactions between the bulky Cp* and aryl substituents. As expected, the Fe—In bond length of 2.509(11) Å is longer than the corresponding Fe—Ga bond length of 2.346(1) Å for **3.2**, reflecting the larger covalent radius of the indium atom compared to gallium (1.44 *vs.* 1.26 Å, respectively).[22]

The preparation of compounds **3.1** and **3.2** in reasonable yields was only successful when diethyl ether was used as the solvent. The complex, $[\{CpFe(CO)_2\}_2Ga_3Cl_3(OSiMe_2OSiMe_2O)_2]$, **3.9**, was isolated as a minor product from the recrystallisation from a toluene solution of $[CpFe(CO)_2Ga(Mes^*)Cl]$ in the presence of adventitious silicone grease.[23] The structure of **3.9** was determined by X-ray crystallography (Figure 4). However, given the low yield of the reaction (four or five crystals) and problems associated with replicating reaction conditions, spectroscopic data was not obtained.

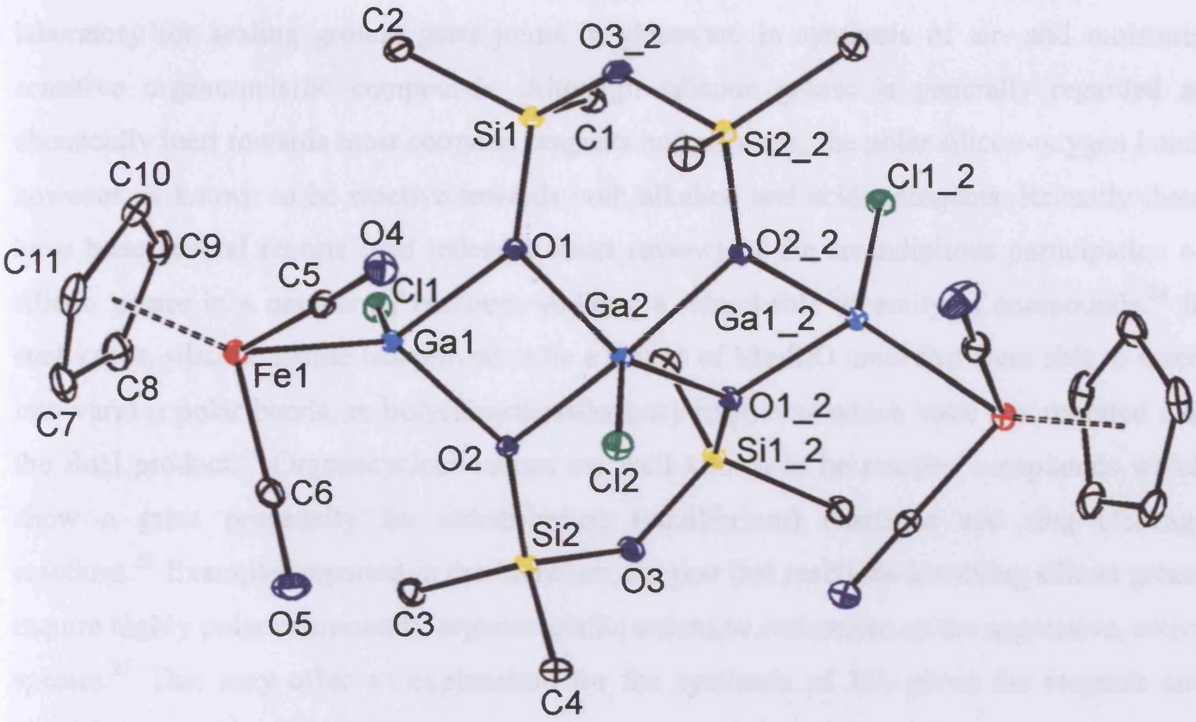
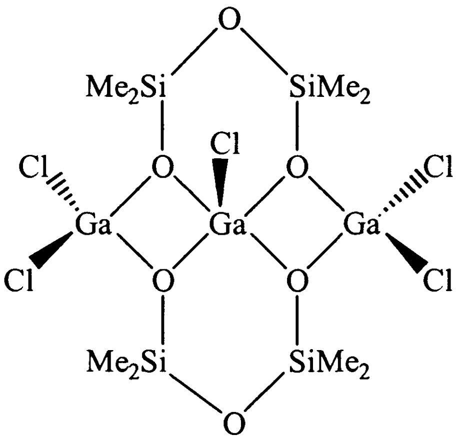


Figure 4: **Molecular structure of [{$CpFe(CO)_2$}$_2Ga_3Cl_3(OSiMe_2OSiMe_2O)_2$] (3.9)**

Selected bond lengths (Å) and angles (°): Ga(1)—Fe(1) 2.3258(6), Ga(1)—Cl(1) 2.2145(8), Ga(1)—O(1) 1.9760(18), Ga(1)—O(2) 1.9357(18), Ga(2)—Cl(2) 2.1828(11), Ga(2)—O(1) 1.9020(18), Ga(2)—O(2) 1.9851(18), Fe(1)—C(5) 1.756(3), Fe(1)—C(6) 1.751(3), Fe(1)—Cp centroid 1.718(3), Si(1)—O(1) 1.6764(19), Si(1)—O(3_2) 1.636(2), Si(1)—C(1) 1.846(3), Si(1)—C(2) 1.843(3), Si(2)—O(2) 1.6638(19), Si(2)—O(3) 1.646(2), Si(2)—C(3) 1.849(3), Si(2)—C(4) 1.846(3); O(1)—Ga(1)—C(l1) 103.56(6), O(1)—Ga(1)—O(2) 79.68(8), Cl(1)—Ga(1)—Fe(1) 122.02(3), O(1)—Ga(1)—Fe(1) 118.48(6), O(2)—Ga(1)—Fe(1) 121.24(6), O(1)—Ga(2)—O(2) 80.26(8), O(1)—Ga(2)—O(1_2) 122.53(11), O(1)—Ga(2)—O(2_2) 94.20(8), O(2)—Ga(2)—O(2_2) 168.55(11), O(1)—Ga(2)—Cl(2) 118.74(6), O(2)—Ga(2)—Cl(2) 95.73(5), C(5)—Fe(1)—C(6) 95.46(14).

Silicone grease is a dimethylsiloxane polymer, $(Me_2SiO)_x$, that is routinely used in the laboratory for sealing ground glass joints in glassware in synthesis of air- and moisture-sensitive organometallic compounds. Although silicone grease is generally regarded as chemically inert towards most common reagents and solvents, the polar silicon-oxygen bond, however, is known to be reactive towards both alkaline and acidic reagents. Recently there have been several reports (and indeed a short review) of the serendipitous participation of silicon grease in a number of reactions yielding a remarkable diversity of compounds.[24] In such cases, silicone grease has proved to be a source of Me_2SiO units that were able to insert into various polar bonds, or poly(dimethylsiloxane) fragments which were incorporated into the final product.[24] Organocyclosiloxanes are well known to be reactive compounds which show a great propensity for redistribution (equilibrium) reactions and ring cleavage reactions.[25] Examples reported in the literature, suggest that reactions involving silicon grease require highly polar compounds, organometallic anions or carbanions as the aggressive, active species.[25] This may offer an explanation for the synthesis of **3.9**, given the reagents and conditions.

The formation of **3.9** can be compared with the reaction of poly(dimethylsiloxanes), cyclic or linear, with $GaCl_3$ which are known to yield the interesting organometallosiloxane compound, $[Ga_3Cl_5(OSiMe_2OSiMe_2O)_2]$, **3.10**.[24,26]



(3.10)

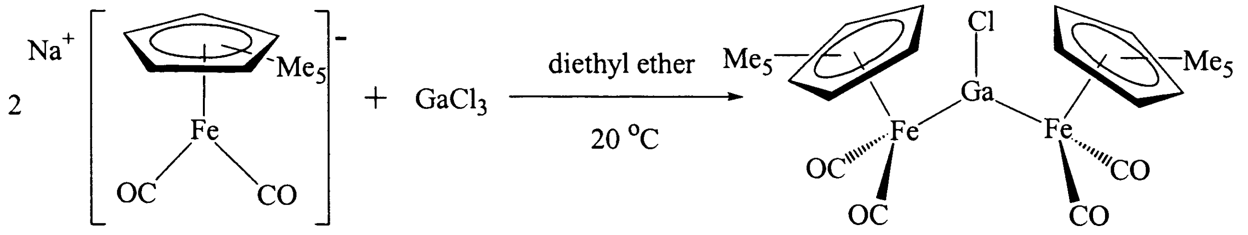
The structure of the trigallasiloxane core of **3.9**, is very similar to that found in the corresponding pentachloride species [$Ga_3Cl_5(OSiMe_2OSiMe_2O)_2$], **3.10**,[24,25] with symmetry equivalent fragments being related through a two-fold rotation axis aligned along Ga(2)—Cl(2). The Fe—Ga bond lengths to the cis-orientated pendant [$CpFe(CO)_2$] groups are within the expected range for bonding to four coordinate gallium centres (2.29-2.44 Å), as determined from a survey of the Cambridge Crystallographic Database.

3.5.2 Bridging gallylene complexes

Using the same methodology employed to synthesise complexes **3.1** - **3.8**, an attempt was made to selectively substitute both of the halide atoms of Mes*$GaCl_2$ with [$CpFe(CO)_2$] fragments. Two equivalents of Na[$CpFe(CO)_2$] were stirred with Mes*$GaCl_2$ in diethyl ether at 20 °C for 1 week. Despite the 2:1 reaction stoichiometry, only [$CpFe(CO)_2$GaMes*Cl], **3.1**, was generated (as ascertained by ^1H NMR and IR), presumably due to the large steric hindrance associated with the desired product [{$CpFe(CO)_2$}$_2$Ga(Mes*)]. Ogino *et al.*, have shown that the corresponding bridging gallylene complexes featuring somewhat less bulky aryl groups, [{(η^5-C_5R_5)$Fe(CO)_2$}$_2$Ga(2,4,6-$Me_3C_6H_2$)] (R = H, Me), **1.55**, can be prepared from the reaction of [2,4,6-$Me_3C_6H_2GaCl_2$] with an appropriate anion.[27]

3.5.3 Bridging halodiyl complexes

Using similar chemistry to that employed to the preparation of **3.1** and **3.2**, the bridging halogallanediyl complex [{Cp*$Fe(CO)_2$}$_2$GaCl], **3.11**, was synthesised. Reaction of two equivalents of Na[Cp*$Fe(CO)_2$] and $GaCl_3$ in diethyl ether at 20 °C over 12 h gave the compound **3.11** as a pale yellow insoluble powder in a 58 % yield (Scheme 7).[28] In contrast to corresponding boron-containing complexes,[16,17] the preparation of **3.11** is best accomplished in diethyl ether, with much lower yields being obtained from the analogous reactions in toluene. Furthermore, **3.11** can be compared to analogous complexes containing the less bulky [$CpFe(CO)_2$] fragment, **1.21**,[29] in which recrystallization from coordinating solvents such as diethyl ether and THF is accompanied by coordination of the oxygen donor at the group 13 centre.[20,30]



(3.11)

Scheme 7

Compound **3.11** has been fully characterised by multinuclear NMR, IR and mass spectrometry. Spectroscopic data are consistent with the proposed structure. For instance, the CH_3 groups of the Cp* ring may be identified in the ^1H NMR and ^{13}C NMR spectra as single resonances at δ 1.68 and δ 9.7 ppm, respectively. Resonances associated with the quaternary carbon of Cp* and the carbonyls of the metal fragment can also be assigned in the ^{13}C NMR spectrum at δ 94.4 and 217.2 ppm, respectively. IR spectroscopy indicates three strong C—O stretches at 1955, 1932, 1919 cm^{-1}. Mass spectrometry data reveals the correct isotope distribution for 2 Fe, 1 Ga and 1 Cl atom together with significant fragment ions corresponding to $[M]^+$, $[M\text{-}CO]^+$ and $[M\text{-}2CO]^+$. The exact mass of the molecular ion has also been determined, giving satisfactory agreement with theory. These spectroscopic inferences were subsequently confirmed crystallographically. Single crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a THF solution of **3.11** at – 50 °C; the molecular structure of **3.11** is illustrated in Figure 5.

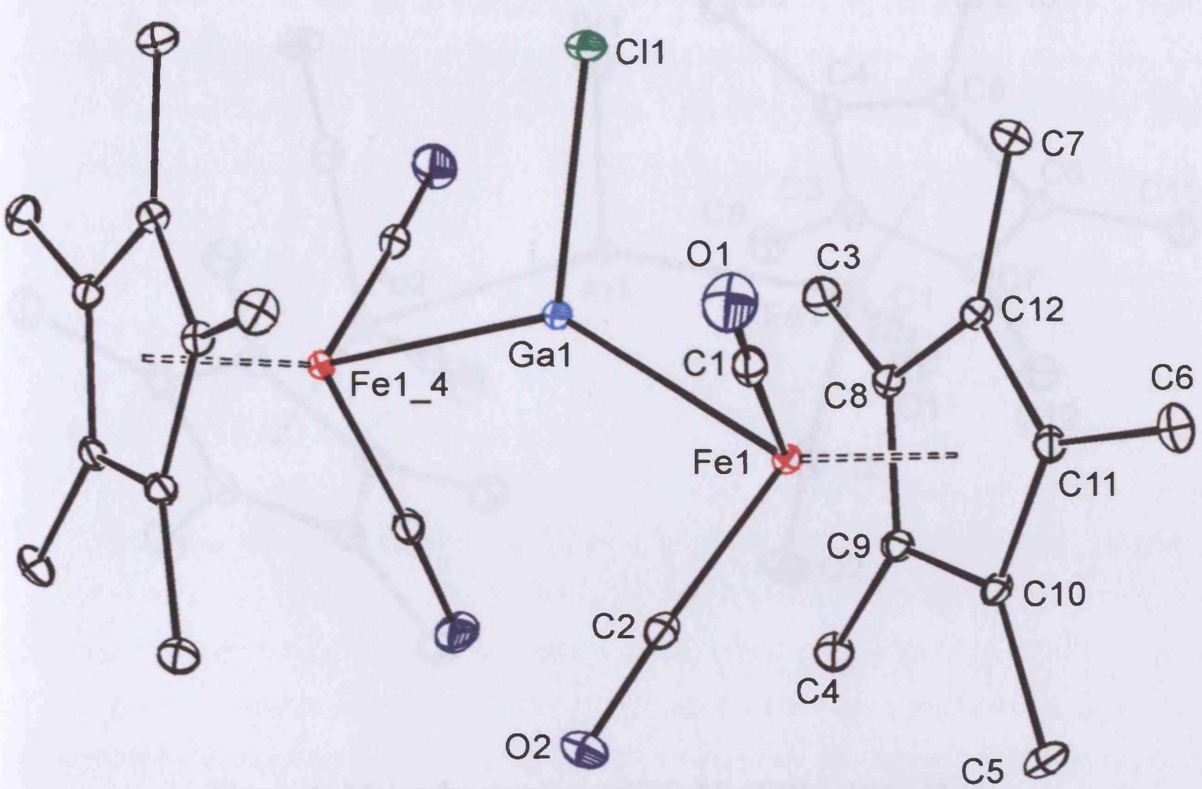


Figure 5: Molecular structure of [{Cp*Fe(CO)$_2$}$_2$GaCl] (**3.11**)

Selected bond lengths (Å) and angles (°): Fe(1)—Ga(1) 2.352(1), Fe(1)—C(1) 1.760(3), Fe(1)—Cp centroid 1.725(3), Ga(1)—Cl(1) 2.283(1), Fe(1)—Ga(1)—Fe(1_4) 138.90(3), Fe(1)—Ga(1)—Cl(1) 110.55(1).

Within our research group, the corresponding indium analogue [Cp*Fe(CO)$_2$]$_2$InBr, **3.12**, has also been prepared using the same methodology (work carried out by Dr D. Coombs). Reaction of two equivalents of the [Cp*Fe(CO)$_2$]$^-$ anion with InBr$_3$ in diethyl ether gave the bridging halodiyl complex **3.12**, in isolated yields of 47 %. Spectroscopic data are consistent with the proposed formulation, which was subsequently confirmed crystallographically (Figure 6).

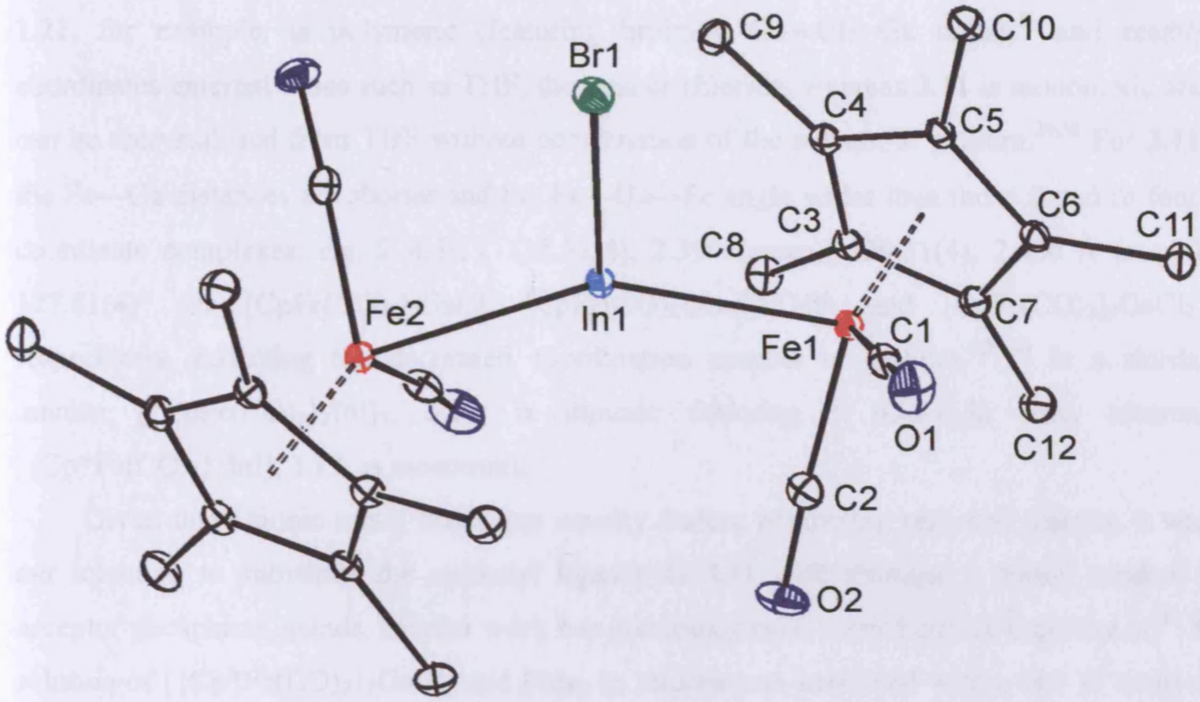


Figure 6: Molecular structure of [{Cp*Fe(CO)$_2$}$_2$InBr] (**3.12**)
(This crystal structure was obtained by Dr. D. Coombs)

Selected bond lengths (Å) and angles (°): Fe(1)—In(1) 2.513(1), Fe(2)—In(1) 2.509(1), Fe(1)—C(11) 1.754, Fe(1)—Cp centroid 1.722(2), Fe(2)—Cp centroid 1.720(2) In(1)—Br(1) 2.641, Fe(1)—In(1)—Fe(2) 141.45(2), Fe(1)—In(1)—Br(1) 107.77(2), Fe(2)—In(1)—Br(1) 110.64(2).

The analogous indium complex [{Cp*Fe(CO)$_2$}$_2$InI], **3.13**, has also been prepared using an alternative methodology (work carried out by Dr D. Coombs), which is discussed in more detail in chapter four. Both the bridging gallanediyl complex, **3.11**, and the indanediyl complexes, **3.12** and **3.13**, are monomeric with trigonal planar geometries. As expected, the Fe—Ga bond length of 2.352(1) Å of **3.11**, is shorter than the corresponding Fe—In (mean) bond lengths of 2.516(1) and 2.511(1) Å for **3.12** and **3.13**, respectively.

The large steric hindrance of the [Cp*Fe(CO)$_2$] fragment seems to have a strong influence on the structural and reaction chemistry of complexes **3.11** - **3.13**. For instance, the trigonal planar ligand geometries of **3.11** - **3.13** strongly contrast with those observed for analogous complexes containing the less bulky Cp ligand. The complex [CpFe(CO)$_2$]$_2$GaCl,

1.21, for example, is polymeric (featuring bridging Ga—Cl—Ga units),[30] and readily coordinates external bases such as THF, dioxane or chloride, whereas **3.11** is monomeric and can be recrystallised from THF without coordination of the solvent at gallium.[20,30] For **3.11**, the Fe—Ga distances are shorter and the Fe—Ga—Fe angle wider than those found in four-coordinate complexes, *e.g.* 2.365(1), 135.58(4); 2.390 (mean), 129.51(4); 2.430 Å (mean), 127.81(4)° for $[CpFe(CO)_2]_2GaCl$, $[CpFe(CO)_2]_2GaCl\cdot THF$, and $[CpFe(CO)_2]_2GaCl_2^-$, respectively, reflecting the decreased coordination number at gallium.[2,29,30] In a similar manner $[\{CpFe(CO)_2\}_2InI]_2$, **3.14**, is dimeric featuring a $In(\mu\text{-}I)_2In$ core, whereas $[\{Cp^*Fe(CO)_2\}_2InI]$, **3.13**, is monomeric.

Given that anionic metal fragments usually feature competing carbonyl ligands, it was our intention to substitute the carbonyl ligands of **3.11** with stronger σ donor, weaker π acceptor phosphine ligands. Similar work has previously been carried out by Ogino *et al.*[31] A solution of $[\{Cp^*Fe(CO)_2\}_2GaCl]$ and PMe_3 in toluene was irradiated with a 100 W lamp at 20 °C for 48 h. Despite extensive variation of reaction conditions (irradiation time, solvent, temperature, concentration and source of irradiation *etc*) only a complex mixture of products was obtained. A similar reaction was also attempted using dppe instead of PMe_3 as the phosphine donor but again only a mixture of products was generated. Presumably, in both cases, this was due to decomposition of **3.11** as it was invariably heated during the photolysis process. The possibility of coordination of the phosphine donor at competing Fe and Ga sites may also offer an explanation for the mixture of products generated.

3.6 Conclusions and Suggestions For Further Work

Transition metal complexes containing three coordinate halo-gallium ligands represent important precursors to unsaturated cationic species of the type $[L_nM(EX)]^+$ *via* halide abstraction chemistry. This chapter describes the syntheses of such precursors by a convenient one-pot salt elimination methodology utilising organometallic anions.[32] The desired monomeric trigonal planar gallyl complexes of the type L_nM—Ga(Aryl)X and halodiyl systems of the type $(L_nM)_2GaX$ have been prepared. Furthermore, the crucial role of steric factors in preventing halide bridged oligomerisation has also been emphasized, *e.g.* by the comparison of $[(\eta^5\text{-}C_5R_5)Fe(CO)_2]_2GaCl$ (R = H, Me). Salt elimination reactions of this type are, however, hampered by the narrow range and predominantly carbonyl based ligand frameworks of the transition metal anions available. Attempts to synthesise phosphine-substituted analogues, however, were unsuccessful with only a mixture of products generated. Presumably, this can be explained by the possibility of coordination of the phosphine donor at competing Fe and Ga sites in $[\{Cp^*Fe(CO)_2\}_2GaCl]$.

This work could be extended to investigate the synthesis of transition metal complexes containing three coordinate halo-gallium ligands from other sources of organometallic anions, such as $Na[CpW(CO)_3]$, and other sterically hindered aryl groups, *e.g.* (C_6H_3-2,6-$Trip_2$). The synthesis of analogous complexes containing heteroatoms, *ie.* amides, could also be investigated. Given that the reactivity of transition metal gallyl complexes has been little explored, the substitution chemistry of such compounds could also be thoroughly investigated.

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Chapter Four

Synthesis of Precursors *via* Insertion/Substitution Methodology

4.1 Introduction

This chapter explores an alternative approach for the synthesis of key halo-gallyl and bridging gallylene precursors of the types L_nM—Ga(Aryl)X and $(L_nM)_2GaX$ (X = halide) featuring three-coordinate gallium centres suitable for the synthesis of two coordinate cationic systems *via* halide abstraction chemistry. The preparation of transition metal halogallyl precursors *via* a two-step process involving initial insertion of a gallium(I) halide into a metal—halogen (or metal—metal) bond, followed by subsequent substitution at the group 13 center by an suitably sterically hindered anionic nucleophile has been investigated.

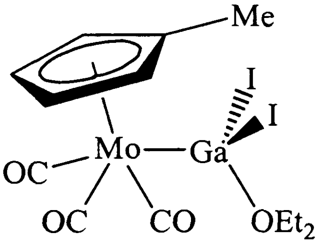
4.2 Preparation and Reactivity of 'GaI'

In 1990, Green *et al.*, reported a new convenient synthesis of 'GaI' by the ultrasonic activation of gallium metal with 0.5 equivalents of I_2 in toluene.[1] The powder diffraction pattern of the resulting pale green precipitate was shown to differ from that of 'GaI', previously reported by Corbett and McMullan, and from that of pure $[Ga_2I_3]$. It was however, similar to that prepared by Wilkinson and Worral. It is worth noting that the exact formulation of 'GaI' remains unknown but has been proposed to be $[Ga]_2^+[Ga_2I_6]^{2-}$, based on Raman spectroscopic studies.[2]

Although not a homogeneous material, this highly reactive pale green powder behaves as a monovalent gallium system. Its reactivity has indicated that it can be used as a source of gallium(I), *e.g.* the conversion of organometallic and organic iodides (RI) to gallyl derivatives of the type $RGaI_2$.[2] Jones, *et al.* have shown that 'GaI' reacts with primary and secondary amines or secondary phosphines to give a variety of gallium(II) iodide complexes of the type $[Ga_2I_4(L)_2]$, **4.1**, (L = NR_2H, NRH_2, PR_2H) *via* disproportionation reactions.[3,4] It is noteworthy that others have seen similar reactivity of gallium subhalides with tertiary amines,[5] phosphines[6] and arsines,[7] to give gallium (I) and (II) iodide complexes, *e.g.* $[Ga_2I_4(NEt_3)_2]$, **4.2**,[5] $[Ga_3I_5(PEt_3)_3]$, **4.3**,[6] and $[Ga_2I_4(AsEt_3)_2]$, **4.4**.[7]

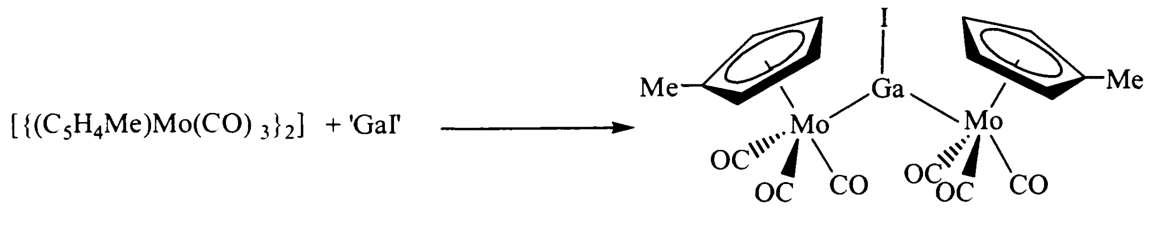
4.3 Introduction To Insertion Chemistry of Group 13 Metal(I) Halides

A number of compounds with transition metal—gallium bonds have been made as a result of a formal insertion reaction of 'GaI' into metal—halogen or metal—metal bonds. For example, Green investigated whether 'GaI' would undergo insertion reactions with metal—iodine bonds. The reaction between $[CpFe(CO)_2I]$ and 'GaI' followed by recrystallisation from ether yielded the compound $[CpFe(CO)_2GaI_2.(Et_2O)_n]$, **1.7**. Analogously, the reactions between 'GaI' and $[MoI(CO)_2(\eta\text{-}C_7H_7)]$ and $[MoI(CO)_3(\eta\text{-}C_5H_4Me)]$ gave similar complexes, $[Mo(\eta\text{-}C_7H_7)(CO)_2GaI_2.(THF)]$, **1.8**, and $[Mo(CO)_3(\eta C_5H_4Me)GaI_2.Et_2O]$, **1.9**, respectively.[1]



(1.9)

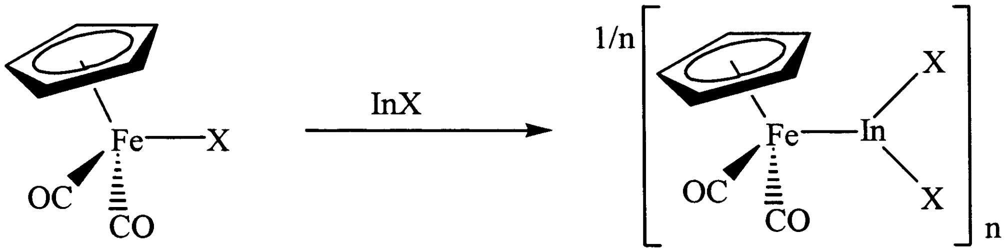
There are also several examples of insertion reactions of 'GaI' into metal—metal bonds, which have been reported in the literature. Reaction of $[\{(C_5H_4Me)Mo(CO)_3\}_2]$ with 'GaI', for example, gives a trimetallic system formulated as $[\{(C_5H_4Me)Mo(CO)_3\}_2GaI]$, **4.5** (Scheme 1).[1]



(4.5)

Scheme 1

The corresponding insertion of InX (X = halide) into metal—metal and metal—halide bonds have also been reported. Early work by Mays *et al.*, demonstrated the insertion of indium (I) chloride into the Fe—Fe bond of [$Fe_2(CO)_4Cp_2$], which afforded the diiron chloro—indanediyl complex [InCl{$Fe(CO)_2Cp$}$_2$], **1.4**. Analogous insertion of InX, (X = halide), into iron—halogen bonds yielded the monoiron complexes [InX_2{$Fe(CO)_2Cp$}], **1.5**, (Scheme 2), and [$InBr_2$(THF)$Fe(CO)_2Cp$], **1.6**.[8] Norman and co-workers later structurally characterised the dimeric complex, [InCl{$Fe(CO)_2Cp$}$_2$], **1.4**.[9]

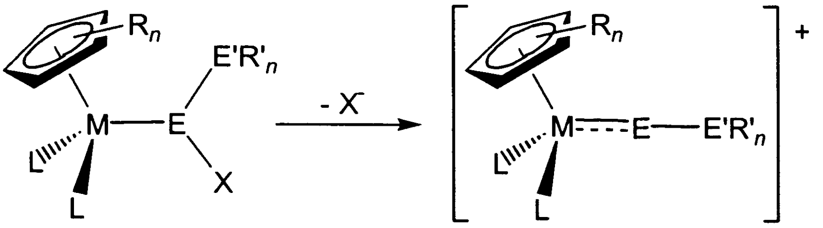


(1.5)

Scheme 2

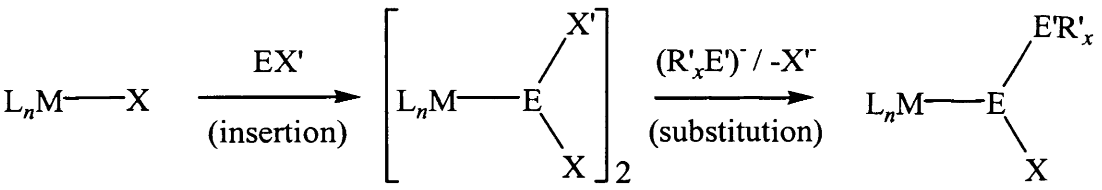
4.4 Research Proposal

The primary aim of this project was to examine the use of halide abstraction chemistry to generate two coordinate cationic derivatives of the heavier group 13 elements in an attempt to broaden the scope of synthetic methodologies available for the synthesis of unsaturated group 13 systems (Scheme 3).



Scheme 3

However, given the small number of reported examples of neutral three-coordinate systems of the type $L_nM—E(X)(E'R'_x)$ (E = Ga, In; X = halide),[10,11] the preparation of key halogallyl precursors suitable for halide abstraction, was first necessary. Therefore it was our intention to synthesise such three coordinate gallium systems among other approaches *via* a two step strategy involving insertion of a gallium(I) halide into a metal—halogen (or metal—metal) bond,[1,3,8,9,12,13] followed by substitution at the group 13 centre by an suitably sterically hindered anionic nucleophile (Scheme 4).[14] The latter step, although not widely precedented, was thought likely to be necessary to prevent the halide-bound oligomerization typically seen for less sterically encumbered systems.



Scheme 4

4.5 Experimental

[CpFe(CO)$_2$Ga(I)Br]$_2$ (4.6)

To a suspension of 'GaI', prepared by sonicating gallium (0.136 g, 1.95 mmol) and iodine (0.247 g, 0.97 mmol) in toluene (50 ml) was added a solution/suspension of [CpFe(CO)$_2$Br] (0.500 g, 1.95 mmol) in toluene (30 ml), and the reaction mixture was stirred at 20 °C for 12 h. Filtration, concentration and standing at 20 °C for 12 h yielded pale orange crystals of **4.6** suitable for X-ray diffraction. Yield: 0.425 g, 48 %. ^{1}H NMR (300MHz, CD$_2$Cl$_2$): δ 4.91 (s, 5H, Cp). ^{13}C NMR (76 MHz, CD$_2$Cl$_2$): δ 84.3 (Cp), 213.3 (CO). IR (CD$_2$Cl$_2$): ν(CO) 2015, 1968 cm^{-1}. Mass spec. (EI): m/z 499.7 (5 %) [CpFe(CO)$_2$GaI$_2$]$^+$, 471.7 (38 %) [CpFe(CO)$_2$GaI$_2$ – CO]$^+$, 443.7 (25 %) [CpFe(CO)$_2$GaI$_2$ – 2CO]$^+$, 454 (3 %) [CpFe(CO)$_2$Ga(I)Br]$^+$, 425.7 (28 %) [CpFe(CO)$_2$Ga(I)Br – CO]$^+$, 397.7 (30 %) [CpFe(CO)$_2$Ga(I)Br – 2CO]$^+$, 406 (2 %) [CpFe(CO)$_2$GaBr$_2$]$^+$, 378 (18 %) [CpFe(CO)$_2$GaBr$_2$ – CO]$^+$, 349.7 (13 %) [CpFe(CO)$_2$GaBr$_2$ – 2CO]$^+$; exact mass: calc. for [CpFe(CO)$_2$GaI$_2$]$^+$ 499.6979, exp. 499.6973.

[CpFe(CO)$_3$]$^+$[CpFe(CO)$_2$Ga(I)Br$_2$]$^-$ (4.9)

To a suspension of 'GaI', prepared by sonicating gallium (0.136 g, 1.95 mmol) and iodine (0.247 g, 0.97 mmol) in toluene (50 ml) was added a solution/suspension of [CpFe(CO)$_2$Br] (0.500 g, 1.95 mmol) in toluene (30 ml), and the reaction mixture was stirred at 20 °C for 12 h. The mixture was then filtered and volatiles removed *in vacuo*. The mixture was then re-dissolved in THF, layered with hexane and cooled to – 30 °C to yield pale yellow crystals of **4.9** suitable for X-ray diffraction. Yield: 0.120 g, 9 %. ^{1}H NMR (300MHz, CD$_2$Cl$_2$): δ 4.88 (s, 5H, Cp), 4.85 (s, 5H, Cp). ^{13}C NMR (76 MHz, CD$_2$Cl$_2$): δ 84.6 (Cp), 84.8 (Cp), 213.5 (CO), 214.2 (CO). IR (CD$_2$Cl$_2$): ν(CO) 2001, 1949 cm^{-1}.

[CpFe(CO)$_2$GaI$_2$(μ-I)Fe(CO)$_2$Cp] (4.11)

To a suspension of 'GaI', prepared by sonicating gallium (0.138 g, 1.97 mmol) and iodine (0.250 g, 0.98 mmol) in toluene (50 ml) was added dropwise a solution/suspension [CpFe(CO)$_2$I] (0.600 g, 1.97 mmol) in toluene (20 ml), and the reaction mixture stirred at 20 °C for 12 h. Filtration, layering with hexane and cooling to –30 °C yielded dark red crystals of **4.11** suitable for X-ray diffraction. Yield: 0.570 g, 72 %. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 4.24 (s, 5H, Cp), 4.25 (s, 5H, Cp). ^{13}C NMR (76 MHz, C$_6$D$_6$): δ 83.8 (Cp), 84.2 (Cp), 212.0 (CO), 215.1 (CO). IR (C$_6$D$_6$): ν(CO) 2037, 2003, 2000, 1957. Mass spec. (EI):

m/z 499.7 (5 %) $[CpFe(CO)_2GaI_2]^+$, 471.7 (75 %) $[CpFe(CO)_2GaI_2 - CO]^+$, 443.7 (52 %) $[CpFe(CO)_2GaI_2 - 2CO]^+$, all with correct isotope distribution for 1 Fe, 1 Ga and 2 I atoms, 303.8 (45 %) $[CpFe(CO)_2I]^+$, 275.8 (47 %) $[CpFe(CO)_2I - CO]^+$, 247.8 (80 %) $[CpFe(CO)_2I - 2CO]^+$; exact mass: calc. for $[CpFe(CO)_2GaI_2 - CO]^+$ 471.7030, exp. 471.7030.

Attempted reaction between $[CpFe(CO)_2GaI_2(\mu\text{-}I)Fe(CO)_2Cp]$ and CO

Carbon monoxide was bubbled through a solution of **4.11** (0.030 g, 0.037 mmol) in toluene (30 ml) at 20 °C over a period of 6 h but no reaction occurred (as ascertained by ^1H NMR and IR spectroscopy).

$[CpFe(CO)_2GaI_2]_2$ (4.12)

To a suspension of 'GaI', prepared by sonicating gallium (0.205 g, 2.94 mmol) and iodine (0.373 g, 1.47 mmol) in toluene (50 ml) was added a solution/suspension of $[CpFe(CO)_2I]$ (0.300 g, 0.98 mmol) in toluene (20 ml), and the reaction mixture stirred at 20 °C for 48 h. Filtration, layering with hexanes and cooling to –30 °C yielded crystals of **4.12** suitable for X-ray diffraction. Yield: 0.300 g, 27 %. ^1H NMR (300 MHz, C_6D_6): δ 4.12 (s, 5H, Cp). ^{13}C NMR (76 MHz, C_6D_6): δ 84.0 (Cp), 213.4 (CO). IR (C_6D_6): ν(CO) 2012, 1970 cm^{-1}. Mass spec. (EI): m/z 500 (5 %) $[CpFe(CO)_2GaI_2]^+$, correct isotope distribution for 1 Fe, 1 Ga and 2 I atoms, significant fragment ions at m/z 472 (100 %) $[CpFe(CO)GaI_2]^+$, 444 (75 %) $[CpFeGaI_2]^+$, 373 (50 %) $[CpFe(CO)_2GaI]^+$; exact mass: calc. for $[CpFe(CO)_2GaI_2]^+$ 499.6979, exp. 499.6975.

$[Cp^*Fe(CO)_2GaI_2]_2$ (4.18)

To a suspension of 'GaI', prepared by sonicating gallium (0.169 g, 2.42 mmol) and iodine (0.307g, 1.21 mmol) in toluene (50 ml) was added a solution of $[Cp^*Fe(CO)_2]_2$ (0.300 g, 0.61 mmol) in toluene (30 ml), and the reaction mixture stirred at 20 °C for 120 h, during which time **4.18** precipitated out of solution as a yellow powder. Recrystallisation from CH_2Cl_2 at –30 °C yielded pale yellow crystals suitable for X-ray diffraction. Yield: 0.641 g, 47 %. ^1H NMR (300 MHz, C_6D_6): δ 1.60 (s, 30H, Cp*). ^{13}C NMR (76 MHz, C_6D_6): δ 9.8 (CH_3 of Cp*), 95.4 (quaternary of Cp*), 216.4 (CO). IR (C_6D_6) ν(CO) 2001, 1954 cm^{-1}. Mass spec. (EI): m/z 569.8 (15 %) $[Cp^*Fe(CO)_2GaI_2]^+$, 541.8 (100 %) $[Cp^*Fe(CO)_2GaI_2 - CO]^+$, 513.8 (60 %) $[Cp^*Fe(CO)_2GaI_2 - 2CO]^+$; exact mass: calc. For $[Cp^*Fe(CO)_2GaI_2]^+$ 569.7761; exp. 569.7753.

[(dppe)PtI$_2$] (4.14)

To a suspension of 'GaI', prepared by sonicating gallium (67 mg, 0.96 mmol) and iodine (122 mg, 0.48 mmol) in toluene (20 ml) was added a suspension of [(dppe)PtCl$_2$] (320 mg, 0.48 mmol) in toluene (10 ml), and the reaction mixture was stirred at 20 °C for 3 h. Filtration, concentration and cooling to –30 °C yielded **4.14** as a yellow powder. Yield: 0.196 g, 48 %. ^{31}P NMR (121 MHz, THF)):δ 46.6 (Pt(dppe)I$_2$, J_{Pt-P} 3384 Hz). EI-MS: 846.5 (15 %) [(dppe)PtI$_2$]$^+$, 719.8 (100 %) [(dppe)PtI]$^+$. Spectroscopic data are consistent with quoted literature values.[15]

[Cp(dppe)RuI] (4.16)

To a suspension of 'GaI', prepared by sonicating gallium (0.037 g, 0.53 mmol) and iodine (0.068 g, 0.27 mmol) in toluene (50 ml), was added a solution of [Cp(dppe)RuCl] (0.320 g, 0.53 mmol) in toluene (10 ml). The reaction mixture was stirred at 20 °C for 12 h. Filtration yielded **4.16** as a red-brown powder, which was subsequently dried *in vacuo*. Single crystals of **4.16** suitable for X-ray diffraction were grown by recrystallisation from a CH$_2$Cl$_2$/hexane mixture (*ca.* 1:2) and cooling to – 50 °C. Yield: 0.2 g, 56 %. ^{31}P NMR (300 MHz, C$_6$D$_6$) δ 80.3 (s). ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 2.17-2.23 (2 H, m, dppe H), 2.74-2.79 (2H, m, dppe H), 4.55 (5 H, s, Cp), 6.89 (6H, m, aromatic H), 7.02 (6H, m, aromatic H), 7.91-7.95 (3H, m, aromatic H). Mass Spec. (EI): m/z 691.9 (62 %) [M$^+$], 565.1 (100 %) [(CpRu(dppe))$^+$]. Spectroscopic data are consistent with quoted literature values.[16]

Attempted Reaction with BBrCat

To a suspension of 'GaI', prepared by sonicating gallium (0.105 g, 1.51 mmol) and iodine (0.192 g, 0.756 mmol) in toluene (50 ml), was added a solution of B-bromocatecholborane (0.300 g, 1.51 mmol) in toluene (20 ml). Despite extensive variation of reaction conditions (temperature, solvent *etc.*), no reaction occurred (as determined by ^{11}B NMR).

Attempted Reaction with Zircocene Dichloride

To a suspension of 'GaI', prepared by sonicating gallium (0.143 g, 2.05 mmol) and iodine (0.261 g, 1.02 mmol) in toluene (50 ml), was added a solution of [Cp$_2$ZrCl$_2$] (0.3 g, 1.02 mmol) in toluene (20 ml). Despite stirring the reaction mixture at 20 °C then heating at reflux for 3 days no reaction occurred (as ascertained by ^{1}H NMR).

[CpFe(CO)$_2$GaI$_2$·(4-pic)] (4.22)

To a solution of **4.6** (0.100 g, 0.11 mmol) in toluene (15 ml) was added dropwise a solution of 4-picoline in toluene (10 ml containing 0.020 g, 0.22 mmol of 4-picoline), and the reaction mixture stirred at 20 °C for 12 h. Filtration, concentration, addition of hexane (40 ml) and cooling to –30 °C yielded **4.22** as part of a pale yellow microcrystalline mixture. Yield: 0.030 g, 25 %. Crystals of [CpFe(CO)$_2$GaI$_2$.(4-pic)] **4.22** suitable for X-ray diffraction were obtained by the slow diffusion of hexane into a benzene solution. Characterizing data for crude (microcrystalline) product: ^{1}H NMR (300 MHz, C_6D_6): δ 1.35 (b, 3H, CH$_3$), 4.27, 4.29, 4.31 (s, 5H, Cp), 6.13 (b, 2H, CH of pic), 8.62 (b, 2H, CH of pic). ^{13}C NMR (76 MHz, C_6D_6): δ 20.6, 20.8 (CH$_3$), 83.4, 84.0, 84.6 (Cp), 125.8, 125.9 (CH of pic), 145.9, 146.0 (CH of pic), 153.5, 153.6 (quaternary of pic), 215.6, 216.1 (CO). IR (C_6D_6): ν(CO) 1985, 1979, 1950, 1934 cm^{-1}. Mass spec. (EI): m/z 500 (weak) [CpFe(CO)$_2$GaI$_2$]$^+$, 472 (10 %) [CpFe(CO)$_2$GaI$_2$ – CO]$^+$, 454 (2 %) [CpFe(CO)$_2$Ga(I)Br]$^+$, 444 (8 %) [CpFe(CO)$_2$GaI$_2$ – 2CO]$^+$, 426 (25 %) [CpFe(CO)$_2$Ga(I)Br – CO]$^+$, 406 (2 %) [CpFe(CO)$_2$GaBr$_2$]$^+$, 398 (25 %) [CpFe(CO)$_2$Ga(I)Br – 2CO]$^+$, 378 (18 %) [CpFe(CO)$_2$GaBr$_2$ – CO]$^+$, 350 (30 %) [CpFe(CO)$_2$GaBr$_2$ – 2CO]$^+$, 93.1 (100 %) [4-pic]$^+$. Characterizing data for the crystalline product **4.22** were identical to those of a crystalline sample prepared independently from [CpFe(CO)$_2$GaI$_2$]$_2$, **4.12**, and 4-picoline and recrystallized from toluene/hexane: ^{1}H NMR (300 MHz, C_6D_6): δ 1.34 (s, 3H, CH$_3$), 4.33 (s, 5H, Cp), 6.09 (b m, 2H, CH of pic), 8.82 (b, 2H, CH of pic). ^{13}C NMR (76 MHz, C_6D_6): δ 20.3 (CH$_3$), 84.6 (Cp), 125.5, (CH of pic), 146.2 (CH of pic), 153.3 (quaternary of pic), 216.1 (CO). IR (C_6D_6): ν(CO) 1985, 1933 cm^{-1}. Mass spec. (EI): m/z 565 (weak) [M – CO]+, correct isotope distribution for 1 Fe, 1 Ga and 2 I atoms, significant fragment ions at m/z 500 (4 %) [M – pic]+, 472 (75 %) [M - pic - CO]$^+$, 444 (60 %) [M – pic – 2CO; exact mass: calc. for [M - CO]$^+$ 564.7608, exp. 564.7611.

[Et$_3$NH]$^+$[CpFe(CO)$_2$GaI$_3$]$^-$ (4.24)

To a solution of [CpFe(CO)$_2$GaBrI]$_2$, **4.6** (0.188 g, 0.207 mmol) in toluene (20 ml) was added dropwise a solution of NEt$_3$ (0.042 g, 0.414 mmol) in toluene (20ml), and the reaction mixture stirred at 20 °C for 12 h. Filtration, concentration and addition of hexane (20 ml) followed by cooling to –30 °C led to the formation of pale yellow crystals of **4.24** suitable for X-ray diffraction. Yield: 0.085 g, 60 %. ^{1}H NMR (300 MHz, C_6D_6): δ 0.52 (t, 9H, CH$_3$ of HNEt$_3^+$), 2.29 (q, 6H, CH$_2$ of HNEt$_3^+$), 4.36 (s, 5H, Cp), 7.44 (b, 1H, H of HNEt$_3^+$). ^{13}C NMR (76 MHz, C_6D_6) δ 9.1 (CH$_3$ of HNEt$_3^+$), 47.2 (CH$_2$ of HNEt$_3^+$), 83.8 (Cp). Carbonyl carbons undetected. IR (CD_2Cl_2): ν(CO) 1996, 1944 cm^{-1}. Mass spec (EI) m/z 627 (15 %) [$FpGaI_3^-$ – $HNEt_3$] $^+$, correct isotope distribution for 1 Fe, 1 Ga and 3 halides, significant fragment ions at m/z 580.6 (50 %) [$FpGaBrI_2^-$ – $HNEt_3$] $^+$, 532.6 (55 %) [$FpGaIBr_2^-$ – $HNEt_3$] $^+$, 484.6 (35 %) [$FpGaBr_3^-$ – $HNEt_3$] $^+$, 102.1 ($HNEt_3$]$^+$.

$[tmpH_2]^+[CpFe(CO)_2GaBr_3]^-$ (4.25)

To a solution of $[CpFe(CO)_2GaIBr]_2$, **4.6** (0.100 g, 0.110 mmol) in toluene (20 ml) was added dropwise a solution of Li[tmp] (0.032 g, 0.218 mmol) in toluene (20ml), and the reaction mixture stirred at 20 °C for 12 h. Filtration, concentration and cooling to –30 °C led to the formation of pale yellow crystals of **4.25** suitable for X-ray diffraction. Yield: 0.030 g, 52 %. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.45 (b, 12H, CH_3 of tmp), 1.65 (b, 4H, CH_2CMe_2 of tmp), 1.82 (b, 2H, CH_2 of tmp), 2.26 (s, 3H, CH_3 of toluene), 4.73 (s, 5H, Cp), 5.62 (b, 2H, NH_2), 7.10 (m, 5H, aromatic toluene). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 15.9 (CH_3 of toluene), 21.2 (CH_3 of tmp), 29.3 (CH_2CMe_2 of tmp), 36;.1 (CH_2 of tmp), 60.1 (quaternary of tmp), 84.2 (Cp), 125.3 (quaternary of toluene), 128.2 (quaternary of toluene), 129.0 (quaternary of toluene), 138.0 (quaternary of toluene), 215.8 (CO). IR (CD_2Cl_2): ν(CO) 1995, 1944 cm^{-1}. Mass spec (ES-) 626.6 (30 %) $[CpFe(CO)_2GaI_3]^-$, 580.6 (95 %) $[CpFe(CO)_2GaI_2Br]^-$, 532.7 (100 %) $[CpFe(CO)_2GaIBr_2]^-$, 484.7 (45 %) $[CpFe(CO)_2GaBr_3]^-$, 126.9 (50 %) $[I]^-$.

$[tmpH_2]^+[Cp^*Fe(CO)_2GaI_3]^-$ (4.28)

To a solution of $[Cp^*Fe(CO)_2GaI_2]_2$, **4.18** (0.100 g, 0.088 mmol) in toluene (20 ml) was added dropwise a solution of Li[tmp] (0.026 g, 0.18 mmol) in toluene (20ml), and the reaction mixture stirred at 20 °C for 12 h. Filtration, concentration and cooling to –30 °C led to the formation of **4.28** as pale yellow crystals suitable for X-ray diffraction. Yield: 0.041 g, 28 %. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.57 (b, 12H, CH_3 of tmp), 1.66 (b, 4H, CH_2CMe_2 of tmp), 1.76 (s, 15H, CH_3 of Cp*), 1.89 (b, 2H, CH_2 of tmp), 6.49 (b, 2H, NH_2). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 8.4 (CH_3 of Cp*), 15.2 (CH_3 of tmp), 27.6 (CH_2CMe_2 of tmp), 35.2 (CH_2 of tmp), 59.1 (quaternary of tmp), 93.6 (quaternary of Cp*), 217.0 (CO). IR (C_6D_6): ν(CO) 1980, 1933cm^{-1}. Mass spec (ES-): 696.7 (10 %) $[Cp^*Fe(CO)_2GaI_3]^-$, 668.7 (1 %), $[Cp^*Fe(CO)_2GaI_3$ - $CO]^-$, 569.7 (5 %) $[Cp^*Fe(CO)_2GaI_3$ - $I]^-$; exact mass: calc. for $[Cp^*Fe(CO)_2GaI_3]^-$ (^{69}Ga): 696.6817, measured 696.6815. Mass spec (ES+): 142.1 (100 %) $[tmpH_2]^+$.

[Cp*Fe(CO)$_2$]$_2$GaI (4.20)

To a solution/suspension of Na[Cp*Fe(CO)$_2$] (0.040 g, 0.148 mmol) in diethyl ether (10 ml) was added dropwise a solution of [Cp*Fe(CO)$_2$GaI$_2$]$_2$, **4.18** (0.085 g, 0.074 mmol) in diethyl ether (20 ml). The reaction mixture was then stirred at 20 °C for 12 h, during which time **4.20** precipitated out of solution as a yellow powder. Filtration, washing with hexane and drying *in vacuo* led to the isolation of **4.20**. Yield: 0.060 g, 61 %. Crystalline samples could be obtained by slow diffusion of hexanes into a THF solution of **4.20** at –30 °C. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 1.77 (s, 30H, Cp*). ^{13}C NMR (76 MHz, CD$_2$Cl$_2$): δ 9.2 (CH$_3$ of Cp*), 94.1 (quaternary of Cp*), 217.4 (CO). IR (CD$_2$Cl$_2$): ν(CO) 1964, 1928 and 1912 cm^{-1}. Mass spec. (EI): m/z 662 (45 %) [M - CO]$^+$, correct isotope distribution for 2 Fe, 1 Ga and 1 I atoms, significant fragment ion at m/z 634 (30 %) [M – 2CO]$^+$; exact mass: calc. for [M - CO]$^+$ 661.9189, exp. 661.9191.

[Cp*Fe(CO)$_2$Ga(Mes*)I] (3.6)

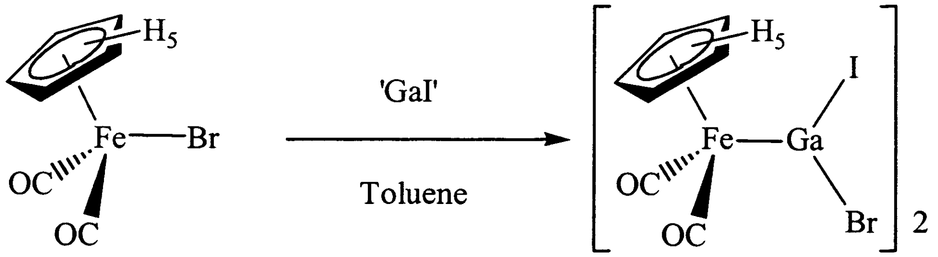
To a solution of [Cp*Fe(CO)$_2$GaI$_2$]$_2$, **4.18** (0.100 g, 0.088 mmol) in diethyl ether (20 ml) was added dropwise a solution of Li[Mes*] (0.044 g, 0.17 mmol) in diethyl ether (15 ml). The resulting mixture was then stirred at 20 °C for 12 h. The reaction mixture was subsequently filtered and concentrated. Hexane (30 ml) was then added and the solution cooled to –30 °C for 12 h to yield **3.6** as a pale yellow powder. Yield: 0.040 g, 33 %. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 1.24 (s, 9H, para ^{t}Bu), 1.78 (s, 18H, ortho ^{t}Bu), 1.89 (s, 15H, CH$_3$ of Cp*), 7.10 (s, 2H, aryl CH). ^{13}C NMR (76 MHz, CD$_2$Cl$_2$): δ 9.4 (CH$_3$ of Cp*), 25.0 (CH$_3$ of para ^{t}Bu), 31.4 (CH$_3$ of ortho ^{t}Bu), 34.7 (quaternary of para ^{t}Bu), 37.9 (quaternary of ortho ^{t}Bu), 95.2 (quaternary of Cp*), 119.5 (aryl CH), 150.1 (aryl para), 155.6 (aryl ortho), 211.8 (CO). IR (CD$_2$Cl$_2$): ν(CO) 1981, 1931 cm^{-1}. Mass spec. (EI): m/z 688.1 (weak) [M]$^+$, correct isotope distribution for 1 Fe, 1 Ga and 1 I atoms, significant fragment ion peaks at m/z 660.1 (weak) [M – CO]$^+$, 632.1 (10 %) [M – 2CO]$^+$; exact mass: calc. for [M]$^+$ 688.0986, exp. 688.0999; calc. for [M-CO]$^+$ 660.1037, exp. 660.1043.

4.6 Results and Discussion

The synthesis of three coordinate halo-gallium ligand systems has been investigated. A two step strategy involving initial insertion of 'GaI' into a metal—halogen (or metal—metal) bond, followed by substitution at the gallium centre by a suitably sterically hindered anionic nucleophile was employed.

4.6.1 Insertion of 'GaI' into metal-halide bonds

Reaction between sonically prepared 'GaI' and [CpFe(CO)$_2$Br] in toluene at 20 °C leads to the formal insertion of 'GaI' into the metal—bromine bond to give the dimeric complex [CpFe(CO)$_2$Ga(I)Br]$_2$, **4.6**, in a isolated yield of 48 % (Scheme 5).



(4.6)

Scheme 5

Complex **4.6** is a pale orange crystalline solid, which has been fully characterised by multinuclear NMR, IR and mass spectrometry. All spectroscopic data are consistent with the proposed formulation. For example, a single resonance is observed for the Cp ring at δ 4.91 ppm in the ^{1}H NMR spectrum. Resonances are visible at *δ* 84.3 and 213.3 ppm in the ^{13}C NMR spectrum corresponding to the Cp and carbonyl ligands, respectively. IR spectroscopy indicates two strong C—O stretches at 2015 and 1968 cm^{-1}. Mass spectrometry reveals ready fragmentation into a mixture of monomeric species, *i.e.* [CpFe(CO)$_2$GaBr$_2$], [CpFe(CO)$_2$Ga(I)Br] and [CpFe(CO)$_2$GaI$_2$], under electron impact conditions, however the dimeric structure of **4.6** was subsequently confirmed crystallographically. Pale orange crystals suitable for X-ray diffraction were grown by concentration of a toluene solution of **4.6** at 20 °C (Figure 1).

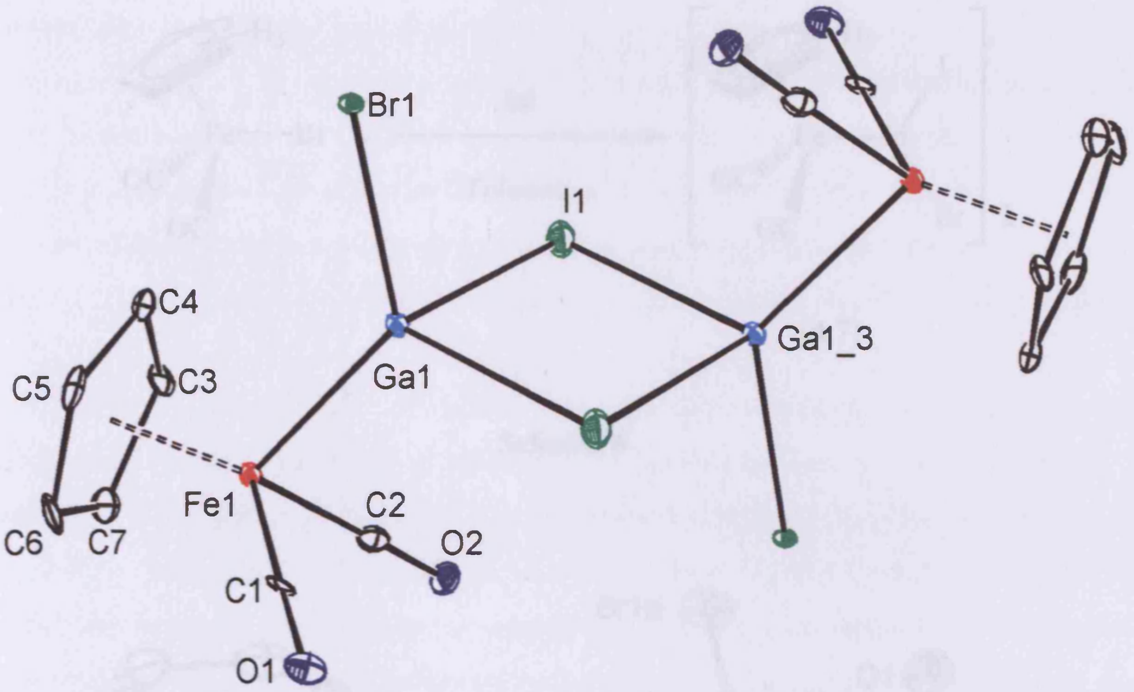
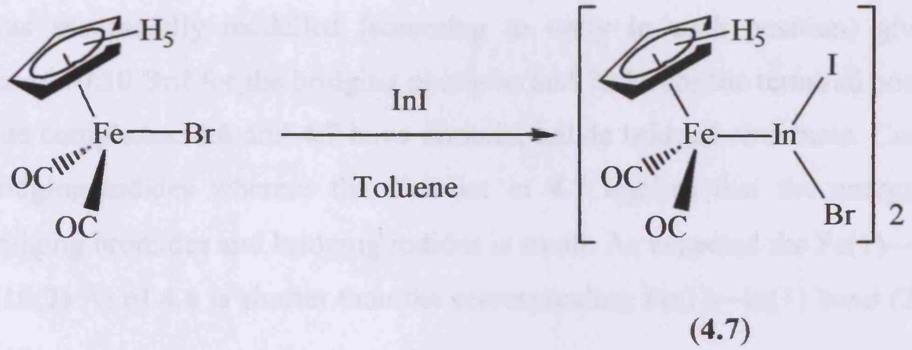


Figure 1: Molecular structure of $[CpFe(CO)_2Ga(I)Br]_2$, **4.6**

Selected bond lengths (Å) and angles (°): Fe(1)—Ga(1) 2.310(2), Fe(1)—C(1) 1.736(14), Fe(1)—Cp centroid 1.730(8), Ga(1)—Br(1) 2.445(18), Ga(1)—I(1) 2.642(18), Fe(1)—Ga(1)—I(1) 116.87 (8), I(1)—Ga(1)—I(1_3) 92.1(6).

X-ray crystallography confirms that compound **4.6** adopts a dimeric structure with bridging iodines and terminal bromine groups. This is expected given the relative steric hindrance of the gallium-bound substituents, *i.e.* halides and Cp ring, and the propensity of halo-gallium and –indium systems in general to augment the coordination number at the group 13 center through bridging halide ligands.[17]

The analogous dimeric indium-containing species has also been synthesised within our research group (work carried out by Dr. D. Coombs), *via* the same methodology using commercially available InI. The corresponding reaction of InI with $[CpFe(CO)_2Br]$ gives the dimeric complex $[CpFe(CO)_2In(I)Br]_2$, **4.7**, in a isolated yield of 80 % (Scheme 6). Spectroscopic data were consistent with the proposed formulation, and the dimeric structure was subsequently determined crystallographically (Figure 2), enabling a direct structural comparison with **4.6**.



(4.7)

Scheme 6

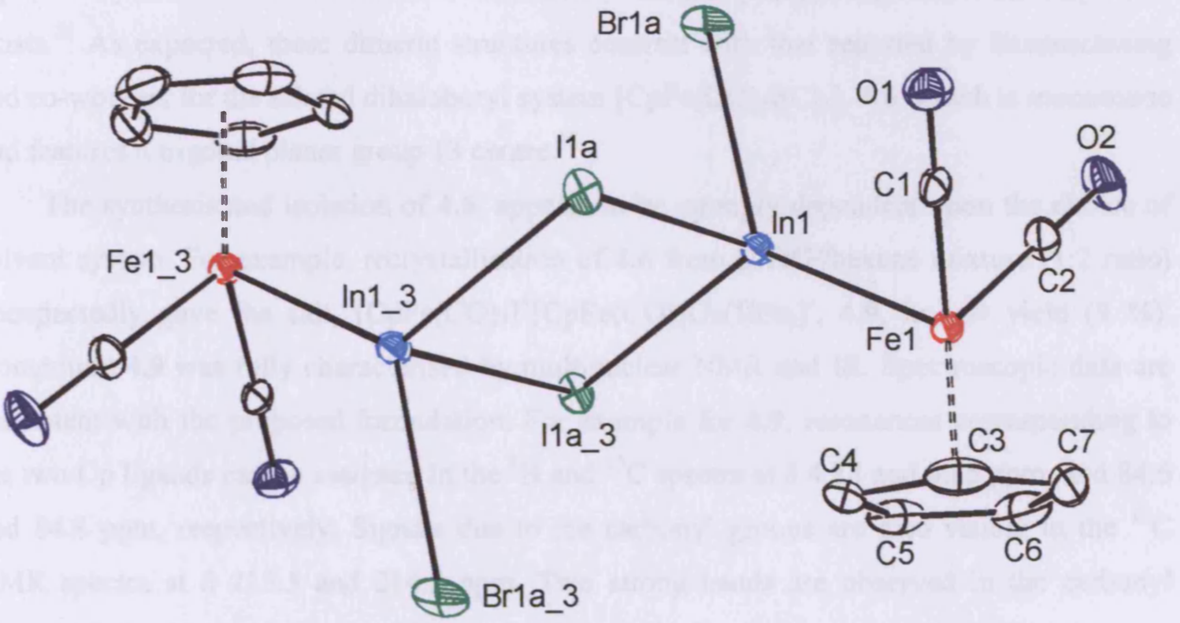


Figure 2: Molecular Structure of $[CpFe(CO)_2In(I)Br]_2$, **4.7**

(This crystal structure was obtained by Dr. D. Coombs)

Selected bond lengths (Å) and angles (°): Fe(1)—In(1) 2.480(1), Fe(1)—C(1) 1.770(9), Fe(1)—Cp centroid 1.730(8), In(1)—Br(1b) 2.974(10), In(1)—Br(1b') 2.623(10), In(1)—I(1b) 2.704(3), Fe(1)—In(1)—I(1b) 130.71(6), Br(1b)—In(1)—Br(1b') 82.7(3).

The halide ligands in **4.7** are disordered between bridging and terminal positions. This disorder was successfully modelled (summing to unity in each position) giving refined occupancies of 70:30 Br:I for the bridging positions and 30:70 for the terminal positions. Both mixed halide complexes, **4.6** and **4.7** have dimeric, halide bridged structures. Compound **4.6** features bridging iodides whereas the disorder in **4.7** implies that the energy difference between bridging bromides and bridging iodides is small. As expected the Fe(1)—Ga(1) bond length (2.310(2) Å) of **4.6** is shorter than the corresponding Fe(1)—In(1) bond (2.480(1) Å) of **4.7**.[18]

Dimeric, halide-bridged structures **4.6** and **4.7** represent the first structurally characterized neutral base-free dihalogallyl or -indyl species to be reported in the literature.[19,20] Comparisons, however, can be drawn with $[CpFe(CO)_2GaCl_2]_2(GaCl_3)_2$, **1.18**, reported by Barron and co-workers, in which a similar $[L_nME(X)(\mu\text{-}X)_2E(X)ML_n]$ motif exists.[21] As expected, these dimeric structures contrast with that reported by Braunschweig and co-workers for the related dihaloboryl system $[CpFe(CO)_2BCl_2]$, **4.8**, which is monomeric and features a trigonal planar group 13 centre.[22]

The synthesis and isolation of **4.6**, appears to be strongly dependent upon the choice of solvent system. For example, recrystallisation of **4.6** from a THF/hexane mixture (1:2 ratio) unexpectedly gave the salt, $[CpFe(CO)_3]^+[CpFe(CO)_2Ga(I)Br_2]^-$, **4.9**, in low yield (9 %). Compound **4.9** was fully characterised by multinuclear NMR and IR. Spectroscopic data are consistent with the proposed formulation. For example for **4.9**, resonances corresponding to the two Cp ligands can be assigned in the ^1H and ^{13}C spectra at δ 4.88 and 4.85 ppm, and 84.6 and 84.8 ppm, respectively. Signals due to the carbonyl groups are also visible in the ^{13}C NMR spectra at δ 213.5 and 214.2 ppm. Two strong bands are observed in the carbonyl region of the IR spectrum, at 2001 and 1949 cm^{-1}. These spectroscopic inferences were subsequently confirmed crystallographically, the molecular structure of **4.9** being depicted in Figure 3.

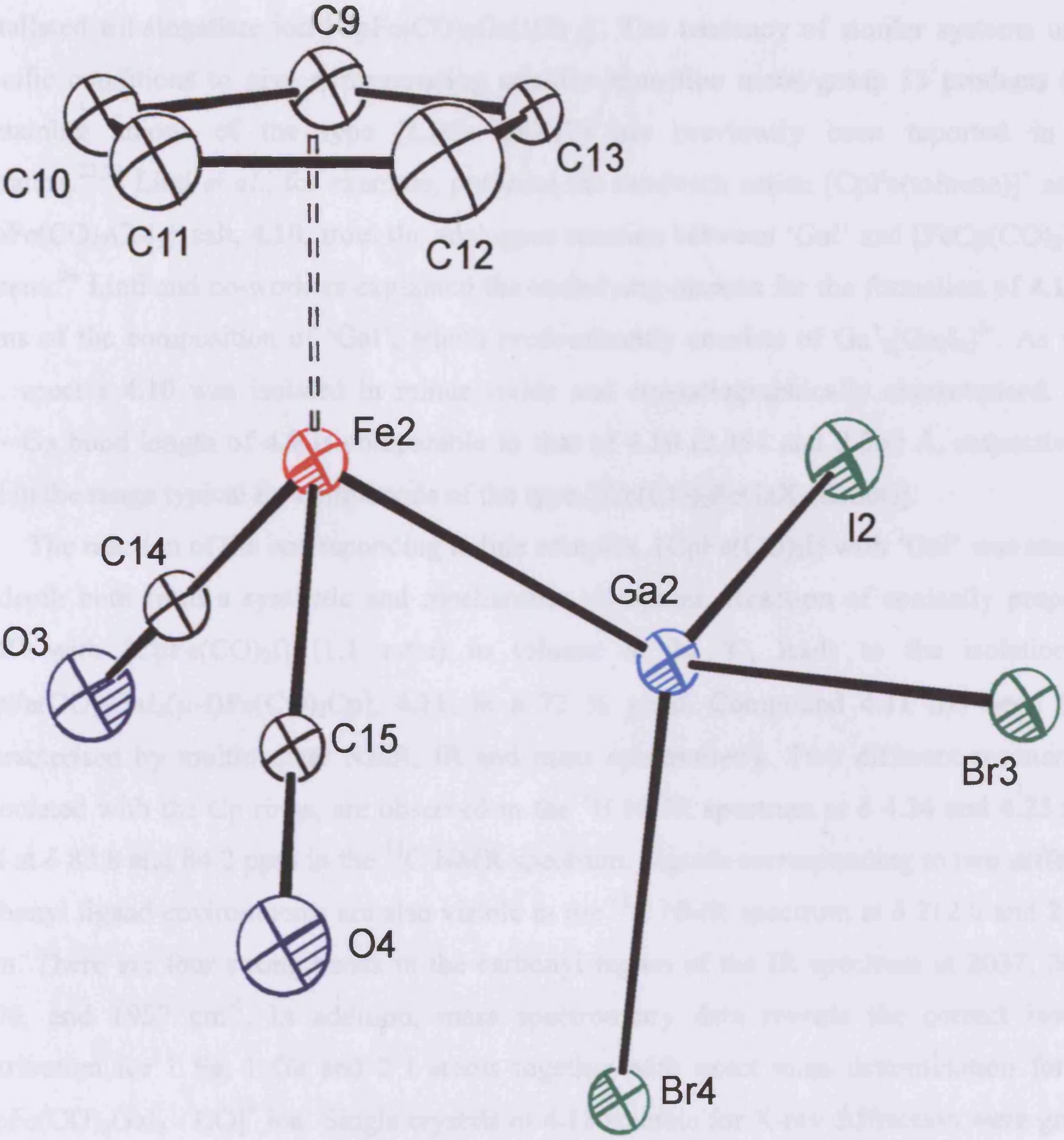


Figure 3: Structure of the anionic component of $[CpFe(CO)_3]^+[CpFe(CO)_2Ga(I)Br_2]^-$, **4.9**

Selected bond lengths (Å) and angles (°): Fe(2)—Ga(2) 2.354(2), Ga(2)—I(2) 2.551(19), Fe(2)—Cp centroid 1.706(2), Ga(2)—Br(3) 2.450(2), Ga(2)—Br(4) 2.535(19), Fe(2)—Ga(2)—I(2) 116.90(8), Br(3)—Ga(2)—Br(4) 102.19(7).

X-ray crystallography has confirmed that **4.9** adopts a salt-like structure featuring the metallated trihalogallate ion $[CpFe(CO)_2Ga(I)Br_2]^-$. The tendency of similar systems under specific conditions to give corresponding salt-like transition metal/group 13 products (*e.g.* containing anions of the type $[L_nM—GaX_3]^-$) has previously been reported in the literature.[23,24] Linti *et al.*, for example, prepared the sandwich cation $[CpFe(toluene)]^+$ as the $[CpFe(CO)_2GaI_3]^-$ salt, **4.10**, from the analogous reaction between 'GaI' and $[FeCp(CO)_2]_2$ in toluene.[24] Linti and co-workers explained the underlying reasons for the formation of **4.10** in terms of the composition of 'GaI', which predominantly consists of $Ga^+_2[Ga_2I_6]^{2-}$. As with **4.9**, species **4.10** was isolated in minor yields and crystallographically characterised. The Fe—Ga bond length of **4.9** is comparable to that of **4.10** (2.354 and 2.360 Å, respectively) and in the range typical for compounds of the type, $[Cp(CO)_2FeGaX_2(donor)]$.

The reaction of the corresponding iodide complex, $[CpFe(CO)_2I]$ with 'GaI' was studied in depth both from a synthetic and mechanistic viewpoint. Reaction of sonically prepared 'GaI' with $[CpFe(CO)_2I]$ (1:1 ratio) in toluene at 20 °C, leads to the isolation of $[CpFe(CO)_2GaI_2(\mu\text{-}I)Fe(CO)_2Cp]$, **4.11**, in a 72 % yield. Compound **4.11** has been fully characterised by multinuclear NMR, IR and mass spectrometry. Two different resonances, associated with the Cp rings, are observed in the ^1H NMR spectrum at δ 4.24 and 4.25 ppm and at δ 83.8 and 84.2 ppm in the ^{13}C NMR spectrum. Signals corresponding to two different carbonyl ligand environments are also visible in the ^{13}C NMR spectrum at δ 212.0 and 215.1 ppm. There are four strong bands in the carbonyl region of the IR spectrum at 2037, 2003, 2000, and 1957 cm^{-1}. In addition, mass spectrometry data reveals the correct isotope distribution for 1 Fe, 1 Ga and 2 I atoms together with exact mass determination for the $[CpFe(CO)_2GaI_2 - CO]^+$ ion. Single crystals of **4.11** suitable for X-ray diffraction were grown by recrystallisation from a toluene/hexane mixture (*ca.* 1:2). The molecular structure of **4.11** is depicted in Figure 4 and is in agreement with spectroscopic data.

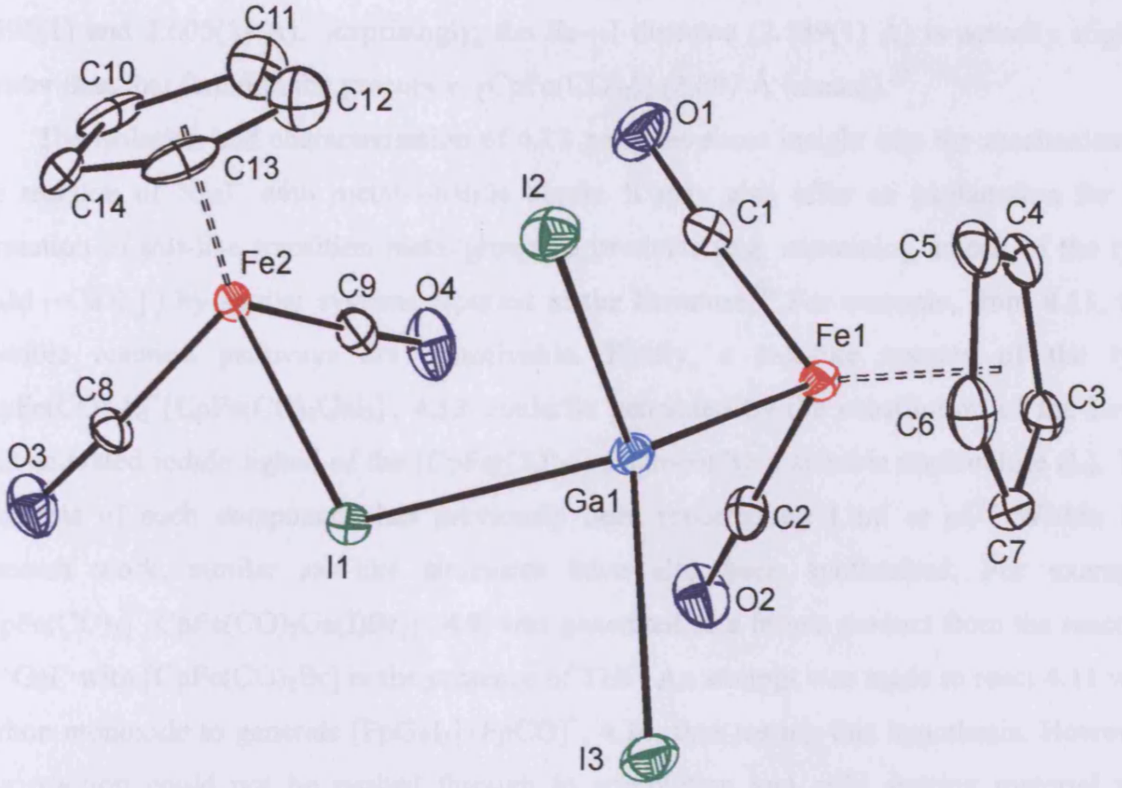


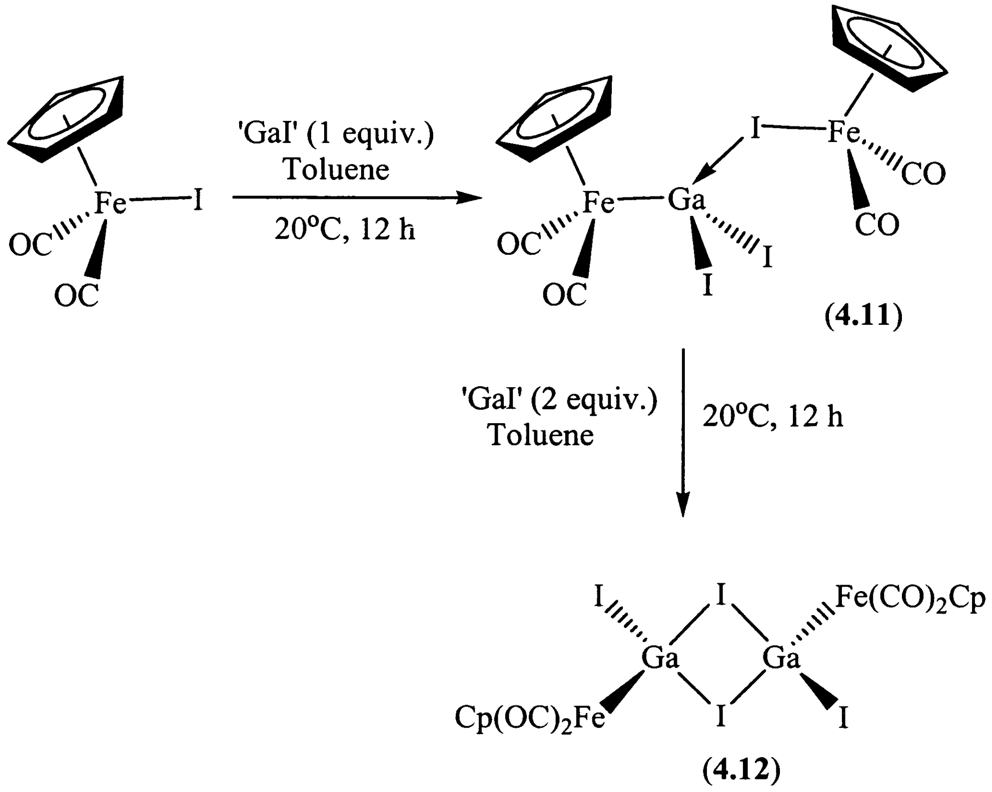
Figure 4: **Molecular structure of [CpFe(CO)$_2$GaI$_2$(μ-I)Fe(CO)$_2$Cp], 4.11**

Selected bond lengths (Å) and angles (°): Fe(1)—Ga(1) 2.331(2), Fe(1)—C(1) 1.740(11), Fe(1)—Cp centroid 1.726(9), Ga(1)—I(1) 2.788(1), Ga(1)—I(2) 2.596(1), Ga(1)—I(3) 2.605(1), Fe(2)—I(1) 2.589(1), Fe(2)—C(8) 1.760(8), Fe(2)—Cp centroid 1.727(8), Fe(1)—I(1)—Fe(2) 116.01(4), I(2)—Ga(1)—I(3) 106.60(4), Fe(1)—Ga(1)—I(1) 114.54(8), Fe(1)—Ga(1)—I(3) 117.98(5).

Complex **4.11** can be considered to be a 1:1 adduct formed between [CpFe(CO)$_2$I] and [CpFe(CO)$_2$GaI$_2$] *via* an I→Ga donor/acceptor interaction (Scheme 7). One possible mechanism for the synthesis of **4.11** presumably involves trapping of the initial product formed by 'GaI' insertion (into the Fe—I bond of [CpFe(CO)$_2$I]) with unreacted [CpFe(CO)$_2$I]. Therefore the structure of **4.11**, can be considered as an intermediate in the reaction pathway from [CpFe(CO)$_2$I] and 'GaI' to [CpFe(CO)$_2$GaI$_2$]$_2$, **4.12**. The molecular structure of **4.11** is consistent with its description as a donor/acceptor adduct. As expected, the bridging Ga—I bond is significantly longer than the terminal Ga—I bonds (2.788(1) *vs.* 2.596(1) and 2.605(1) Å). Surprisingly, the Fe—I distance (2.589(1) Å) is actually slightly shorter than that found in the precursor, [CpFe(CO)$_2$I] (2.607 Å (mean)).[25]

The isolation and characterisation of **4.11** provides some insight into the mechanism of the reaction of 'GaI' with metal—halide bonds. It may also offer an explanation for the formation of salt-like transition metal/group 13 products (*e.g.* containing anions of the type [L$_n$M—GaX$_3$]$^-$) by similar systems reported in the literature.[24] For example, from **4.11**, two possible reaction pathways are conceivable. Firstly, a salt-like species of the type [CpFe(CO)$_2$L]$^+$[CpFe(CO)$_2$GaI$_3$]$^-$, **4.13**, could be generated by the substitution of the Lewis acid activated iodide ligand of the [CpFe(CO)$_2$I] fragment by a suitable nucleophile (L). The synthesis of such compounds has previously been reported by Linti *et al.*[24] Within this research work, similar salt-like structures have also been synthesised. For example, [CpFe(CO)$_3$]$^+$[CpFe(CO)$_2$Ga(I)Br$_2$]$^-$, **4.9**, was generated as a minor product from the reaction of 'GaI' with [CpFe(CO)$_2$Br] in the presence of THF. An attempt was made to react **4.11** with carbon monoxide to generate [FpGaI$_3$]$^-$[FpCO]$^+$, **4.14**, thus testing this hypothesis. However, this reaction could not be pushed through to completion and only starting material was isolated.

Alternatively, from **4.11**, dimeric [CpFe(CO)$_2$GaI$_2$]$_2$, **4.12**, could be generated by further insertion of 'GaI' into the remaining and presumably significantly weakened Fe—I bond coupled with the simultaneous formation of a further I→ Ga interaction. Such a mechanism would require an excess of 'GaI'. Indeed, under more forcing conditions, with three equivalents of 'GaI', compound **4.12** is formed as the predominant product (Scheme 7).



Scheme 7

Reaction of sonically prepared ‘GaI’ (3 equiv.) with [CpFe(CO)$_2$I] in toluene at 20 °C for 48 h yields **4.12**. Compound **4.12** has been fully characterised by multinuclear NMR, IR and mass spectrometry. Spectroscopic data are consistent with the proposed formulation. For example signals due to the Cp-ligand are visible in the ^{1}H and ^{13}C NMR spectra at δ 4.12 and δ 84.0 ppm, respectively. A single resonance associated with the carbonyl groups could also be assigned in the ^{13}C NMR spectrum at δ 213.4 ppm. Two strong bands were observed in the carbonyl region of the IR spectrum at 2012 and 1970 cm^{-1}. Mass spectral data, including exact mass determination, are also consistent with the proposed formulation, revealing ready fragmentation into a mixture of monomeric species, *e.g.* [CpFe(CO)GaI$_2$]$^+$, [CpFeGaI$_2$]$^+$, and [CpFe(CO)$_2$GaI]$^+$, under electron impact conditions. Single crystals suitable for X-ray diffraction were grown by layering a toluene solution of **4.12** with hexane and cooling to –30 °C. The molecular structure of **4.12** is depicted in Figure 5.

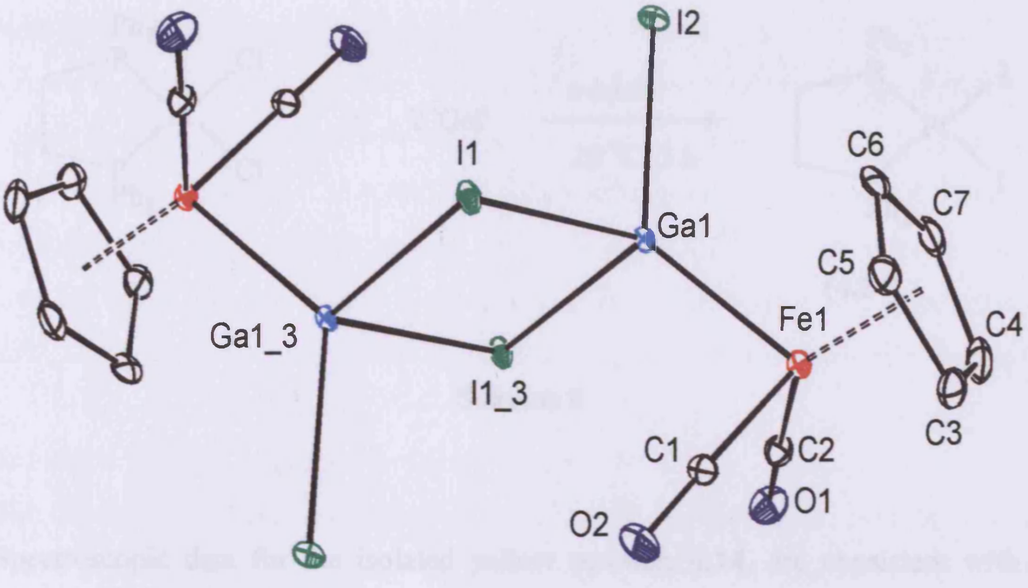
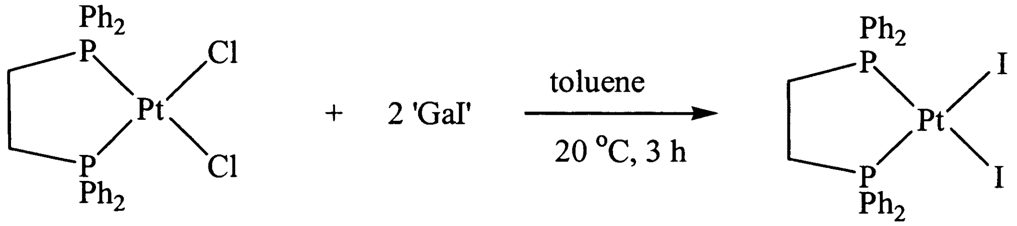


Figure 5: Structure of [$CpFe(CO)_2GaI_2]_2$, **4.12**

Selected bond lengths (Å) and angles (°): Fe(1)—Ga(1) 2.321(1), Fe(1)—C(1) 1.757(8), Fe(1)—Cp centroid 1.717(8), Ga(1)—I(1) 2.799(1), Ga(1)—I(1_3) 2.731(1), Ga(1)—I(2) 2.557(1), Fe(1)—Ga(1)—I(2) 126.48(4), I(1)—Ga(1)—I(1_3) 91.59(2).

X-ray crystallography reveals that compound **4.12** adopts the expected dimeric geometry with bridging and terminal iodide groups. Together with **4.6**, the dimeric halide-bridged structure of **4.12** represents the first structurally characterized neutral base-free dihalogallyl species to be reported. Therefore the molecular structure of **4.12** can be compared with that of dimeric mixed halide species **4.6**. Both compounds contain bridging iodides and similar Fe—Ga bonds distances (2.310(2) *vs.* 2.321(1) Å for **4.6** and **4.12**, respectively).

The formation of compounds **4.6** and **4.12** by insertion chemistry can be contrasted with the reaction of 'GaI' with [(dppe)$PtCl_2$] which results in substitution of the chloride atoms. Reaction between 'GaI' (2 equiv.) and [(dppe)$PtCl_2$] in toluene at 20 °C over 3 h gives the yellow powder [(dppe)PtI_2], **4.14**, rather than [(dppe)Pt(GaICl)$_2$], **4.15**, the expected product of insertion chemistry. (Scheme 8).

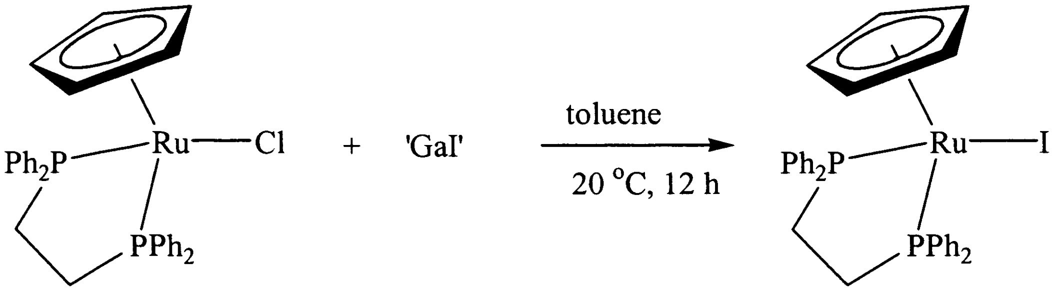


(4.14)

Scheme 8

Spectroscopic data for the isolated yellow powder, **4.14**, are consistent with quoted literature values for [(dppe)PtI$_2$],[15] thus confirming its identity. A single peak, for example, is observed in the ^{31}P NMR spectrum at δ 46.6 ppm (with satellites, $J_{Pt\text{-}P}$ 3384 Hz). The molecular ion is also visible in the mass spectrum at m/z 846.5.

A similar reaction is also observed between 'GaI' and [CpRu(dppe)Cl] in toluene at 20 °C, which yields [Cp(dppe)RuI], **4.16**, instead of [CpRu(dppe)GaICl], **4.17** (Scheme 9).



(4.16)

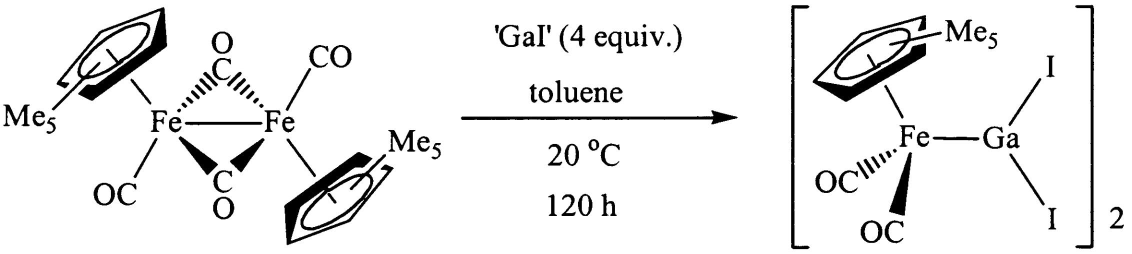
Scheme 9

Compound **4.16** was fully characterised by multinuclear NMR and mass spectrometry. Spectroscopic data are consistent with the formation of **4.16** and previously reported literature values.[16] For example, a single peak was observed in the ^{31}P NMR spectrum at δ 80.3 ppm. Resonances associated with both the dppe fragment and Cp-ring were also visible in the ^{1}H

NMR spectrum. Mass spectral data revealed both the molecular ion and fragmentation consistent with the proposed formulation. Single crystals of **4.16** suitable for X-ray diffraction were grown by recrystallisation from a CH_2Cl_2/hexane mixture and although there were of poor quality they did serve to confirm the empirical composition. The underlying reasons why halide substitution reactions occur between [(dppe)$PtCl_2$] and [CpRu(dppe)Cl] and 'GaI' is unclear. Presumably factors such as bond strength and sterics are key aspects. Attempts to react both B-bromocatecholborane and zirconocene dichloride with 'GaI', were unsuccessful. Despite extensive variation of reaction conditions, in both cases, no reaction was observed.

4.6.2 Insertion of 'GaI' into metal—metal bonds

The insertion of 'GaI' into metal—metal bonds has also been investigated in some depth. Reaction of sonically prepared 'GaI' with [Cp*Fe$(CO)_2$]$_2$ in toluene at 20 °C, over the course of 120 h, gives [Cp*Fe$(CO)_2$GaI_2]$_2$, **4.18**, in an isolated yield of 47 % (Scheme 10).



(4.18)

Scheme 10

Complex **4.18** is a pale yellow solid, which has been fully characterised by multinuclear NMR, IR and mass spectrometry. All spectroscopic data are consistent with the proposed formulation. For example, resonances due to the Cp* ring, are observed in the ^1H NMR and ^{13}C NMR spectra at δ 1.60 and δ 9.8 ppm, respectively. Resonances associated with the quaternary carbon of Cp* ring and the carbonyl groups of the metal fragment are also identifiable in the ^{13}C NMR spectrum at δ 95.4 and 216.4 ppm, respectively. IR spectroscopy indicates two strong C—O stretches at 2001 and 1954 cm^{-1}. Mass spectrometry data reveals fragment ions corresponding to [Cp*Fe$(CO)_2$GaI_2]$^+$, [Cp*Fe$(CO)_2$GaI_2 - CO]$^+$, [Cp*Fe$(CO)_2$GaI_2 – 2CO]$^+$ Pale yellow single crystals of **4.18** suitable for X-ray diffraction were grown by recrystallisation from CH_2Cl_2 at – 30 °C. The molecular structure of **4.18** is depicted in Figure 6.

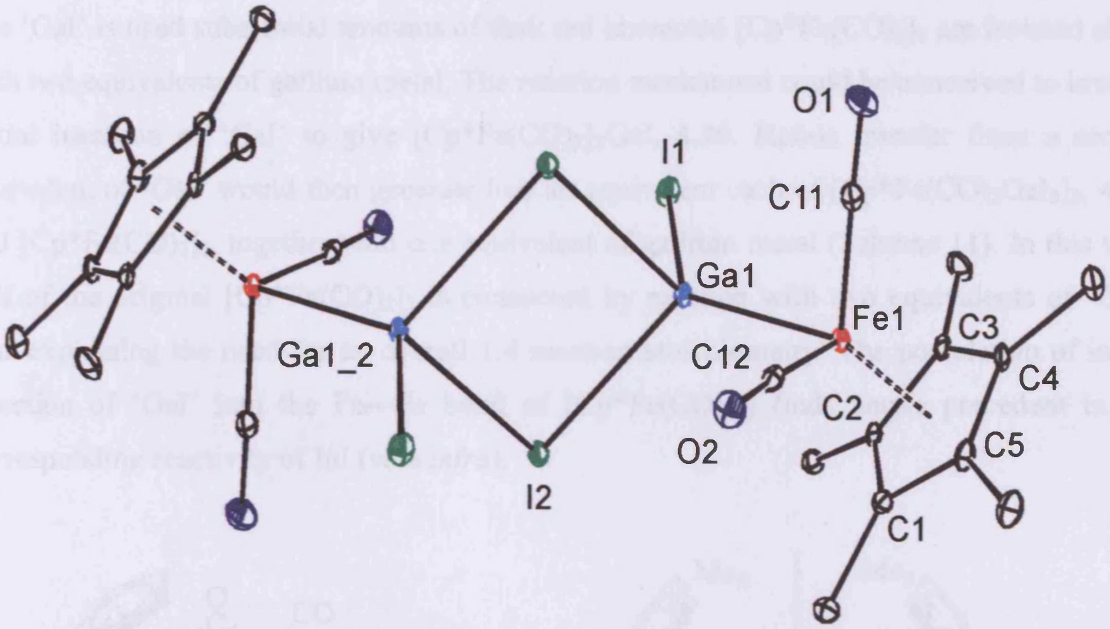
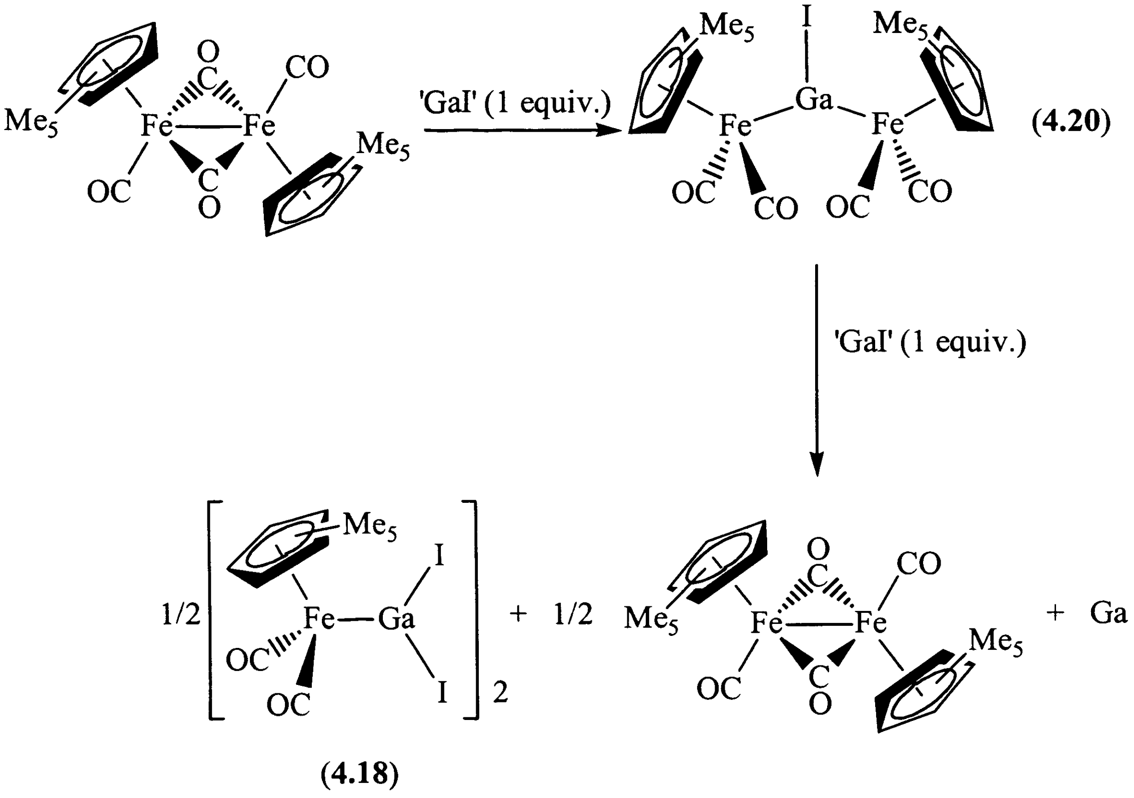


Figure 6: Molecular structure of $[Cp^*Fe(CO)_2GaI_2]_2$, **4.18**

Selected bond lengths (Å) and angles (°): Fe(1)—Ga(1) 2.314(1), Fe(1)—C(11) 1.746(6), Fe(1)—Cp centroid 1.725(4), Ga(1)—I(1) 2.585(1), Ga(1)—I(2) 2.756(1), Fe(1)—Ga(1)—I(1) 124.72(3).

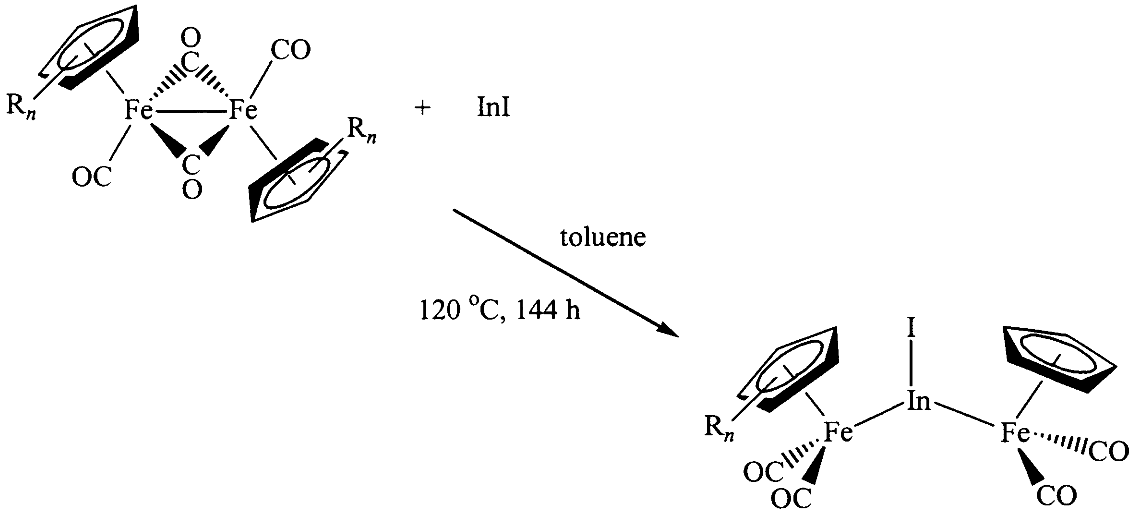
X-ray crystallography has confirmed that compound **4.18** adopts the expected dimeric geometry with bridging and terminal iodide groups. The molecular structure of **4.18** can be compared with that of the corresponding Cp complex **4.12**. Both compounds contain both bridging and terminal iodide ligands and similar Fe—Ga linkages (2.314(1) *vs.* 2.321(1) Å). The bridging Fe—I bond distances in **4.18**, however, are markedly longer than those of **4.12** (2.756(1) *vs.* 2.731(1) Å). Presumably this reflects the increased steric demands of the Cp* ring.

Irrespective of reaction stoichiometry, complex **4.18**, is the only Fe/Ga containing product isolated from the reaction between 'GaI' and $[Cp^*Fe(CO)_2]_2$. This can be contrasted with the corresponding reaction of $[CpFe(CO)_2]_2$ and 'GaI' reported in the literature by Linti *et al.*[24] In this case, a mixture of organometallic species was synthesised although the salt, $[CpFe(CO)_2GaI_3]^-$, **4.19**, was the only isolated Fe/Ga/I containing product. For the formation of **4.18**, at least four equivalents of 'GaI' are required to drive this reaction to completion. If less 'GaI' is used substantial amounts of dark red unreacted $[Cp^*Fe(CO)_2]_2$ are isolated along with two equivalents of gallium metal. The reaction mechanism could be conceived to involve initial insertion of 'GaI' to give $[Cp^*Fe(CO)_2]_2GaI$, **4.20**. Halide transfer from a second equivalent of 'GaI' would then generate half an equivalent each of $[Cp^*Fe(CO)_2GaI_2]_2$, **4.18**, and $[Cp^*Fe(CO)_2]_2$, together with one equivalent of gallium metal (Scheme 11). In this way, half of the original $[Cp^*Fe(CO)_2]_2$ is consumed by reaction with two equivalents of 'GaI', thus explaining the need for an overall 1:4 reaction stoichiometry. The postulation of initial insertion of 'GaI' into the Fe—Fe bond of $[Cp^*Fe(CO)_2]_2$ finds ample precedent in the corresponding reactivity of InI (*vide infra*).



Scheme 11

The analogous reactions of InCl and InI with $[Cp^*Fe(CO)_2]_2$ have also been investigated within our research group (work carried out by Dr. D. Coombs). Reaction between InI and $[Cp^*Fe(CO)_2]_2$ (1:1 stoichiometry) in refluxing toluene over 144 h yields the simple insertion product, $[Cp^*Fe(CO)_2]_2InI$, **3.13**, in 53 % yield (Scheme 12). This can be contrasted with the formation of dimeric **4.18**. Single crystals of **3.13** suitable for X-ray diffraction were grown by the slow diffusion of hexane into a toluene solution of **3.13** at –30 °C. The molecular structure of **3.13** is depicted in Figure 7.



(3.13)

Scheme 12

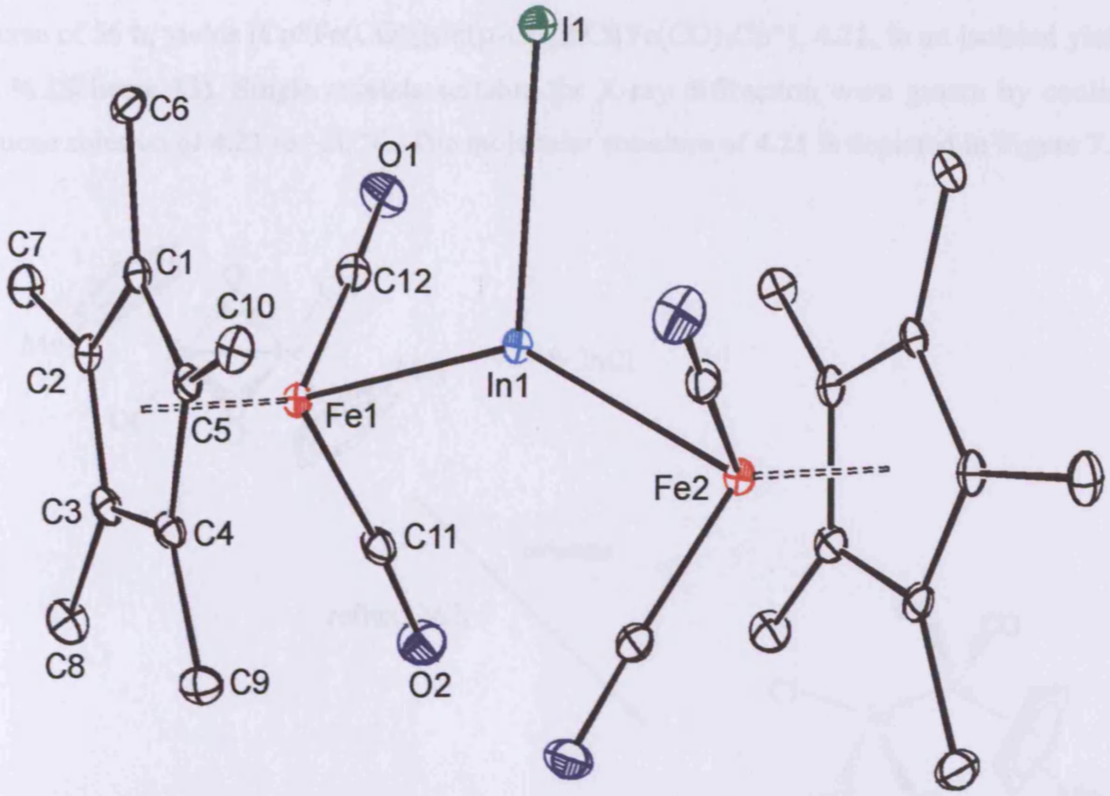
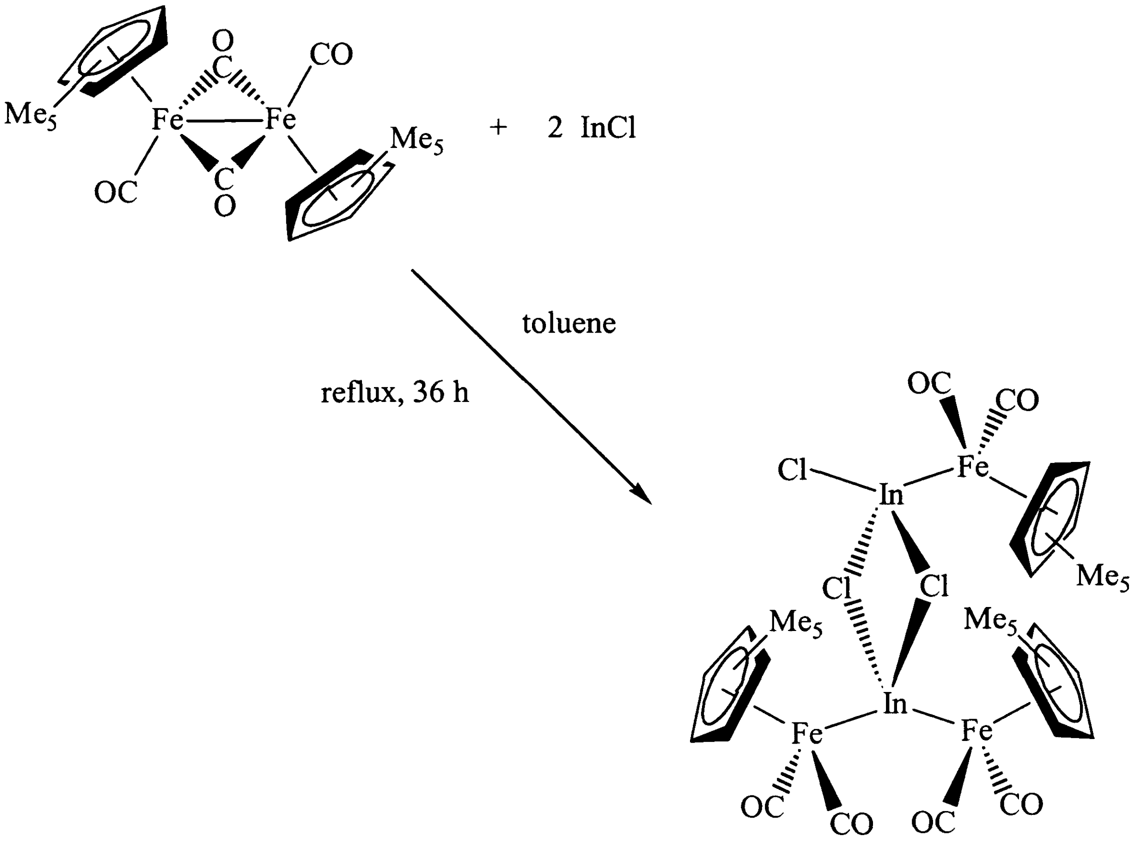


Figure 7: Molecular structure of $[Cp^*Fe(CO)_2]_2InI$, **3.13**
(This crystal structure was obtained by Dr. D. Coombs)

Selected bond lengths (Å) and angles (°): Fe(1)—In(1) 2.513(1), Fe(2)—In(1) 2.519(1), Fe(1)—C(11) 1.754(5), Fe(1)—Cp centroid 1.726(5), In(1)—I(1) 2.854(4), Fe(1)—In(1)—Fe(2) 141.98(2), Fe(1)—In(1)—I(1) 110.30(2), Fe(2)—In(1)—I(1) 107.61(2).

The structure of **3.13** is analogous to the molecular structure of $[\{Cp^*Fe(CO)_2\}_2GaCl]$ **3.11**, which was synthesised using salt elimination methodology (discussed in Chapter 3). The synthesis of **3.13** demonstrates that in the presence of sufficient steric bulk, subvalent metal halide insertion chemistry represents a direct one-step route to three-coordinate group 13 ligand systems. Therefore this methodology can be used as an alternative to the more limited salt elimination route.

However, for the corresponding reaction of InCl with $[Cp^*Fe(CO)_2]_2$, the predominant product generated is not simply the insertion product (work carried out by Dr. D. Coombs). Reaction between InCl and $[Cp^*Fe(CO)_2]_2$ (2:1 stoichiometry) in toluene, refluxing over the course of 36 h, yields $[Cp^*Fe(CO)_2]_2In(\mu\text{-}Cl)_2InCl[Fe(CO)_2Cp^*]$, **4.21,** in an isolated yield of 20 % (Scheme 13). Single crystals suitable for X-ray diffraction were grown by cooling a toluene solution of **4.21** to –30 °C. The molecular structure of **4.21** is depicted in Figure 7.



(4.21)

Scheme 13

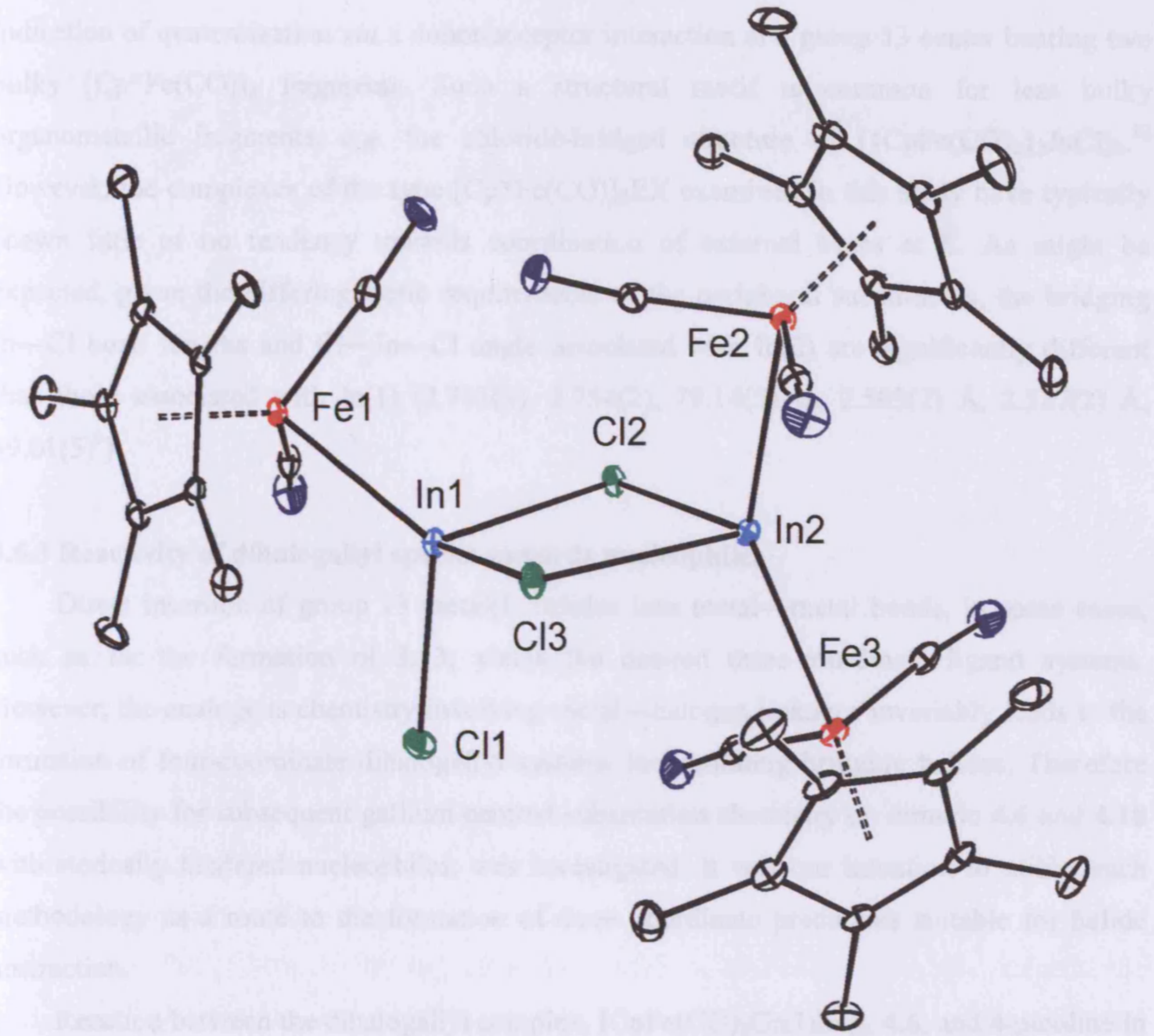


Figure 7: Molecular structure of $[Cp^*Fe(CO)_2]_2In(\mu\text{-}Cl)_2InCl[Fe(CO)_2Cp^*]$, **4.21**
(This crystal structure was obtained by Dr. D. Coombs)

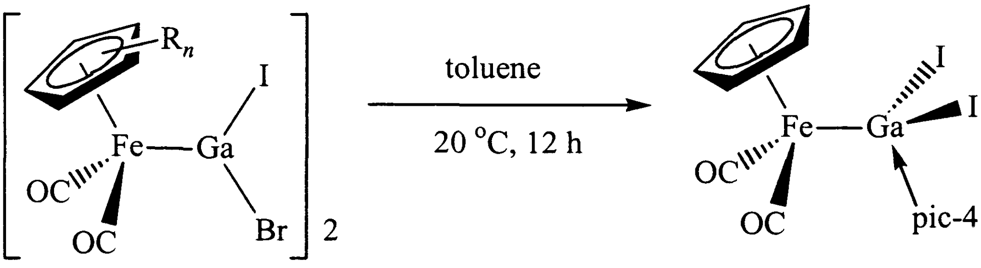
Selected bond lengths (Å) and angles (°): Fe(1)—In(1) 2.488(1), Fe(2)—In(2) 2.546(1), Fe(3)—In(2) 2.540(1), In(1)—Cl(1) 2.403(2), In(1)—Cl(2) 2.527(2), In(1)—Cl(3) 2.503(2), In(2)—Cl(2) 2.754(2), In(2)—Cl(3) 2.782(2), Cl(2)—In(1)—Cl(3) 89.04(5), Cl(2)—In(2)—Cl(3) 79.15(5).

The structure $[Cp^*Fe(CO)_2]_2In(\mu\text{-}Cl)_2InCl[Fe(CO)_2Cp^*]$, **4.21**, can be thought of as a chloride bridged 1:1 adduct between $[Cp^*Fe(CO)]_2InCl$ and $[Cp^*Fe(CO)_2InCl_2]$ fragments and features a highly asymmetric In_2Cl_2 bridging unit. Unusually **4.21** shows the first indication of quaternization *via* a donor/acceptor interaction at a group 13 center bearing two bulky $[Cp^*Fe(CO)]_2$ fragments. Such a structural motif is common for less bulky organometallic fragments, *e.g.* the chloride-bridged structure of $[\{CpFe(CO)_2\}_2InCl]_2$.[12] However, the complexes of the type $[Cp^*Fe(CO)]_2EX$ examined in this study have typically shown little or no tendency towards coordination of external bases at E. As might be expected, given the differing steric requirements of the peripheral substituents, the bridging In—Cl bond lengths and Cl—In—Cl angle associated with In(2) are significantly different than those associated with In(1) (2.781(2), 2.754(2), 79.14(5) *vs.* 2.503(2) Å, 2.527(2) Å, 89.01(5)°).

4.6.3 Reactivity of dihalogallyl species towards nucleophiles

Direct insertion of group 13 metal(I) halides into metal—metal bonds, in some cases, such as for the formation of **3.13**, yields the desired three-coordinate ligand systems. However, the analogous chemistry involving metal—halogen linkages invariably leads to the formation of four-coordinate dihalogallyl systems incorporating bridging halides. Therefore the possibility for subsequent gallium-centred substitution chemistry on dimeric **4.6** and **4.18** with sterically hindered nucleophiles, was investigated. It was our intention to utilise such methodology as a route to the formation of three coordinate precursors suitable for halide abstraction.

Reaction between the dihalogallyl complex, $[CpFe(CO)_2Ga(I)Br]_2$, **4.6**, and 4-picoline in toluene 20 °C over 12 h results in simple adduct formation yielding, $[CpFe(CO)_2GaI_2.Pic]$, **4.22**, in 25 % isolated yield (Scheme 14). Similar reactivity has previously been observed for dihalogallyl complexes. For example, Linti *et al.*, have reported the synthesis of $[CpFe(CO)_2GaCl_2{\cdot}THF]$, **1.23**, from a metathesis reaction between compounds with Ga—Ga and Fe—Fe bonds.[24]



(4.6)   **(4.22)**

Scheme 14

The initially isolated crude microcrystalline product was a mixture with spectroscopic data indicating that it contains three different Cp containing species. For example, three Cp resonances were visible in the ^{1}H NMR and ^{13}C NMR spectra at δ 4.27, 4.29, and 4.31 and 83.4, 84.0, and 84.6 ppm, respectively. Broad signals associated with 4-picoline were also observed in the ^{1}H spectrum at δ 1.35, 6.13 and 8.62 ppm, corresponding to the CH_3 and CH groups of 4-picoline. Four strong bands were observed in the carbonyl region of the IR spectrum at 1985, 1979, 1950, and 1934 cm^{-1}. Mass spectrometry data also implied the presence of both dibromo- and diiodogallyl derivatives as well as the mixed iodo(bromo) complex. Single crystals of the picoline-complexed diiodogallyl species, [CpFe(CO)$_2$GaI$_2$·(4-pic)], **4.22**, suitable for X-ray diffraction were grown by careful recrystallization from benzene, followed by slow diffusion of hexane. The structure of **4.22** (as the benzene hemi-solvate) is depicted in Figure 8. Characterizing data for the crystalline product **4.22** were identical to those of a crystalline sample prepared independently from [CpFe(CO)$_2$GaI$_2$]$_2$, **4.12**, and 4-picoline and recrystallized from toluene/hexane. Presumably, the mechanism of formation of **4.22** from [CpFe(CO)$_2$Ga(I)Br] involves N-base coordination together with halide scrambling. Differences in solubility/crystallinity may help to explain the isolation of diiodo complex **4.22**, in preference to the other dihalo complexes.

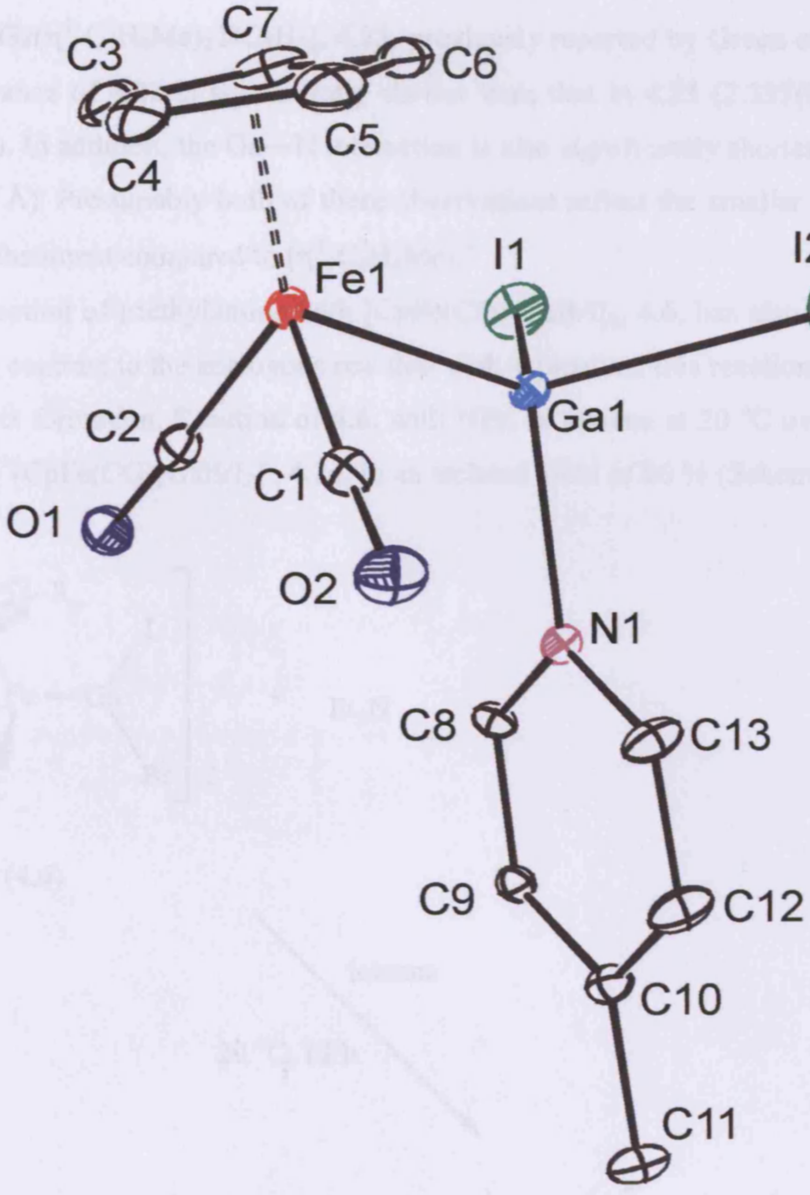
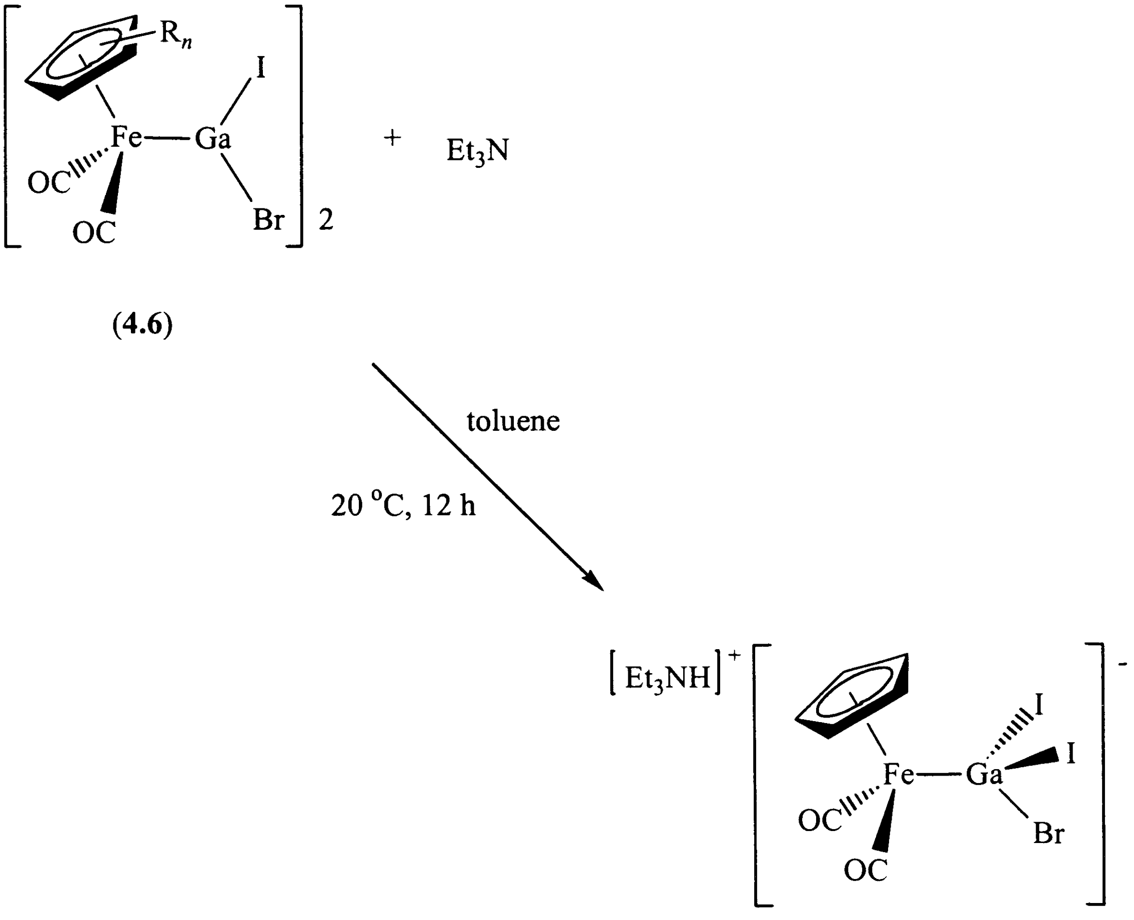


Figure 8: Molecular structure of [CpFe(CO)$_2$GaI$_2$·(4-pic)], **4.22**

Selected bond lengths (Å) and angles (°): Fe(1)—Ga(1) 2.337(1), Fe(1)—C(1) 1.778(10), Fe(1)—Cp centroid 1.719(9), Ga(1)—I(1) 2.451(1), Ga(1)—I(2) 2.501(1), Ga(1)—N(1) 2.054(7), I(1)—Ga(1)—I(2) 103.91(4), Fe(1)—Ga(1)—I(1) 115.67(5), Fe(1)—Ga(1)—I(2) 119.87(5).

The structure of the picoline adduct **4.22** can be compared with the pyridine adduct $[CpFe(CO)_2Ga(\eta^1\text{-}C_5H_4Me)_2{\cdot}NC_5H_5]$, **4.23**, previously reported by Green *et al.* However, the Fe—Ga distance of **4.22** is significantly shorter than that in **4.23** (2.337(1) *vs.* 2.427(1) Å, respectively). In addition, the Ga—N interaction is also significantly shorter in **4.22** (2.054(7) *vs.* 2.101(4) Å). Presumably both of these observations reflect the smaller steric demands of the iodide substituent compared to $(\eta^1\text{-}C_5H_4Me)$.[1]

The reaction of triethylamine with $[CpFe(CO)_2GaBrI]_2$, **4.6**, has also been investigated. However, in contrast to the analogous reaction with 4-picoline, this reaction does not result in simple adduct formation. Reaction of **4.6**, with NEt_3 in toluene at 20 °C over 12 h yields the salt $[Et_3NH]^+[CpFe(CO)_2GaBrI_2]^-$, **4.24**, in an isolated yield of 60 % (Scheme 15).



(4.6)

(4.24)

Scheme 15

Pale yellow crystals of **4.24** suitable for X-ray diffraction were grown by the slow diffusion of hexane into a concentrated toluene solution, **4.24**. The structure of the anionic component of **4.24** is depicted in Figure 9. Compound **4.24** was fully characterised by multinuclear NMR, IR and mass spectrometry. Spectroscopic data are consistent with the crystallographically determined structure. For example, resonances associated with both $[HNEt_3]^+$ and $[CpFe(CO)_2GaBrI_2]^-$ ions are observed in the ^1H NMR spectrum at δ 0.52, 2.29, 7.44 and 4.36 ppm, corresponding to the CH_3 of $HNEt_3^+$, CH_2 of $HNEt_3^+$, proton of $HNEt_3^+$ and the Cp ligand, respectively. Signals corresponding to these two ions could also be assigned in the ^{13}C NMR spectrum at δ 9.1 and 47.2 ppm for $[HNEt_3]^+$ and δ 83.8 for the Cp ligand. However, the carbonyl carbons were undetected despite the use of a long scan and extended relaxation time. Two strong bands were observed in the carbonyl region of the IR spectrum at 1996 and 1944 cm^{-1}. Mass spectral data indicated significant fragment ions for $[FpGaBrI_2^- - HNEt_3]^+$, $[FpGaIBr_2^- - HNEt_3]^+$, $[FpGaBr_3^- - HNEt_3]^+$, and $[HNEt_3]^+$. As with **4.22**, differences in solubility/crystallinity may help to explain the isolation of diiodobromo complex **4.24**, in preference to other trihalo complexes.

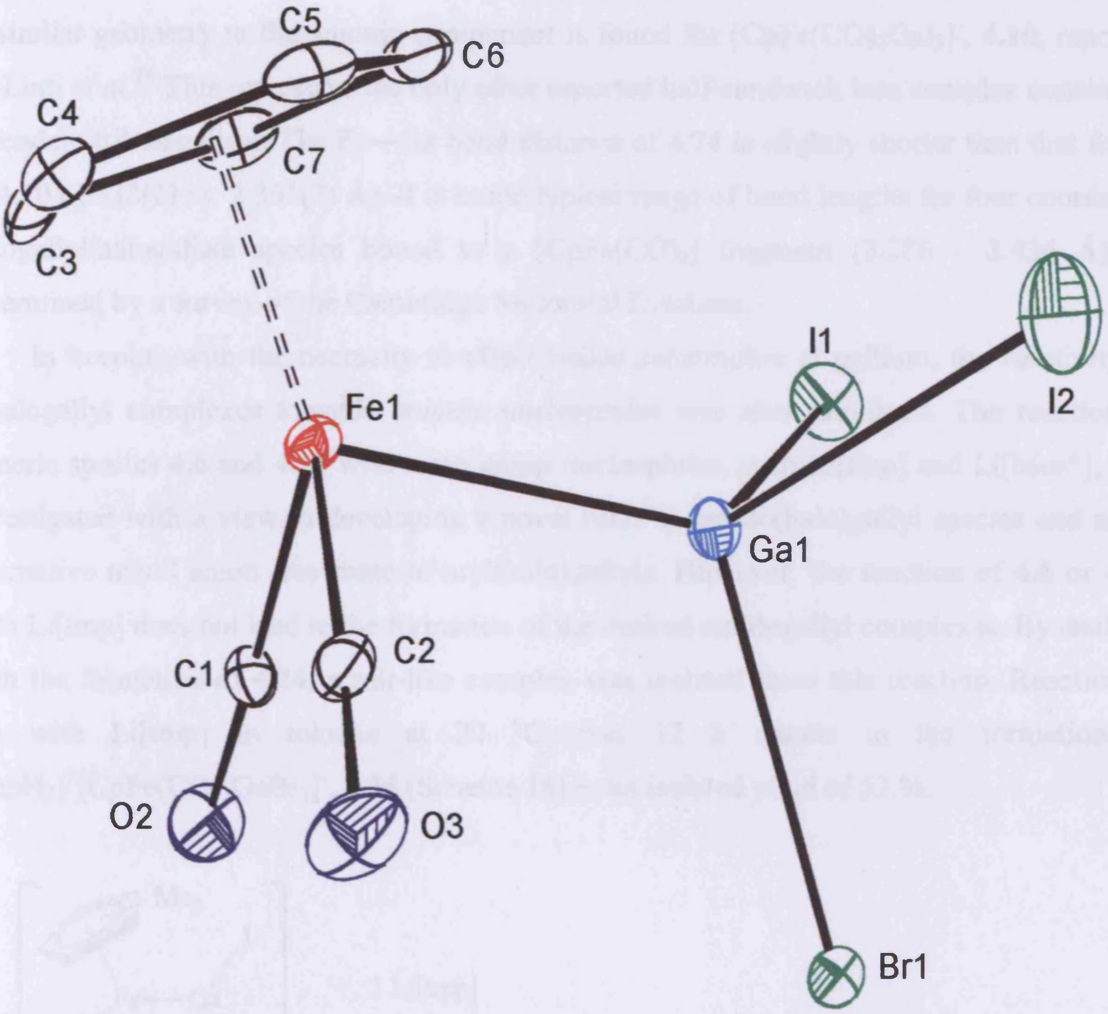
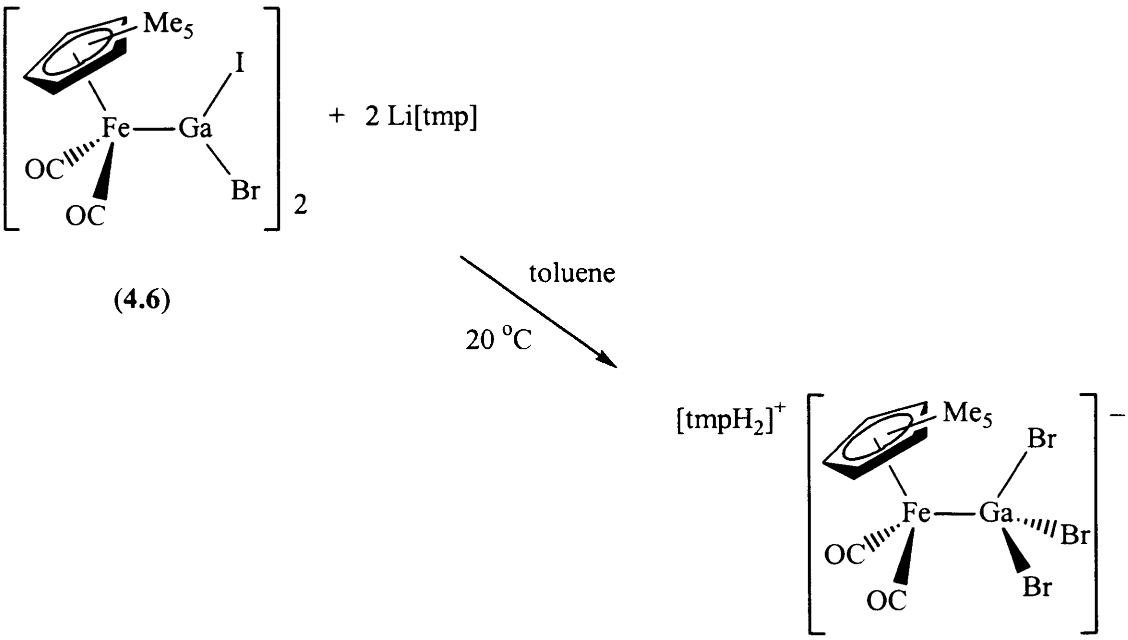


Figure 9: Structure of the anionic component of $[Et_3NH]^+[CpFe(CO)_2GaBrI_2]^-$, **4.24**

Selected bond lengths (Å) and angles (°): Fe(1)—Ga(1) 2.338(2), Fe(1)—C_5H_5 centroid 1.717(11), Fe(1)—C(1) 1.742(12), Ga(1)—I(1) 2.544(2), Ga(1)—I(2) 2.527(2), Ga(1)—Br(1) 2.443(2), C_5H_5 centroid—Fe(1)—Ga(1)—Br(1) 176.6(10).

X-ray crystallography has confirmed the structure of the metallated trihalogallate ion $[CpFe(CO)_2GaBrI_2]^-$ which was isolated as the $[Et_3NH]^+$ salt. The anionic component of **4.24** features a staggered conformation about the Ga—Fe bond (Cp centroid—Fe(1)—Ga(1)—Br(1) 176.6(10)°), which is presumably enforced on steric grounds. The origins of the proton of the $[Et_3NH]^+$ cation are not immediately clear but its location from the X-ray diffraction data is supported by ^{1}H NMR and mass spectrometry data. A similar geometry to the anionic component is found for [CpFe(CO)$_2$GaI$_3$]$^-$, **4.10**, reported by Linti *et al.*[24] This represents the only other reported half-sandwich iron complex containing a pendent trihalogallate. The Fe—Ga bond distance of **4.24** is slightly shorter than that found in **4.10** (2.338(2) *vs.* 2.361(7) Å). It is in the typical range of bond lengths for four coordinate halogallyl/halogallate species bound to a [CpFe(CO)$_2$] fragment (2.286 – 2.436 Å), as determined by a survey of the Cambridge Structural Database.

In keeping with the necessity to effect halide *substitution* at gallium, the reactivity of dihalogallyl complexes towards *anionic* nucleophiles was also examined. The reaction of dimeric species **4.6** and **4.18** with main group nucleophiles, such Li[tmp] and Li[Mes*], was investigated with a view to developing a novel route to amido(halo)gallyl species and as an alternative metal anion free route to aryl(halo)gallyls. However, the reaction of **4.6** or **4.18** with Li[tmp] does not lead to the formation of the desired amidogallyl complexes. By analogy with the formation of **4.24**, a salt-like complex was isolated from this reaction. Reaction of **4.6** with Li[tmp] in toluene at 20 °C over 12 h results in the formation of [tmpH$_2$]$^+$[CpFe(CO)$_2$GaBr$_3$]$^-$, **4.25** (Scheme 16) in an isolated yield of 52 %.



(4.6)

(4.25)

Scheme 16

Pale yellow crystals of **4.25** were grown by the slow diffusion of hexane into a concentrated toluene solution of **4.25** at – 30 °C. The structure of the anionic component of **4.25** is depicted in Figure 10. Spectroscopic data are consistent with the crystallographically determined structure. The origins of the protons of the $[tmpH_2]^+$ cation are not immediately clear but as with **4.24**, their location from X-ray diffraction data is supported by the results of mass spectrometry (ES+) and ^1H NMR experiments. For example, resonances associated with $[tmpH_2]^+$ were visible in the ^1H NMR spectrum at δ 1.45, 1.65, 1.82 and 5.62 ppm, corresponding to the methyl groups, the CH_2CMe_2 of tmp, CH_2 of tmp, and the NH_2 protons, respectively. Signals due to the Cp ligand and toluene, incorporated into the crystal lattice, were also visible in the ^1H NMR spectrum at δ 2.26, 4.73 and 7.10 ppm, respectively. In addition, resonances associated with the Cp ring, $[tmpH_2]^+$ and the toluene in the lattice were observed in the ^{13}C NMR spectrum. Two strong bands were seen in the carbonyl region of the IR spectrum at 1995 and 1944 cm^{-1}. Mass spectral data implied the presence of both tribromo- and triiodogallyl derivatives as well as the mixed iodo(bromo) complex with significant fragment ions corresponding to $[CpFe(CO)_2GaI_3]^-$, $[CpFe(CO)_2GaI_2Br]^-$, $[CpFe(CO)_2GaIBr_2]^-$ and $[CpFe(CO)_2GaBr_3]^-$. Differences in solubility/crystallinity may help to explain the isolation of tribromo complex **4.25**, in preference to other trihalo complexes.

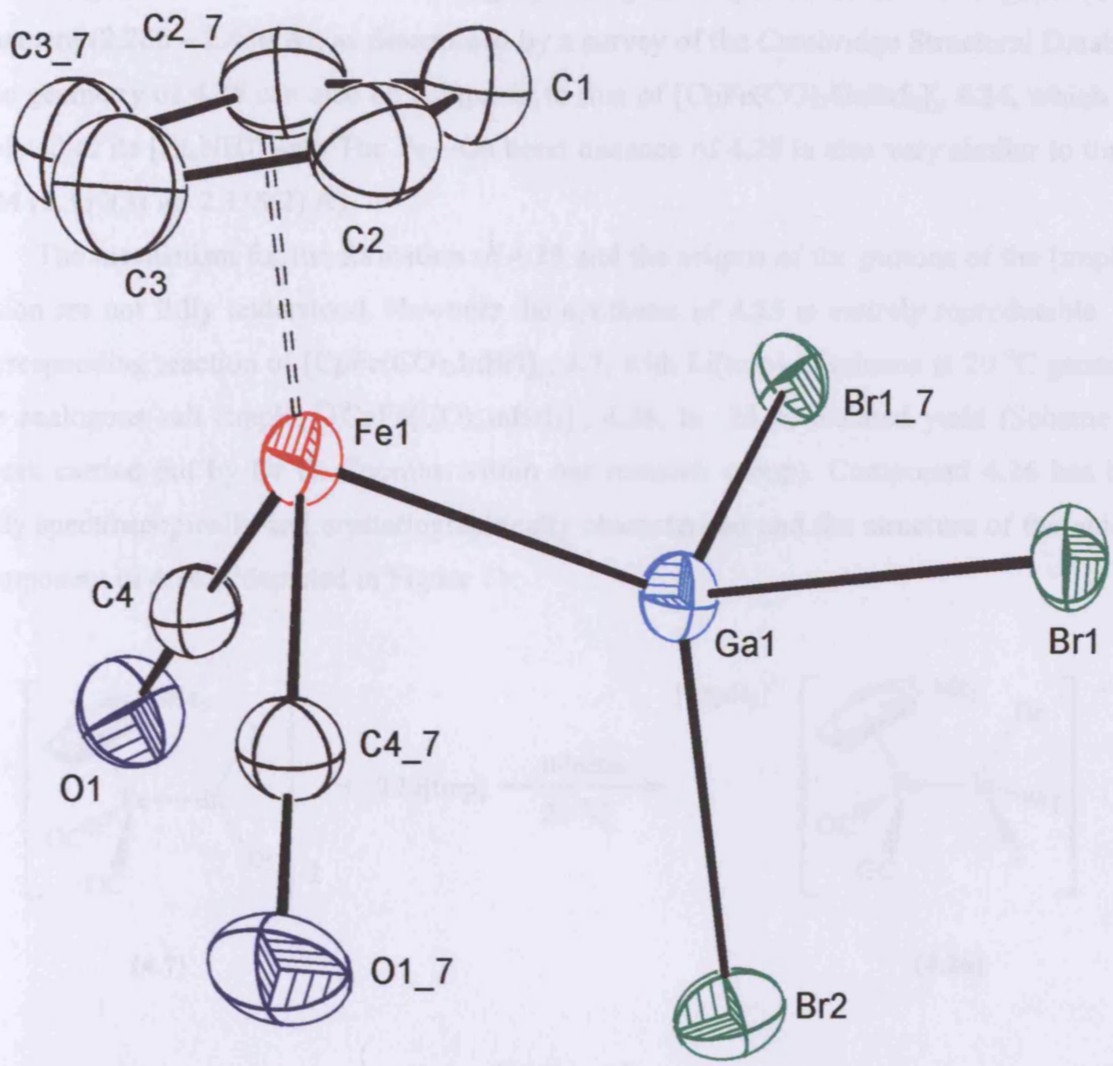
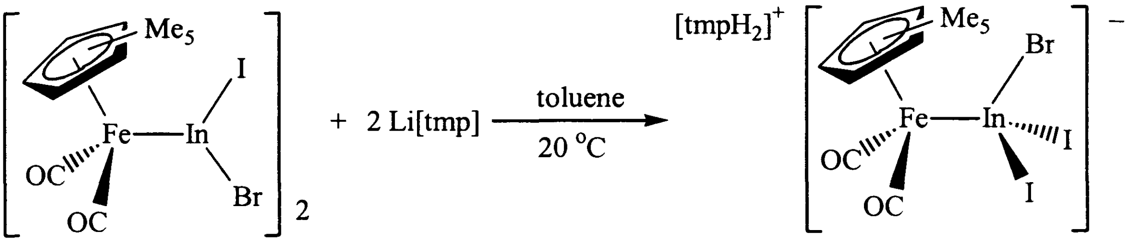


Figure 10: Structure of the anionic component of $[tmpH_2]^+[CpFe(CO)_2GaBr_3]^-$, **4.25**

Selected bond lengths (Å) and angles (°): Fe(1)—Ga(1) 2.330(3), Fe(1)—Cp centroid 1.744(2), Ga(1)—Br(1) 2.5744(17), Ga(1)—Br(2) 2.395(3), Ga(1)—Br(3) 2.5744 (17), C_5H_5 centroid—Fe(1)—Ga(1) 110.69(1).

The structure of the metallated trihalogallate ion **4.25** features a staggered conformation about the Fe—Ga bond (110.69(1)°), which is presumably enforced on steric grounds. The Fe—Ga bond length of **4.25** is very close to that measured previously for the related complex $[CpFe(CO)_3GaI_3]^-$, **4.10**, (2.330(3) *vs.* 2.361(7) Å, respectively).[24] It is in the typical range of bond lengths for four coordinate halogallyl/halogallate species bound to a $[CpFe(CO)_2]$ fragment (2.286 – 2.436 Å), as determined by a survey of the Cambridge Structural Database. The geometry of **4.25** can also be compared to that of $[CpFe(CO)_2GaBrI_2]^-$, **4.24**, which was isolated as its $[Et_3NH]^+$ salt. The Fe—Ga bond distance of **4.25** is also very similar to that of **4.24** (2.330(3) *vs.* 2.338(2) Å).

The mechanism for the formation of **4.25** and the origins of the protons of the $[tmpH_2]^+$ cation are not fully understood. However the synthesis of **4.25** is entirely reproducible. The corresponding reaction of $[CpFe(CO)_2InBrI]_2$, **4.7**, with Li[tmp] in toluene at 20 °C generates the analogous salt $[tmpH_2]^+[CpFe(CO)_2InBrI_2]^-$, **4.26**, in 28 % isolated yield (Scheme 17) (work carried out by Dr D. Coombs within our research group). Compound **4.26** has been fully spectroscopically and crystallographically characterised and the structure of the anionic component of **4.26** is depicted in Figure 11.



(4.7) **(4.26)**

Scheme 17

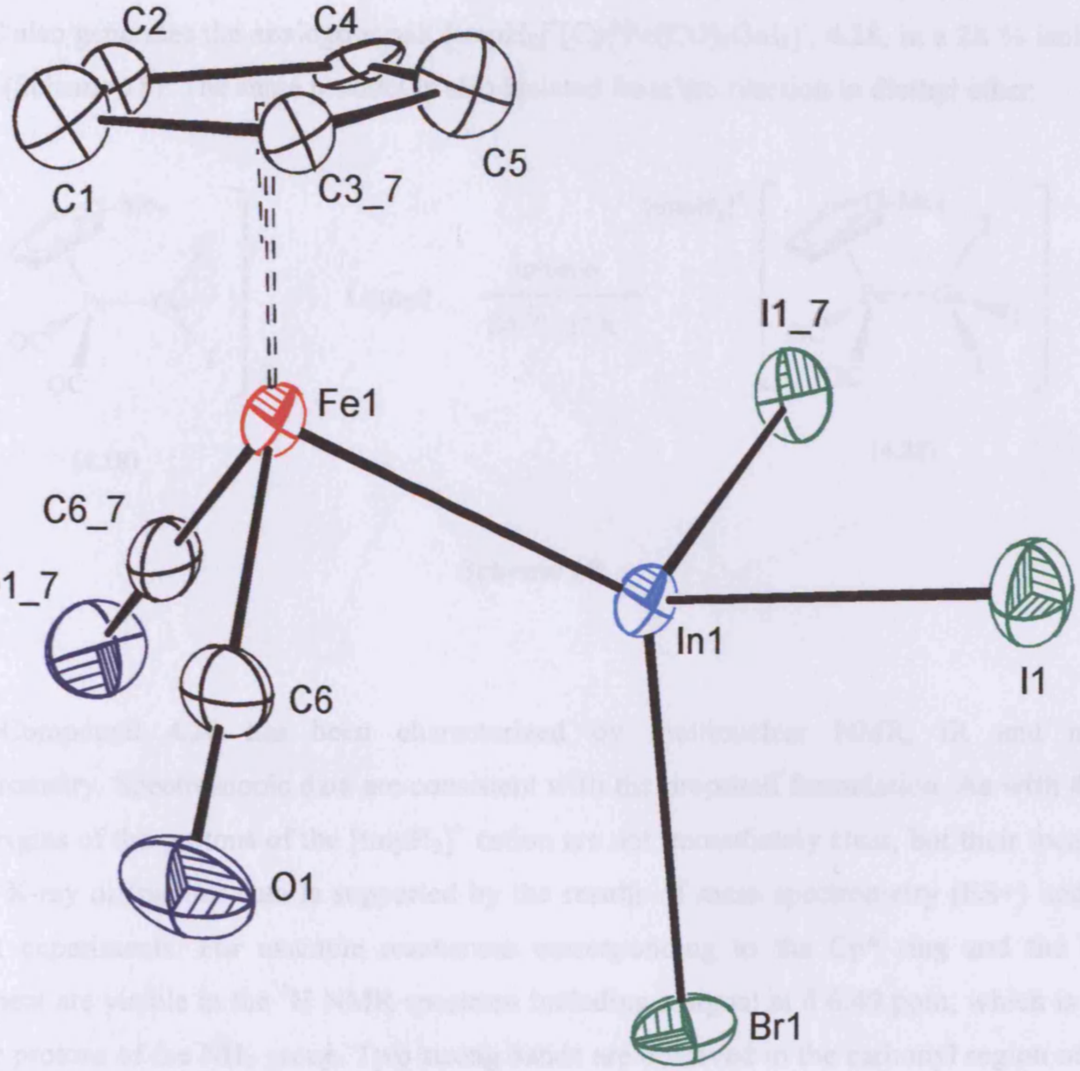
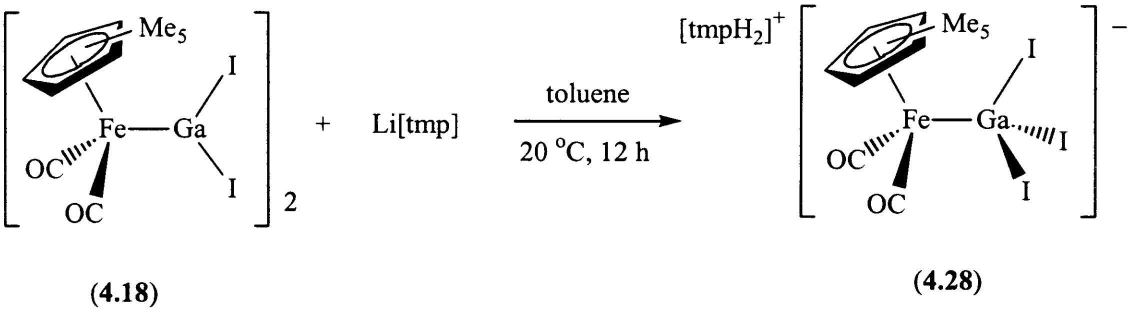


Figure 11: Structure of the anionic component of $[tmpH_2]^+[CpFe(CO)_2InBrI_2]^-$, 4.26
(This crystal structure was obtained by Dr. D. Coombs)

Selected bond lengths (Å) and angles (°): Fe(1)—In(1) 2.491(1), Fe(1)—Cp centroid 1.745(1), In(1)—Br(1) 2.585(3), In(1)—I(1) 2.763(3), C_5H_5 centroid—Fe(1)—In 118.50(1).

By analogy with **4.25**, the metallated trihaloindate ion, **4.26**, adopts a staggered geometry about the Fe—In bond. The Fe—In bond length of **4.26** is consistent with that found for other examples of $[CpFe(CO)_2]$ species bound to four coordinate indium-based ligands, *e.g.* 2.553(1) Å in $[CpFe(CO)_2]_4[In_2(\mu\text{-}Cl)_2]$, **4.27**.[9]

The corresponding reaction between $[Cp^*Fe(CO)_2GaI_2]_2$, **4.18**, and Li[tmp] in toluene at 20 °C also generates the analogous salt $[tmpH_2]^+[Cp^*Fe(CO)_2GaI_3]^-$, **4.28**, in a 28 % isolated yield (Scheme 18). The same product is also isolated from the reaction in diethyl ether.



Scheme 18

Compound **4.28** has been characterized by multinuclear NMR, IR and mass spectrometry. Spectroscopic data are consistent with the proposed formulation. As with **4.25**, the origins of the protons of the $[tmpH_2]^+$ cation are not immediately clear, but their location from X-ray diffraction data is supported by the results of mass spectrometry (ES+) and ^1H NMR experiments. For example resonances corresponding to the Cp* ring and the tmp fragment are visible in the ^1H NMR spectrum including a signal at δ 6.49 ppm, which is due to the protons of the NH_2 group. Two strong bands are observed in the carbonyl region of the IR spectrum at 1980 and 1933 cm^{-1}. Mass spectrometry data reveals significant fragment ions corresponding to $[Cp^*Fe(CO)_2GaI_3]^-$, $[Cp^*Fe(CO)_2GaI_3 - CO]^-$, and $[Cp^*Fe(CO)_2GaI_3 - I]^-$ together with an exact mass determination for $[Cp^*Fe(CO)_2GaI_3]^-$. These spectroscopic inferences were subsequently confirmed crystallographically. Pale yellow crystals of **4.28**, suitable for X-ray diffraction, were grown by the slow cooling of a concentrated toluene solution of **4.28** to –30 °C. The structure of the anionic component of **4.28** is depicted in Figure 12.

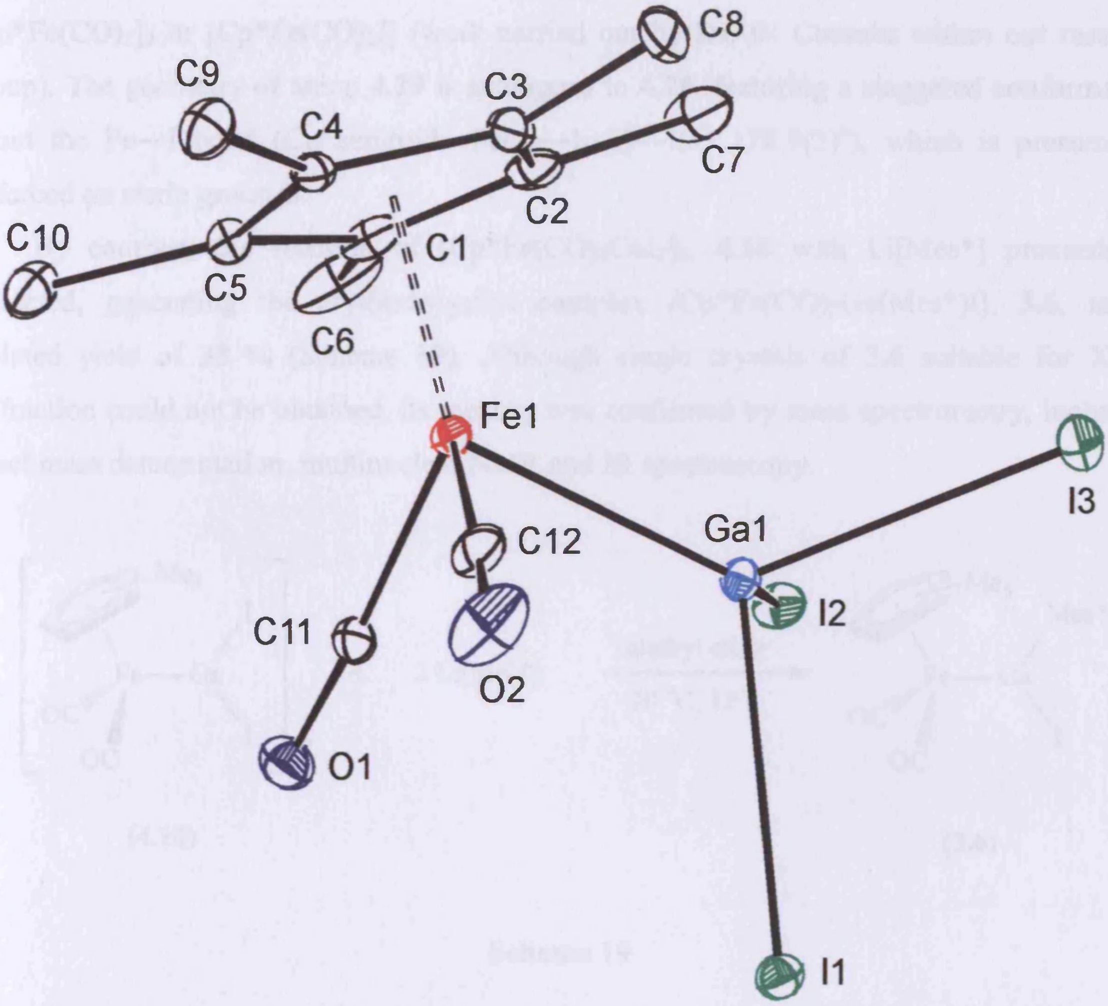
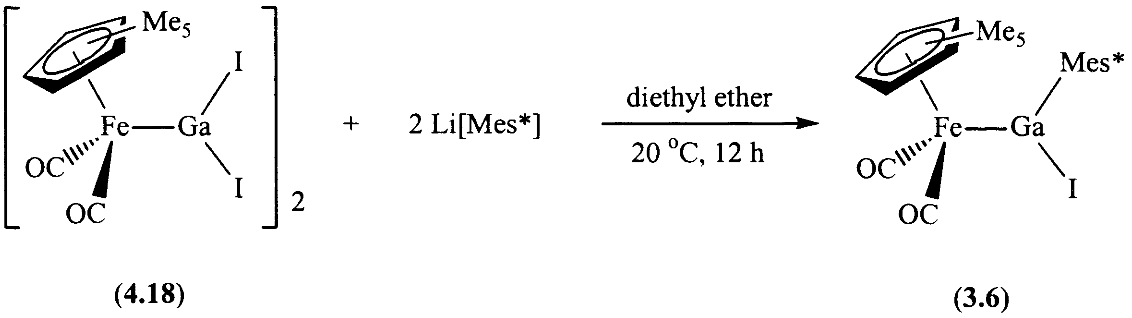


Figure 12: Structure of the anionic component of $[\text{tmpH}_2]^+[\text{Cp*Fe(CO)}_2\text{GaI}_3]^-$, **4.28**

Selected bond lengths (Å) and angles (°): Fe(1)—Ga(1) 2.355(1), Fe(1)—C(11) 1.754(6), Fe(1)—Cp centroid 1.722(5), Ga(1)—I(1) 2.702(1), Ga(1)—I(2) 2.655(1), Ga(1)—I(3) 2.642(1).

Complex **4.28** adopts a similar salt-like structure to that of **4.24** and **4.25**, featuring a staggered conformation about the Fe—Ga bond. The marginally longer Fe—Ga linkage of **4.28** compared to **4.24** and **4.25** (2.355(2) *vs.* 2.338 and 2.330 Å, respectively) is presumably a result of the increased steric hindrance of the Cp* ring in **4.28**. Complex **4.28** can also be compared to the metallated trihaloindate ion $[\text{Cp*Fe(CO)}_2\text{InI}_3]^-$, **4.29**, which was isolated as the $[Cp^*Fe(\eta^6\text{-}C_6H_5Me)]^+$ salt as a minor product from the reaction of InI with either $[Cp^*Fe(CO)_2]_2$ or $[Cp^*Fe(CO)_2I]$ (work carried out by Dr. D. Coombs within our research group). The geometry of anion **4.29** is analogous to **4.28**, featuring a staggered conformation about the Fe—I bond (Cp*centroid—Fe(1)—In(1)—I(3) 178.9(3)°), which is presumably enforced on steric grounds.

By contrast, the reaction of $[Cp^*Fe(CO)_2GaI_2]_2$, **4.18** with Li[Mes*] proceeds as expected, generating the aryl(iodo)gallyl complex [Cp*Fe(CO)₂Ga(Mes*)I], **3.6**, in an isolated yield of 33 % (Scheme 19). Although single crystals of **3.6** suitable for X-ray diffraction could not be obtained, its identity was confirmed by mass spectrometry, including exact mass determination, multinuclear NMR and IR spectroscopy.

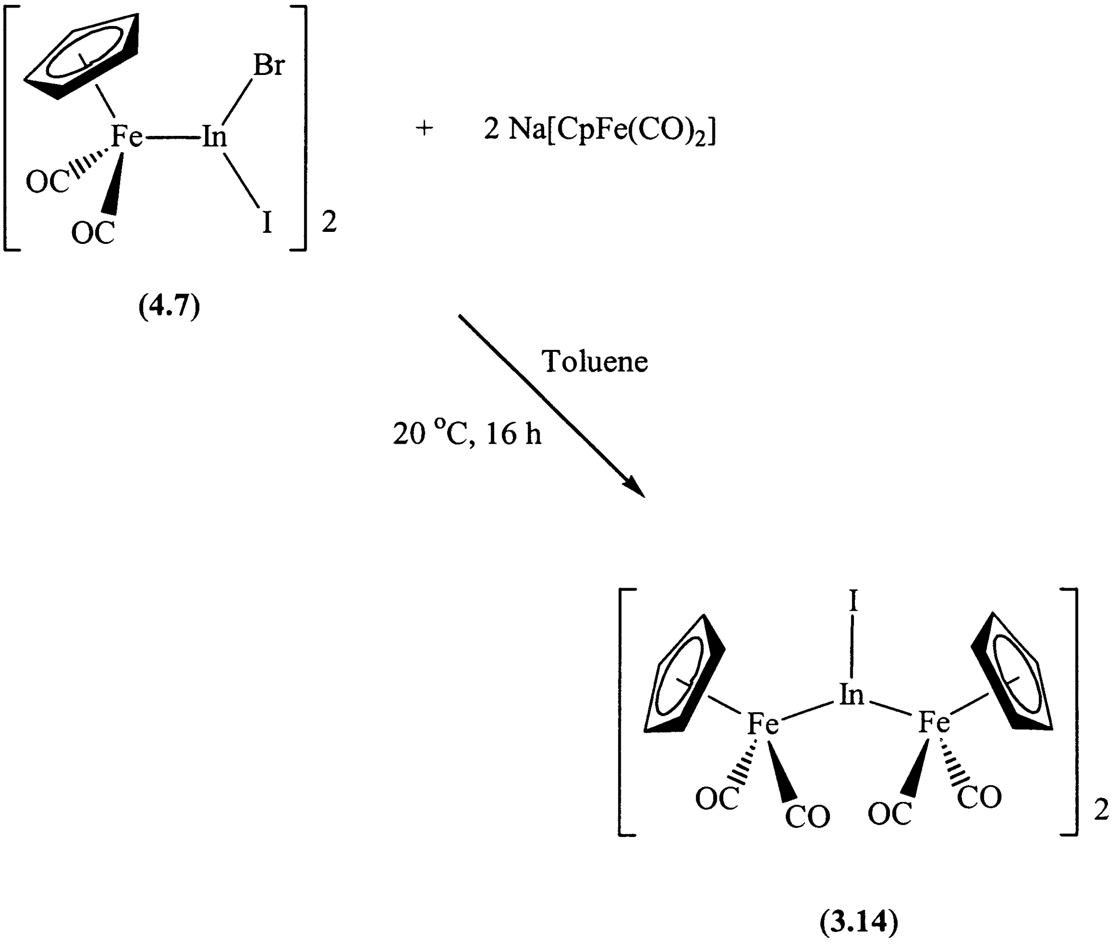


Scheme 19

Spectroscopic data for **3.6** are essentially identical to that obtained for the structurally characterized chloride analogue **3.2**. The synthesis and characterisation of **3.6** are discussed in Chapter 3. For example, both compounds **3.2** and **3.6** show single resonances corresponding to the CH_3 groups of the Cp* ring in the ^1H NMR spectra at δ 1.77 and 1.89 ppm and in the ^{13}C NMR spectra at δ 9.2 and 9.4 ppm for **3.2** and **3.6**, respectively. Resonances associated with the Mes* group can be identified in the ^1H NMR spectrum of **3.6** at *δ* 1.24, 1.78, and 7.10 ppm, corresponding to the para ^{t}Bu, ortho ^{t}Bu and aryl CH of the Mes* group. Mass spectrometry data reveals the correct isotope distribution for 1 Fe, 1 Ga and 1 I atoms for the molecular ion $[M^+]$ at m/z 688.1. Two bands are observed in the IR spectrum at 1983, 1933 cm^{-1} *vs*. 1981 and 1931 cm^{-1} for **3.2** and **3.6**, respectively.

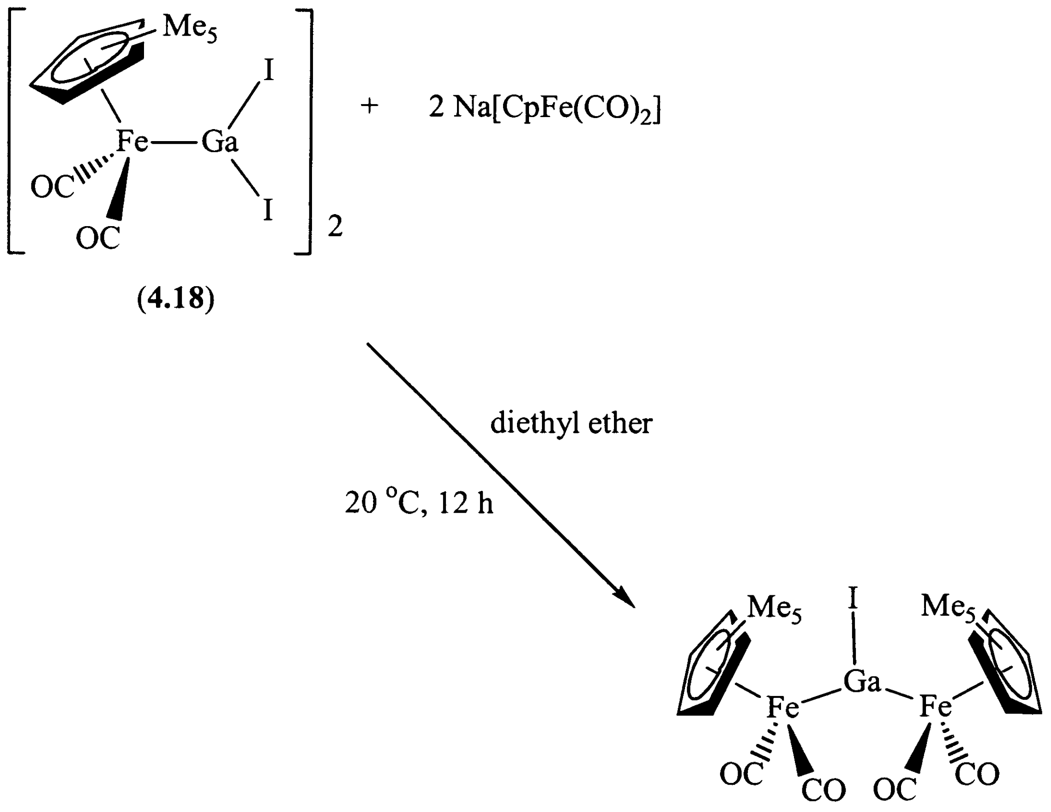
Previous work carried out within our research group (by Dr. D. Coombs), has demonstrated that dimeric **4.7** reacts at room temperature in toluene with two equivalents of

Na[CpFe(CO)$_2$] *via* halide substitution to give the bis-metallated species [CpFe(CO)$_2$]$_2$InI, **3.14** (Scheme 20).



Scheme 20

This reaction illustrates the possibility of substitution at existing gallyl/indyl ligand systems. However it is evident that reaction with an anion and/or dimer with greater steric hindrance are required to generate the desired three-coordinate derivatives. Therefore the analogous reactivity of Cp* substituted [Cp*Fe(CO)$_2$GaI$_2$]$_2$, **4.18**, was investigated. The reaction of **4.18** with Na[Cp*Fe(CO)$_2$] was examined as a possible route to the bridging iodogallylene [Cp*Fe(CO)$_2$]$_2$GaI, **4.20**, given the lack of success in isolating this compound by direct insertion of 'GaI' into the Fe—Fe bond of [Cp*Fe(CO)$_2$]$_2$. Indeed, reaction of 2 equivalents of Na[Cp*Fe(CO)$_2$] with [Cp*Fe(CO)$_2$GaI$_2$]$_2$, **4.18**, in diethyl ether at 20 °C over 12 h yields **4.20** as a pale yellow powder in a 61 % isolated yield (Scheme 21).



(4.18)

(4.20)

Scheme 21

Multinuclear NMR, IR and mass spectral data for **4.20** are consistent with the proposed formulation and comparable to those mentioned for $[Cp^*Fe(CO)_2]_2GaCl$, **3.11**, synthesised *via* the alternative salt elimination methodology (Chapter 3). For example, single resonances associated with the Cp* rings are observed in the ^{1}H and ^{13}C NMR spectra at δ 1.77 and 9.2 ppm, respectively. Mass spectrometry data reveals the correct isotope distribution for 2 Fe, 1 Ga and 1 I atoms and exact mass determination for $[M - CO]^+$ together with a significant fragment ion corresponding to $[M - 2CO]^+$. Three strong bands were observed in the carbonyl region of the IR spectrum at 1964, 1928 and 1912 cm^{-1} *vs.* 1960, 1925 and 1910 cm^{-1} for **4.20** and **3.11**, respectively. These spectroscopic inferences were subsequently confirmed crystallographically. Crystals of **4.20** suitable for X-ray diffraction were grown by the slow diffusion of hexane into a THF solution of **4.20** at –30 °C. The molecular structure of **4.20** is depicted in Figure 13.

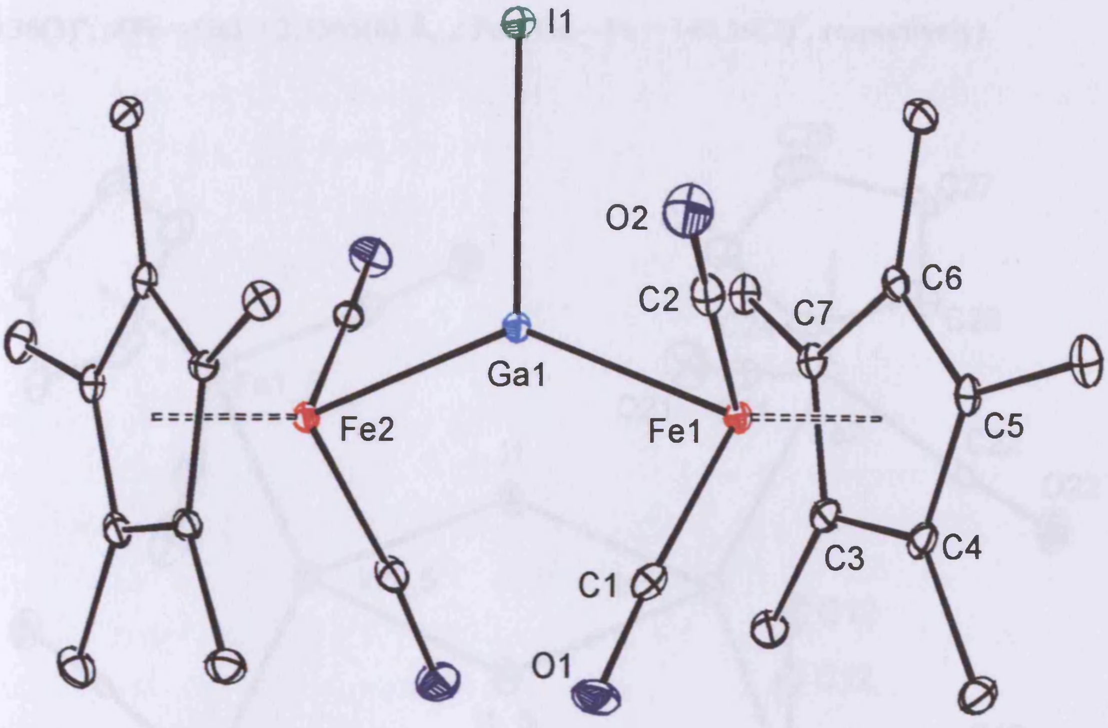


Figure 13: Structure of [Cp*Fe(CO)$_2$]$_2$GaI, **4.20**

Selected bond lengths (Å) and angles (°): Fe(1)—Ga(1) 2.3565(6), Fe(2)—Ga(1) 2.3505(6), Fe(1)—C(1) 1.749(4), Fe(1)—Cp centroid 1.732(3), Fe(2)—Cp centroid 1.727(3), Ga(1)—I(1) 2.7005(4), Fe(1)—Ga(1)—Fe(2) 140.14(2), Fe(1)—Ga(1)—Cl(1) 109.011(18).

The spectroscopic and structural data for bridging gallylene **4.20** are comparable to that of the chlorogallylene analogue [{Cp*Fe(CO)$_2$}$_2$GaCl], **3.11**. Both species are monomeric with trigonal planar geometries and similar Fe—Ga bond distances (2.3565(6) *vs.* 2.352(1) Å for **4.20** and **3.11**, respectively). The trigonal planar ligand geometry of **4.20** contrasts with those observed for the corresponding complexes containing the less bulky Cp ligand.[21,24] For example, the results of a single X-ray diffraction study showed that species **3.14** has an iodide-bridged dimeric structure [{CpFe(CO)$_2$}$_2$InI]$_2$ analogous to that reported for the corresponding chloride complex (Figure 14).[9] Steric influences are most likely responsible for the structural differences between **3.14** and **4.20** (*d*(Fe—In) = 2.549(1) Å, ∠Fe—In—Fe = 130.36(3)°; *d*(Fe—Ga) = 2.3565(6) Å, ∠Fe—Ga—Fe = 140.14(2)°, respectively).

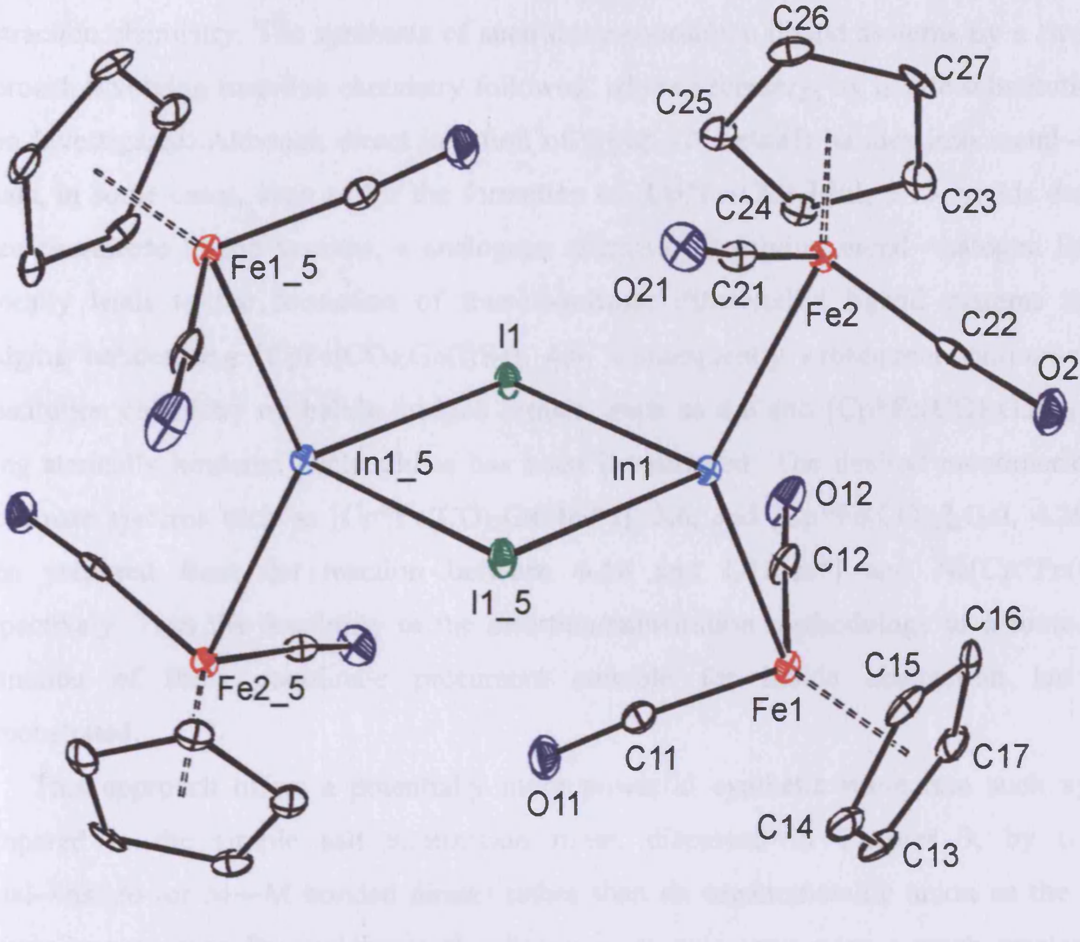


Figure 14: Structure of $[CpFe(CO)_2]_2InI$, **3.14**
(This crystal structure was obtained by Dr. D. Coombs)

Selected bond lengths (Å) and angles (°): Fe(1)—In(1) 2.549(1), Fe(2)—In(1) 2.554(1), Fe(1)—C(11) 1.755(8), Fe(1)—Cp centroid 1.723(6), In(1)—I(1) 3.081(1), In(1)—I(1_5) 2.932(1), Fe(1)—In(1)—Fe(2) 130.36(3), Fe(1)—In(1)—I(1) 102.15(3), Fe(2)—In(1)—I(1) 106.47(3), I(1)—In(1)—I(1_5) 86.59(2).

4.7 Conclusion and Suggestions for Further Work

Transition metal complexes containing three coordinate halo-gallium ligands represent important precursors to unsaturated cationic species of the type $[L_nM(EX)]^+$ *via* halide abstraction chemistry. The synthesis of such three-coordinate ligand systems by a two-stage approach involving insertion chemistry followed, where necessary, by halide substitution has been investigated. Although direct insertion of group 13 metal(I) halides into metal—metal bonds, in some cases, such as for the formation of $[Cp^*Fe(CO)_2]_2InI$, **3.13**, yields desirable three-coordinate ligand systems, a analogous chemistry involving metal—halogen linkages typically leads to the formation of four-coordinate dihalogallyl ligand systems through bridging halides, *e.g* $[CpFe(CO)_2Ga(I)Br]$, **4.6**. Consequently subsequent gallium-centred substitution chemistry on halide bridged dimers, such as **4.6** and $[Cp^*Fe(CO)_2GaI_2]_2$, **4.18**, using sterically hindered nucleophiles has been investigated. The desired monomeric three coordinate systems such as $[Cp^*Fe(CO)_2GaMes^*I]$, **3.6**, and $[Cp^*Fe(CO)_2]_2GaI$, **4.20** have been prepared from the reaction between **4.18** and Li[Mes*] and $Na[Cp^*Fe(CO)_2]$, respectively. Thus the feasibility of the insertion/substitution methodology as a route to the formation of three coordinate precursors suitable for halide abstraction has been demonstrated.

This approach offers a potentially more powerful synthetic route into such systems compared to the simple salt elimination route, discussed in Chapter 3, by using a metal—halide (or M—M bonded dimer) rather than an organometallic anion as the metal-containing precursor. By avoiding such reliance on anionic precursors, a much greater range of complexes are potentially accessible. This leads to the possibility of synthesising cationic diyl systems $[L_nM(EX)]^+$, which do not include appreciably π acidic ligands, *i.e.* carbonyls. Such insertion/substitution methodology, however, does have its disadvantages. Although it is potentially a more powerful route, in terms of the range of complexes accessible, it lacks the inherent convenience of the one-pot salt elimination methodology and can, in some cases, lead to the preparation of undesirable products.

This work could be extended to thoroughly investigate the subsequent substitution chemistry of dimeric species **4.6** and **4.18**, further exploiting this methodology as a viable route to novel three coordinate transition metal gallyl complexes. Insertion reactions of Group 13 metal(I) halides (EX) with other compounds containing metal—halide, metal—metal or multiple metal—metal bonds could also be explored e.g. [CpFe(dppe)I].

4.8 References

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Chapter Five

Synthetic and Reaction Chemistry of Cationic Gallium-Containing Ligand Systems

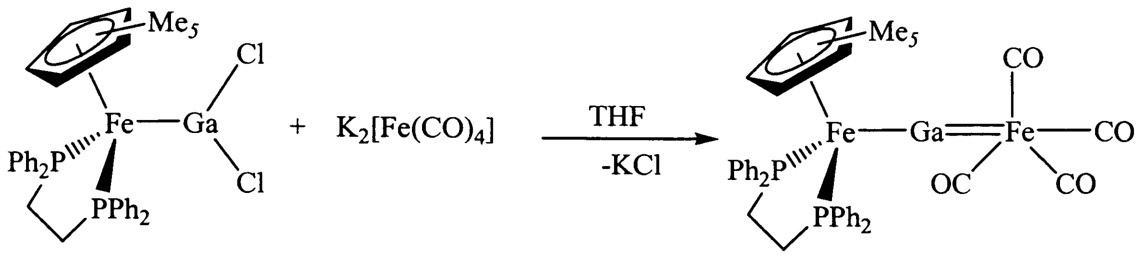
5.1 Introduction

This chapter explores the use of halide abstraction chemistry in heavier group 13 systems, leading to the synthesis of cationic derivatives containing gallium donor atoms. In particular, halide abstraction chemistry has been investigated for two classes of three-coordinate halo-gallium substrate systems: (i) asymmetric halogallyl systems of the type $L_nM—Ga(Mes^*)Cl$ and (ii) bridging halogallanediyl complexes $(L_nM)_2GaCl$. The nature of the M—E bond in the cationic systems so formed has been analysed by spectroscopic, structural and computational studies. In addition, comparison is made with related systems containing indium donors, thus probing the controversial subject of multiple bonding involving the heavier group 13 elements as a function of E. Preliminary studies of the fundamental reactivity of the trimetallic system $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}Ga)]^+$ are also explored.

5.2 Introduction to Multiple Bonding Involving the Heavier Group 13 Elements

Recently there has been much interest in compounds that offer the possibility for multiple bonding between a transition metal and a main group element. Whereas multiple bonding involving terminally bound group 14 systems (alkylidene (CR_2) and silylene (SiR_2) ligands) is well known,[1] the synthetic, structural and reaction chemistries of analogous group 13 systems (BR, AlR, GaR, InR, TlR) are much more poorly understood. The bonding in these systems is currently a matter of great debate, which reflects not only the fundamental questions of structure and bonding in group 13 diyl complexes, but also the scarcity of structural data available.

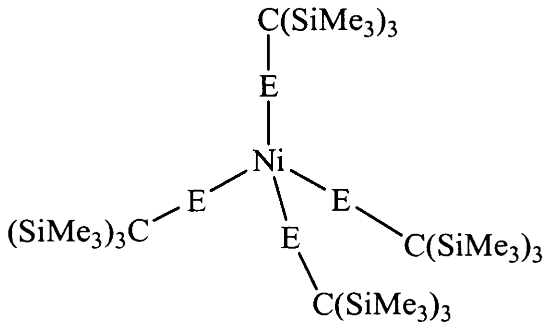
In 2003 Ogino *et al.*, reported the first dinuclear complex bridged by a substituent-free, 'naked' gallium atom $[Cp^*Fe(dppe)(\mu\text{-}Ga)Fe(CO)_4]$, **1.73**, the bonding in which can formally be described as a single bond between the Cp*(dppe)Fe fragment and the Ga atom and a double bond between Ga and $Fe(CO)_4$ (Scheme 1). However, this is only an valence bond formalism and the Fe—Ga distances in **1.73** are actually similar in length (2.2931(10) and 2.2479(10) Å).[2]



(1.73)

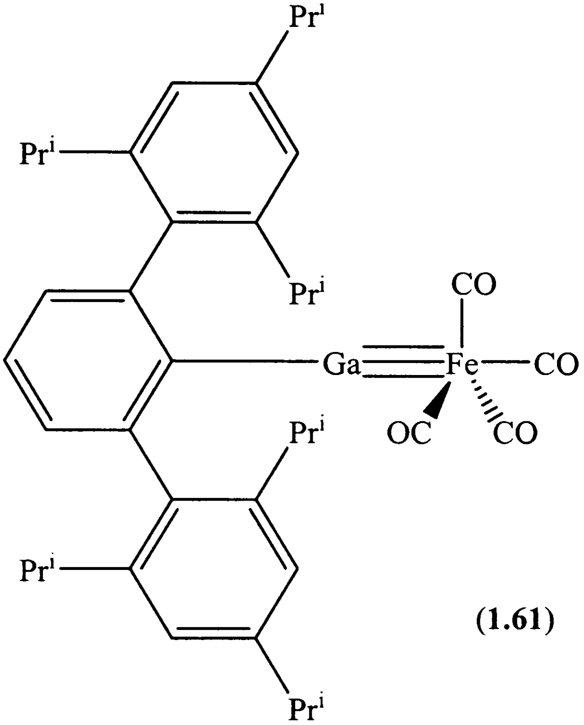
Scheme 1

Interesting transition metal — group 13 element bonding has also been postulated for the unusual and fascinating homoleptic Ni(0) complexes, $[Ni(In\{C(SiMe_3)_3\}_4]$, **1.56**, and $[Ni(Ga\{C(SiMe_3)_3\}_4]$, **1.80**, recently reported by Uhl and co-workers.[3,4] These represent the first examples of transition metal complexes with the metal exclusively coordinated to terminal ER groups in an undistorted tetrahedral coordination sphere and enable direct comparison with the carbonyl analogue $[Ni(CO)_4]$. In the case of $[Ni\{InC(SiMe_3)_3\}_4]$ for example, the Ni—In—C bonds are linear with Ni—In—C bond angles of *ca.* 180°. The short Ni—In bonds (2.310 Å) are thought to be indicative of π back-bonding. Indeed quantum chemical calculations confirm that there is a significant π back-bonding of electron density from nickel to the empty orbitals at gallium or indium.[3]



E = Ga **(1.80)**, In **(1.56)**

The assessment of the degree of π back-bonding in diyl complexes containing competing ancillary π acceptor ligands (*e.g.* CO) is much more controversial and is perhaps most notably exemplified by the iron—gallium diyl complex, $[(Ar^{*}Ga)Fe(CO)_4]$, **1.61**, (Ar^{*} = 2,6-(2,4,6-$Pr^i_3C_6H_2)_2C_6H_3$) reported by Robinson in 1997.[5] X-ray crystallography revealed a linear Fe—Ga—C_{ipso} arrangement and a short Fe—Ga bond, which the authors attributed to a triple Fe—Ga bond. However this was later dismissed by Cotton and Feng who proposed a Ga→ Fe donor acceptor bond on the basis of spectroscopic and DFT analyses.[6]

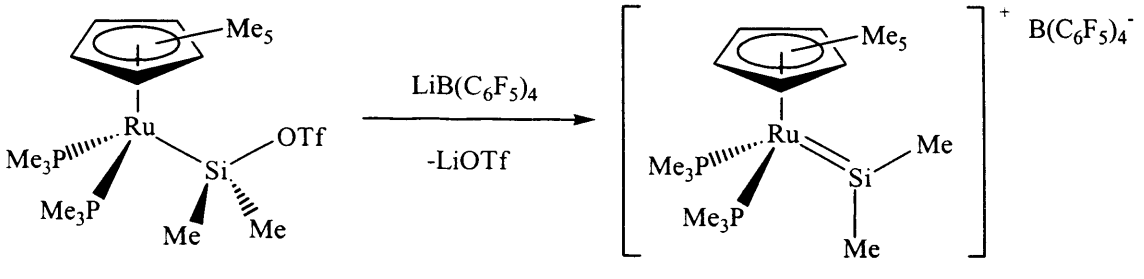


(1.61)

Numerous theoretical studies on this and related complexes have since been carried out and it is now generally accepted that the degree of metal—metal back bonding is minimal due to the relatively high energy of the gallium acceptor p-orbitals.[7] However, studies aimed at a more systematic appraisal of the bonding in two coordinate gallylene complexes have been hindered by the relative scarcity of structural data available. At present synthetic routes to such species are principally confined to salt elimination and ligand substitution methodologies.[8,9,10]

In order to develop the chemistry of base-free systems, Tilley and co-workers developed a novel route to terminal silylene complexes, which has subsequently been used to synthesise a series of new compounds. Reaction of the silyl complex $[Cp^{*}Ru(PMe_3)_2SiMe_2OTf]$ with

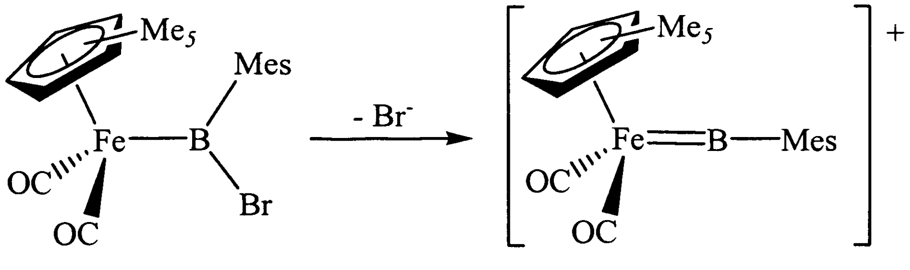
$Li[B(C_6F_5)_4]$ proceeds *via* triflate abstraction chemistry, to yield the first base free terminal silylene complex without π donor stabilisation, **5.1**, (Scheme 2).[11]



(5.1)

Scheme 2

Such methodology has subsequently been extended to group 13 systems. In 2003, Aldridge *et al.*, demonstrated that halide abstraction can be used as a viable route to cationic terminal borylene complexes with an increased metal to ligand bond order.[12] Halide abstraction from a suitable boryl precursor, *i.e.* [Cp*Fe(CO)$_2$B(Mes)Br], is possible by using the salt of a weakly coordinating anion, *e.g.* Na[BAr$^f_4$] or Ag[CB$_{11}$H$_6$Br$_6$]. This reaction generates the cationic terminal borylene complex, [Cp*Fe(CO)$_2$B(Mes)]$^+$, **1.85** (Scheme 3) as the [BAr$^f_4$]$^-$ or [CB$_{11}$H$_6$Br$_6$]$^-$ salt.



(1.85)

Scheme 3

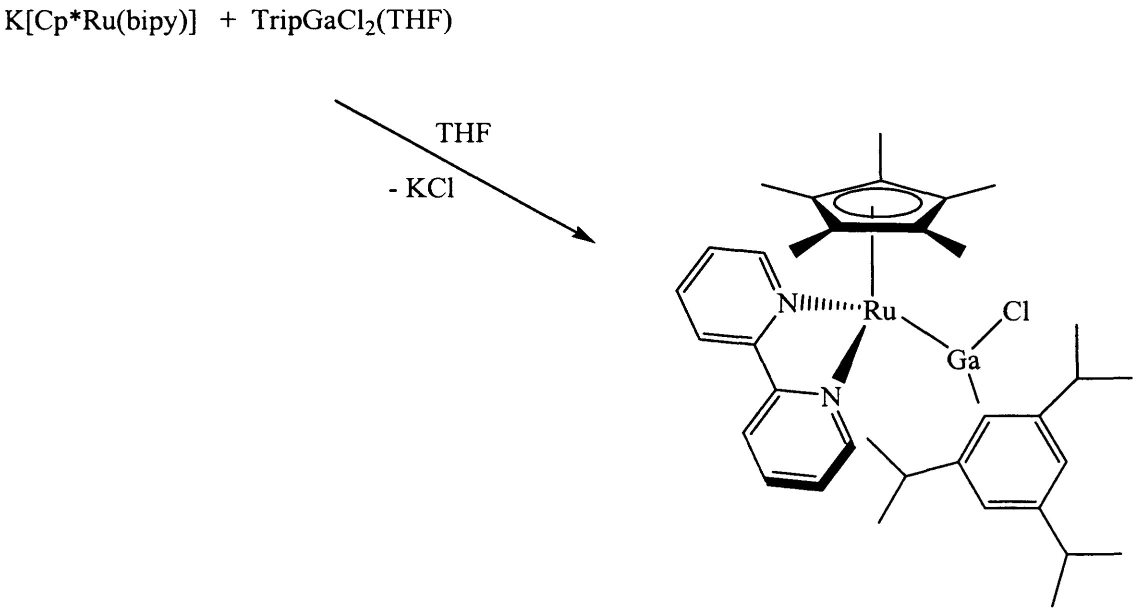
Of particular interest from a structural viewpoint is the linear Fe—B—C unit (∠178.3(6)°) and the Fe—B distance (1.792(8) Å), which is *ca.* 10 % shorter than in the boryl precursor and significantly shorter than any other transition metal to boron linkage previously reported. In fact the iron—boron distance in **1.85** is significantly shorter than similar complexes containing iron—boron single bonds and is within the range expected on going from a single to double bond. It is 11 % shorter than that found in [Cp*BFe(CO)$_4$], **5.2**, (2.010(3) Å) a compound containing a B→ Fe donor/acceptor linkage,[13] 18 % shorter than the σ-only single bond found in the four-coordinate boryl complex [(η^5-C$_5$Me$_4$Et)Fe(CO)$_2$BH$_2$·PMe$_3$], **5.3**, (2.195(14) Å), and 8.5% shorter than the shortest Fe—B distance found for any three-coordinate boryl complex (1.959(6) Å for [CpFe(CO)$_2$Bcat]), **5.4**.[14] By means of comparison, the Fe—C distance in [CpFe(CO)$_2$(=CCl$_2$)]$^+$, **5.5**, (1.808(12) Å) is *ca.* 12 % shorter than that found in typical [CpFe(CO)$_2$] alkyl complexes.[15] The Fe—B distance in **1.85** is therefore consistent with the presence of an Fe═B double bond. Furthermore, preliminary computational analyses have suggested that the positive charge in cationic terminal diyl species, [L$_n$M(EX)]$^+$, primarily rests at the group 13 centre (*e.g.* Mulliken charges of +0.438, +0.680 and +0.309 for [Cp*Fe(CO)$_2$E(Mes)]$^+$, E = B, Al, Ga). They also reveal that M→ E back-bonding may contribute appreciably to the overall metal ligand interaction (*e.g.* a 38 % π contribution to the FeB bonding density in [Cp*Fe(CO)$_2$B(Mes)]$^+$).[16] Therefore the double bond in **1.85** can be simplistically described as comprising of B→ Fe σ donor and Fe→ B π acceptor components.

The reactivity of the cationic terminal borylene complex, **1.85**, has also been investigated in detail.[12c] The primary forms of reactivity can be divided into two distinct types: reactivity towards anionic nucleophiles and reactivity towards unsaturated neutral donor systems. Reactivity towards anionic nucleophiles generally proceeds as expected, *via* addition at the highly electrophilic boron center. However, reactivity towards unsaturated substrates primarily progresses *via* borylene displacement. Reactions with reagents containing CO or CC multiple bonds, for example, result in the dissociation of the BMes ligand and the formation of the corresponding cationic iron complex [Cp*Fe(CO)$_2$L]$^+$[BAr$^f_4$]$^-$ (L = CO, η^1-OCPh$_2$, η^2-H$_2$C=C(H)^{t}Bu). The displacement of such ligands by ketone or alkene donors is surprising given the strong binding energies predicted for borylene ligands to transition metal centres. However, it is proposed that the driving force of such reactions is the irreversible removal of the borylene ligand by insertion into the C—H bond of the solvent.[12c] Attempts to modulate this reactivity by variation in the diyl substituent have led to the synthesis of

$[\mathrm{CpFe(CO)_2B(N^iPr_2)}]^+[\mathrm{BAr}^f_4]^-$, **5.6**, a compound which displays metathesis reactivity towards $\mathrm{Ph_3E{=}X}$ (E = P, As; X = O, S).[17]

In addition, Aldridge *et al.*, have shown when similar halide abstraction chemistry is applied to $[\mathrm{Cp^*Fe(CO)_2B(NMe_2)Br}]$, **5.7**, at –20 °C, the highly reactive aminoborylene, $[\mathrm{Cp^*Fe(CO)_2B(NMe_2)}]^+[\mathrm{BAr}^f_4]^-$, **5.8**, is generated. Compound **5.8** has been fully characterised in solution by multinuclear NMR and IR spectroscopy and chemically trapped by chloride to yield the known compound $[\mathrm{Cp^*Fe(CO)_2B(NMe_2)Cl}]$, **5.9**.[12]

Recently, Tilley has sought to extend his earlier work to group 13 systems, generating a new anionic ruthenium complex supported by Cp* and bipy ligands, and unusually excluding competing carbonyl ligands. The anion $[\mathrm{Cp^*Ru(bipy)}]^-$, **5.10**, was produced *in situ* as its lithium or potassium salt and then reacted to give new examples of ruthenium alkyl, stannyl and gallyl compounds such as [Cp*Ru(bipy)Ga(Cl)Mes*], **5.11** (Scheme 4). Attempts to abstract a chloride anion from **5.11** with $\mathrm{Li(OEt_2)_3B(C_6F_5)_4}$ in fluorobenzene, however were unsuccessful; a complex mixture of products was obtained.[18]



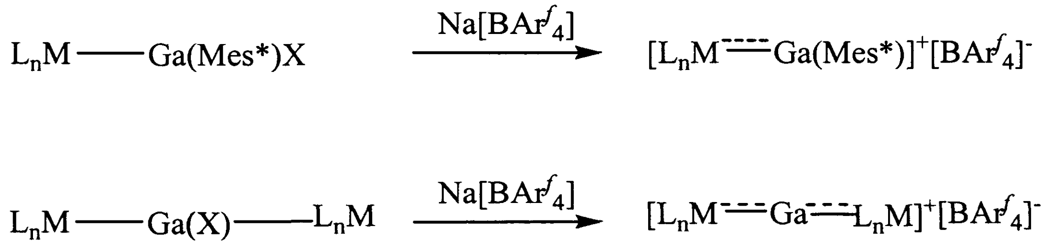
(5.11)

Scheme 4

5.3 Research Proposal

The chemistry of low coordinate or multiply-bonded group 13 ligand systems continues to be the focus of considerable research effort,[8,9,10] and in some cases significant controversy.[5,6] Within this area, a systematic appraisal of both structural and reaction chemistry for diyl systems, $L_nM(EX)$ (E = B, Al, Ga, In), lags behind that of analogous group 14 systems, such as carbenes and silylenes.[1] To a certain extent, this reflects the limited number of structurally authenticated complexes reported so far in the literature which have typically been synthesised *via* salt elimination or ligand substitution methodologies.

With a view to expanding the number of synthetic routes available for the preparation of unsaturated group 13 systems, a new synthetic approach to two-coordinate diyl complexes has recently been developed by our research group, using halide abstraction chemistry to generate the Fe=B double bond in $[Cp^*Fe(CO)_2B(Mes)]^+[BAr^f_4]^-$, **1.85**. Therefore, the aim of this study was to extend this synthetic approach from boron to the heavier group 13 elements and investigate the use of halide abstraction chemistry to generate cationic derivatives of gallium and indium. Halide abstraction chemistry was investigated for two classes of three-coordinate halo-gallium substrate systems, (i) asymmetric halogallyl systems of the type $L_nM—Ga(Mes^*)Cl$ and (ii) bridging halogallanediyl complexes $(L_nM)_2GaCl$ (Scheme 5).



Scheme 5

The nature of the M—E bond in such systems was then to be analysed by comparative spectroscopic, structural and computational studies as a function of the element E, thereby probing the controversial subject of multiple bonding involving the heavier group 13 elements. Furthermore, it was our intention to investigate the preliminary reactivity of any synthesised unsaturated cationic gallium systems.

5.4 Experimental

$[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}Ga)][BAr^f_4]$ (5.12)

To a suspension of $Na[BAr^f_4]$ (0.067 g, 0.075 mmol) in dichloromethane (10 ml) at -78 °C was added a solution of $[Cp^*Fe(CO)_2]_2GaCl$, **3.11**, (0.045 g, 0.075 mmol) in dichloromethane (10 ml), and the reaction mixture was then warmed to 20 °C over 30 min. Further stirring for 20 min, filtration and removal of volatiles *in vacuo* yielded **5.12** as a golden yellow powder. Yield: 0.050 g, 46 %. X-ray quality crystals were grown by layering a dichloromethane solution with hexane at –30 °C. ^1H NMR (300 MHz, CD_2Cl_2): δ 1.93 (s, 30H, Cp*), 7.54 (s, 4H, *p*ara CH of $BAr^f_4{}^-$), 7.70 (s, 8H, *o*rtho CH of $BAr^f_4{}^-$). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 10.3 (CH_3 of Cp*), 97.5 (quaternary of Cp*), 117.5 (*p*ara CH of $BAr^f_4{}^-$), 122.8 (q, $^1J_{CF}$ = 273 Hz, CF_3 of $BAr^f_4{}^-$), 128.8 (q, $^2J_{CF}$ = 34 Hz, meta C of $BAr^f_4{}^-$), 134.8 (ortho CH of $BAr^f_4{}^-$), 160.8 (q, $^1J_{CB}$= 53 Hz, ipso C of $BAr^f_4{}^-$), 211.4 (CO). ^{19}F NMR (283 MHz, CD_2Cl_2): δ -62.8 (CF_3). ^{11}B NMR (96 MHz, CD_2Cl_2): δ -7.6 ($BAr^f_4{}^-$). IR (CH_2Cl_2): ν(CO) 2016, 1994, 1963 cm^{-1}. Mass spec. (ES-): m/z 863 (100 %) $[BAr^f_4]^-$; (ES+): m/z 563 (5 %) $[M]^+$, correct isotope distribution for 2 Fe and 1 Ga atoms. Exact mass: calc. for $[M]^+$ 563.0093, exp. 563.0092.

Attempted synthesis of $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}Ga)][BF_4]$

To a suspension of $Ag[BF_4]$ (0.013 g, 0.0.067 mmol) in dichloromethane-d_2 (1 ml) at –78 °C was added dropwise a solution of $[Cp^*Fe(CO)_2]GaCl$, **3.11**, (0.040 g, 0.0.067 mmol) in dichloromethane-d_2 (3 ml), and the reaction mixture was then warmed to 20 °C over 10 min. The reaction mixture immediately turned dark brown. Monitoring the reaction by multinuclear NMR and IR revealed that a complex mixture of products had formed.

Reaction between $[\{Cp^*Fe(CO)_2\}_2GaCl]$ and $Na[BPh_4]$

To a suspension of $Na[BPh_4]$ (0.074 g, 0.22 mmol) in dichloromethane (10 ml) at –78 °C was added a solution of $[Cp^*Fe(CO)_2]_2GaCl$, **3.11**, (0.080 g, 0.11 mmol) in dichloromethane (10 ml), and the reaction mixture was then warmed slowly to 20 °C. Monitoring the reaction mixture by IR spectroscopy over a period of 72 h led to the gradual disappearance of the peaks due to the starting material (1969, 1957 and 1922 cm^{-1}), and the growth of bands at 2016, 1995, 1970 and 1940 cm^{-1}. Monitoring by ^{11}B NMR spectroscopy also revealed the growth of a strong broad signal at δ_B 67.0. Filtration of the supernatant solution, removal of volatiles *in vacuo* and recrystallization from hexane at –30 °C led to the formation of crops of colourless and dark red microcrystalline material, which were identified as BPh_3 (δ_B 67.0) and [$Cp^*Fe(CO)_2Ph$] (ν(CO) 1995 and 1940 cm^{-1}), respectively, by comparison of multinuclear NMR, IR and mass spectrometric data with previously reported data.[25]

Reaction of 5.12 with [PPN]Cl: synthesis of [$Cp^*Fe(CO)_2$]$_2$GaCl (3.11)

To a solution of [PPN]Cl (0.020 mg, 0.035 mmol) in dichloromethane-d_2 (1 ml) was added a solution of **5.12** (0.050 g, 0.035 mmol) in dichloromethane-d_2 (3 ml) at 20 °C. The reaction mixture was sonicated for 1 h, after which time ^1H NMR spectroscopy revealed complete conversion to **3.11** (quantitative conversion by NMR). Further comparison of multinuclear NMR and IR data (for the isolated compound) with those obtained for an authentic sample of **3.11** confirmed the identity of **3.11** as the sole organometallic product.

Attempted reaction of [{$Cp^*Fe(CO)_2$}$_2$(μ-Ga)][BAr^f_4] with [$^nBu_4N$][BF_4]

To a slurry of [Bu_4N][BF_4] (0.003 mg, 9.12 μmol) in dichloromethane-d_2 (1 ml) was added a solution of **5.12** (0.010 g, 7.00 μmol) in dichloromethane-d_2 (3 ml) at 20 °C. Despite extensive variation of reaction conditions (sonication, heating *etc*), no reaction occurred.

[{$Cp^*Fe(CO)_2$}$_2${μ-Ga(THF)}][BAr^f_4] (5.24)

To a solution of **5.12** in dichloromethane (12 ml) prepared *in situ* from Na[BAr^f_4] (0.059 g, 0.067 mmol) and [$Cp^*Fe(CO)_2$]$_2$GaCl, **3.11**, (0.040 g, 0.067 mmol) at –78 °C, was added THF (2 ml) and the reaction mixture was warmed to 20 °C over 30 min. After stirring for a further 1 h at 20 °C the reaction was judged to be complete by IR spectroscopy. Filtration and cooling to –30 °C led to the isolation of [{$Cp^*Fe(CO)_2$}$_2${μ-Ga(THF)}][BAr^f_4], **5.24**, as a pale yellow microcrystalline solid. Yield: 0.035 g, 35 %. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.80 (br m, 4H, CH_2 of THF), 1.86 (s, 30H, Cp*), 3.65 (br m, 4H, CH_2 of THF), 7.48 (s, 4H, para CH of $BAr^f_4{}^-$), 7.65 (s, 8H, ortho CH of $BAr^f_4{}^-$). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 10.2 (CH_3 of Cp*), 25.5 (CH_2 of THF), 69.0 (CH_2 of THF), 97.4 (quaternary of Cp*), 117.6 (para CH of $BAr^f_4{}^-$), 122.8 (q, $^1J_{CF}$ = 273 Hz, CF_3 of $BAr^f_4{}^-$), 129.1 (q, $^2J_{CF}$ = 34 Hz, meta C of $BAr^f_4{}^-$), 134.9 (ortho CH of $BAr^f_4{}^-$), 160.8 (q, $^1J_{CB}$= 53 Hz, ipso C of $BAr^f_4{}^-$), 211.6 (CO). ^{11}B (96 MHz, CD_2Cl_2): δ –7.6 ($BAr^f_4{}^-$). ^{19}F NMR (283 MHz, CD_2Cl_2): δ – 62.8 (CF_3). IR (CH_2Cl_2/THF): ν(CO) 1978, 1962, 1927 cm^{-1}. Mass spec. (ES+): m/z 635.7 (weak) $[M]^+$, correct isotope distribution for 2 Fe, 1 Ga atoms, significant fragment ions at m/z 563 (45 %) $[M – THF]^+$, 535 (10 %) $[M – THF - CO]^+$, 507 (5 %) $[M – THF - 2CO]^+$. Exact mass: calc.

for [M – THF]$^+$ 563.0093, meas. 563.0095.

[{CpFe(CO)$_2$Ga(Mes*)}$_2$(μ-Cl)][BAr$^f_4$] (5.26)

To a suspension of Na[BAr$^f_4$] (0.042 g, 0.047 mmol) in dichloromethane-d$_2$ (1 ml) at -78 °C was added dropwise a solution of [CpFe(CO)$_2$Ga(Mes*)Cl], **3.1**, (0.025 g, 0.047 mmol) in dichloromethane-d$_2$ (5 ml), and the reaction mixture warmed to 20 °C over 30 min. At this point, the reaction was judged to be complete by ^{1}H NMR spectroscopy; filtration and layering with hexane led to the isolation of **5.26** as crystals suitable for X-ray diffraction. Yield: 0.021 g, 24 %. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 1.25 (s, 9H, para ^{t}Bu), 1.46 (s, 18H, ortho ^{t}Bu), 4.88 (s, Cp), 7.34 (s, 2H, aryl CH of Mes*), 7.55 (s, 4H, para CH of BAr$^f_4{}^-$), 7.71 (s, 8H, ortho CH of BAr$^f_4{}^-$). ^{13}C NMR (76 MHz, CD$_2$Cl$_2$): δ 30.9 (CH$_3$ of para ^{t}Bu), 34.0 (CH$_3$ of ortho ^{t}Bu), 34.7 (quaternary of para ^{t}Bu), 38.2 (quaternary of ortho ^{t}Bu), 83.5 (Cp), 117.4 (para CH of BAr$^f_4{}^-$), 119.4 (meta CH of Mes*), 122.9 (q, $^1J_{CF}$ = 273 Hz, CF$_3$ of BAr$^f_4{}^-$), 128.8 (q, $^2J_{CF}$ = 31 Hz, meta C of BAr$^f_4{}^-$), 134.9 (ortho CH of BAr$^f_4$), 154.9 (para C of Mes*), 155.0 (ortho C of Mes*), 212.7 (CO), ipso carbons undetected. ^{11}B NMR (96 MHz, CD$_2$Cl$_2$): δ –7.6 (BAr$^f_4{}^-$). ^{19}F NMR (283 MHz, CD$_2$Cl$_2$): δ –62.7 (CF$_3$). IR (CD$_2$Cl$_2$): ν(CO) 2016, 2002, 1972, 1954 cm^{-1}. Mass spec. (EI): 963.7 (5 %) [M - 2CO]$^+$, correct isotope distribution for 2 Fe, 2Ga and 1 Cl atoms, significant fragment ions at m/z 527.1 (5 %) [CpFe(CO)$_2$Ga(Mes*)Cl]$^+$, 491.1 (20 %) [CpFe(CO)$_2$Ga(Mes*)]$^+$.

[{Cp*Fe(CO)$_2$Ga(Mes*)}$_2$(μ-Cl)][BAr$^f_4$] (5.30)

To a suspension of Na[BAr$^f_4$] (0.022 g, 0.025 mmol) in dichloromethane-d$_2$ (1 ml) at –78 °C was added dropwise a solution of [Cp*Fe(CO)$_2$Ga(Mes*)Cl], **3.2**, (0.015 g, 0.025 mmol) in dichloromethane-d$_2$ (5 ml), and the reaction mixture warmed to 20 °C over 30 min. At this point, the reaction was judged to be complete by ^{1}H NMR spectroscopy; filtration and layering with hexane led to the isolation of **5.30** as a pale orange powder. Yield: 0.005 g, 26 %: ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 1.25 (s, 18H, para ^{t}Bu), 1.50 (s, 36H, ortho ^{t}Bu), 1.76 (s, 30H, Cp*), 7.30 (s, 4H, aryl CH of Mes*), 7.50 (s, 4H, para CH of BAr$^f_4{}^-$), 7.66 (s, 8H, ortho CH of BAr$^f_4{}^-$). ^{13}C NMR (76 MHz, CD$_2$Cl$_2$): δ 10.0 (CH$_3$ of Cp*), 30.9 (CH$_3$ of para ^{t}Bu), 33.9 (CH$_3$ of ortho ^{t}Bu), 34.7 (quaternary of para ^{t}Bu), 38.5 (quaternary of ortho ^{t}Bu), 95.5 (quaternary of Cp*), 117.5 (para CH of BAr$^f_4{}^-$), 123.4 (meta CH of Mes*), 124.6 (q, $^1J_{CF}$ = 272 Hz, CF$_3$ of BAr$^f_4{}^-$), 128.9 (q, $^2J_{CF}$ = 31 Hz, meta C of BAr$^f_4{}^-$), 134.9 (ortho CH of BAr$^f_4{}^-$), 137.9 (ipso C of Mes*), 151.6 (para C of Mes*), 155.4 (ortho C of Mes*), 161.8 (q, $^1J_{CB}$ = 50

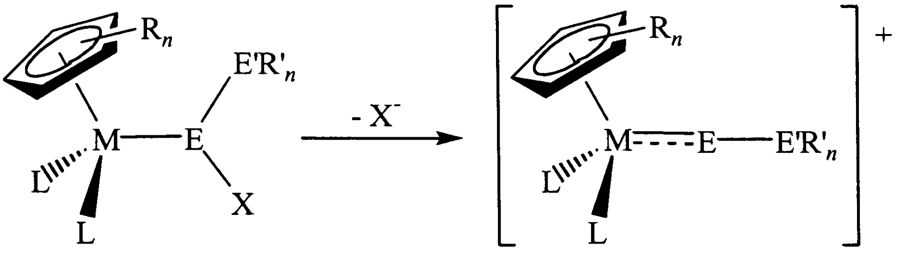
Hz, ipso C of $BAr^{f}_{4}{}^{-}$), 214.5 (CO). ^{11}B NMR (96 MHz, CD_2Cl_2): δ –7.6 ($BAr^{f}_{4}{}^{-}$). ^{19}F NMR (283 MHz, CD_2Cl_2): δ –62.8 (CF_3). ν(CO) 1996, 1986,1954, 1932 cm^{-1}. Mass spec. (EI): 1131.1 (weak) $[M - CO]^+$, correct isotope distribution for 2 Fe, 2Ga and 1 Cl atoms, significant fragment ions at m/z 723.0 (25 %) $[Cp^*Fe(CO)_2Ga(Mes^*)_2Cl - 2CO]^+$, 650.1 (100 %) $[BAr^{f}_{3}]^+$, 631.1 (80 %) $[BAr^{f}_{3} - F]^+$.

$[Cp^*Fe(CO)_2Ga(Mes^*)][BAr^{f}_{4}]$ (5.31)

To a suspension of $Na[BAr^{f}_{4}]$ (0.111 g, 0.125 mmol) in dichloromethane-d_2 (1 ml) at –78 °C was added dropwise a solution of $[Cp^*Fe(CO)_2Ga(Mes^*)Cl]$, **3.2**, (0.075 g, 0.125 mmol) in dichloromethane-d_2 (9 ml), and the reaction mixture stirred and warmed to 20 °C over 1 h. At this point, the reaction was judged to be complete by ^1H NMR and IR spectroscopy. Filtration and layering with hexane led to the isolation of **5.31** as a pale yellow powder. Yield 0.019 g, 27 %. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.19 (s, 9H, para ^tBu), 1.50 (s, 18H, ortho ^tBu), 1.77 (s, 15H, Cp*), 7.29 (s, 2H, aryl CH of Mes*), 7.44 (s, 4H, para CH of $BAr^{f}_{4}{}^{-}$), 7.60 (s, 8H, ortho CH of $BAr^{f}_{4}{}^{-}$). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 10.1 (CH_3 of Cp*), 30.8 (CH_3 of para ^tBu), 31.3 (CH_3 of ortho ^tBu), 35.4 (quaternary of para ^tBu), 38.5 (quaternary of ortho ^tBu), 97.5 (quaternary of Cp*), 117.5 (para CH of $BAr^{f}_{4}{}^{-}$), 122.4 (meta CH of Mes*), 126.1 (q, $^1J_{CF}$ = 272 Hz, CF_3 of $BAr^{f}_{4}{}^{-}$), 129.1 (q, $^2J_{CF}$ = 31 Hz, meta C of $BAr^{f}_{4}{}^{-}$), 134.9 (ortho CH of $BAr^{f}_{4}{}^{-}$), 150.1 (para C of Mes*), 155.5 (ipso C of Mes*), 157.3 (ortho C of Mes*), 162.1 (q, $^1J_{CB}$ = 50 Hz, ipso C of $BAr^{f}_{4}{}^{-}$), 212.4 (CO). ^{11}B NMR (96 MHz, CD_2Cl_2): δ –7.6 ($BAr^{f}_{4}{}^{-}$). ^{19}F NMR (283 MHz, CD_2Cl_2): δ –62.7 (CF_3). ν(CO) 2019, 1998 cm^{-1}. Mass spec. (ES): 562.0 (30 %) $[M]^+$, 534.1 (weak) $[M - CO]^+$.

5.5 Results and Discussion

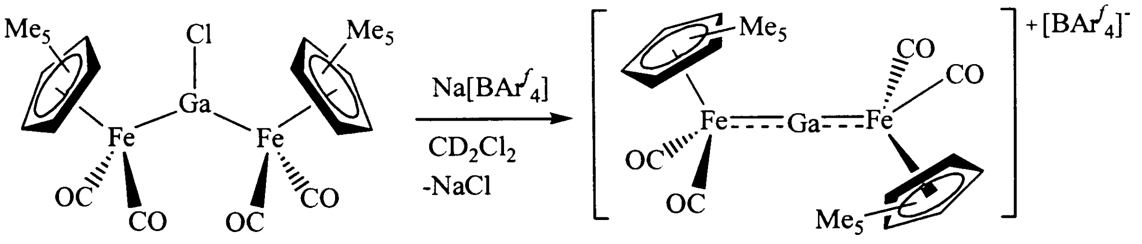
Halide abstraction chemistry has been investigated for two classes of three-coordinate halo-gallium substrate systems, (i) asymmetric halogallyl systems of the type L_nM—Ga(Mes*)Cl and (ii) bridging halogallanediyl complexes $(L_nM)_2GaCl$, with a view to probing this route for the synthesis of cationic diyl and metalladiyl complexes (Scheme 6).



Scheme 6

5.5.1 Halide abstraction chemistry of bridging halogallanediyl systems

The three-coordinate bridging halodiyl complex, $[\{Cp^*Fe(CO)_2\}_2GaCl]$, **3.11**, reacts cleanly and readily with a single equivalent of $Na[BAr^f_4]$ in dichloromethane over a period of *ca.* 2 h to give the expected cationic dinuclear complex $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}Ga)]^+$, **5.12**, and sodium chloride (Scheme 7).[19]



(3.11) **(5.12)**

Scheme 7

Monitoring of the reaction in CD_2Cl_2 (by ^1H NMR and IR) shows quantitative conversion to a single Cp* containing species with significantly higher carbonyl stretching frequencies (2016, 1994, 1963 *vs.* 1960, 1925, 1910 cm^{-1} for **3.11** and **5.12**, respectively). This may be expected for the formation of a base free cationic two-coordinate group 13 system *via* chloride abstraction. The ^{1}H NMR spectrum is consistent with a 2:1 ratio of Cp* and $[BAr^{f}_{4}]^{-}$ components, and ^{13}C, ^{19}F, ^{11}B NMR and mass spectral data for the isolated crystalline product are consistent with the presence of $[\{Cp^{*}Fe(CO)_{2}\}_{2}(\mu\text{-}Ga)]^{+}$ and $[BAr^{f}_{4}]^{-}$ ions. These spectroscopic inferences were subsequently confirmed crystallographically. X-ray quality crystals were grown by layering a dichloromethane solution of **5.12** with hexane and cooling to –30 °C overnight. The molecular structure of the cationic component of **5.12** is depicted in Figure 1.

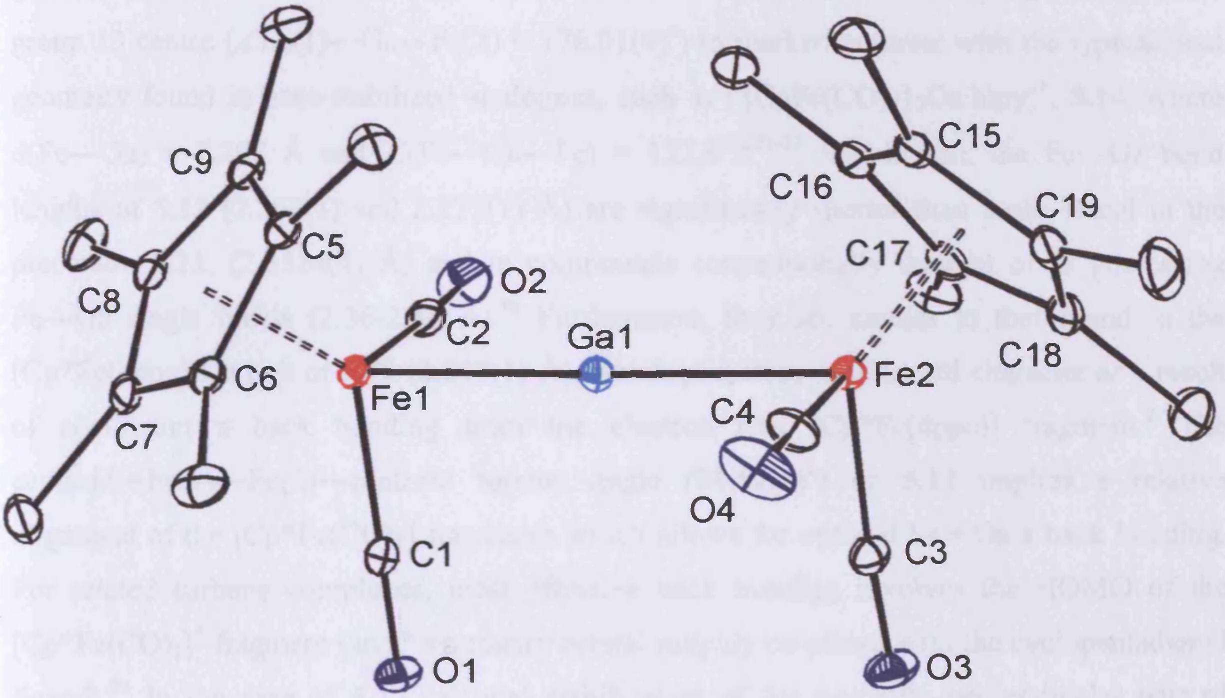


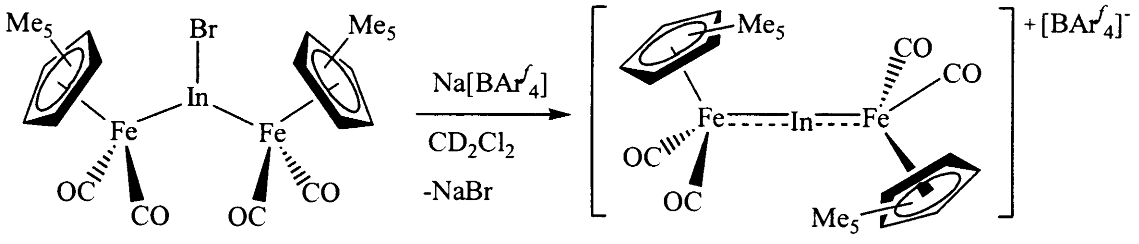
Figure 1: Structure of the cationic component of $[\{Cp^{*}Fe(CO)_{2}\}_{2}(\mu\text{-}Ga)]^{+}[BAr^{f}_{4}]^{-}$, **5.12**

Selected bond lengths (Å) and angles (°): Fe(1)—Ga(1) 2.272(1), Fe(2)—Ga(1) 2.266(1), Fe(1)—Cp* centroid 1.728(3), Fe(1)—C(1) 1.764(3), Fe(1)—Ga(1)—Fe(2) 178.99(2), Cp* centroid—Fe(1)—Fe(2)—Cp* centroid 84.6(1).

Compound **5.12** represents an extremely rare example of a structurally characterized species containing a two-coordinate cationic gallium centre and the first containing metal—group 13 element bonds. Bridging gallylene (gallanediyl) complexes featuring two coordinate gallium centres have only previously been reported in association with extremely bulky aryl substituents, such as $[\{2,6\text{-}Mes_2C_6H_3\}_2Ga]^+Li[Al\{OCH(CF_3)_2\}_4]^{2-}$, **5.13**.[20]

There are a number of interesting structural features to note about **5.12**. Firstly, the linear Fe—Ga—Fe unit (∠Fe(1)—Ga(1)—Fe(1') = 178.99(2)°) is consistent with a two-coordinate gallium center engaging in no significant secondary interactions (*e.g.* with an anion).[2] This geometry can be compared with that found in the neutral species $[Cp^*Fe(dppe)](\mu\text{-}Ga)[Fe(CO)_4]$, **1.76**, reported by Ueno and co-workers,[2] a compound which represents the only other example of a transition metal complex containing a 'naked' bridging gallium atom. Like **5.12**, this complex also features a near-linear coordination geometry at the group 13 centre (∠Fe(1)—Ga—Fe(2) = 176.01(4)°) in marked contrast with the typical bent geometry found in base-stabilized analogues, such as $[\{CpFe(CO)_2\}_2Ga{\cdot}bipy]^+$, **5.14**, where d(Fe—Ga) = 2.397 Å and ∠(Fe—Ga—Fe) = 132.8°.[2,21-23] In addition, the Fe—Ga bond lengths of **5.12** (2.266(1) and 2.272(1) Å) are significantly shorter than those found in the precursor, **3.11**, (2.3524(4) Å) and in compounds conventionally thought of as possessing Fe—Ga single bonds (2.36-2.46 Å).[9a] Furthermore, they are similar to that found in the [Cp*Fe(dppe)]Ga unit of **1.76** (2.248(1) Å), which possesses unsaturated character as a result of significant π back bonding from the electron rich [Cp*Fe(dppe)] fragment.[2] The centroid—Fe(1)—Fe(2)—centroid torsion angle (84.62(3)°) of **5.12** implies a relative alignment of the $[Cp^*Fe(CO)_2]$ fragments which allows for optimal Fe→ Ga π back bonding. For related carbene complexes, most effective back bonding involves the HOMO of the $[Cp^*Fe(CO)_2]^+$ fragment (an a'' symmetry orbital roughly co-planar with the cyclopentadienyl ligand).[24] In the case of **5.12**, optimal stabilization of the mutually perpendicular pair of formally vacant Ga p orbitals would therefore be achieved by orthogonal alignment of the HOMOs of the two $[Cp^*Fe(CO)_2]$ fragments and consequently by a torsion angle of *ca.* 90°.

The corresponding cationic dinuclear complex $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}In)]^+[BAr^f_4]^-$, **5.15**, has also been synthesized using the same methodology. Work discussed on saturated indium complexes was carried out within our research group by Dr D. L. Coombs. Reaction between a single equivalent of $Na[BAr^f_4]$ and $[\{Cp^*Fe(CO)_2\}_2InBr]$, **3.12**, in dichloromethane over a period of 2 h gave the analogous cationic dinuclear complex **5.15**, and sodium bromide (Scheme 8).



(3.12) (5.15)

Scheme 8

The molecular structure of the cationic component of **5.15** is depicted in Figure 2. This has enabled direct structural comparison with the base-free cationic two-coordinate gallium analogue, **5.12**.

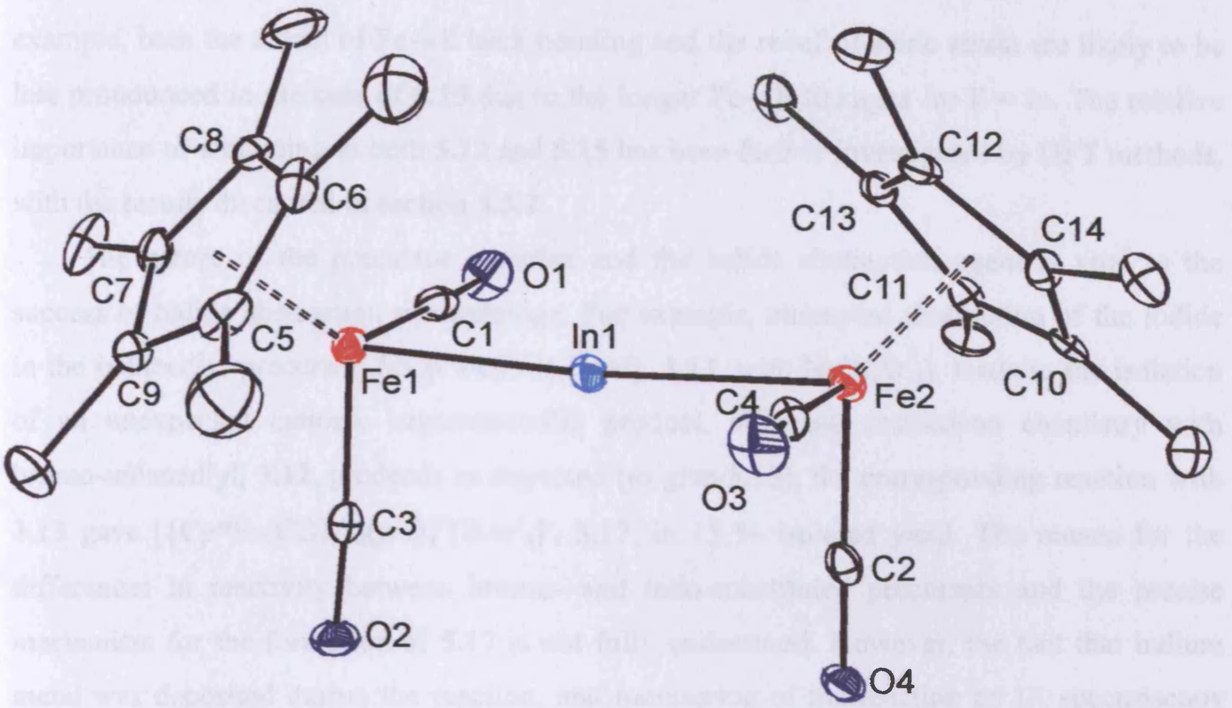


Figure 2: Structure of the cationic component of $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}In)]^+[BAr^f_4]^-$, **5.15**

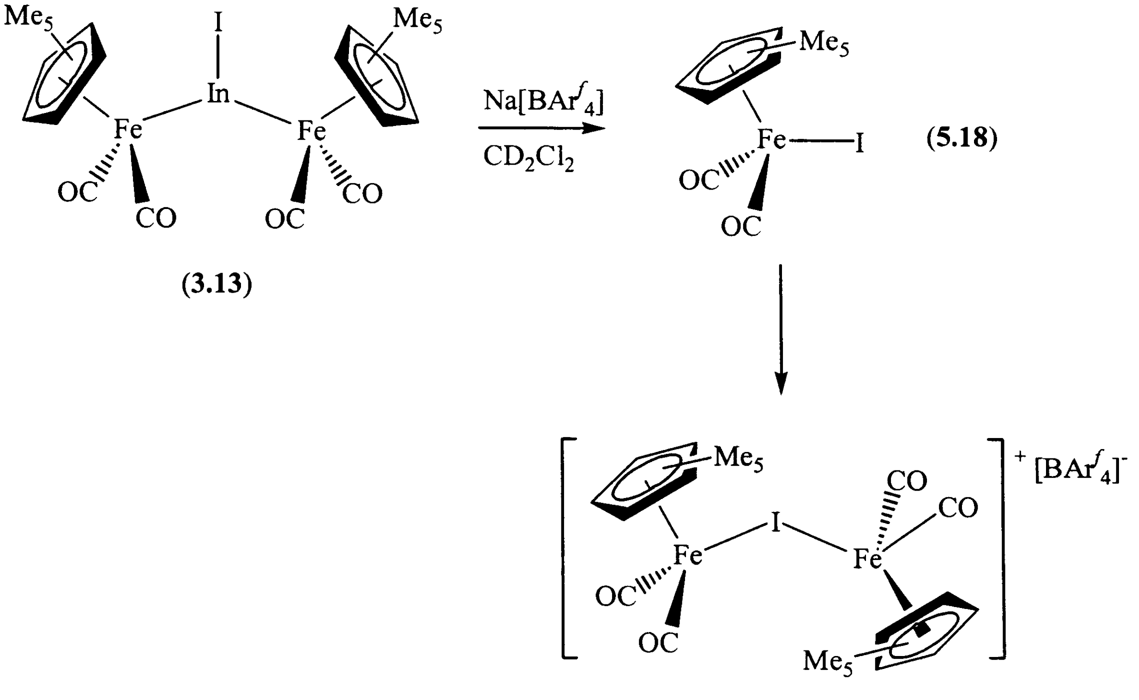
(This crystal structure was obtained by Dr. D. Coombs)

Selected bond lengths (Å) and angles (°): Fe(1)—In(1) 2.460(2), Fe(2)—In(1) 2.469(2), Fe(1)—Cp* centroid 1.725(10), Fe(1)—C(1) 1.757(13), Fe(1)—In(1)—Fe(2) 175.32(6), Cp* centroid—Fe(1)—Fe(2)—Cp* centroid 86.8(3).

As with **5.12**, the Fe—In bond lengths of **5.15** (2.460(2) and 2.469(2) Å) are shorter than those found in the corresponding bridging halodiyl precursor $[Cp^*Fe(CO)_2]_2InBr$, **3.12**, (2.509(3) Å) and in related three-coordinate base-stabilized cationic systems, *e.g.* $[\{Cp^*Fe(CO)_2\}_2\{\mu\text{-}In(THF)\}]^+[BAr^f_4]^-$, **5.16**, (2.498(2) and 2.494(2) Å).

Clearly the shortening observed on halide abstraction from **3.11** (to give **5.12**) (*ca.* 3.5 %) is consistent with both steric and electronic factors, *i.e.* with a reduction in the coordination number at gallium or with an increase in the extent of Fe→Ga back bonding. However, the extent of bond shortening accompanying the halide abstraction process is significantly less in the case of the indium complex, **5.15**, (*ca.* 1.8 % with respect to **3.12**). Such an observation is consistent with both the underlying steric and electronic factors. For example, both the extent of Fe→E back bonding and the relief of steric strain are likely to be less pronounced in the case of **5.15** due to the longer Fe—E linkages for E = In. The relative importance of π bonding in both **5.12** and **5.15** has been further investigated by DFT methods, with the results discussed in section **5.5.2**.

The nature of the precursor complex and the halide abstraction agent is vital to the success of halide abstraction methodology. For example, attempted abstraction of the iodide in the indanediyl precursor, $[\{Cp^*Fe(CO)_2\}_2InI]$, **3.13**, with $Na[BAr^f_4]$, leads to the isolation of an unexpected cationic organometallic product. Whereas abstraction chemistry with bromo-indanediyl, **3.12**, proceeds as expected (to give **5.15**), the corresponding reaction with **3.13** gave $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}I)]^+[BAr^f_4]^-$, **5.17**, in 15 % isolated yield. The reason for the differences in reactivity between bromo- and iodo-substituted precursors and the precise mechanism for the formation of **5.17** is not fully understood. However, the fact that indium metal was deposited during the reaction, and monitoring of the reaction by IR spectroscopy revealed that $[Cp^*Fe(CO)_2I]$, **5.18**, is an intermediate on the overall reaction pathway, gives clues to a possible mechanistic route (Scheme 9).



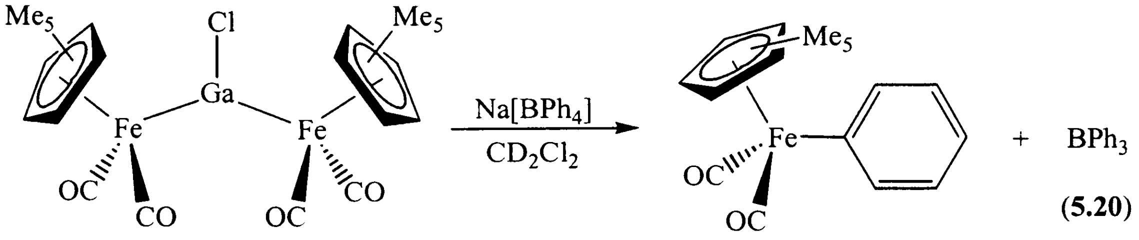
(3.13)

(5.18)

(5.17)

Scheme 9

The nature of the abstraction agent also plays a critical role in the success of the halide abstraction process. Attempted reaction of **3.11** with Ag[BF$_4$] instead of Na[BAr$^f_4$] leads to the isolation of no tractable iron/gallium products. Whereas reaction of **3.11** using Na[BPh$_4$] as the halide abstraction agent, gives [Cp*Fe(CO)$_2$Ph], **5.19**, and BPh$_3$, **5.20** (Scheme 10).



(3.11)

(5.19)

(5.20)

Scheme 10

Monitoring the reaction mixture by IR spectroscopy over a period of 72 h revealed the gradual disappearance of the carbonyl stretching bands of the starting material (1969, 1957 and 1922 cm^{-1}), and the growth of bands at 2016, 1995, 1970 and 1940 cm^{-1}. The ^{11}B NMR spectrum also revealed the growth of a strong broad signal at δ_B 67.0. Filtration of the supernatant solution, removal of volatiles *in vacuo* and recrystallization from hexane at –30°C led to the formation of crops of colourless and dark red microcrystalline material, which were identified as BPh_3, **5.20**, (δ_B 67.0) and [Cp*Fe$(CO)_2$Ph], **5.19**, (ν(CO) 1995 and 1940 cm^{-1}), respectively, by comparison of multinuclear NMR, IR and mass spectrometric data with that reported previously.[25] Compounds **5.19** and **5.20**, are formed as a result of abstraction of a phenyl group from the tetraphenylborate counterion.[26] The analogous reaction of [{Cp*Fe$(CO)_2$}$_2$InBr], **3.12** with Na[BPh_4] also proceeds *via* a similar route. The difference in reactivity of Na[BPh_4] compared to Na[BAr^f_4], as a halide abstraction agent, can be explained in terms of the more reactive nature of the [BPh_4]$^-$ anion compared to [BAr^f_4]$^-$ Similar reactivity has previously been observed with highly electrophilic group 13 complexes of iron.[12] Consequently Na[BAr^f_4] has generally been preferred for halide abstraction chemistry. Weakly coordinating anions such as [$CB_{11}H_6Br_6$]$^-$ can be used as an alternative to Na[BAr^f_4] but then the rate of halide abstraction chemistry is typically much slower.

5.5.2 DFT studies of bonding

In order to provide a fuller basis for the discussion of the bonding in cationic dinuclear complexes **5.12** and **5.15**, DFT analyses were carried out, in collaboration with Dr. D. Willock, Dr. A. Rossin and Miss N. Coombs at Cardiff University. The DFT calculations were carried out at the BLYP/TZP level using established methods and salient parameters relating to the fully optimised geometries of [{Cp*Fe$(CO)_2$}$_2$E]$^+$ (E = Ga, In) are detailed in Table 1.[27]

Table 1: Calculated and crystallographically determined structural parameters for the cationic components of $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}E)]^+[BAr^f_4]^-$ (**5.12** E = Ga; **5.15** E = In)

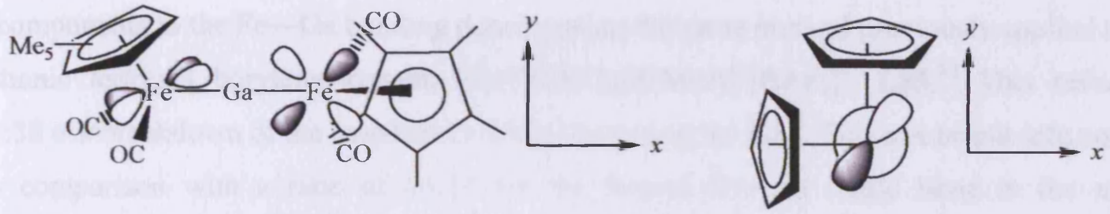
Compound	**Fe-E distances (Å)**	**Fe-E-Fe angle (^{o})**	**Ct-Fe-Fe-Ct torsion angle (^{o})**	**σ:π breakdown**	**Mulliken charges (Fe, E)**[a]
5.12 (exp.)	2.266(1), 2.272(1)	178.99(2)	84.6(1)	-	-
5.12 (calc.)	2.338, 2.337	177.93	86.5	61:38	
5.15 (exp.)	2.460(2), 2.469(2)	175.32(6)	86.8(3)	-	-
5.15 (calc.)	2.463, 2.463	179.40	161.8	74:26	0
5.15 (calc.)	2.469, 2.469	179.87	82.8	74:26	+1.78

[a] Calculated energy relative to minimum energy conformation.

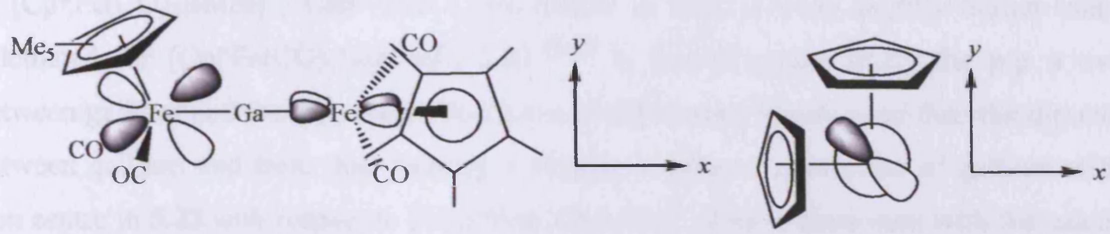
In general the agreement between calculated and experimentally derived geometric parameters is very good. The fully optimised geometry (*d*(Fe—Ga) = 2.338, 2.337 Å; ∠(Fe—Ga—Fe) = 177.9^{o}, ∠ (Ct—Fe—Fe—Ct) = 86.5^{o}) is consistent with that determined crystallographically. The 2-3 % overestimate in the calculated Fe—E bond lengths is comparable to that found in related systems and can be attributed to solid-state effects which lead to a shortening of donor/acceptor bonds together with a general overestimate in bond lengths by generalized gradient approximation (GGA) methods.[12,27,28] In addition, the near linear Fe—Ga—Fe geometry (178.99(2) *vs.* 177.93^{o}, experimental and calculated values, respectively) and almost orthogonal alignments of the $[Cp^*Fe(CO)_2]$ fragments were accurately reproduced (84.6(10) *vs.* 86.5^{o}, experimental and calculated values, respectively).

In the case of **5.15**, the minimum energy conformation calculated by DFT corresponds to a centroid—Fe—Fe—centroid torsion angle of 161.8°, in contrast to the experimentally determined value of 86.3(3)°. Closer inspection, however, reveals that there is a very shallow potential energy surface for rotation about this axis and that the energy difference between the minimum energy conformer and that corresponding to the approximately orthogonal alignment found in the solid state is very small (e.g. $\Delta E = 1.78$ kcal mol^{-1} between rotamers corresponding to torsion angles of 161.8 and 82.4°). σ and π contributions to the overall Fe—In bonding density have therefore been calculated for both of these conformations.

The (Fe—Ga—Fe) π system of **5.12** consists of pairs of nearly degenerate orbitals, with components that are both of x and y type. They do not possess exactly the same energy because one orbital uses the HOMO of each $Cp^{*}Fe(CO)_2^{+}$ fragment whereas the other uses the HOMO-2. The mixing of x and y coordinates is necessary to achieve optimal stabilization *via* simultaneous overlap of the central gallium atomic orbitals with both iron fragments orbitals, which are mutually perpendicular to each other (as shown by the torsion angle close to 90°).[29] This is depicted in Figure 3.



HOMO (Fe1) + HOMO (Fe2) Px + Py (Ga)



HOMO-2(Fe1) + HOMO-2(Fe2) Px-Py(Ga)

Figure 3

Thus the 'corkscrew' appearance of the HOMO-3 (Figure 4) is derived from interaction of the HOMOs of the pair of orthogonal $[Cp^*Fe(CO)_2]^+$ fragments with a combination of the formally vacant $4p_x$ and $4p_y$ orbitals at gallium. The corresponding anti-bonding MOs are the LUMO+1 to LUMO+4.

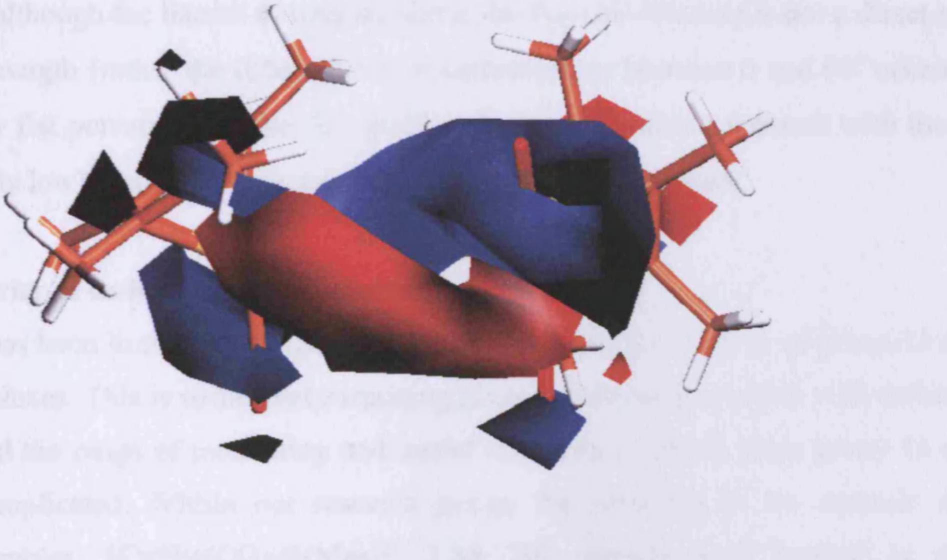


Figure 4

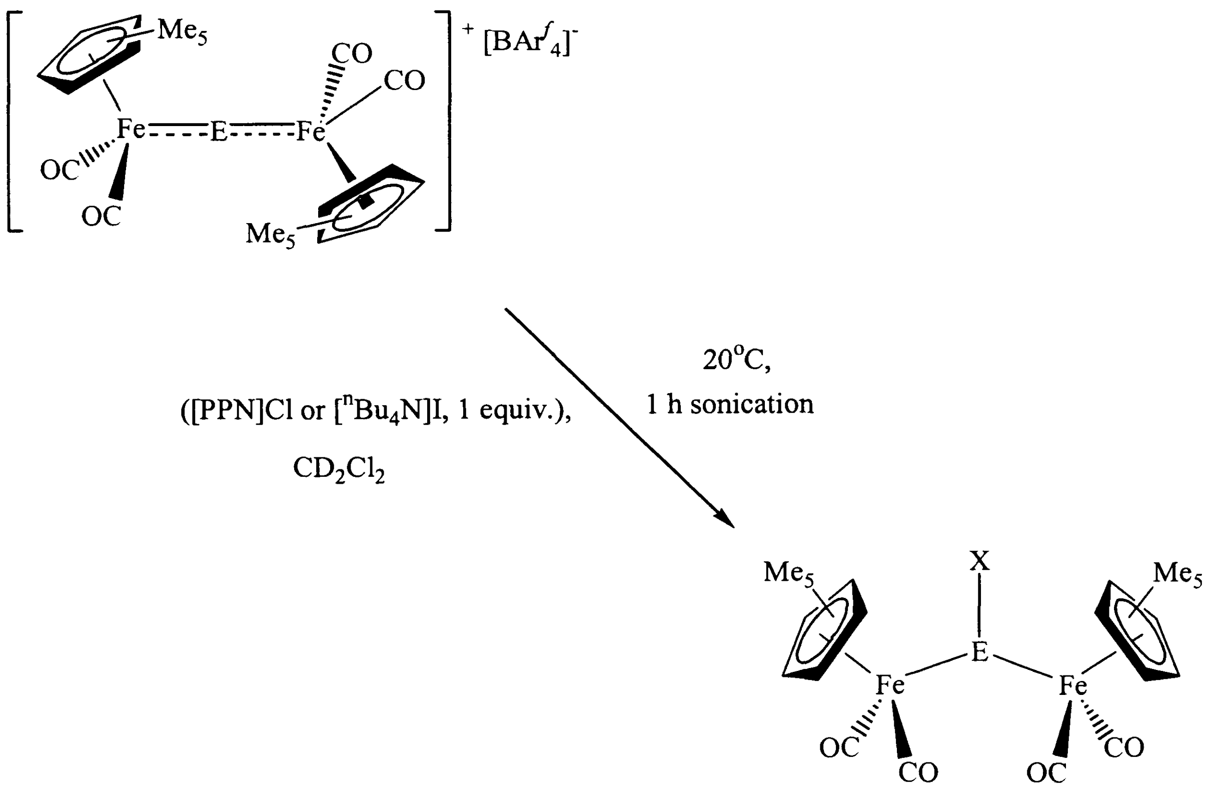
A bond partitioning analysis was carried out to quantify the relative importance of σ and π components to the Fe—Ga bonding density using the same method previously applied to the cationic terminal borylene system, $[Cp^*Fe(CO)_2B(Mes)]^+[BAr^f_4]^-$, **1.85**.[12] This reveals a 61:38 σ:π breakdown of the covalent Fe—Ga interaction for **5.12**. This can be put into context by comparison with a ratio of 86:14 for the formal Fe—Ga single bond in the model compound $[CpFe(CO)_2GaCl_2]$, **5.21**. and a calculated ratio of 62:38 for the Fe=B double bond in $[Cp^*Fe(CO)_2BMes]^+$, **1.85**. The π component in **5.12** is even slightly higher than that calculated for $[Cp^*Fe(CO)_2GaMes]^+$, **5.22**.[27a,29] It would appear likely the p-p π overlap between gallium and the ipso mesityl carbon in **5.22** is more pronounced than the d-p overlap between gallium and iron, thus causing a slightly smaller π interaction of gallium with the iron centre in **5.22** with respect to $[\{Cp^*Fe(CO)_2\}_2Ga]^+$. This is consistent with the calculated Fe—Ga bond lengths in the two cases (*c.f.* 2.309 Å for $[Cp^*Fe(CO)_2GaMes]^+$ and 2.269 Å for **5.12**).

Similar analyses for the indium-centred cation $[\{Cp^*Fe(CO)_2\}_2In]^+$, **5.15**, are consistent with a significantly smaller π contribution to the metal – group 13 element bond. Thus, the σ:π breakdown in this case is 74:26 (for the conformation corresponding to a torsion angle of 82.4°) and 74:26 (at 161.8°); these values can be compared to an 11 % calculated π contribution for the formal Fe—In single bond in the model compound $[CpFe(CO)_2InCl_2]$, **5.23**.[30] The significantly smaller π contribution for E = In than E = Ga is as expected on the well precedented basis of diminished π orbital overlap for the heavier main group elements.[31] In addition, although the barrier to rotation about the Fe—In—Fe axis is not a direct measure of π bond strength (rather the difference in π contributions between 0 and 90° orientations), the relatively flat potential function for rotation about his bond is consistent with the similar (and relatively low) π contributions calculated for both conformations.

5.5.3 Reactivity of cationic systems towards nucleophiles

There has been limited investigation into the fundamental reactivity of group 13 diyl and related complexes. This is somewhat surprising given the obvious parallels with carbenes and silylenes, and the range of interesting and useful reactivity in which these group 14 systems have been implicated. Within our research group, the reactivity of the cationic terminal borylene complex, $[Cp^*Fe(CO)_2B(Mes)]^+$, **1.85**, has recently been studied in detail.[12c] Preliminary studies of **1.85** have indicated that subsequent reactivity chemistry, which implies dominant electrophilic character, can be divided into two distinct types. Reactivity towards anionic neutral nucleophiles proceeds *via* addition at the highly electrophilic boron center, whereas, reactivity towards neutral unsaturated substrates primarily progresses *via* borylene displacement. Attempts to modulate this reactivity by variation in the diyl substituent have led to the synthesis of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2B(N^iPr_2)]^+[BAr^f_4]^-$, **5.6**, a compound which displays metathesis reactivity towards $Ph_3E{=}X$ (E = P, As; X = O, S).[17]

The reactivities of the two-coordinate metalladiyls **5.12** and **5.15** towards neutral and anionic two-electron donors were investigated. Both compounds **5.12** and **5.15** rapidly react with sources of halide ions in dichloromethane solution to generate the bridging halodiyl complexes $[Cp^*Fe(CO)_2]_2EX$ (**3.11**: E = Ga, X = Cl; **3.13**: E = In, X = I) (Scheme 11).

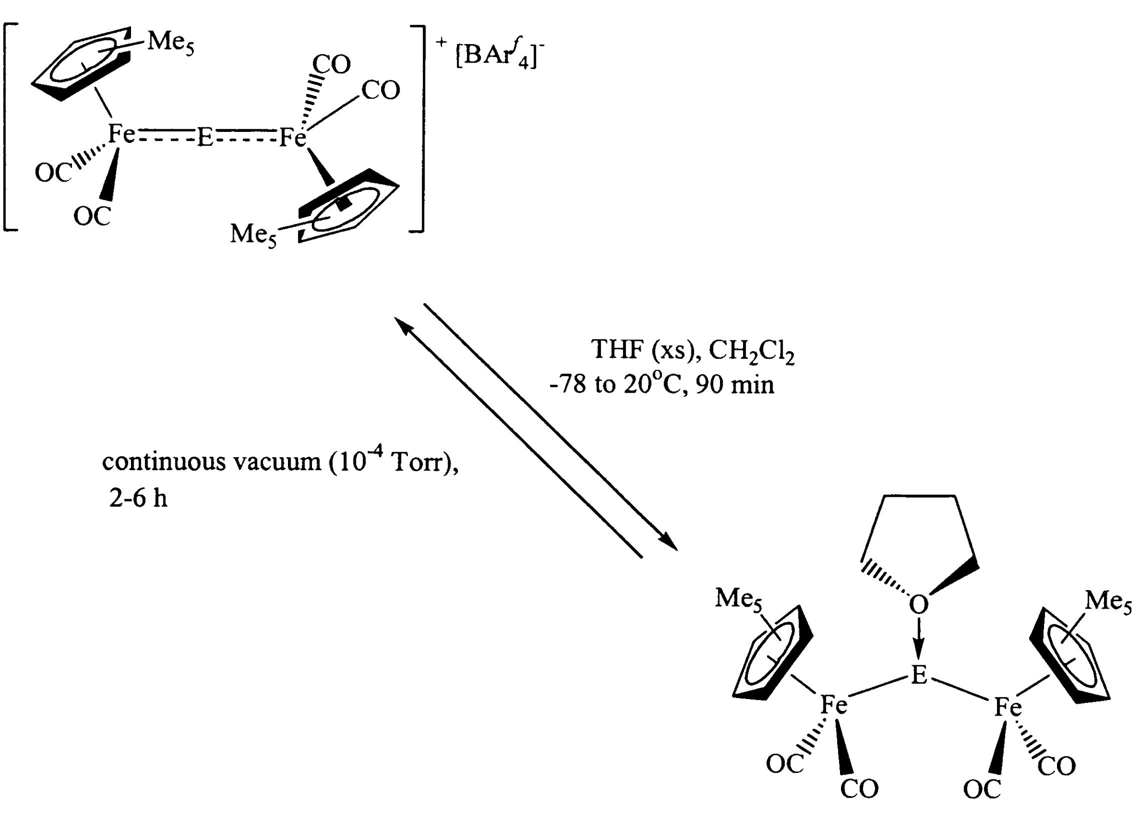


3.11: E = Ga, X = Cl
3.13: E = In, X = I

Scheme 11

Compound **5.12** reacts cleanly and swiftly (*ca.* 1 h) with [PPN]Cl in dichloromethane at 20 °C to regenerate **3.11**. Monitoring of the reaction (by ^1H NMR) reveals quantitative conversion to a single Cp* containing species. Further comparison of multinuclear NMR and IR data (for the isolated compound) with those obtained for an authentic sample of **3.11**, confirmed the identity of **3.11** as the sole organometallic product. Analogously, the two-coordinate metalladiyl **5.15** rapidly reacts with [^{n}Bu$_4$N]I in dichloromethane to yield **3.13** quantitively. Multinuclear NMR and IR data (for the isolated compound) are identical with those obtained for an authentic sample of **3.13** thus confirming the identity of **3.13** as the sole organometallic product. This can be compared to similar reactivity which is observed towards halides for the terminal borylene complex, $[Cp^*Fe(CO)_2B(Mes)]^+$, **1.85**.[12] However, whereas **1.87** is sufficiently Lewis acidic to abstract fluoride from $[BF_4]^-$ and generate $[Cp^*Fe(CO)_2B(Mes)F]$, gallium-centred cation **5.12**, for example, is unreactive towards sources of $[BF_4]^-$ under similar conditions. Therefore the gallium centre of **5.12** is presumed to be somewhat less electrophilic in character than the corresponding boron centre of $[Cp^*Fe(CO)_2B(Mes)]^+$, **1.85**.

The reactivity of two coordinate metalladiyls **5.12** and **5.15** towards neutral two-electron donors, such as THF, has also been investigated. In the presence of THF, the cationic trimetallic species **5.12** readily coordinates a single molecule of THF to generate the 1:1 adduct, $[\{Cp^*Fe(CO)_2\}_2\{\mu\text{-}Ga(THF)\}]^+[BAr^f_4]^-$, **5.24**. Filtration and cooling to –30 °C leads to the isolation of **5.24** as a pale yellow microcrystalline solid in a 35 % yield. Indium-containing compound **5.15** also reacts with THF in a similar manner to generate $[\{Cp^*Fe(CO)_2\}_2\{\mu\text{-}In(THF)\}]^+[BAr^f_4]^-$, **5.16**, in an isolated yield of 41 % (Scheme 12).



(**5.24**) E = Ga
(**5.16**) E = In

Scheme 12

Compounds **5.16** and **5.24** have been fully characterised by multinuclear NMR, IR and mass spectrometry, including exact mass determination. Spectroscopic data are consistent with the proposed formulation. For both adducts **5.16** and **5.24**, the 1:1 stoichiometry is implied by integration of the ^{1}H NMR signals due to THF and Cp* groups. The coordination of the donor oxygen of THF at the group 13 centre is consistent with the significant shifts to lower wavenumber in the CO stretching bands (1978, 1962, 1927 and 2016, 1994, 1963 cm^{-1} for **5.24** and **5.12**, respectively; 1974, 1958, 1922 and 2005, 1983, 1951 cm^{-1} for **5.16** and **5.15**, respectively). Furthermore, in the case of **5.16**, the structure of the adduct was subsequently confirmed crystallographically. Single crystals suitable for X-ray diffraction were grown by filtering and cooling of the reaction mixture to –30 °C. The molecular structure of **5.16** is depicted in Figure 6.

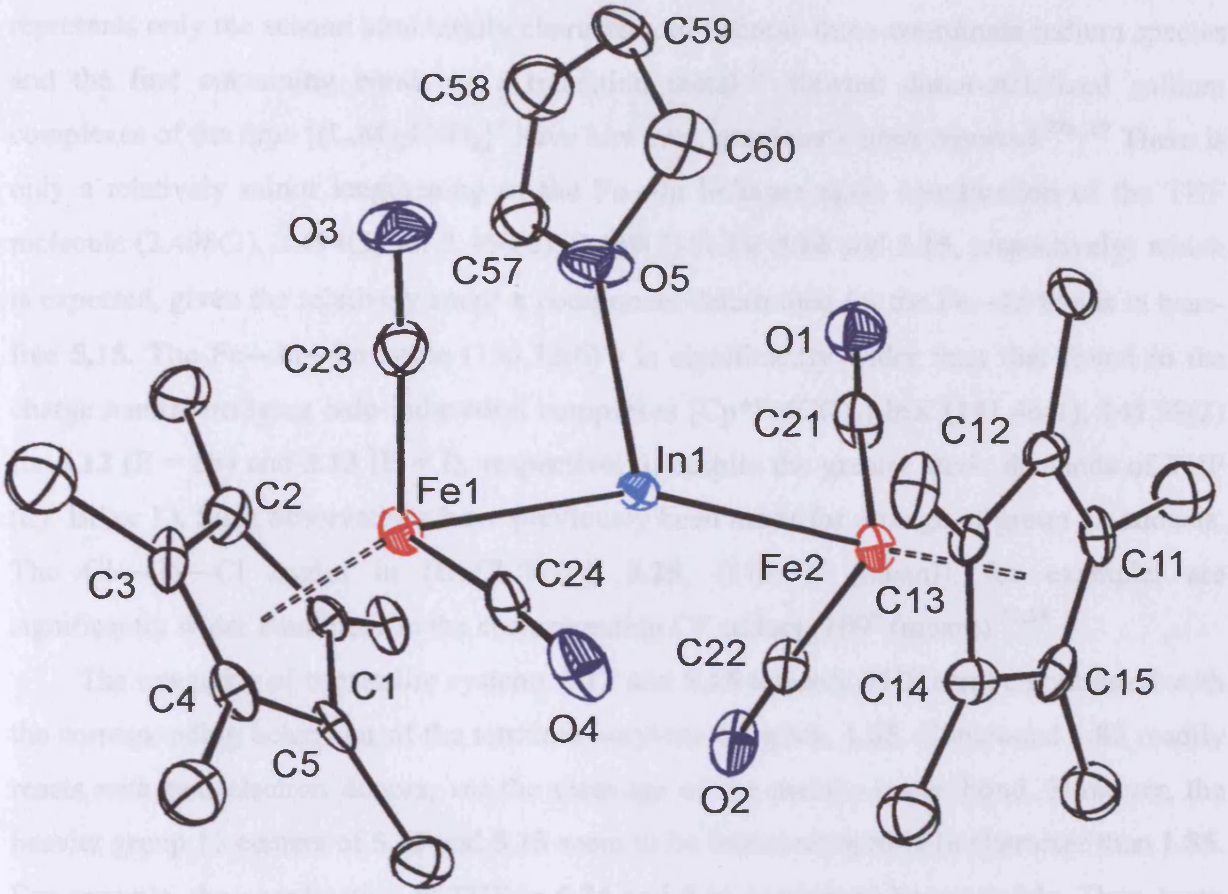


Figure 6: Structure of the cationic component of $[\{Cp^*Fe(CO)_2\}_2\{\mu\text{–}In(THF)\}]^+[BAr^f_4]^-$, **5.16**
(This crystal structure was obtained by Dr. D. Coombs)

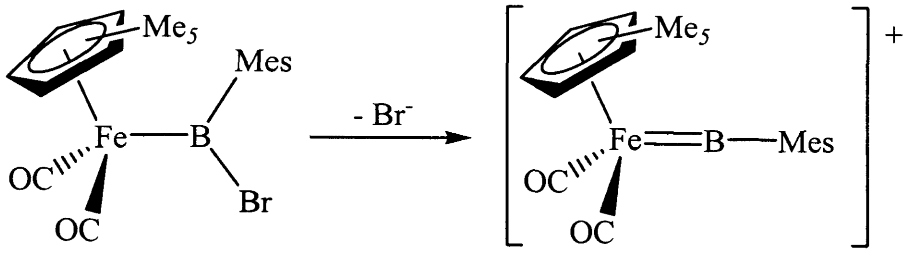
Selected bond lengths (Å) and angles (°): Fe(1)—In(1) 2.498(2), Fe(2)—In(1) 2.494(2), Fe(1)—Cp* centroid 1.729(12), Fe(1)—C(23) 1.748(13), Fe(1)—In(1)—Fe(2) 156.72(6), Fe(1)—In(1)—O(5) 100.1(3), Fe(2)—In(1)—O(5) 103.2(3), Fe(1)—In(1)—O(5)—C(57) 80.0(4).

The molecular structure of the THF-stabilized complex $[\{Cp^*Fe(CO)_2\}_2\{\mu\text{-}In(THF)\}]^+[BAr^f_4]^-$, **5.16**, is consistent with the proposed 1:1 formulation and spectroscopic data. The indium centre is trigonal planar (sum of angles at indium = 360.0(3)°). Presumably, the approximately orthogonal alignment of Fe_2In and OC_2 planes (torsion Fe(1)—In(1)—O(5)—C(57) = 80.0(4)°) is imposed on steric grounds. Compound **5.16** represents only the second structurally characterized cationic three-coordinate indium species and the first containing bonds to a transition metal.[32] Related donor-stabilized gallium complexes of the type $[(L_nM)_2GaD_2]^+$ have however, previously been reported.[27a, 29] There is only a relatively minor lengthening of the Fe—In linkages upon coordination of the THF molecule (2.498(2), 2.494(2) *vs.* 2.460(2), 2.469(2) Å for **5.16** and **5.15**, respectively) which is expected, given the relatively small π component determined for the Fe—In bonds in base-free **5.15**. The Fe—In—Fe angle (156.72(6)°) is significantly wider than that found in the charge neutral bridging halo-indanediyl complexes $[Cp^*Fe(CO)_2]_2InX$ (141.46(1), 141.98(2) for **3.12** (E = Br) and **3.13** (E = I), respectively), despite the greater steric demands of THF (*c.f.* Br^- or I^-). Such observations have previously been made for a range of group 13 adducts. The Cl—Ga—Cl angles in $[GaCl_3{\cdot}THF]$, **5.25**, (113.07° (mean)), for example, are significantly wider than those in the corresponding Cl^- adduct (109° (mean)).[33,34]

The reactivity of trimetallic systems **5.12** and **5.15** towards THF can be contrasted with the corresponding behaviour of the terminal borylene complex, **1.85**. Compound **1.85** readily reacts with two electron donors, *via* the cleavage of the metal—boron bond. However, the heavier group 13 centers of **5.12** and **5.15** seem to be less electrophilic in character than **1.85**. For example, the coordination of THF in **5.24** and **5.16** appears to be reversible. Thus, upon prolonged exposure to continuous vacuum (10^{-4} Torr) spectroscopic data for both compounds are consistent with loss of coordinated THF. Monitoring of this process by IR and ^1H NMR spectroscopies reveals that in the case of **5.24**, a mixture of the donor-stabilized complex and the 'naked' two-coordinate species **5.12** is obtained. In the case of **5.16** complete loss of THF is observed over a period of 6 h, leading to the regeneration of $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}In)]^+[BAr^f_4]^-$, **5.15**. Such behaviour is consistent with a relatively weak Lewis acid/base interaction. The greater ease at which the indium-bound THF ligand is lost compared to that of gallium is mirrored with previous reports of the thermodynamics of oxygen donor coordination to gallium and indium based Lewis acids.[35,36]

5.5.4 Halide abstraction chemistry of asymmetric halogallyl systems

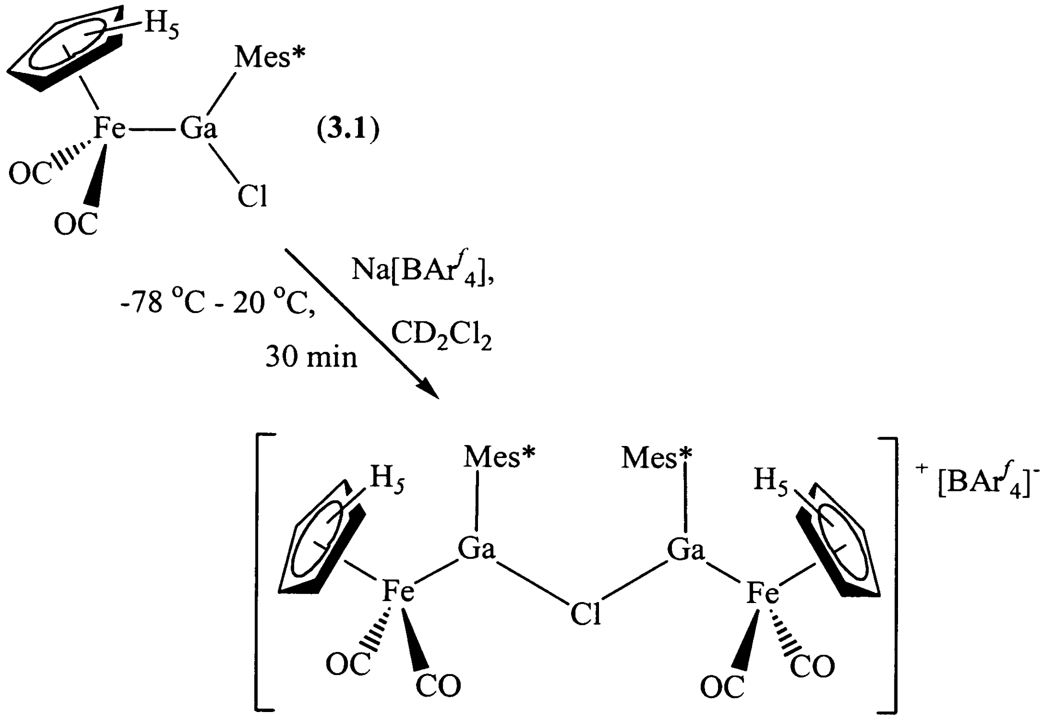
Given the successful synthesis of the cationic dinuclear complexes, **5.12** and **5.15**, *via* halide abstraction, it was decided to investigate the corresponding reactivity of asymmetric halo-gallium containing precursors. Similar abstraction methodology has previously been reported for the analogous cationic terminal borylene complex, **1.85**, featuring the first reported Fe=B bond (Scheme 13).[12]



(1.85)

Scheme 13

Halide abstraction was firstly attempted with the aryl(chloro)gallyl precursor complex, [CpFe(CO)$_2$Ga(Mes*)Cl], **3.1**. This compound contains the sterically hindered super-mesityl group, the role of which is to provide kinetic stabilisation to the putative cationic terminal gallylene and reduce any tendency for aggregation. This precursor is readily synthesised *via* the salt elimination reaction between [CpFe(CO)$_2$]$^-$ and Mes*GaCl$_2$, as discussed in detail in Chapter 3. Reaction between **3.1** and Na[BAr$^f_4$] in dichloromethane over a period of 30 min, however, gives the chloride-bridged dinuclear species [{CpFe(CO)$_2$Ga(Mes*)}$_2$(μ-Cl)]$^+$[BAr$^f_4$]$^-$, **5.26**, in a 24 % yield (Scheme 14). Complex **5.26** was always formed from the halide abstraction reaction of **3.1** with Na[BAr$^f_4$] in dichloromethane, irrespective of stoichiometry, timescale or order of reagent addition. Presumably, the mechanism of formation of bridged species **5.26** involves trapping the highly electrophilic first-formed intermediate species [CpFe(CO)$_2$Ga(Mes*)]$^+$, **5.27**, with a second equivalent of the chlorogallyl starting material, **3.1**.



(3.1)

(5.26)

Scheme 14

Monitoring of the reaction in CD_2Cl_2 (by ^1H NMR and IR) reveals quantitative conversion to **5.26** and a 2:1 ratio of the resonances associated with the Cp and $[BAr^f_4]^-$ groups. In addition, IR data shows the shifts in the carbonyl stretching frequencies to higher wavenumbers (2016, 2002, 1972, 1954 *vs.* 1999, 1952 cm^{-1} for **5.26** and **3.1**, respectively), as expected on halide abstraction. Multinuclear NMR, IR and mass spectral data for the isolated crystalline product are consistent with the proposed formulation. For example, resonances associated with the super-mesityl group are visible in the ^1H NMR spectrum at δ 1.25, 1.46 and 7.34 ppm, corresponding to the para ^tBu, ortho ^tBu and aryl CH of the Mes* group, respectively. Resonances associated with the Cp and $[BAr^f_4]^-$ groups are also observed in the ^1H NMR spectrum at δ 4.88, 7.55, 7.71 ppm, respectively. Mass spectrometry revealed the correct isotope distribution for 2 Fe, 2 Ga and 1 Cl atoms together with the $[M-2CO]^+$ ion and significant fragment ions corresponding to $[CpFe(CO)_2Ga(Mes^*)Cl]^+$ and $[CpFe(CO)_2Ga(Mes^*)]^+$. These spectroscopic inferences were subsequently confirmed crystallographically. Single yellow crystals suitable for X-ray diffraction were grown by the slow diffusion of hexane into a dichloromethane solution of **5.26**, the molecular structure of which is depicted in Figure 7.

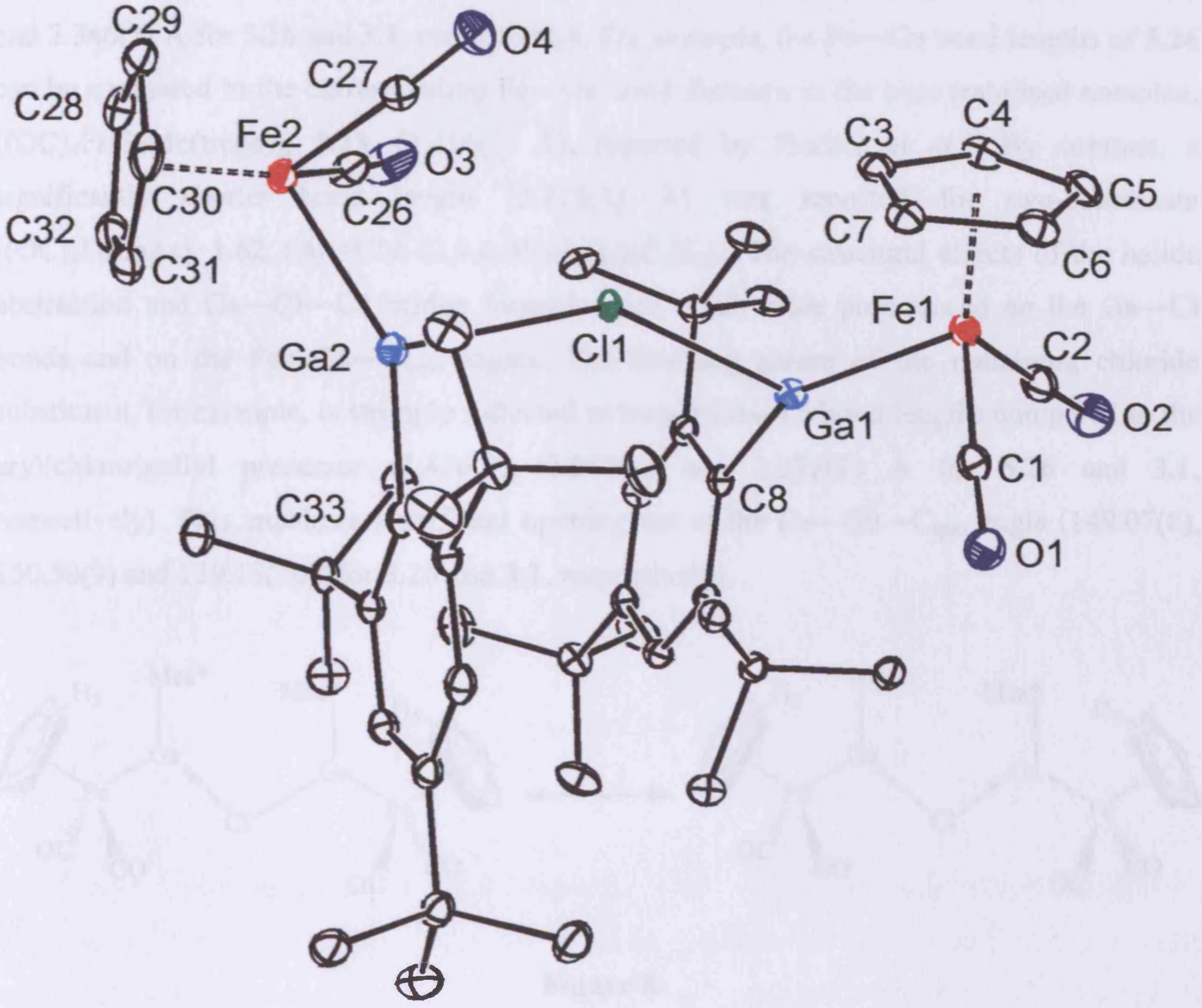


Figure 7: Structure of the cationic component of $[\{CpFe(CO)_2Ga(Mes^*)\}_2(\mu\text{-}Cl)]^+[BAr^f_4]^-$, **5.26**

Selected bond lengths (Å) and angles (°): Fe(1)—Ga(1) 2.333(1), Fe(2)—Ga(2) 2.328(1), Fe(1)—Cp* centroid 1.724(4), Fe(1)—C(1) 1.755(4), Ga(1)—Cl(1) 2.552(1), Ga(2)—Cl(1) 2.476(1), Fe(1)—Ga(1)—C(8) 149.07(8), Fe(2)—Ga(2)—C(33) 150.50(9), Ga(1)—Cl(1)—Ga(2) 142.16(3).

The structure of **5.26** can be regarded as a base-stabilized gallanediyl complex, in which the gallium-coordinated donor is the bridging chloride ligand (Figure 8). In common with other base-stabilised diyl complexes, the metal—group 13 distance is more similar to that expected for related single bonds, than that for unsaturated species (*e.g.* 2.333(1), 2.328(1) and 2.346(1) Å for **5.26** and **3.1**, respectively). For example, the Fe—Ga bond lengths of **5.26** can be compared to the corresponding Fe—Ga bond distance in the base stabilised complex, $[(OC)_4FeGaMe(tmpa)]$, **5.23**, (2.416(3) Å), reported by Fischer *et al.*[37] By contrast, a significantly shorter bond length (2.225(1) Å) was reported for two-coordinate $[(OC)_4FeGaAr]$, **1.62**, ($Ar = 2,6\text{-}(2,4,6\text{-}{}^iPr_3C_6H_2)_2C_6H_3$).[5] The structural effects of the halide abstraction and Ga—Cl—Ga bridge formation are much more pronounced on the Ga—Cl bonds and on the Fe—Ga—C_{ipso} angles. The bridging nature of the remaining chloride substituent, for example, is strongly reflected in longer Ga—Cl bond lengths compared to the aryl(chloro)gallyl precursor (2.476(1), 2.552(1) and 2.272(1) Å for **5.26** and **3.1**, respectively). This enables a significant opening out of the Fe—Ga—C_{ipso} angle (149.07(8), 150.50(9) and 139.18(10)° for **5.26** and **3.1**, respectively).

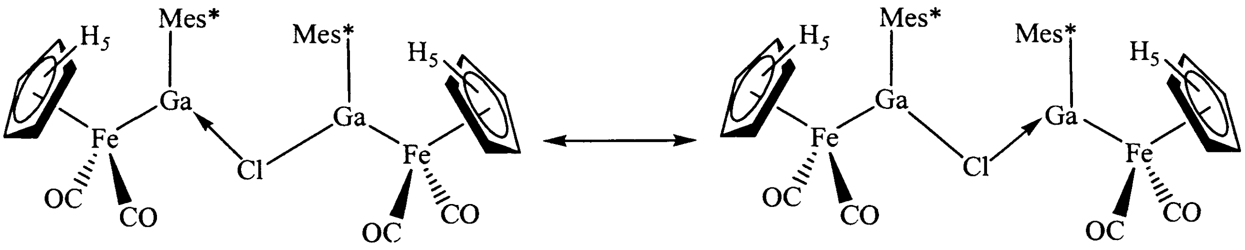
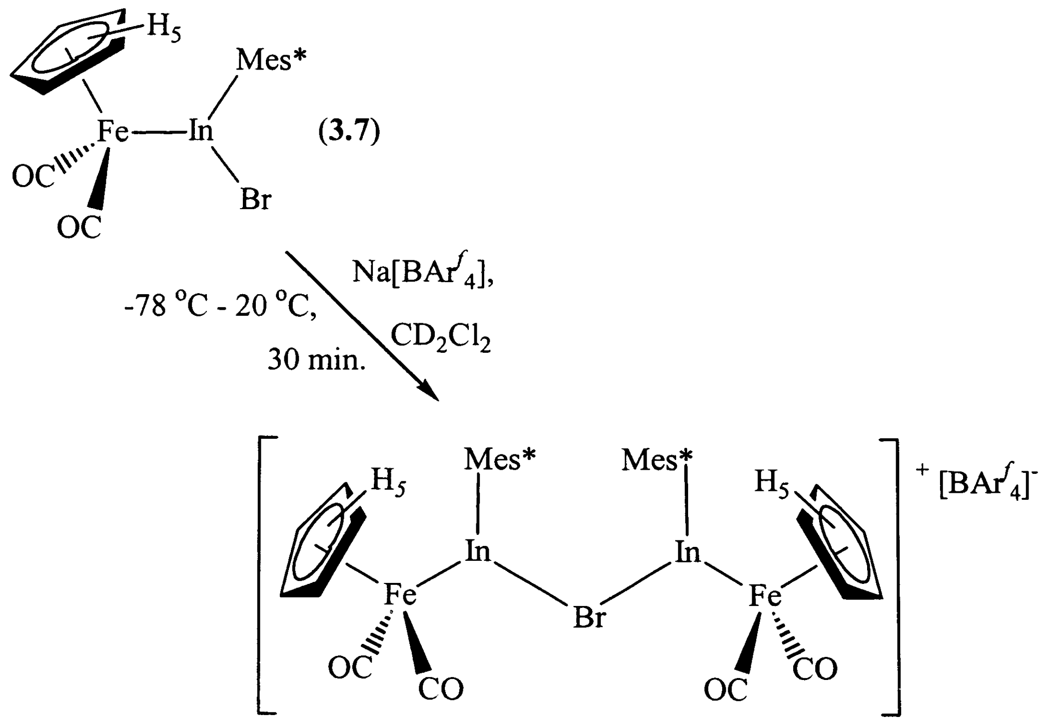


Figure 8

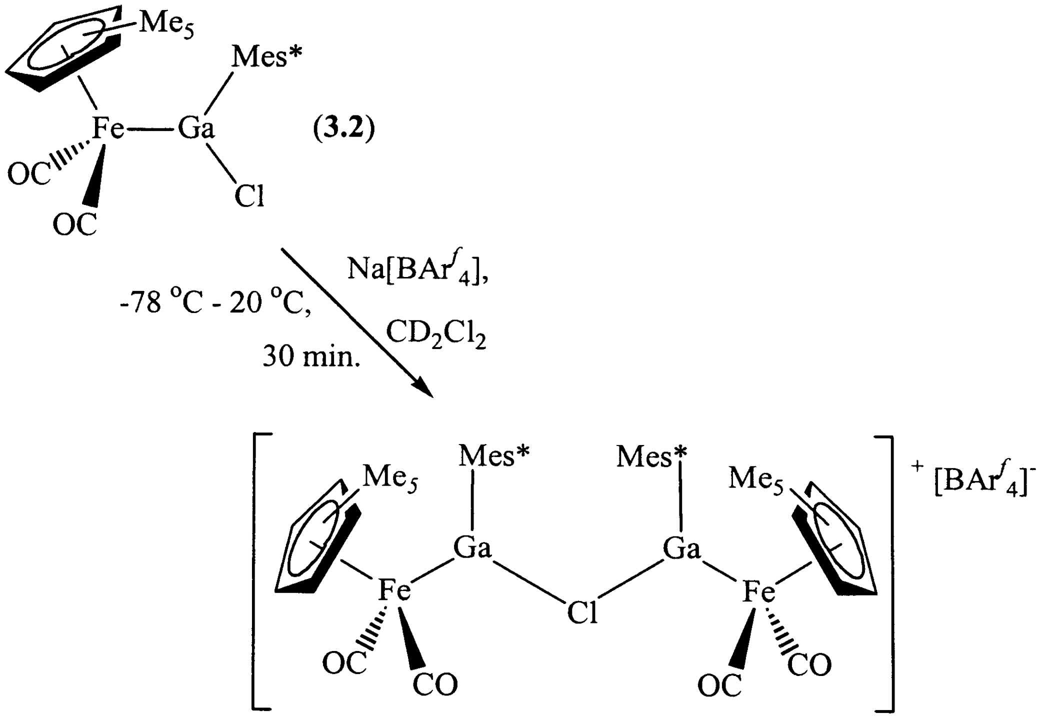
The corresponding halide abstraction reaction between bromoindyl complex, $[CpFe(CO)_2In(Mes^*)Br]$, **3.7**, and $Na[BAr^f_4]$ was also investigated (work carried out by Miss N. Coombs within our research group). By analogy with **3.1**, the reaction between precursor complex **3.7** and $Na[BAr^f_4]$ in dichloromethane yields the bromide bridged dinuclear species, $[\{CpFe(CO)_2In(Mes^*)\}_2(\mu\text{-}Br)]^+[BAr^f_4]^-$, **5.29**, in an isolated yield of 28 % (Scheme 15).



(5.29)

Scheme 15

Given the extremely facile trapping of the presumed diyl complexes $[CpFe(CO)_2E(Mes^*)]^+$ implied by the formation of **5.26** and **5.29**, a potential route to isolable mononuclear cationic systems may involve the use of more sterically hindered and/or more electron releasing substituents at the metal center. Therefore the reactivity of $[Cp^*Fe(CO)_2Ga(Mes^*)Cl]$, **3.2**, towards $Na[BAr^f_4]$ was investigated. However, in this case, the nature of the cationic species generated was strongly dependent upon reaction conditions. Reaction of precursor **3.2** with a single equivalent of $Na[BAr^f_4]$ in dichloromethane-d_2, on a NMR scale, resulted in the formation of the analogous dinuclear compound $[\{Cp^*Fe(CO)_2Ga(Mes^*)\}_2(\mu\text{-}Cl)]^+[BAr^f_4]^-$, **5.30**, (Scheme 16). Subsequent filtration and the slow diffusion of hexane into the reaction mixture led to the isolation of **5.30** as a pale orange powder.

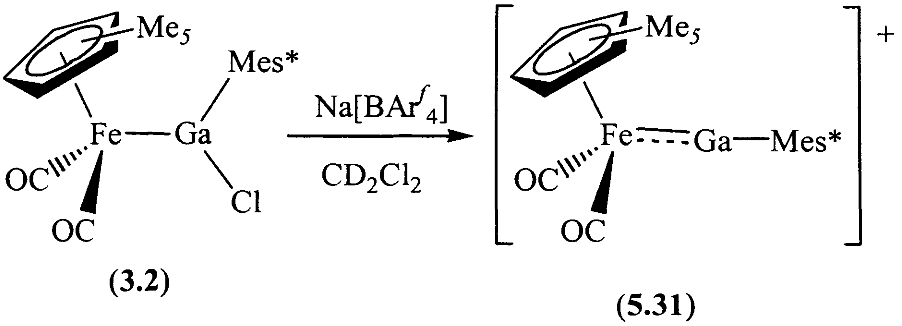


(5.30)

Scheme 16

Compound **5.30** has been characterized by multinuclear NMR, IR and mass spectrometry. All spectroscopic data are consistent to the proposed formulation. However, single crystals suitable for X-ray diffraction could not be grown. A 2:1 integrated ratio of the Cp* and $[\mathrm{BAr}^f_4]^-$ signals is observed in the ^{1}H NMR spectrum. A similar *pattern* of carbonyl stretching frequencies compared to **5.26** (1996, 1986, 1954, 1932 *vs*. 2016, 2002, 1972, 1954 cm^{-1} for **5.26** and **5.30**, respectively) is visible in the IR spectrum. Analysis of the mass spectra data reveals the presence of the $[\mathrm{M - CO}]^+$ ion together with the correct isotope distribution for 2 Fe, 2Ga and 1 Cl atoms. Together this spectroscopic data provides compelling evidence that the molecular structure of **5.30** is analogous to the chloride bridged structure of **5.26**.

The effect of reaction conditions and timescale on the nature of the cationic species formed from this reaction was investigated. The cation so generated is strongly dependent upon reaction conditions. This can be contrasted with the analogous Cp chemistry, being formed from the corresponding halide abstraction reaction irrespective of reaction stoichiometry, timescale or order of reagent addition. Reaction of the three-coordinate aryl(chloro)gallyl complex, [Cp*Fe(CO)$_2$Ga(Mes*)Cl], **3.2**, with a single equivalent of Na[BAr$^f{}_4$] on a NMR scale over a period of *ca.* 30 min yielded dinuclear **5.30**. However, upon repeating the reaction in more dilute solution, on a larger scale (0.125 mmol) and allowing a longer period reaction time (1 h), a complex identified spectroscopically as [Cp*Fe(CO)$_2$Ga(Mes*)]$^+$[BAr$^f{}_4$]$^-$, **5.31**, is generated (Scheme 17).



Scheme 17

Monitoring of the reaction in CD$_2$Cl$_2$ (by ^{1}H NMR and IR) shows quantitative conversion to a single Cp* containing species and shifts to significantly higher carbonyl stretching frequencies (2019, 1998 *vs.* 1983, 1933 cm^{-1} for **5.31** and **3.2**, respectively), as expected for the formation of a base free cationic two-coordinate group 13 system *via* chloride abstraction. Multinuclear NMR, IR and mass spectral data for the isolated crystalline product are consistent and with the proposed formulation and comparable to that of the corresponding terminal borylene complex, **1.85**. Although single crystals suitable for X-ray diffraction could not be grown, spectroscopic data provides compelling evidence for the structural identity of **5.31**.

5.6 Conclusion and Suggestions for Further Work

In conclusion, this chapter describes the use of halide abstraction chemistry as a viable synthetic route to cationic two-coordinate derivatives featuring the heavier group 13 elements gallium and indium as donor atoms. In particular, halide abstraction chemistry has been investigated for two classes of three-coordinate halo-gallium substrate systems, (i) asymmetric halogallyl systems of the type L_nM—Ga(Mes*)Cl and (ii) bridging halogallanediyl complexes $(L_nM)_2GaCl$. This has led to the preparation and structural characterisation of a number of cationic gallium-containing systems. Thus, the linear trimetallic species $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}E)]^+$ (**5.12** E = Ga; **5.15** E = In) featuring 'naked' bridging gallium or indium atoms can be synthesized by the reaction of the corresponding chloro- or bromo-substituted bridging diyl complexes with $Na[BAr^f]_4$. Analogous reactions utilising the super-mesityl substituted gallyl or indyl precursors of the type $[(\eta^5\text{-}C_5R_5)Fe(CO)_2E(Mes^*)X]$, on the other hand, typically lead to the synthesis of halide-bridged species of the type $[\{(\eta^5\text{-}C_5R_5)Fe(CO)_2E(Mes^*)\}_2(\mu\text{-}X)]^+$, presumably by trapping the highly electrophilic putative cationic diyl complex $[(\eta^5\text{-}C_5R_5)Fe(CO)_2E(Mes^*)]^+$. The success of this halide abstraction methodology in generating tractable cationic derivatives, is also strongly dependent on the nature of the precursor complex, the halide abstraction agent and on reaction conditions.

The nature of the M—E bond in such systems has been analysed by comparative spectroscopic, structural and computational studies as a function of the element E, thereby probing the controversial subject of multiple bonding involving the heavier group 13 elements. Compound **5.12** represents an extremely rare example of a structurally characterized species containing a two-coordinate cationic gallium center and the first containing transition metal—gallium bonds. This complex contains delocalised partial Fe—Ga multiple bond character. In contrast, the analogous indium-bridged complex **5.15**, features a much smaller π component to the metal-ligand interaction. Compound **5.31**, which represents a mononuclear cationic gallium system comparable to the previously reported cationic terminal borylene complex, **1.85**, has been characterised spectroscopically.

Preliminary studies have shown trimetallic systems **5.12** and **5.15** to be reactive towards neutral and anionic two-electron donors. However, the reversible coordination of THF is indicative of surprisingly weak Lewis acidic behaviour. In fact, it appears that the group 13 metal centres, of **5.12** and **5.15**, are less electrophilic in character than

$[Cp^*Fe(CO)_2B(Mes)]^+$, **1.85**.

This research work could be extended to modified systems, such as **3.1** and **3.2**, by the introduction of bulky, strongly σ-basic phosphine ligands at the group 8 metal centre, *via* photolysis, and investigate the subsequent halide abstraction chemistry. Phosphine ligated systems offer little competing back-bonding from the metal, therefore subsequent halide abstraction chemistry could potentially lead to greater M=E bond orders (E = Group 13 element).

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Appendix One
Computational Methodology

Details of the computational methodology used in this study are similar to those reported recently, and salient points are outlined here.[1]

Gradient corrected DFT calculations were carried out using the ADF2000.01 code,[2] with functionals for exchange and correlation due to Becke[3] and Lee, Yang and Parr,[4] respectively. A basis set constructed from Slater type orbitals at the triple zeta with polarization functions level was used for all calculations (ADF IV). The level of frozen core approximation for Ga, C, N, O and F was the 1s orbital and for P, Cl and Fe was the 2p orbital. All structures, unless otherwise stated, were fully optimised with no symmetry restrictions. Convergence was accepted when the following limits were met: (i) energy change on next step < $1\text{x}10^{-3}$ Ha; (ii) gradient < $1\text{x}10^{-3}$ Ha Å^{-1}; and (iii) uncertainty in cartesian coordinates < $1\text{x}10^{-2}$ Å. The multiplicity of each structure was determined by using unrestricted calculations with spin states set to reasonable alternatives to determine the lowest energy configuration which conformed to the aufbau principle.

To calculate the degree of σ and π-bonding between the metal centre and gallium atom the optimised structures were re-orientated so that the bond was aligned with the z-axis. A bonding analysis was then carried out following the approach discussed below to give contributions to the bonding density segregated according to the symmetry of the atomic orbitals involved.

The one electron wavefunctions, ψ_i, used to represent the density in these DFT calculations are constructed in the usual manner as a linear combination of atomic basis functions, ϕ:

$$\psi_i = \sum_k^M c_{ik}\phi_k \qquad (1)$$

where c_{ik} is the coefficient of the k^{th} basis function in the i^{th} molecular orbital and there are a total of M basis functions. The density, ρ, is then given by summation over the occupied orbitals of the one electron densities:

$$\rho = 2\sum_{i}^{N/2}\sum_{l}^{M} c_{il}\phi_l \sum_{k}^{M} c_{ik}\phi_k = 2\sum_{l}^{M}\sum_{k}^{M}\phi_l\phi_k \sum_{i}^{N/2} c_{il}c_{ik} \qquad (2)$$

Where N is the total number of electrons and we only consider the restricted spin paired situation for simplicity, extension to the spin unrestricted case is straightforward. The rearranged form of the density expression allows the calculation to be performed *via* the definition of two square matrices with the dimension M. The first is usually referred to as the density matrix, **P**, and its components depend only on the calculated coefficients:

$$P_{lk} = \sum_{i}^{N/2} c_{il}c_{ik} \qquad (3)$$

The second, the overlap matrix, **S**, depends on the basis set and the geometry of the molecule:

$$S_{lk} = \phi_l\phi_k \qquad (4)$$

The density can then be represented as a matrix multiplication:

$$\rho = 2\sum_{l}^{M}\sum_{k}^{M} S_{lk}P_{kl} \qquad (5)$$

Since the basis set consists of atom centred functions, **P** and **S** will contain some contributions which are wholly centred on a given atom and some which are due to the overlap of basis functions on pairs of atoms. The latter contribution is related to the bonding between atoms and the most straightforward way to address the character of bonding is to examine this portion in isolation. By identifying the basis functions centred on a pair of atoms, A and B say, we can identify the bonding density, ρ_{AB}, by summing only the relevant contributions in equation 5:

$$\rho_{AB} = 2\sum_{l\in A}\sum_{k\in B} S_{lk}P_{kl} \qquad (6)$$

This is the bonding density as defined by Mulliken.[5] To differentiate π and σ contributions to the bonding density we simply align the bond of interest with the *z*-direction and separate the basis functions according to their symmetry, *e.g.* p_z is of σ type and p_x and p_y are of π type. Equation 6 can then be further sub-divided:

$$\rho_{AB} = 2\sum_{l\in A}^{\sigma}\sum_{k\in B}^{\sigma} S_{lk}P_{kl} + 2\sum_{l\in A}^{\pi}\sum_{k\in B}^{\pi} S_{lk}P_{kl} + 2\sum_{l\in A}^{\delta}\sum_{k\in B}^{\delta} S_{lk}P_{kl} + \ldots\ldots\ldots \qquad (7)$$

where the symmetry labels on the summations indicate the basis function symmetry to be considered. We report the two terms in equation 7 separately to judge the degree of π bonding in MGa bonds.

This decomposition of the molecular orbital representation of the density to give bonding density is not unique and so to ensure the reliability of our analysis we also consider a bonding density analysis proposed by Mayer.[6] In the Mayer analysis the product of the density and overlap matrices is first calculated and then the elements of this product matrix are selected according to the basis functions belonging to the atoms of interest. Again we further partition the matrix in terms of π and σ symmetry:

$$\rho^{M}_{AB} = 2\sum_{l\in A}^{\sigma}\sum_{k\in B}^{\sigma} (\mathrm{PS})_{kl} + 2\sum_{l\in A}^{\pi}\sum_{k\in B}^{\pi} (\mathrm{PS})_{kl} \qquad (8)$$

As part of this work the application of equations (7) and (8) to the data provided by an ADF output was automated by the development of a dedicated program. The coding was tested by calculation of the Mulliken atomic densities which are output by ADF and by analysis of simple test cases such as ethane, ethene, ethyne *etc.* (these analyses are included in reference 1). The Mayer bond order calculation was tested by comparing values obtained from our analysis of ADF outputs and those generated at a similar basis set level by the MSI code, Dmol.[7] The results of decomposition into σ and π contributions from Mulliken and Mayer approaches consistently showed the same trends and so only the former is reported in the main text.

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Appendix Two

Publications in support of this thesis

- Natalie R. Bunn, Simon Aldridge, Deborah L. Coombs, Andrea Rossin, David J. Willock, Cameron Jones and Li-ling Ooi. Fe—Ga multiple bonding? Synthesis, spectroscopic and structural characterisation of a transition metal complex containing a cationic two-coordinate gallium centre. *Chem. Comm.*, 2004, 1732-1733.

- Additionally, the above paper was featured as a highlight in the German Chemical Society review of 2004. *Nachrichten aus der Chemie*, 2005, **53**, 226.

- Natalie R. Bunn, Simon Aldridge and Cameron Jones. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2Ga_3Cl_3(OSiMe_2OSiMe_2O)_2$: a diiron complex of a tetracyclic trigallasiloxane. *Appl. Organomet. Chem.*, 2004, **18**, 425-426.

- Natalie R. Bunn, Simon Aldridge, Deborah L. Kays (née Coombs), Natalie D. Coombs, Joanne K. Day, Li-ling Ooi, Simon J. Coles, and Michael B Hursthouse. Towards cationic gallane- and indanediyl complexes: synthetic approaches to three-coordinate halogallyl and -indyl precursors. *Organometallics*, 2005, **24**,5879-5890.

- Natalie R. Bunn, Simon Aldridge, Deborah L. Kays (née Coombs), Natalie D. Coombs, Joanne K. Day, Li-ling Ooi, Simon J. Coles, and Michael B Hursthouse. Halide abstraction as a route to cationic transition metal complexes containing two-coordinate gallium and indium ligand systems. *Organometallics*, 2005, **24**, 5891-5900.

- Simon Aldridge, Deborah L. Kays, Natalie R. Bunn, Natalie D. Coombs and Li-ling Ooi. Structures of the metallated trihalogallate and indate ions $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2InI_3]^-$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2GaI_2Br]^-$, *Main Group Metal Chem.*, in press.

APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2004; **18**: 425–426

Crystallographic report

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2Ga_3Cl_3(OSiMe_2OSiMe_2O)_2$: a diiron complex of a tetracyclic trigallasiloxane

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Received 30 March 2004; Revised 14 April 2004; Accepted 15 April 2004

The structure of the penta-metallic diiron trigallasiloxane, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2Ga_3Cl_3(OSiMe_2OSiMe_2O)_2$, reveals two distinct gallium coordination environments and Fe–Ga bond lengths (2.3258(6) Å), consistent with bonding of the iron centres to four-coordinate gallyl ligands. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: crystal structure; iron; gallium; gallyl; siloxane

COMMENT

The title complex (**I**) was isolated as a minor product from the recrystallization of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Ga(^sMes)Cl$ (Bunn NR, Aldridge S, unpublished results; $^sMes = 2, 4, 6\text{-}^tBu_3C_6H_3$) from toluene solution in the presence of adventitious silicone grease. The structure of the trigallasiloxane core (Fig. 1) is very similar to that found in the corresponding pentachloride species $Ga_3Cl_5(OSiMe_2OSiMe_2O)_2$,[1,2] with symmetry-equivalent fragments being related through a twofold rotation axis aligned along Ga(2)–Cl(2). The Fe–Ga bond lengths to the cis-orientated pendant $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ groups are within the range expected for bonding to four-coordinate gallium centres (2.29–2.44 Å), as determined from a survey of the Cambridge Crystallographic Database.

EXPERIMENTAL AND RESULTS

A solution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Ga(^sMes)Cl$ (0.52 mmol) in toluene (5 ml) was cooled to −30 °C over a period of 1 week. Reaction with adventitious grease yielded the title compound (**I**) as colourless blocks in low yield (four or five crystals). Intensity data for **I** were collected at 150 K on a Nonius Kappa CCD diffractometer for a colourless crystal 0.15 × 0.25 × 0.25 mm³. $C_{22}H_{34}Cl_3Fe_2Ga_3O_{10}Si_4$, $M = 998.06$, monoclinic, $C2/c$, $a = 16.338(3)$, $b = 13.349(3)$, $c = 17.854(4)$ Å, $\beta = 105.16(3)°$, $V = 3758.4(13)$ Å^3, $Z = 4$, 4224 unique data (θ_{max} 27.5°),

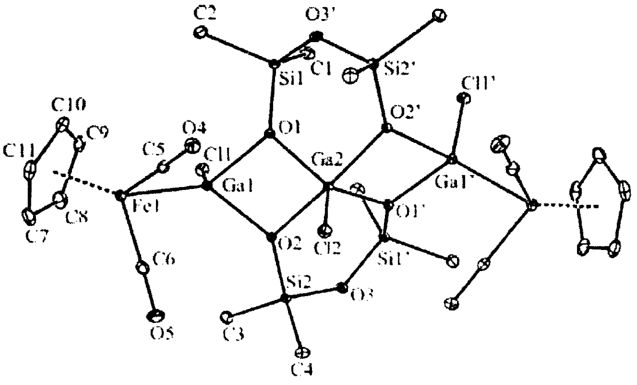

Figure 1. Molecular structure of **I**; hydrogen atoms omitted for clarity. Key geometric parameters: Ga1–Fe1 2.3258(6), Ga1–Cl1 2.2145(8), Ga1–O1 1.9760(18), Ga1–O2 1.9357(18), Ga2–Cl2 2.1828(11), Ga2–O1 1.9020(18), Ga2–O2 1.9851(18), Fe1–C5 1.756(3), Fe1–C6 1.751(3), Fe1–Cp centroid 1.718(3), Si1–O1 1.6764(19), Si1–O3′ 1.636(2), Si1–C1 1.846(3), Si1–C2 1.843(3), Si2–O2 1.6638(19), Si2–O3 1.646(2), Si2–C3 1.849(3), Si2–C4 1.846(3) Å; O1–Ga1–Cl1 103.15(6), O2–Ga1–Cl1 103.56(6), O1–Ga1–O2 79.68(8), Cl1–Ga1–Fe1 122.02(3), O1–Ga1–Fe1 118.48(6), O2–Ga1–Fe1 121.24(6), O1–Ga2–O2 80.26(8), O1–Ga2–O1′ 122.53(11), O1–Ga2–O2′ 94.20(8), O2–Ga2–O2′ 168.55(11), O1–Ga2–Cl2 118.74(6), O2–Ga2–Cl2 95.73(5), C5–Fe1–C6 95.46(14)°. Symmetry transformations used to generate primed atoms: $1 - x, y, 3/2 - z$.

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Contract/grant sponsor: EPSRC.

3625 data $I \geq 2\sigma(I)$, $R = 0.033$, $wR = 0.082$ (all data). Programs used: SHELXS-97, SHELXL-97, X-seed and ORTEP. CCDC deposition number: 234501.

Acknowledgements

We gratefully acknowledge financial support from the EPSRC.

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COMMUNICATION

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Fe–Ga multiple bonding? Synthesis, spectroscopic and structural characterization of a transition metal complex containing a cationic two-coordinate gallium centre†

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Received (in Cambridge, UK) 21st April 2004, Accepted 1st June 2004
First published as an Advance Article on the web 28th June 2004

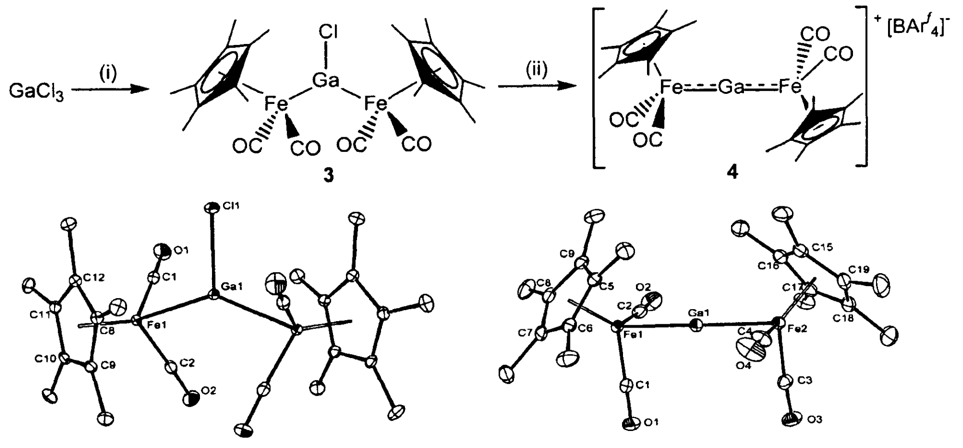
This communication reports the synthesis and characterization of the cationic iron complex $[\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}_2Ga]^+$-$[BAr^f{}_4]^-$ [Ar^f = $C_6H_3(CF_3)_2$-3,5] containing a symmetrically bridging two-coordinate gallium atom and a delocalised Fe–Ga–Fe π system incorporating partial Fe–Ga multiple bond character.

The chemistry of transition metal complexes featuring low coordinate Group 13 ligands continues to attract significant research interest,[1] in part with a view to better understanding the fundamental issues of structure and bonding. Thus, the nature of the interaction between the ligand and the metal centre in diyl systems [$L_nM(ER)$], such as $(OC)_4Fe(GaAr)$ [**1**, Ar = $C_6H_3(2,4,6\text{-}{}^iPr_3C_6H_2)_2$-2,6] has been the subject of considerable debate.[2] The description of superficially similar complexes as being bound *via* multiple bonds (*e.g.* $L_nM{=}ER$ or $L_nM{\equiv}ER$) or *via* donor–acceptor interactions (*e.g.* $L_nM{\leftarrow}ER$) reflects not only the fundamental questions of structure and bonding posed by such systems, but also the scarcity of structural data available.[1–3]

Although several recent theoretical studies have sought to characterize the metal–Group 13 element bond by quantifying its various components,[4] experimental validation has been impaired by the paucity of available synthetic routes. For the heavier Group 13 elements these are confined principally to salt elimination {as used for $[(\eta^5\text{-}C_5Me_5)Fe(dppe)]Ga[Fe(CO)_4]$, **2**},[2a,5] and to reactions of suitable alkyl or aryl precursors, $(RE)_n$, with transition metal complexes containing labile ligands (*e.g.* $Ni\{Ga[C(SiMe_3)_3]\}_4$[3a]). Recently we have demonstrated a new synthetic approach to two-coordinate diyl complexes, using halide abstraction to generate the Fe=B double bond in $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(BMes)]^+[BAr^f{}_4]$ [Ar^f = $C_6H_3(CF_3)_2$-3,5].[6] Given the continuing debate surrounding charge neutral diyl systems, we have sought to extend this methodology to *cationic* species offering the potential for M=E multiple bonding involving the heavier Group 13 elements. Herein we report the synthesis of $[\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}_2Ga]^+$ which features a naked symmetrically bridging gallium atom and a significant Fe–Ga π bonding component.

Reaction of gallium trichloride with two equivalents of $Na[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]$ leads to the formation of chlorogallylene complex **3** (Scheme 1).‡ Spectroscopic data are consistent with the proposed formulation,§ which was confirmed crystallographically.¶ The steric bulk of the $(\eta^5\text{-}C_5Me_5)Fe(CO)_2$ fragment appears to have a strong influence on structural and reaction chemistry. Hence, in contrast to the corresponding $(\eta^5\text{-}C_5H_5)$ derivative, **3** is monomeric in the solid state [Σ(angles at Ga) = 360.00(3)°],‖ shows no hint of oligomerization *via* Ga–Cl–Ga bridges, and can be crystallised from thf without coordination at gallium.[7] **3** therefore represents a suitable precursor for the formation of a two-coordinate cationic gallium centre by halide abstraction.

Monitoring of the reaction of **3** with a single equivalent of $Na[BAr^f{}_4]$ in CD_2Cl_2 (by ^1H NMR) reveals quantitative conversion to a single η^5-C_5Me_5 containing species;‡ the significantly higher carbonyl stretching frequencies (2016, 1994, 1963 *vs.* 1960, 1925, 1910 cm^{-1}) are consistent with the development of a net positive charge implied by chloride abstraction.[6] Multinuclear NMR, IR and mass spectral data for the isolated crystalline product are consistent with $[\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}_2Ga]^+$ and $[BAr^f{}_4]$ ions,§ and these spectroscopic inferences were subsequently confirmed crystallo-



Scheme 1 Syntheses of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2GaCl$ (**3**) and $[\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}_2Ga]$ $[BAr^f{}_4]$ (**4**). Reagents and conditions: (i) $Na[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]$ 2 equiv., toluene, 20 °C, 12 h; (ii) $Na[BAr^f{}_4]$ 1 equiv., dichloromethane, −78 °C to 20 °C, 30 min. Relevant bond lengths (Å), angles (°) and torsion angles (°): for **3** Fe(1)–Ga(1) 2.3524(4), Fe(1)–C(1) 1.760(3), Fe(1)–centroid 1.725(3), Ga(1)–Cl(1) 2.283(1), Fe(1)–Ga(1)–Fe(1′) 138.90(3), Fe(1)–Ga(1)–Cl(1) 110.55(1); for the cationic component of **4** Fe(1)–Ga(1) 2.272(1), Fe(2)–Ga(1) 2.266(1), Fe(1)–C(1) 1.764(3), Fe(1)–centroid 1.728(3), Fe(1)–Ga(1)–Fe(2) 178.99(2), centroid-Fe(1)–Fe(2)-centroid 84.62(3).

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† Electronic supplementary information (ESI) available: *xyz* file corresponding to the fully optimised geometry of $[\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}_2Ga]^+$ and full details of the crystal structures of 3 and 4. See http://www.rsc.org/suppdata/cc/b4/b405943c/

DOI: 10.1039/b405943c

graphically.¶ Thus halide abstraction from **3** proceeds cleanly as outlined in Scheme 1, leading to the generation of the cationic dinuclear complex $[\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}_2Ga][BAr^f_4]$ (**4**). To our knowledge **4** represents the second structurally characterized example of a two-coordinate cationic gallium centre, and the first featuring bonds to a transition metal.[8]

A number of structural features are worthy of further comment. (i) The linear Fe–Ga–Fe unit [∠ Fe(1)–Ga(1)–Fe(1′) = 178.99(2)°] is consistent with a two-coordinate gallium centre engaging in no significant secondary interactions (*e.g.* with the anion).[8] This geometry is consistent with that found in the only other complex containing a 'naked' bridging gallium atom (*i.e.* **2**) and contrasts with the bent geometry found in base-stabilized analogues.[5,9–11] (ii) The Fe–Ga bond lengths [2.266(1) and 2.272(1) Å] are significantly shorter than those found in **3** [2.3524(4) Å] and in compounds conventionally thought of a possessing Fe–Ga single bonds (2.36–2.46 Å).[1a] Furthermore, they are similar to that found in the $[(\eta^5\text{-}C_5Me_5)Fe(dppe)]Ga$ unit of **2** [2.248(1) Å], which possesses unsaturated character as a result of significant π back-bonding from the electron-rich $(\eta^5\text{-}C_5Me_5)Fe(dppe)$ fragment.[5] (iii) The centroid–Fe(1)–Fe(2)–centroid torsion angle [84.62(3)°] implies a relative alignment of the $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]$ fragments which allows for optimal Fe→Ga π back-bonding. For related carbene complexes, most effective back-bonding involves the HOMO of the $[(\eta^5\text{-}C_5R_5)Fe(CO)_2]^+$ fragment (an a″ symmetry orbital roughly co-planar with the cyclopentadienyl ligand).[12] In the case of **4**, optimal stabilization of the mutually perpendicular pair of formally vacant Ga p orbitals would therefore be achieved by orthogonal alignment of the HOMOs of the two $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]$ fragments and consequently by a torsion angle of *ca.* 90°.

In order to provide a fuller basis for discussion of the bonding in **4**, DFT analysis was carried out at the BLYP/TZP level using established methods.[13] The fully optimised geometry [*d*(Fe–Ga) = 2.338, 2.337 Å; ∠(Fe–Ga–Fe) = 177.9°, ∠(Ct–Fe–Fe–Ct) = 86.5°] is consistent with that determined crystallographically. A *bond population analysis* was carried out to quantify the relative importance of σ and π components to the Fe–Ga covalent interaction using a method previously applied to the borylene cation $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(BMes)]^+$ and to boryl complexes of the type $(\eta^5\text{-}C_5R_5)Fe(CO)_2(BX_2)$.[6,13] This reveals a 61 : 38 σ : π breakdown of the covalent Fe–Ga interaction {*c.f.* 86 : 14 for the Fe–Ga single bond in the model compound $(\eta^5\text{-}C_5H_5)Fe(CO)_2GaCl_2$, and a 62 : 38 breakdown for $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(BMes)]^+$}.[6,13b] Further evidence for a significant Fe–Ga π component is provided by analysis of the atomic orbital contributions to the MOs HOMO-3 to HOMO-6, each of which features in-phase contributions from gallium- and iron-centred π symmetry orbitals (Ga $4p_x$ and $4p_y$ and Fe $3d_{xz}$ and $3d_{yz}$).

We thank the EPSRC for funding and for access to the National Mass Spectrometry Centre, Swansea. Calculations were carried out using the Cardiff University Helix facility.

Notes and references

‡ *Syntheses of* $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2GaCl$ (**3**) *and* $[\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}_2Ga][BAr^f_4]$ (**4**). Reaction of $GaCl_3$ (0.163 g, 0.93 mmol) with a suspension of $Na[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]$ (0.500 g, 1.85 mmol) in toluene (30 cm^3) at 20 °C for 12 h, followed by filtration, concentration to *ca.* 10 cm^3 and cooling to −50 °C yielded **3** as a bright yellow microcrystalline material (0.200 g, 36%). X-ray quality crystals were grown by layering a solution in thf with hexanes, and cooling to −50 °C for 1 week. Treatment of **3** (0.045 g, 0.075 mmol) with 1 equiv. of $Na[BAr^f_4]$ in CH_2Cl_2 (20 ml) at −78 °C, followed by warming to 20 °C over 30 min., filtration and removal of volatiles *in vacuo* yielded **4** as a golden yellow powder (0.050 g, 46%). X-ray quality crystals were grown by layering a CH_2Cl_2 solution with hexanes.

§ *Spectroscopic data for* **3** *and* **4**. **3**: ^1H NMR (300 MHz, C_6D_6): δ 1.68 (s, 30H, $\eta^5\text{-}C_5Me_5$); (300 MHz, CD_2Cl_2): δ 1.85 (s, 30H, $\eta^5\text{-}C_5Me_5$). ^{13}C NMR (76 MHz, C_6D_6): δ 9.7 (Me of $\eta^5\text{-}C_5Me_5$), 94.4 ($\eta^5\text{-}C_5Me_5$ quaternary), 217.2 (CO). IR (cm^{-1}): ν(CO) (KBr disc) 1955 st, 1932 st, 1919 m sh; (CH_2Cl_2 solution) 1960 st, 1925 st, 1910 m sh. EI-MS: *m/z* 598 (M^+, 5%), correct isotope distribution for 2 Fe, 1 Ga and 1 Cl atoms, significant fragment ions at *m/z* 570 ($[M - CO]^+$, 35 %), 542 ($[M - 2CO]^+$, 25%). Exact mass (M^+): calc. 597.9782, meas. 597.9780. **4**: ^1H NMR (300 MHz, CD_2Cl_2): δ 1.93 (s, 30H, $\eta^5\text{-}C_5Me_5$), 7.54 (s, 4H, *p*-H of $BAr^f_4{}^-$), 7.70 (s, 8H, *o*-H of $BAr^f_4{}^-$). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 10.3 (Me of $\eta^5\text{-}C_5Me_5$), 97.5 ($\eta^5\text{-}C_5Me_5$ quaternary), 117.5 (*p*-CH of $BAr^f_4{}^-$), 122.8 (q, $^1J_{CF}$ = 273 Hz, CF_3 of $BAr^f_4{}^-$), 128.8 (q, $^2J_{CF}$ = 34 Hz, *m*-C of $BAr^f_4{}^-$), 134.8 (*o*-CH of $BAr^f_4{}^-$), 160.8 (q, $^1J_{CB}$ = 53 Hz, *ipso*-C of $BAr^f_4{}^-$), 211.4 (CO). ^{19}F NMR (283 MHz, CD_2Cl_2): δ −62.8 (CF_3). ^{11}B NMR (96 MHz, CD_2Cl_2): δ −7.6 ($BAr^f_4{}^-$). IR (cm^{-1}): ν(CO) (CH_2Cl_2 solution) 2016 m, 1994 st, 1963 st. ES-MS (neg.): *m/z* 863 ($BAr^f_4{}^-$); ES-MS (pos.): *m/z* 563 (M^+, 5%), correct isotope distribution for 2 Fe and 1 Ga atoms. Exact mass (M^+): calc. 563.0093, meas. 563.0092.

¶ *Crystallographic data for* **3** *and* **4**. $C_{24}H_{30}ClFe_2GaO_4$, **3**: orthorhombic, *Pcnb*, a = 11.1946(2), b = 12.9307(3), c = 16.9269(4) Å, U = 2450.24(9) Å^3, Z = 4, d_c = 1.625 Mg m^{-3}, M_r = 599.34, T = 150(2) K. 29314 reflections collected, 3574 independent [R(int) = 0.1124] which were used in all calculations. R_1 = 0.0486, wR_2 = 0.0981 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and R_1 = 0.0678, wR_2 = 0.1050 for all unique reflections. Max. and min. residual electron densities: 1.310 and −0.761 e Å^{-3}, respectively. $C_{56}H_{42}BF_{24}Fe_2GaO_4$, **4**: triclinic, $P\bar{1}$, a = 14.442(3), b = 15.004(3), c = 15.541(3) Å, α = 66.25(3), β = 71.75(3), γ = 75.17(3)°, U = 2894.5(10) Å^3, Z = 2, d_c = 1.637 Mg m^{-3}, M_r = 1427.13, T = 150(2) K. 43319 reflections collected, 13120 independent [R(int) = 0.0770] which were used in all calculations. R_1 = 0.0443, wR_2 = 0.1038 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and R_1 = 0.0599, wR_2 = 0.1119 for all unique reflections. Max. and min. residual electron densities: 1.069 and −0.699 e Å^{-3}, respectively. CCDC 237193 and 237194. See http://www.rsc.org/suppdata/cc/b4/b405943c/ for crystallographic data in .cif or other electronic format.

‖ Bridging gallylene (gallanediyl) complexes featuring three-coordinate gallium centres have previously been reported only in association with very bulky gallylene substituents.[14]

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Organometallics **2005,** *24,* 5879–5890

Toward Cationic Gallane- and Indanediyl Complexes: Synthetic Approaches to Three-Coordinate Halogallyl and -indyl Precursors

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Received July 26, 2005

Transition metal complexes containing ligands featuring three-coordinate, halide-functionalized gallium or indium donors represent key precursors to unsaturated cationic species of the type $[L_nM(EX)]^+$ via halide abstraction chemistry. Two routes to these three-coordinate systems have been demonstrated: (i) salt elimination, such as the reaction between $Na[Cp^*Fe(CO)_2]$ and Mes^*GaCl_2 or Mes^*InBr_2 ($Mes^* = C_6H_2{}^tBu_3$-2,4,6, supermesityl) to generate $Cp^*Fe(CO)_2E(Mes^*)X$ (**3a**, E = Ga, X = Cl; **5**, E = In, X = Br), and (ii) insertion of a gallium(I) or indium(I) halide into a metal–halogen or metal–metal bond followed, where necessary, by substitution by a sterically bulky anionic nucleophile. Crystallographic studies have confirmed the presence of the target trigonal planar ligand systems both in gallyl/indyl complexes of the type L_nM-E(Aryl)X and in halide-functionalized gallane- and indanediyl systems of the type $(L_nM)_2EX$.

Introduction

The chemistry of low-coordinate or multiply bonded group 13 ligand systems continues to attract considerable research effort,[1–3] due, at least in part, to a desire to resolve fundamental questions of structure and bonding.[4,5] Despite this, a systematic appraisal of both structural and reaction chemistry, e.g., for terminal diyl systems, $L_nM(EX)$ (E = B, Al, Ga, In), lags behind that of analogous group 14 systems (such as carbenes and silylenes),[6] reflecting the relatively small number of authenticated complexes in the literature. To date, such species have predominantly been derived from either salt elimination or ligand substitution chemistries (Scheme 1).[1–3]

Scheme 1. Ligand Substitution and Salt Elimination Routes to Group 13 Diyl Complexes [E = group 13 element; R = bulky substituent (e.g., amino or aryl group); X = halide; L, L′ = generic ligands coordinated to transition metal M]

$$1/n\,(RE)_n + L_nML' \xrightarrow{-L'} L_nM(ER) \xleftarrow{-2\,X^-} REX_2 + [L_nM]^{2-}$$

Recently we have been successful in developing a halide abstraction methodology for the synthesis of the first base-free *cationic* group 13 diyl systems (Scheme 2).[7,8] The predominant localization of the positive charge at the group 13 center (E) in such complexes has been demonstrated by density functional theory (DFT) and in the case of $[Cp^*Fe(CO)_2(BMes)]^+$ (**1**, Mes = mesityl, 2,4,6-$Me_3C_6H_2$), for example, leads to an appreciable M→E π back-bonding component.[7] Thus a bonding description as an Fe=B double bond, comprised of B→Fe σ and Fe→B π contributions has been proposed.[7]

We have been seeking to expand this abstraction methodology to the heavier group 13 elements,[9] with a

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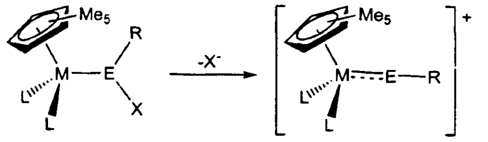
10.1021/om050630f CCC: $30.25
Publication on Web 10/26/2005

Scheme 2. Halide Abstraction Route to Cationic Transition Metal Complexes Containing Two-Coordinate Group 13 Ligands (E = group 13 element; R = bulky substituent; X = halide; L = generic ligand coordinated to transition metal M)



view to exploring the structural and reaction chemistry of cationic diyl complexes featuring, for example, gallium and indium donors. Central to this approach is ready access to a range of halo-substituted precursors featuring *three-coordinate* gallium or indium centers (Scheme 3). Given the propensity of halogallium and -indium systems in general to augment the coordination number at the group 13 center through bridging halide ligands,[10] it is not surprising that, to date, there have been almost no literature reports of neutral three-coordinate systems of the type L$_n$M-E(X)(E′R′$_x$) (E = Ga, In; X = halide).[9,11,12] From a synthetic standpoint, sterically bulky metal (L$_n$M) and/or gallyl/indyl substituents (E′R′$_x$) are therefore likely to be key factors in enforcing a trigonal planar ligand geometry.[13]

During the course of this study two parallel approaches to these key halogallyl and -indyl precursors have been examined: (i) direct substitution of a gallium- or indium-bound halide by an organometallic anion[11] and (ii) a two-step process involving initial insertion of a gallium(I) or indium(I) halide into a metal−halogen (or metal−metal) bond,[2a,14,15] followed by substitution at the group 13 center by an appropriately bulky anionic nucleophile. On paper at least, the latter route offers much greater versatility in the nature of the metal fragment (L$_n$M) by employing a metal halide (or M−M bonded dimer) rather than an organometallic anion as the metal-containing precursor. However, given the likely importance of sterically bulky gallyl/indyl substituents (E′R′$_x$), a significant synthetic challenge lies in the second (substitution) step; previous reports of substitution chemistry at existing group 13 ligand systems (e.g., boryls, gallyls etc.) that proceed with retention of the M−E bond are very rare.[7c,8b]

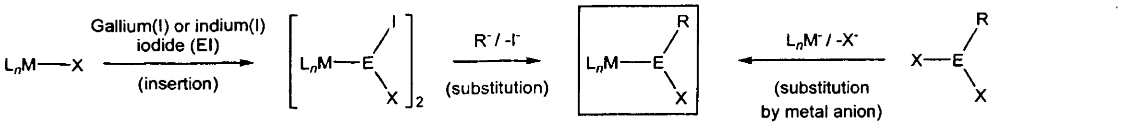
Experimental Section

(i) General Considerations. All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk line or drybox techniques. Solvents were predried over sodium wire (hexanes, toluene, thf) or molecular sieves (dichloromethane) and purged with nitrogen prior to distillation from the appropriate drying agent (hexanes: potassium, toluene; thf: sodium; dichloromethane: CaH$_2$). Benzene-d_6 and dichloromethane-d_2 (both Goss) were degassed and dried over the appropriate drying agent (potassium or molecular sieves) prior to use. InI, InCl, InBr$_3$, and GaCl$_3$ were used as received without further purification; Li[Mes*] (Mes* = C$_6$H$_2$^{t}Bu$_3$-2,4,6, supermesityl), Li[tmp] (tmp = N$\overline{\text{CMe}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}}Me_2$ tetramethylpiperamide), Mes*GaCl$_2$, Mes*InBr$_2$, GaI, CpFe(CO)$_2$X (X = Br, I), [Cp*Fe(CO)$_2$]$_2$, and Na[(η^5-C$_5$R$_5$)Fe(CO)$_2$] (R = H, Me) were prepared by literature methods.[14a,16−20]

NMR spectra were measured on a Bruker AM-400 or JEOL 300 Eclipse Plus FT-NMR spectrometer. Residual signals of solvent were used for reference for ^{1}H and ^{13}C NMR spectroscopy. Infrared spectra were measured for each compound either pressed into a disk with excess dry KBr or as a solution in the appropriate solvent, on a Nicolet 500 FT-IR spectrometer. Mass spectra were measured by the EPSRC National Mass Spectrometry Service Centre, University of Wales Swansea. Perfluorotributylamine was used as the standard for high-resolution EI mass spectra. Despite repeated attempts, satisfactory elementary microanalysis for new gallium and indium complexes was often frustrated by their extreme air, moisture, and (in some cases) thermal instability. With the exceptions of compounds **6a**, **6b**, **8**, **11**, and **12** (for which satisfactory analyses could be obtained), characterization of the new compounds is therefore based upon multinuclear NMR, IR, and mass spectrometry data (including accurate mass measurement), supplemented by single-crystal X-ray diffraction studies in the cases of **2**, **3a**, and **5**−**16**. In all cases the purity of the bulk material was established by multinuclear NMR to be >95% (see Supporting Information). Abbreviations: b = broad, s = singlet, d = doublet, t = triplet, m = multiplet.

(ii) Syntheses. (η^5-C$_5$R$_5$)Fe(CO)$_2$Ga(Mes*)Cl (2: R = H; 3a: R = Me). The two compounds were prepared using an identical method, exemplified for **2**. To a solution of Na[CpFe(CO)$_2$] (0.052 g, 0.26 mmol) in diethyl ether (10 mL) was added a solution of Mes*GaCl$_2$ (0.100 g, 0.26 mmol) in diethyl ether (10 mL), and the reaction mixture was stirred at 20 °C for 12 h. Filtration, concentration of the reaction mixture, and cooling to −50 °C yielded pale yellow crystals suitable for X-ray diffraction. Yields: 0.040 g, 29% (for **2**); 0.100 g, 30% (for **3a**). Characterizing data for **2**: ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 1.25 (s, 9H, para ^{t}Bu), 1.52 (s, 18H, ortho ^{t}Bu), 4.75 (b s, 5H, Cp), 7.34 (s, 2H, aryl CH). ^{13}C NMR (76 MHz, CD$_2$Cl$_2$): δ 31.0 (CH$_3$ of para ^{t}Bu), 34.0 (CH$_3$ of ortho ^{t}Bu), 34.7 (quaternary of para ^{t}Bu), 38.3 (quaternary of ortho ^{t}Bu), 82.8 (Cp), 119.5 (aryl CH), 142.1 (aryl ipso), 150.1 (aryl para), 154.8 (aryl ortho), 214.6 (CO). IR (KBr): ν(CO) 2004, 1948 cm^{-1}; (C$_6$D$_6$) ν(CO) 1996, 1951; (CD$_2$Cl$_2$) ν(CO) 1999, 1952. MS (EI): *m/z* 526.1 (weak) [M]$^+$, correct isotope distribution for 1 Fe, 1 Ga, and 1 Cl atom, significant fragment ion peaks at *m/z* 498.1 (5%) [M − CO]$^+$, 470.1 (8%) [M − 2CO]$^+$; exact mass calc for [M]$^+$ 526.0847, found 526.0845. Characterizing data for **3a**: ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 1.27 (s, 9H, para ^{t}Bu), 1.53 (s, 18H, ortho ^{t}Bu), 1.74 (s, 15H, CH$_3$ of Cp*), 7.33 (s, 2H, aryl CH). ^{13}C NMR (76 MHz, CD$_2$Cl$_2$): δ 10.0 (CH$_3$ of Cp*), 31.0 (CH$_3$ of para ^{t}Bu), 33.9 (CH$_3$ of ortho ^{t}Bu), 34.7 (quaternary of para ^{t}Bu), 38.6 (quaternary of ortho ^{t}Bu), 94.1 (quaternary of Cp*), 122.6 (aryl CH), 151.0 (aryl para), 154.7 (aryl ortho), 212.9 (CO), ipso carbon of Mes* not observed. IR (KBr): ν(CO) 1983, 1931 cm^{-1}. MS (EI): *m/z* 596.1 (3%) [M]$^+$, correct isotope distribution for

Scheme 3. Insertion/Substitution and Direct Metal Anion Substitution Routes to Key Halogallyl and -indyl Precursors (E = group 13 element; R = bulky substituent; X = halide; L generic ligand coordinated to transition metal M)



1 Fe, 1 Ga, and 1 Cl atom, significant fragment ion peaks at *m/z* 568.1 (22%) $[M - CO]^+$, 540.1 (40%) $[M - 2CO]^+$; exact mass calc for $[M]^+$ 596.1630, found 596.1634.

Cp*Fe(CO)$_2$Ga(Mes*)I, 3b. To a solution of $[Cp^*Fe(CO)_2GaI_2]_2$ (**12**, 0.100 g, 0.088 mmol) in diethyl ether (20 mL) was added dropwise a solution of Mes*Li (0.044 g, 0.17 mmol) in diethyl ether (15 mL), and the resulting mixture stirred at 20 °C for 12 h. The reaction mixture was filtered and concentrated; hexane (30 mL) was then added and the solution cooled to −30 °C for 12 h to yield **3b** as a pale yellow powder. Yield: 0.040 g, 33%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.24 (s, 9H, para ^{t}Bu), 1.78 (s, 18H, ortho ^{t}Bu), 1.89 (s, 15H, CH_3 of Cp*), 7.10 (s, 2H, aryl CH). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 9.4 (CH_3 of Cp*), 25.0 (CH_3 of para ^{t}Bu), 31.4 (CH_3 of ortho ^{t}Bu), 34.7 (quaternary of para ^{t}Bu), 37.9 (quaternary of ortho ^{t}Bu), 95.2 (quaternary of Cp*), 119.5 (aryl CH), 150.1 (aryl para), 155.6 (aryl ortho), 211.8 (CO), ipso carbon of Mes* not observed. IR (CD_2Cl_2): ν(CO) 1982, 1932 cm^{-1}. MS (EI): *m/z* 688.1 (weak) $[M]^+$, correct isotope distribution for 1 Fe, 1 Ga, and 1 I atom, significant fragment ion peaks at *m/z* 660.1 (weak) $[M - CO]^+$, 632.1 (10%) $[M - 2CO]^+$; exact mass calc for $[M]^+$ 688.0986, found 688.0999; calc for $[M - CO]^+$ 660.1037, found 660.1043.

(η^5-C$_5$R$_5$)Fe(CO)$_2$In(Mes*)Br (4: R = H; 5: R = Me). The two compounds were prepared using an identical method, exemplified for **4**. To a solution of $Na[CpFe(CO)_2]$ (0.183 g, 0.90 mmol) in diethyl ether (5 mL) was added a solution of Mes*InBr$_2$ (0.499 g, 0.96 mmol) in diethyl ether (10 mL), yielding a dark yellow solution and pale white precipitate. The reaction mixture was stirred at 20 °C for 16 h, then filtered to yield a dark yellow solution. Volatiles were then removed in vacuo, yielding a dark yellow solid. The solid was washed with hexane (3 × 10 mL) and dried in vacuo, yielding a yellow powder. Crystalline samples could be obtained by slow diffusion of hexanes into a solution in toluene at −30 °C. Yields: 0.135 g, 22% (for **4**); 0.124 g, 25% (for **5**). Characterizing data for **4**: ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.25 (s, 9H, para ^{t}Bu), 1.50 (s, 18H, ortho ^{t}Bu), 4.89 (s, 5H, Cp), 7.34 (s, 2H, aryl CH). ^{13}C NMR (76 MHz, CD_2Cl_2): 31.1 (CH_3 of para ^{t}Bu), 33.5 (CH_3 of ortho ^{t}Bu), 34.8 (quaternary of para ^{t}Bu), 37.9 (quaternary of ortho ^{t}Bu), 82.7 (Cp), 122.0 (aryl CH), 150.3 (aryl para), 155.4 (aryl ortho), 213.9 (CO), ipso carbon of Mes* not observed. IR (CD_2Cl_2): ν(CO) 1996, 1945 cm^{-1}. MS (EI): *m/z* 616.1 (weak) $[M]^+$, correct isotope distribution for 1 Fe, 1 In, and 1 Br atom, significant fragment ions at *m/z* 588.1 (7%) $[M - CO]^+$, 560.1 (5%) $[M - 2CO]^+$, 537.1 (6%) $[M - Br]^+$; exact mass calc for $[M - CO]^+$ 588.0176, found 588.0163. Characterizing data for **5**: ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.26 (s, 9H, para ^{t}Bu), 1.48 (s, 18H, ortho ^{t}Bu), 1.87 (s, 15H, CH_3 of Cp*), 7.28 (s, 2H, aryl CH). ^{13}C NMR (76 MHz, CD_2Cl_2): 9.6 (CH_3 of Cp*), 30.3 (CH_3 of para ^{t}Bu), 32.8 (CH_3 of ortho ^{t}Bu), 33.9 (quaternary of para ^{t}Bu), 37.3 (quaternary of ortho ^{t}Bu), 94.3 (quaternary of Cp*), 121.2 (aryl CH), 150.7 (aryl para), 154.9 (aryl ortho), 215.4 (CO), ipso carbon of Mes* not observed. IR (CD_2Cl_2): ν(CO) 1977, 1928 cm^{-1}. MS (EI): *m/z* 686.1 (weak) $[M]^+$, correct isotope distribution for 1 Fe, 1 In, and 1 Br atom, significant fragment ions at *m/z* 658.1 (4%) $[M - CO]^+$, 630.1 (7%) $[M - 2CO]^+$, 607.2 (9%) $[M - Br]^+$; exact mass calc for $[M]^+$ 686.0907, found 686.0889.

[Cp*Fe(CO)$_2$]$_2$GaCl, 6a. To a solution/suspension of $Na[Cp^*Fe(CO)_2]$ (0.500 g, 1.85 mmol) in diethyl ether (30 mL) was added a solution of $GaCl_3$ (0.163 g, 0.93 mmol) in diethyl ether (20 mL), and the reaction mixture stirred at 20 °C for 12 h, during which time **6a** precipitated out of solution as a yellow powder. Filtration and recrystallization from dichloromethane/hexane at −30 °C led to the isolation of microcrystalline **6a** (yield: 0.320 g, 58%). A lower yield is obtained if toluene is used as the reaction solvent, rather than diethyl ether (0.200 g, 36%). X-ray quality crystals could be grown by slow diffusion of hexanes into a solution in thf at −50 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 1.68 (s, 30H, Cp*); (CD_2Cl_2): δ 1.85 (s, 30H, Cp*). ^{13}C NMR (76 MHz, C_6D_6): δ 9.7 (CH_3 of Cp*), 94.4 (quaternary of Cp*), 217.2 (CO). IR (KBr): ν(CO) 1955, 1932, 1919; (CH_2Cl_2) 1960, 1925, 1910. MS (EI): *m/z* 598 (5%) $[M]^+$, correct isotope distribution for 2 Fe, 1 Ga, and 1 Cl atom, significant fragment ions at *m/z* 570 (35%) $[M - CO]^+$, 542 (25%) $[M - 2CO]^+$; exact mass calc for $[M]^+$ 597.9782, found 597.9780. Anal Calc for $C_{24}H_{30}ClFe_2GaO_4$: C 48.09, H 5.05. Found: C 47.82, H 5.33.

[Cp*Fe(CO)$_2$]$_2$GaI, 6b. To a solution/suspension of $Na[Cp^*Fe(CO)_2]$ (0.040 g, 0.148 mmol) in diethyl ether (10 mL) was added dropwise a solution of $[Cp^*Fe(CO)_2GaI_2]_2$ (**12**, 0.085 g, 0.074 mmol) in diethyl ether (20 mL), and the reaction mixture stirred at 20 °C for 12 h, during which time **6b** precipitated out of solution as a yellow powder. Filtration, washing with hexanes, and drying in vacuo led to the isolation of **6b** (yield: 0.060 g, 61%). Crystalline samples could be obtained by slow diffusion of hexanes into a solution in thf at −30 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.77 (s, 30H, Cp*). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 9.2 (CH_3 of Cp*), 94.1 (quaternary of Cp*), 217.4 (CO). IR (CD_2Cl_2): ν(CO) 2003, 1964, 1928 cm^{-1}. MS (EI): *m/z* 662 (45%) $[M - CO]^+$, correct isotope distribution for 2 Fe, 1 Ga, and 1 I atom, significant fragment ion at *m/z* 634 (30%) $[M - 2CO]^+$; exact mass calc for $[M - CO]^+$ 661.9189, found 661.9191. Anal. Calc for $C_{24}H_{30}Fe_2GaIO_4$: C 41.73, H 4.38. Found: C 41.67, H 4.21.

[Cp*Fe(CO)$_2$]$_2$InBr, 7a. To a suspension of $Na[Cp^*Fe(CO)_2]$ (0.201 g, 0.74 mmol) in diethyl ether (20 mL) was added a solution of $InBr_3$ (0.131 g, 0.37 mmol) in diethyl ether (10 mL), and the reaction mixture stirred at 20 °C for 16 h. Filtration of the supernatant solution, removal of volatiles in vacuo, and recrystallization from toluene (60 mL) at −30 °C yielded **7a** as an orange microcrystalline solid (0.121 g, 47%). X-ray quality crystals could be grown by slow diffusion of hexanes into a solution in toluene at −30 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.83 (s, 30H, Cp*). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 10.0 (CH_3 of Cp*), 94.2 (quaternary of Cp*), 216.1 (CO). IR (CD_2Cl_2): ν(CO) 1979, 1946, 1925 cm^{-1}. MS (EI): *m/z* 687.9 (5%) $[M]^+$, correct isotope distribution for 2 Fe, 1 In, and 1 Br atom, significant fragment ion peaks at *m/z* 661.9 (100%) $[M - CO]^+$, 663.9 (20%) $[M - 2CO]^+$; exact mass calc for $[M]^+$ 687.9060, found 687.9066.

[Cp*Fe(CO)$_2$]$_2$InI, 7b. To a suspension of InI (0.245 g, 1.01 mmol) in toluene (10 mL) was added a solution of $[Cp^*Fe(CO)_2]_2$ (0.501 g, 1.01 mmol) in toluene (50 mL), and the reaction mixture refluxed for 144 h. Filtration, concentration, and cooling of the solution to −30 °C yielded **7b** as a microcrystalline solid (0.396 g, 53%). Single crystals suitable for X-ray diffraction could be obtained by slow diffusion of

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hexanes into a toluene solution at −30 °C. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 1.71 (s, 30H, Cp*). ^{13}C NMR (76 MHz, CD$_2$Cl$_2$): δ 9.6 (CH$_3$ of Cp*), 93.7 (quaternary of Cp*), 216.3 (CO). IR (CH$_2$Cl$_2$): ν(CO) 1969, 1957, 1922 cm^{-1}. MS (EI): *m/z* 736 (weak) [M]$^+$, correct isotope distribution for 2 Fe, 1 In, and 1 I atom, significant fragment ions at *m/z* 708 (100%) [M − CO]$^+$, 680 (8%) [M − 2CO]$^+$; exact mass calc for [M − CO]$^+$ 707.8972, found 707.8961.

[CpFe(CO)$_2$Ga(I)Br]$_2$, 8. To a suspension of GaI, prepared by sonicating gallium (0.136 g, 1.95 mmol) and iodine (0.247 g, 0.97 mmol) in toluene (50 mL), was added a solution/suspension of CpFe(CO)$_2$Br (0.500 g, 1.95 mmol) in toluene (30 mL), and the reaction mixture was stirred at 20 °C for 12 h. Filtration, concentration, and standing at 20 °C for 12 h yielded pale orange crystals suitable for X-ray diffraction (0.425 g, 48%). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 4.91 (s, 5H, Cp). ^{13}C NMR (76 MHz, CD$_2$Cl$_2$): δ 84.3 (Cp), 213.3 (CO). IR (CD$_2$Cl$_2$): ν(CO) 2015, 1968 cm^{-1}. MS (EI): *m/z* 499.7 (5%) [CpFe(CO)$_2$GaI$_2$]$^+$, 471.7 (38%) [CpFe(CO)$_2$GaI$_2$ − CO]$^+$, 443.7 (25%) [CpFe(CO)$_2$GaI$_2$ − 2CO]$^+$, 454 (3%) [CpFe(CO)$_2$Ga(I)Br]$^+$, 425.7 (28%) [CpFe(CO)$_2$Ga(I)Br − CO]$^+$, 397.7 (30%) [CpFe(CO)$_2$Ga(I)Br − 2CO]$^+$, 406 (2%) [CpFe(CO)$_2$GaBr$_2$]$^+$, 378 (18%) [CpFe(CO)$_2$GaBr$_2$ − CO]$^+$, 349.7 (13%) [CpFe(CO)$_2$GaBr$_2$ − 2CO]$^+$; exact mass calc for [CpFe(CO)$_2$GaI$_2$]$^+$ 499.6979, found 499.6973. Anal. Calc for C$_{14}$H$_{10}$Br$_2$Fe$_2$Ga$_2$I$_2$O$_4$: C 18.54, H 1.11. Found: C 18.22, H 0.99.

[CpFe(CO)$_2$In(I)Br]$_2$, 9. To a suspension of InI (0.247 g, 1.0 mmol) in toluene (5 mL) was added a solution/suspension of CpFe(CO)$_2$Br (0.262 g, 1.0 mmol) in toluene (40 mL), and the reaction mixture stirred at 20 °C for 144 h, during which time **9** precipitated out of solution as a yellow powder. Recrystallization by slow diffusion of hexanes into a toluene solution at −30 °C yielded orange crystals of **9** suitable for X-ray diffraction (0.407 g, 80%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 4.96 (s, 10H, Cp). ^{13}C NMR (76 MHz, CD$_2$Cl$_2$): δ 82.8 (Cp), carbon of CO ligands not observed. IR (CH$_2$Cl$_2$): ν(CO) 2012, 1969 cm^{-1}. MS (EI): 916 (25%) [M − Br]$^+$, 870 (30%) [M − I]$^+$, 546 (10%) [CpFe(CO)$_2$InI$_2$]$^+$, 518 (6%) [CpFe(CO)$_2$InI$_2$ − CO]$^+$, 498 (2%) [CpFe(CO)$_2$In(I)Br]$^+$, 490 (23%) [CpFe(CO)$_2$InI$_2$ − 2CO]$^+$, 470 (2%) [CpFe(CO)$_2$In(I)Br − CO]$^+$, 442 (20%) [CpFe(CO)$_2$In(I)Br − 2CO]$^+$, 419 (100%) [CpFe(CO)$_2$InI]$^+$, 391 (8%) [CpFe(CO)$_2$InI − CO]$^+$, 371 (60%) [CpFe(CO)$_2$InBr]$^+$, 363 (7%) [CpFe(CO)$_2$InI − 2CO]$^+$, 343 (7%) [CpFe(CO)$_2$InBr − CO]$^+$, 315 (3%) [CpFe(CO)$_2$InBr − 2CO}$^+$, 3%]; exact mass calc for [CpFe(CO)$_2$InI$_2$]$^+$ 545.6762, found 545.6760.

CpFe(CO)$_2$GaI$_2$(μ-I)Fe(CO)$_2$Cp, 10. To a suspension of GaI, prepared by sonicating gallium (0.138 g, 1.97 mmol) and iodine (0.250 g, 0.98 mmol) in toluene (50 mL), was added dropwise a solution/suspension CpFe(CO)$_2$I (0.600 g, 1.97 mmol) in toluene (20 mL), and the reaction mixture stirred at 20 °C for 12 h. Filtration, layering with hexanes, and cooling to −30 °C yielded dark red crystals suitable for X-ray diffraction (0.570 g, 72%). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 4.24 (s, 5H, Cp), 4.25 (s, 5H, Cp). ^{13}C NMR (76 MHz, C$_6$D$_6$): δ 83.8 (Cp), 84.2 (Cp), 212.0 (CO), 215.1 (CO). IR (C$_6$D$_6$): ν(CO) 2037, 2003, 2000, 1957. MS (EI): *m/z* 499.7 (5%) [CpFe(CO)$_2$GaI$_2$]$^+$, 471.7 (75%) [CpFe(CO)$_2$GaI$_2$ − CO]$^+$, 443.7 (52%) [CpFe(CO)$_2$GaI$_2$ − 2CO]$^+$, all with correct isotope distribution for 1 Fe, 1 Ga, and 2 I atom, 303.8 (45%) [CpFe(CO)$_2$I]$^+$, 275.8 (47%) [CpFe(CO)$_2$I − CO]$^+$, 247.8 (80%) [CpFe(CO)$_2$I − 2CO]$^+$; exact mass calc for [CpFe(CO)$_2$GaI$_2$ − CO]$^+$ 471.7030, found 471.7030.

[CpFe(CO)$_2$GaI$_2$]$_2$, 11. To a suspension of GaI, prepared by sonicating gallium (0.205 g, 2.94 mmol) and iodine (0.373 g, 1.47 mmol) in toluene (50 mL), was added a solution/suspension of CpFe(CO)$_2$I (0.300 g, 0.98 mmol) in toluene (20 mL), and the reaction mixture stirred at 20 °C for 48 h. Filtration, layering with hexanes, and cooling to −30 °C yielded crystals suitable for X-ray diffraction (0.300 g, 27%). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 4.12 (s, 5H, Cp). ^{13}C NMR (76 MHz, C$_6$D$_6$): δ 84.0 (Cp), 213.4 (CO). IR (C$_6$D$_6$): ν(CO) 2012, 1970 cm^{-1}. MS (EI): *m/z* 500 (5%) [CpFe(CO)$_2$GaI$_2$]$^+$, correct isotope distribution for 1 Fe, 1 Ga, and 2 I atom, significant fragment ions at *m/z* 472 (100%) [CpFe(CO)GaI$_2$]$^+$, 444 (75%) [CpFeGaI$_2$]$^+$, 373 (50%) [CpFe(CO)$_2$GaI]$^+$; exact mass calc for [CpFe(CO)$_2$GaI$_2$]$^+$ 499.6979, found 499.6975. Anal. Calc for C$_{14}$H$_{10}$Fe$_2$Ga$_2$I$_4$O$_4$: C 16.80, H 1.01. Found: C 16.48, H 0.91.

[Cp*Fe(CO)$_2$GaI$_2$]$_2$, 12. To a suspension of GaI, prepared by sonicating gallium (0.169 g, 2.42 mmol) and iodine (0.307 g, 1.21 mmol) in toluene (50 mL), was added a solution of [Cp*Fe(CO)$_2$]$_2$ (0.300 g, 0.61 mmol) in toluene (30 mL), and the reaction mixture stirred at 20 °C for 120 h, during which time **12** precipitated out of solution as a yellow powder. Recrystallization from dichloromethane at −30 °C yielded pale yellow crystals suitable for X-ray diffraction (0.324 g, 47%). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 1.60 (s, 30H, Cp*). ^{13}C NMR (76 MHz, C$_6$D$_6$): δ 9.8 (CH$_3$ of Cp*), 95.4 (quaternary of Cp*), 216.4 (CO). IR (C$_6$D$_6$) ν(CO) 2001, 1954 cm^{-1}. MS (EI): *m/z* 569.8 (15%) [Cp*Fe(CO)$_2$GaI$_2$]$^+$, 541.8 (100%) [Cp*Fe(CO)$_2$GaI$_2$ − CO]$^+$, 513.8 (60%) [Cp*Fe(CO)$_2$GaI$_2$ − 2CO]$^+$; exact mass calc For [Cp*Fe(CO)$_2$GaI$_2$]$^+$ 569.7761; found 569.7753. Anal. Calc for C$_{24}$H$_{30}$Fe$_2$Ga$_2$I$_4$O$_4$: C 25.26, H 2.65. Found: C 24.98, H 2.43.

[Cp*Fe(CO)$_2$]$_2$In(μ-Cl)$_2$InCl[Fe(CO)$_2$Cp*], 13. To a suspension of InCl (0.182 g, 1.22 mmol) in toluene (10 mL) was added a solution of [Cp*Fe(CO)$_2$]$_2$ (0.298 g, 0.60 mmol) in toluene (40 mL), and the reaction mixture refluxed for 36 h. Filtration, concentration, and cooling of the solution to −30 °C yielded **13** as single crystals suitable for X-ray diffraction (0.065 g, 20%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 1.81 (s, 15H, Cp*), 1.87 (s, 30H, Cp*). ^{13}C NMR (76 MHz, CD$_2$Cl$_2$): δ 10.0 (CH$_3$ of Cp*), 10.2 (CH$_3$ of Cp*), 94.1 (quaternary of Cp*), 94.3 (quaternary of Cp*), 215.4 (CO), 216.5 (CO). IR (CD$_2$Cl$_2$): ν(CO) 1987, 1967, 1954, 1939, 1919 cm^{-1}. MS (EI): *m/z* 616 (13%) [{Cp*Fe(CO)$_2$}$_2$InCl − CO]$^+$, correct isotope distribution for 2 Fe, 1 In, and 1 Cl atom, significant fragment ions at *m/z* 588 (5%) [{Cp*Fe(CO)$_2$}$_2$InCl − 2CO]$^+$, 397 (12%) [Cp*Fe(CO)$_2$InCl]$^+$; exact mass calc for [{Cp*Fe(CO)$_2$}$_2$InCl − CO]$^+$ 615.9616; found 615.9616.

Reaction of [CpFe(CO)$_2$Ga(I)Br]$_2$ (8) with 4-Picoline. To a solution of **8** (0.100 g, 0.11 mmol) in toluene (15 mL) was added dropwise a solution of 4-picoline in toluene (10 mL containing 0.020 g, 0.22 mmol of 4-picoline), and the reaction mixture stirred at 20 °C for 12 h. Filtration, concentration, addition of hexane (40 mL), and cooling to −30 °C yielded a pale yellow microcrystalline material (0.030 g, 25%). Crystals of CpFe(CO)$_2$GaI$_2$·(4-pic) (**14**) suitable for X-ray diffraction could be obtained by slow diffusion of hexanes into a benzene solution. Characterizing data for crude (microcrystalline) product: ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 1.35 (b, 3H, CH$_3$), 4.27, 4.29, 4.31 (s, 5H, Cp), 6.13 (b, 2H, CH of pic), 8.62 (b, 2H, CH of pic). ^{13}C NMR (76 MHz, C$_6$D$_6$): δ 20.6, 20.8 (CH$_3$), 83.4, 84.0, 84.6 (Cp), 125.8, 125.9 (CH of pic), 145.9, 146.0 (CH of pic), 153.5, 153.6 (quaternary of pic), 215.6, 216.1 (CO). IR (C$_6$D$_6$): ν(CO) 1985, 1979, 1950, 1934 cm^{-1}. MS (EI): *m/z* 500 (weak) [CpFe(CO)$_2$GaI$_2$]$^+$, 472 (10%) [CpFe(CO)$_2$GaI$_2$ − CO]$^+$, 454 (2%) [CpFe(CO)$_2$Ga(I)Br]$^+$, 444 (8%) [CpFe(CO)$_2$GaI$_2$ − 2CO]$^+$, 426 (25%) [CpFe(CO)$_2$Ga(I)Br − CO]$^+$, 406 (2%) [CpFe(CO)$_2$GaBr$_2$]$^+$, 398 (25%) [CpFe(CO)$_2$Ga(I)Br − 2CO]$^+$, 378 (18%) [CpFe(CO)$_2$GaBr$_2$ − CO]$^+$, 350 (30%) [CpFe(CO)$_2$GaBr$_2$ − 2CO]$^+$, 93.1 (100%) [4-pic]$^+$. Characterizing data for the crystalline product **14** were identical to those of a crystalline sample prepared independently from [CpFe(CO)$_2$GaI$_2$]$_2$ (**11**) and 4-picoline and recrystallized from toluene/hexanes: ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 1.34 (s, 3H, CH$_3$), 4.33 (s, 5H, Cp), 6.09 (b m, 2H, CH of pic), 8.82 (b, 2H, CH of pic). ^{13}C NMR (76 MHz, C$_6$D$_6$): δ 20.3 (CH$_3$), 84.6 (Cp), 125.5, (CH of pic), 146.2 (CH of pic), 153.3 (quaternary of pic), 216.1 (CO). IR (C$_6$D$_6$): ν(CO) 1985, 1933 cm^{-1}. MS (EI): *m/z* 565 (weak) [M − CO]$^+$, correct isotope distribution for 1 Fe, 1 Ga, and 2 I atom, significant fragment ions at *m/z* 500 (4%) [M − pic]$^+$, 472 (75%) [M − pic − CO]$^+$, 444 (60%) [M − pic − 2CO]; exact mass calc for [M − CO]$^+$ 564.7608, found 564.7611.

Table 1. Details of Data Collection, Structure Solution and Refinement for Compounds 2, 3a, 5, 6a, and 7b

	2	**3a**	**5**	**6b**	**7b**
empirical formula	$C_{25}H_{34}ClFeGaO_2$	$C_{30}H_{44}ClFeGaO_2$	$C_{30}H_{44}BrFeInO_2$	$C_{24}H_{30}Fe_2GaIO_4$	$C_{24}H_{30}Fe_2IInO_4$
fw	527.54	597.67	687.23	690.80	735.90
temperature (K)	150(2)	150(2)	180(2)	150(2)	150(2)
CCDC deposit number	271129	271128	272450	271131	271132
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	*Pcab*	*Cmca*	*Cmca*	$P2_1/c$	$P2_1/c$
unit cell dimens (Å, deg) *a*	16.8447(3)	15.2046(4)	15.0781(4)	13.4340(2)	13.4349(3)
b	17.0707(4)	19.8952(5)	20.5262(6)	11.2410(2)	11.5133(3)
c	17.7094(4)	20.2595(7)	20.4631(8)	17.0130(3)	17.0644(5)
α	90	90	90	90	90
β	90	90	90	94.1360(10)	94.3400(10)
γ	90	90	90	90	90
volume (Å^3)	5092.35(19)	6128.5(3)	6333.2(4)	2562.47(4)	2631.95(12)
density (calcd, Mg m^{-3})	1.376	1.296	1.422	1.791	1.857
Z	8	8	8	4	4
absorp coeff (mm^{-1})	1.750	1.463	2.470	3.393	3.156
F(000)	2192	2512	2800	1368	1440
cryst size (mm^3)	0.50 × 0.30 × 0.20	0.20 × 0.15 × 0.15	0.35 × 0.22 × 0.10	0.25 × 0.25 × 0.20	0.18 × 0.15 × 0.10
θ range (deg)	2.91 to 27.48	3.52 to 26.37	3.59 to 26.37	3.54 to 26.37	2.98 to 27.47
index ranges *h*	−21 to 21	−18 to 18	−18 to 18	−16 to 16	−17 to 17
k	−21 to 22	−20 to 24	−25 to 25	−14 to 14	−14 to 14
l	−22 to 23	−25 to 25	−25 to 25	−21 to 21	−21 to 22
no. of reflns collected	38 720	21 350	20 540	29 428	18 768
no. of indep reflns	5780 [*R*(int) = 0.1282]	3245 [*R*(int) = 0.0981]	3356 [*R*(int) = 0.1051]	5232 [*R*(int) = 0.0774]	5991 [*R*(int) = 0.0778]
completeness to *θ* max	99.0%	99.5%	99.6%	99.8%	99.5%
absorp corr	semiempirical from equivs	semiempirical from equivs	semiempirical from equivs	semiempirical from equivs	semiempirical from equivs
max. and min. transmn	0.7210 and 0.4748	0.8104 and 0.7585	0.7902 and 0.4785	0.5502 and 0.4842	0.7432 and 0.6004
refinement method	full-matrix least-squares (F^2)	full-matrix least-squares (F^2)	full-matrix least-squares (F^2)	full-matrix least-squares (F^2)	full-matrix least-squares (F^2)
no. of data/restraints/params	5780/0/280	3245/6/183	3356/0/168	5232/0/299	5991/0/299
goodness-of-fit on F^2	1.031	1.057	1.030	1.025	1.036
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0532, wR2 = 0.1076	R1 = 0.0735, wR2 = 0.1880	R1 = 0.0517, wR2 = 0.1071	R1 = 0.0321, wR2 = 0.0651	R1 = 0.0401, wR2 = 0.0782
R indices (all data)	R1 = 0.1327, wR2 = 0.1304	R1 = 0.1121, wR2 = 0.2062	R1 = 0.0935, wR2 = 0.1206	R1 = 0.0448, wR2 = 0.0701	R1 = 0.0586, wR2 = 0.0846
largest diff pk and hole (e Å^{-3})	0.623 and −0.916	2.393 and −1.046	0.730 and −0.672	0.542 and −0.720	0.697 and −1.096

$\{[CpFe(CO)_2]_2InI\}_2$, 15. To a suspension of $Na[CpFe(CO)_2]$ (0.023 g, 0.12 mmol) in toluene (10 mL) was added a solution of **9** (0.057 g, 0.06 mmol) in toluene (10 mL), and the reaction mixture stirred at 20 °C for 16 h. Filtration and crystallization by slow diffusion of hexanes into a toluene solution at −30 °C led to the formation of orange-yellow crystals suitable for X-ray diffraction (0.055 g, 77%). ^1H NMR (400 MHz, C_6D_6): δ 4.34 (s, 20H, Cp). ^{13}C NMR (76 MHz, C_6D_6): δ 82.8 (Cp), 215.5 (CO). IR (C_6D_6): ν(CO) 1997, 1972, 1927 cm^{-1}. MS (EI): 596 (2%) $[\{CpFe(CO)_2\}_2InI]^+$, correct isotope distribution for 2 Fe, 1 In, and 1 I atom, 568 (33%) $[\{CpFe(CO)_2\}_2InI - CO]^+$, 540 (20%) $[\{CpFe(CO)_2\}_2InI - 2CO]^+$, 419 (53%) $[CpFe(CO)_2InI]^+$, 391 (8%) $[CpFe(CO)_2InI - CO]^+$, 363 (35%) $[CpFe(CO)_2InI - 2CO]^+$; exact mass calc for $[\{CpFe(CO)_2\}_2InI]^+$ 595.7356, found 595.7364.

$[tmpH_2]^+[Cp^*Fe(CO)_2GaI_3]^-$, 16. To a solution of $[Cp^*Fe(CO)_2GaI_2]_2$ (**12**, 0.100 g, 0.088 mmol) in toluene (20 mL) was added dropwise a solution of Li[tmp] (0.026 g, 0.18 mmol) in toluene (20 mL), and the reaction mixture stirred at 20 °C for 12 h. Filtration, concentration, and cooling to −30 °C led to the formation of pale yellow crystals suitable for X-ray diffraction (0.041 g, 28%). ^1H NMR (300 MHz, CD_2Cl_2): δ 1.57 (b, 12H, CH_3 of tmp), 1.66 (b, 4H, CH_2CMe_2 of tmp), 1.76 (s, 15H, CH_3 of Cp*), 1.89 (b, 2H, CH_2 of tmp), 6.49 (b, 2H, NH_2). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 8.4 (CH_3 of Cp*), 15.2 (CH_3 of tmp), 27.6 (CH_2CMe_2 of tmp), 35.2 (CH_2 of tmp), 59.1 (quaternary of tmp), 93.6 (quaternary of Cp*), 217.0 (CO). IR (C_6D_6): ν(CO) 1980, 1933 cm^{-1}. MS (ES−): 696.7 (10%) $[Cp^*Fe(CO)_2GaI_3]^-$, 668.7 (1%), $[Cp^*Fe(CO)_2GaI_3 - CO]^-$, 569.7 (5%) $[Cp^*Fe(CO)_2GaI_3 - I]^-$; exact mass calc for $[Cp^*Fe(CO)_2GaI_3]^-$ (^{69}Ga): 696.6817, found 696.6815. MS (ES+): 142.1 (100%) $[tmpH_2]^+$.

(iii) Crystallographic Method. Data for compounds **2**, **3a**, and **5**–**16** were collected on an Bruker Nonius Kappa CCD diffractometer. Data collection and cell refinement were carried out using DENZO and COLLECT; structure solution and refinement used DIRDIFF-99 (Patterson methods), SIR-92 (direct methods), and SHELXL-97, respectively; absorption corrections were performed using SORTAV.[21] Details of each data collection, structure solution, and refinement can be found in Tables 1 and 2. Relevant bond lengths and angles are included in the figure captions, and complete details of each structure have been deposited with the CCDC (numbers as listed in Table 1). In addition, complete details for each structure (including CIF files) have been included in the Supporting Information. The crystal structure of compound **6a** has been reported in a preliminary communication;[9] the structures of **7a**, **8**, **14**, and **16** were obtained predominantly for compound verification and show geometric features very similar to related derivatives. Hence these three structures, together with those of $[tmpH_2]^+[CpFe(CO)_2GaBr_3]^-$ and

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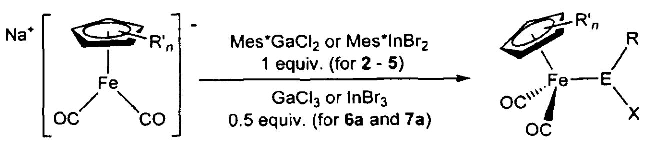
Table 2. Details of Data Collection, Structure Solution, and Refinement for Compounds 9–13 and 15

	9	**10**	**11**	**12**	**13·1/4(C_6H_6)**	**15**
empirical formula	$C_{14}H_{10}Br_2Fe_2I_2In_2O_4$	$C_{14}H_{10}Fe_2GaI_3O_4$	$C_{14}H_{10}Fe_2Ga_2I_4O_4$	$C_{24}H_{30}Fe_2Ga_2I_4O_4$	$C_{37.5}H_{46.5}Cl_3Fe_3In_2O_6$	$C_{28}H_{20}Fe_4I_2In_2O_8$
fw	997.18	804.34	1000.96	1141.22	1096.79	1191.28
temperature (K)	150(2) K	150(2)	150(2)	150(2)	150(2)	150(2)
CCDC deposit number	271135	271136	271137	271138	271139	271141
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	monoclinic	triclinic	orthorhombic	orthorhombic
space group	*P*21/*n*	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	*Pcab*	*Pcab*
unit cell dimens (Å, deg) *a*	7.6338(3)	7.9200(3)	8.9422(3)	8.4507(2)	14.9810(2)	7.5598(2)
b	14.8212(6)	9.8960(3)	8.7431(3)	9.6929(3)	21.5210(3)	18.7946(5)
c	9.9594(5)	15.2600(6)	14.4917(6)	11.4642(3)	29.8390(4)	23.1101(6)
α	90	100.5820(10)	90	75.9390(10)	90	90
β	90.796(2)	97.6700(10)	90.301(1)	74.028(2)	90	90
γ	90	113.333(2)	90	67.5600(10)	90	90
volume (Å^3)	1126.72(9)	1050.98(7)	1132.98(7)	824.33(4)	9620.3(2)	3283.56(15)
density (calcd, Mg m^{-3})	2.939	2.542	2.934	2.299	1.515	2.410
Z	2	2	2	1	8	4
absorp coeff (mm^{-1})	9.585	7.054	9.073	6.250	2.031	5.028
F(000)	904	736	904	532	4372	2240
cryst size (mm^3)	0.30 × 0.13 × 0.10	0.15 × 0.10 × 0.05	0.35 × 0.28 × 0.25	0.15 × 0.15 × 0.13	0.18 × 0.15 × 0.10	0.25 × 0.08 × 0.03
θ range (deg)	3.00 to 27.42	3.52 to 26.37	3.54 to 26.37	2.93 to 27.47	3.53 to 26.37	3.04 to 27.47
index ranges *h*	−9 to 9	−9 to 9	−11 to 11	−10 to 10	−18 to 18	−9 to 9
k	−19 to 19	−12 to 12	−9 to 10	−12 to 12	−26 to 26	−24 to 24
l	−12 to 12	−19 to 19	−17 to 18	−14 to14	−35 to 37	−29 to 30
no. of reflns collected	9748	14 311	7086	13 459	47 982	24 421
no. of indep reflns	2554 [*R*(int) = 0.0807]	4287 [*R*(int) = 0.0907]	2302 [*R*(int) = 0.0594]	3761 [*R*(int) = 0.0878]	9794 [*R*(int) = 0.1115]	3757 [*R*(int) = 0.1148]
completeness to *θ* max	99.4%	99.7%	99.4%	99.7%	99.5%	99.9%
absorp corr	semiempirical from equivs	semiempirical from equivs	semiempirical from equivs	semiempirical from equivs	semiempirical from equivs	semiempirical from equivs
max. and min. transmn	0.4474 and 0.1611	0.7193 and 0.4176	0.2101 and 0.1434	0.4971 and 0.4541	0.8227 and 0.7113	0.8638 and 0.3662
refinement method	full-matrix least-squares (F^2)	full-matrix least-squares (F^2)	full-matrix least-squares (F^2)	full-matrix least-squares (F^2)	full-matrix least-squares (F^2)	full-matrix least-squares (F^2)
no. of data/restraints/params	2554/30/137	4287/12/217	2302/0/118	3761/0/168	9794/0/484	3757/0/200
goodness-of-fit on F^2	1.142	1.021	1.148	1.031	1.023	1.031
final R indices [$I > 2\sigma(I)$]	R1 = 0.0491, wR2 = 0.1179	R1 = 0.0503, wR2 = 0.1174	R1 = 0.0424, wR2 = 0.1049	R1 = 0.0408, wR2 = 0.0902	R1 = 0.0527, wR2 = 0.1356	R1 = 0.0465, wR2 = 0.0852
R indices (all data)	R1 = 0.0592, wR2 = 0.1241	R1 = 0.0851, wR2 = 0.1331	R1 = 0.0492, wR2 = 0.1087	R1 = 0.0571, wR2 = 0.0977	R1 = 0.0835, wR2 = 0.1499	R1 = 0.0888, wR2 = 0.0980
largest diff pk and hole (e Å^{-3})	1.336 and −2.099	1.405 and −1.667	0.948 and −2.532	1.100 and −1.586	1.626 and −0.620	1.106 and −1.357

Scheme 4. Direct Substitution by Organometallic Anions as a One-Step Route to Three-Coordinate Halogallium and -indium Ligand Systems



2: E = Ga, X = Cl, R = Mes*, R'_n = H_5
3a: E = Ga, X = Cl, R = Mes*, R'_n = Me_5
4: E = In, X = Br, R = Mes*, R'_n = H_5
5: E = In, X = Br, R = Mes*, R'_n = Me_5
6a: E = Ga, X = Cl, R = (η^5-C_5Me_5)Fe(CO)$_2$, R'_n = Me_5
7a: E = In, X = Br, R = (η^5-C_5Me_5)Fe(CO)$_2$, R'_n = Me_5

$[CpFe(CO)_3]^+[CpFe(CO)_2Ga(I)Br_2]^-$, are included only in the Supporting Information. The halide ligands in $[CpFe(CO)_2In(I)Br]_2$, **9**, are disordered between bridging and terminal positions. This disorder was successfully modeled (summing to unity in each position) giving refined occupancies of 70:30 Br:I for the bridging positions and 30:70 for the terminal positions.

Results and Discussion

(i) Synthesis from Metal Anions. Synthesis from anionic organometallic precursors has been applied to two classes of three-coordinate gallium- or indium-containing ligand system, namely, (i) asymmetric halogallyl and -indyl systems of the type L_nM-E(Mes*)X (Mes* = supermesityl, 2,4,6-^{t}Bu$_3$C$_6$H$_2$) and (ii) bridging halogallanediyl and -indanediyl complexes $(L_nM)_2EX$. The former class of compound is exemplified by complexes **2**–**5**, which can be synthesized by the reaction of Na[(η^5-C_5R_5)Fe(CO)$_2$] (R = H, Me) with Mes*GaCl$_2$ or Mes*InBr$_2$ (Scheme 4).

Given the observation for boron-based systems that subsequent halide abstraction chemistry leads to tractable cationic diyl derivatives *only* in the presence of bulky aryl or amino groups,[7] the supermesityl substituent was employed in complexes **2**–**5**.[11] Although Mes*BBr$_2$ is itself inert to boron-centered substitution chemistry with anions of the type [(η^5-C_5R_5)Fe(CO)$_2$]$^-$, presumably on steric grounds,[22c] substitution at the larger group 13 centers in Mes*EX$_2$ (E = Ga, In) has previously been shown to offer a viable route of generating monomeric, three-coordinate group 13 systems [e.g., Mes*Ga(Cl)N(SiMe$_3$)$_2$ and (OC)$_5$MnGa(Mes*)Cl[11,23]]. For complexes **2** and **3a**, Mes*GaCl$_2$ represents a convenient,

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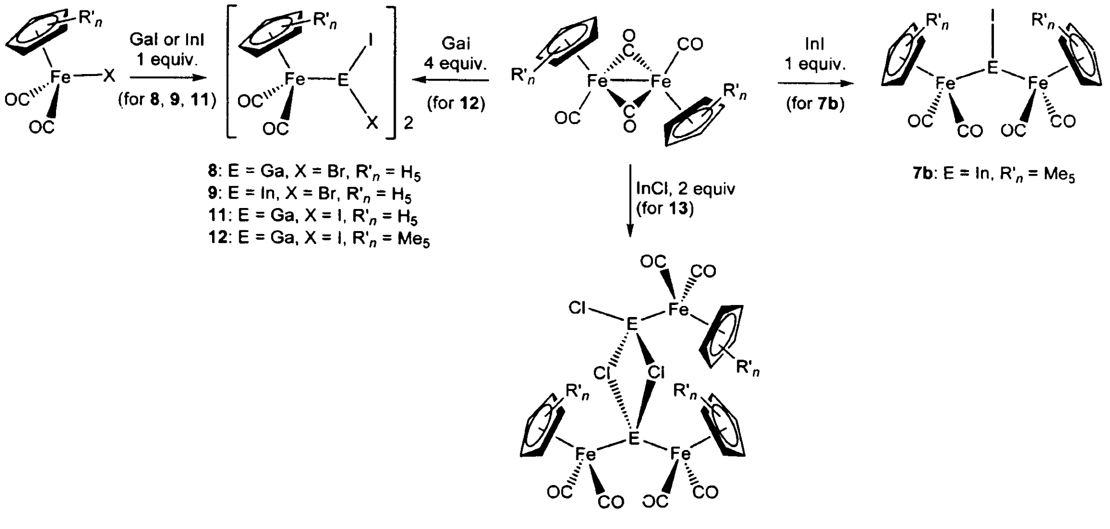
[22] (a) Aldridge, S.; Coombs, D. L.; Jones, C. *Chem. Commun.* **2002**, 856. (b) Coombs, D. L.; Aldridge, S.; Jones, C. *Dalton Trans.* **2002**, 3851. (c) Coombs, D. L.; Aldridge, S.; Jones, C. *Appl. Organomet. Chem.* **2003**, *6*–*7*, 356.

Scheme 5. Insertion Chemistry as a Route to Gallium- and Indium-Based Ligand Systems Containing Pendant Halides



8: E = Ga, X = Br, $R'_n = H_5$
9: E = In, X = Br, $R'_n = H_5$
11: E = Ga, X = I, $R'_n = H_5$
12: E = Ga, X = I, $R'_n = Me_5$

7b: E = In, $R'_n = Me_5$

13: E = In, $R'_n = Me_5$

readily synthesized precursor, with the corresponding bromide Mes^*InBr_2 being employed for indyl complexes **4** and **5** because of reported difficulties obtaining Mes^*InCl_2 free from $InCl_3$.[16b,c] Complexes **2**–**5** are pale yellow crystalline solids, which have been characterized by multinuclear NMR and IR spectroscopies, by mass spectrometry (including exact mass determination), and, in the cases of **2**, **3a** and **5**, by single-crystal X-ray diffraction. Similar chemistry can also be employed in the synthesis of bridging gallanediyl and indanediyl complexes **6a** and **7a** (Scheme 4). Thus, reaction of 2 equiv of the bulky $[Cp^*Fe(CO)_2]^-$ anion with $GaCl_3$ or $InBr_3$ leads to selective substitution of two of the halide ligands to give the bridging halodiyl complexes $[Cp^*Fe(CO)_2]_2EX$ (**6a**: E = Ga, X = Cl; **7a**: E = In, X = Br) in isolated yields of 36 and 47%, respectively. A related salt elimination approach, albeit with *dianionic* organometallic reagents, has been exploited by Hüttner and co-workers in the synthesis of complexes of the type $\{[(OC)_5Cr]_2EX\}^{2-}$ (E = In, Tl; X = Cl, Br, I).[12]

Spectroscopic data for **6a** and **7a** are in accordance with the proposed formulations, which are confirmed in both cases by the results of a single-crystal X-ray diffraction study. In contrast to the corresponding complexes featuring the less bulky $CpFe(CO)_2$ fragment, **6a** and **7a** are monomeric in the solid state (vide infra) and can be recrystallized from coordinating solvents such as diethyl ether and thf without coordination at the group 13 center.[24,25]

(ii) Synthesis by Combined Insertion/Substitution Methodology. (a) Insertion Chemistry. An alternative approach to the synthesis of the requisite three-coordinate halo-gallium and -indium ligand systems involves initial insertion of EI (E = Ga, In) into a M–X or M–M bond to give a dihalogallyl or -indyl, $[L_nM\text{-}E(I)X]_n$, or halogallanediyl/indanediyl complex, $(L_nM)_2EI$. This approach offers a potentially more powerful route to such systems than the simple organometallic anion substitution methodology discussed above. By avoiding reliance on such anionic precursors, a much greater range of complexes is potentially accessible, leading ultimately to the possibility of cationic diyl systems $[L_nM(EX)]^+$ without competing ancillary π acidic ligands (i.e., carbonyls[26]). Relevant reaction chemistry of GaI and InX (X = Cl, I) toward metal–halogen and metal–metal bonds is shown in Scheme 5. The insertion of sonochemically generated GaI into M–I bonds (M = Fe, Mo) was originally demonstrated by Green and co-workers in 1990,[14a] and in similar fashion both GaI and InI readily insert into the Fe–Br bond of $CpFe(CO)_2Br$ to give dimeric $[CpFe(CO)_2E(I)Br]_2$ (**8**: E = Ga; **9**: E = In) in yields of 48 and 80%, respectively. In each case IR and multinuclear NMR data are consistent with the proposed formulations, although the mass spectra reveal ready fragmentation into a mixture of monomeric species $CpFe(CO)_2EBr_2$, $CpFe(CO)_2E(I)Br$, and $CpFe(CO)_2EI_2$ under electron impact conditions. The halide-bridged dimeric structures of **8** and **9** were subsequently deduced from single-crystal X-ray diffraction studies (vide infra).

The reaction of $CpFe(CO)_2I$ with GaI has also been investigated in some depth and provides some insight into the mechanism of the reaction, together with the reported tendency of similar systems under certain conditions to give salt-like transition metal/group 13 products (e.g., containing anions of the type $[L_nM\text{-}GaX_3]^-$).[24,27] Thus, under mild reaction conditions, reaction of $CpFe(CO)_2I$ with GaI generates a deep red compound, **10**, which can be recrystallized from a

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(23) Leung, W.-P.; Chan, C. M. Y.; Wu, B. M.; Mak, T. C. W. *Organometallics* **1996**, *15*, 5179.

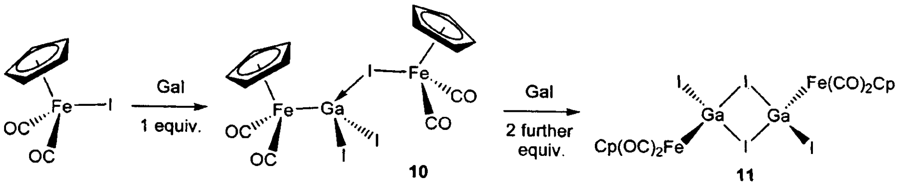
(24) Linti, G.; Li, G.; Pritzkow, H. *J. Organomet. Chem.* **2001**, *626*, 82.

(25) A previous report of the synthesis of **11** from GaI_3 and of its hydrolytic reactivity makes no comment as to its state of aggregation and reports slightly different spectroscopic data than those detailed in the present study: Borovik, A. S.; Bott, S. G.; Barron, A. R. *Organometallics* **1999**, *18*, 2668.

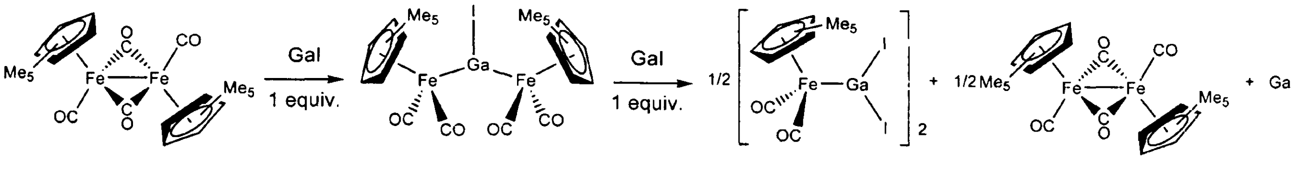
(26) Mork, B. V.; McMillan, A.; Yuen, H.; Tilley, T. D. *Organometallics* **2004**, *23*, 2855.

(27) Although the reaction of $CpFe(CO)_2FeBr$ with GaI in toluene gives $[CpFe(CO)_2Ga(I)Br]_2$ in ca. 50% isolated yields, in the presence of traces of thf $[CpFe(CO)_3]^+[CpFe(CO)_2Ga(I)Br_2]^-$ is obtained. Details of the structure of this salt-like product are included in the Supporting Information.

Scheme 6. Reaction of the Isolated Intermediate 10 with GaI via Further Insertion to Give Dimeric $[CpFe(CO)_2GaI_2]_2$



Scheme 7. Proposed Mechanism for the Formation of $[Cp^*Fe(CO)_2]_2GaI$ from $[Cp^*Fe(CO)_2]_2$ and GaI



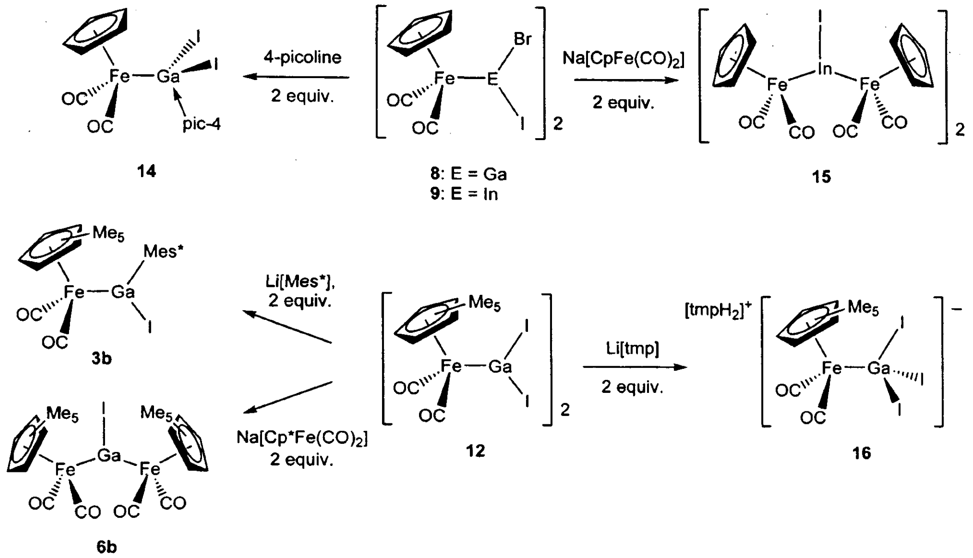
toluene/hexane mixture (ca. 1:2) as large block-like crystals. Spectroscopic and crystallographic studies indicate that **10** is a 1:1 adduct formed between $CpFe(CO)_2I$ and $CpFe(CO)_2GaI_2$ via an I→Ga donor/acceptor interaction (Scheme 6). It seems likely that **10** arises from the trapping of the initial product of GaI insertion [into the Fe−I bond of $CpFe(CO)_2I$] by unreacted $CpFe(CO)_2I$. From **10** two possible reaction pathways are plausible. First, in the presence of an excess of GaI, insertion into the remaining (and presumably weakened) Fe−I bond with concomitant formation of a further I→Ga interaction would create dimeric $[CpFe(CO)_2GaI_2]_2$ (**11**). Indeed, under more forcing conditions (using 3 equiv of GaI) **11** is indeed the predominant product from this reaction and is shown from spectroscopic and structural data to possess the expected dimeric structure.[25] Alternatively, in the presence of a suitable nucleophile (L) substitution of the (Lewis acid activated) iodide ligand of the $CpFe(CO)_2I$ fragment would generate a salt-like species of the type $[CpFe(CO)_2L]^+[CpFe(CO)_2GaI_3]^-$. Species containing similar $[CpFe(CO)_2GaX_3]^-$ anions have been reported by Linti and co-workers from related GaI chemistry, and we have also isolated $[CpFe(CO)_3]^+[CpFe(CO)_2Ga(I)Br_2]^-$ as a minor product from the reaction of GaI with $CpFe(CO)_2Br$ in the presence of traces of thf (see Supporting Information).[24,27]

Insertion of InI into *metal−metal* bonds can also be exploited to generate three-coordinate halo-indium ligand systems under appropriate conditions. Accordingly, reaction of InI with $[Cp^*Fe(CO)_2]_2$ generates $[Cp^*Fe(CO)_2]_2InI$, **7b** (in ca. 50% yield), which, unlike its Cp counterpart, has been shown to contain a trigonal planar indium center (vide infra). Thus, in the presence of sufficient steric bulk, subvalent metal halide insertion chemistry represents a direct one-step route to three-coordinate group 13 ligand systems. The reactions for GaI and InCl with $[Cp^*Fe(CO)_2]_2$ have also been examined. In contrast to InI, however, the predominant products generated from reaction with these two reagents are not the simple products of EX insertion into the Fe−Fe bond. Instead $[Cp^*Fe(CO)_2GaI_2]$ (**12**) and $[Cp^*Fe(CO)_2]_2In(\mu\text{-}Cl)_2InCl[Fe(CO)_2Cp^*]$ (**13**) are isolated in yields of 47 and 20%, respectively. In the reaction with GaI, **12** is the only Fe/Ga-containing product isolated, irrespective of reaction stoichiometry, and its formation contrasts markedly with the reactivity reported for $[CpFe(CO)_2]_2$ toward the same reagent. Linti and co-workers have reported that this reaction generates a mixture of organometallic species, among which a $[CpFe(CO)_2GaI_3]^-$ salt represents the only Fe/Ga/I-containing product.[24] In the case of **12**, at least 4 equiv of GaI are required to drive this reaction to completion, with substantial amounts of $[Cp^*Fe(CO)_2]_2$ otherwise being retained; in addition 2 equiv of gallium metal are deposited during the reaction. Presumably the reaction mechanism involves initial insertion of GaI to give $[Cp^*Fe(CO)_2]_2GaI$ in a manner analogous to the corresponding InI chemistry (which generates **7b**). Halide transfer from a second equivalent of GaI would then generate half an equivalent each of $[Cp^*Fe(CO)_2GaI_2]_2$ and $[Cp^*Fe(CO)_2]_2$, together with 1 equiv of gallium metal (Scheme 7). In this way, half of the original $[Cp^*Fe(CO)_2]_2$ is consumed by reaction with 2 equiv of GaI, and the need for an overall 1:4 reaction stoichiometry is justified.

The reaction of InCl with $[Cp^*Fe(CO)_2]_2$ finds a precedent of sorts in the chemistry of the corresponding Cp derivative; a mixture of the two halide-bridged dimers $[CpFe(CO)_2InCl_2]_2$ and $\{[CpFe(CO)_2]_2InCl\}_2$ is thought to be formed in this case.[15e,f] ^1H and ^{13}C NMR analyses of the isolated crystalline product for the permethylated system are consistent with the formation of two Cp*- and carbonyl-containing moieties in a 2:1 ratio. In addition, the IR spectrum contains *five* carbonyl stretching bands (1987, 1967, 1954, 1939, 1919 cm^{-1}), the observed pattern appearing to correspond to the superposition of the two-band spectrum observed for derivatives of the type $[Cp^*Fe(CO)_2EX_2]_2$ (e.g., 2001, 1954 cm^{-1} for **12**, E = Ga, X = I) with the three stretches observed for species of the type $[Cp^*Fe(CO)_2]_2EX$ (e.g., 1979, 1946, 1925 cm^{-1} for **7a**, E = In, X = Br). The structure of the product $[Cp^*Fe(CO)_2]_2In(\mu\text{-}Cl)_2InCl[Fe(CO)_2Cp^*]$, **13**, has been determined crystallographically (vide infra) and, consistent with the IR and NMR data, can be thought of as a chloride-bridged 1:1 adduct between $[Cp^*Fe(CO)]_2InCl$ and $Cp^*Fe(CO)_2InCl_2$ fragments.

(b) Substitution Chemistry. Although direct insertion into metal−metal bonds, such as that demonstrated for InI with $[Cp^*Fe(CO)_2]_2$, can in some cases be used to give access to the required three-coordinate ligand systems, analogous chemistry involving metal−halogen linkages invariably results in four-coordinate dihalogal-

Scheme 8. Substitution and Addition Chemistry at Gallium- and Indium-Based Ligands Containing Pendant Halides



lyl or -indyl systems. Thus, gallium- or indium-centered substitution chemistry with appropriately bulky nucleophiles is required to generate the desired three-coordinate group 13 center. Given this, and the scarcity of reports concerning substitution at existing group 13 ligand systems,[7c,8b] we have therefore examined the reactivity of **8**, **9**, and **12** toward a range of nucleophiles, with the results outlined in Scheme 8.

Simple adduct formation has been observed for dihalogallyl complexes in previous studies [e.g., $CpFe(CO)_2GaCl_2{\cdot}thf$[24]], and the reaction of $[CpFe(CO)_2Ga(I)X]_2$ (**8**: X = Br; **11**: X = I) with neutral donors, exemplified by 4-picoline, appears to proceed along similar lines. Formation of the picoline adduct $CpFe(CO)_2GaI_2{\cdot}(4\text{-pic})$ (**14**) can be demonstrated spectroscopically and has been confirmed by crystallographic study (see Supporting Information). In keeping with the necessity to effect halide *substitution* at gallium/indium, the reactivity of dihalogallyl and -indyl complexes toward *anionic* nucleophiles has also been examined. Thus, $[CpFe(CO)_2In(I)Br]_2$, **9**, reacts at room temperature with $Na[CpFe(CO)_2]$ via halide substitution to yield the bis-metalated species $[CpFe(CO)_2]_2InI$, **15**, which has been characterized spectroscopically and shown crystallographically to adopt an iodide-bridged dimeric structure $\{[CpFe(CO)_2]_2InI\}_2$ analogous to that reported for the corresponding chloride complex.[15f] Although this chemistry demonstrates the feasibility of substitution at existing gallyl/indyl ligand systems, it is apparent that a greater degree of steric bulk is required to generate three- rather than four-coordinate derivatives. Hence the corresponding reactivity of Cp*-substituted $[Cp^*Fe(CO)_2GaI_2]_2$ (**12**) was examined. Initial focus was centered upon the main group nucleophiles Li[tmp] and Li[Mes*] with a view to developing a route to amido(halo)gallyl species such as $Cp^*Fe(CO)_2Ga(tmp)I$[28] and an alternative (metal anion free) route to aryl(halo)gallyls [e.g., $Cp^*Fe(CO)_2Ga(Mes^*)I$]. Additionally, the reaction of **12** with $Na[Cp^*Fe(CO)_2]$ was examined as a possible route to the bridging iodogallylene $[Cp^*Fe(CO)_2]_2GaI$ (**6b**), given the lack of success in isolating this compound by direct insertion of GaI into the Fe–Fe bond of $[Cp^*Fe(CO)_2]_2$.

The reaction of **12** with Li[tmp] in toluene, however, proceeds not to the desired amidogallyl complex, but to the salt $[tmpH_2]^+[Cp^*Fe(CO)_2GaI_3]^-$ (**16**) in 28% yield. The same product is also isolated from the corresponding reaction in diethyl ether and has been characterized both spectroscopically and crystallographically. The origins of the protons of the $[tmpH_2]^+$ cation are unclear, but their location from X-ray diffraction data is supported by the results of mass spectrometry (ES+) and ^{1}H NMR experiments. Although the mechanism for the formation of **16** is not obvious, its formation is entirely reproducible and in accordance with the corresponding reaction of $[CpFe(CO)_2Ga(I)Br]_2$ (**8**) with Li[tmp], which generates the analogous salt $[tmpH_2]^+[CpFe(CO)_2GaBr_3]^-$ (see Supporting Information).

By contrast, the reaction of **12** with Li[Mes*] proceeds as expected, generating the aryl(iodo)gallyl complex $Cp^*Fe(CO)_2Ga(Mes^*)I$, **3b**, in 33% isolated yield. Although single crystals of **3b** suitable for X-ray diffraction could not be obtained, its identity was confirmed by mass spectrometry (including exact mass determination) and by multinuclear NMR and IR data, which are essentially identical to those for the structurally characterized chloride analogue **3a**. Thus by analogy with $(\eta^5\text{-}C_5R_5)Fe(CO)_2Ga(Mes^*)Cl$ (**2**: R = H; **3a**: R = Me) a mononuclear complex containing a three-coordinate gallyl ligand would be expected. In a similar fashion, the reaction of **12** with $Na[Cp^*Fe(CO)_2]$ generates $[Cp^*Fe(CO)_2]_2GaI$ (**6b**) in reasonable yield, with the identity of the product (and its tricoordinate geometry at gallium) being confirmed by a combination of spectroscopic and crystallographic data.

Two routes to three-coordinate halogallium and -indium ligand systems have therefore been demonstrated: (i) simple salt elimination and (ii) insertion chemistry followed, where necessary, by halide substi-

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[28] For a previous example of a group 13 ligand system featuring a tmp substituent, see: Anand, B. N.; Crossing, I.; Nöth, H. *Inorg. Chem.* **1997**, *36*, 6, 1979.

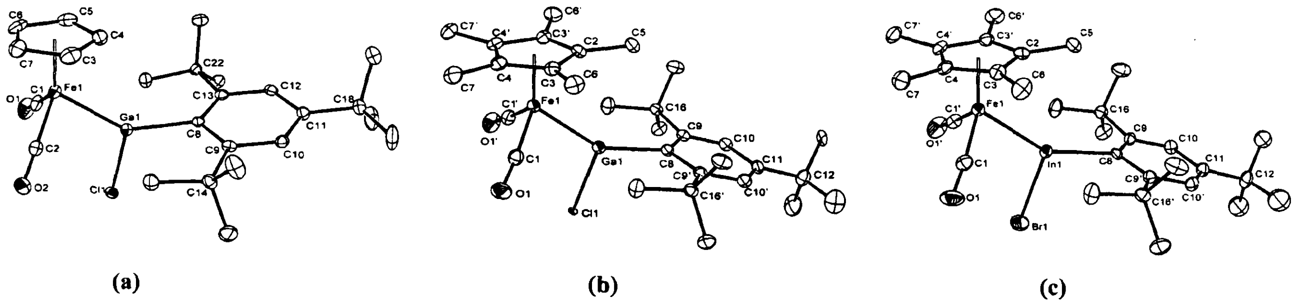

Figure 1. Structures of (a) CpFe(CO)$_2$Ga(Mes*)Cl, **2**; (b) Cp*Fe(CO)$_2$Ga(Mes*)Cl, **3a**; and (c) Cp*Fe(CO)$_2$In(Mes*)Br, **5**. Hydrogen atoms have been omitted for clarity and ORTEP ellipsoids set at the 50% probability level. Important bond lengths (Å) and angles (deg): (for **2**) Fe(1)−Ga(1) 2.346(1), Fe(1)−Cp centroid 1.713(4), Fe(1)−C(1) 1.758(5), Ga(1)−Cl(1) 2.272(1), Ga(1)−C(8) 1.997(3), Fe(1)−Ga(1)−C(8) 139.18(10), Fe(1)−Ga(1)−Cl(1) 112.62(3), Cl(1)−Ga(1)−C(8) 108.21(10), Cp centroid−Fe(1)−Ga(1)−C(8) 2.40(10), Fe(1)−Ga(1)−C(8)−C(9) 97.51(18); (for **3a**) Fe(1)−Ga(1) 2.372(2), Fe(1)−Cp* centroid 1.729(7), Fe(1)−C(1) 1.749(7), Ga(1)−Cl(1) 2.358(2), Ga(1)−C(8) 2.025(8), Fe(1)−Ga(1)−C(8) 146.7(2), Fe(1)−Ga(1)−Cl(1) 111.5(1), Cl(1)−Ga(1)−C(8) 101.8(2), Cp* centroid−Fe(1)−Ga(1)−C(8) 0.0(1), Fe(1)−Ga(1)−C(8)−C(9) 93.6(3); (for **5**) Fe(1)−In(1) 2.509 (1), Fe(1)−Cp* centroid 1.719(5), Fe(1)−C(1) 1.747(6), In(1)−Br(1) 2.610(1), In(1)−C(8) 2.178(7), Fe(1)−In(1)−C(8) 148.9(2), Fe(1)−In(1)−Br(1) 111.4(1), Br(1)−In(1)−C(8) 100.7(2), Cp* centroid−Fe(1)−In(1)−C(8) 0.0(1), Fe(1)−In(1)−C(8)−C(9) 94.2(2).

tution. The latter route, although potentially more powerful, in terms of the range of complexes accessible, typically lacks the convenience inherent in the one-pot salt elimination methodology.

(iii) Structural Studies. Single-crystal X-ray diffraction studies were undertaken on compounds **2**, **3a**, and **5**−**16**; of these, the structures of **7a**, **8**, **14**, and **16** were obtained predominantly for compound verification and show geometric features very similar to related derivatives. Hence these three structures, together with those of [tmpH$_2$]$^+$[CpFe(CO)$_2$GaBr$_3$]$^-$ and [CpFe(CO)$_3$]$^+$[CpFe(CO)$_2$Ga(I)Br$_2$]$^-$, are included only in the Supporting Information. The crystal structure of compound **6a** has been reported in a preliminary communication.[9] For the remaining compounds, details of data collection, structure solution, and refinement parameters are given in Table 1; relevant bond lengths and angles are included in the figure captions. Complete details of *all* structures are given in the Supporting Information and have been deposited with the Cambridge Structural Database.

Other than the complex (OC)$_5$MnGa(Mes*)Cl reported by Cowley and co-workers as a cocrystallite with (OC)$_5$MnGa(Mes*)(μ_2-O)Ga(Mes*)Mn(CO)$_5$,[11] aryl(chloro)gallyl species **2** and **3a** (Figure 1) represent the only structurally authenticated three-coordinate halogallyl systems to be reported in the literature; **5** represents the first simple neutral haloindyl complex to be structurally characterized.[12,29] As expected, the gallium/indium center in each case is trigonal planar [sum of angles = 360.0(1)°, 360.0(6)°, and 360.0(2)° for **2**, **3a**, and **5**, respectively], and the orientation of the gallyl/indyl ligand is such that it lies essentially coplanar with the Cp centroid−Fe−Ga plane [$\angle$Cp centroid−Fe−Ga−C$_{\text{ipso}}$ = 2.40(10)°, 0.0(1)°, and 0.0(1)° for **2**, **3a**, and **5**, respectively, the latter two angles being enforced by a crystallographic mirror plane]. This ligand orientation and the near perpendicular alignment of the gallyl and supermesityl planes [$\angle$Fe−Ga−C$_{\text{ipso}}$−C$_{\text{ortho}}$ = 97.5(2)°, 93.6(3)° and 94.2(2)° for **2**, **3a** and **5**, respectively] mirror those seen for boryl complexes of the type (η^5-C$_5$R$_5$)Fe(CO)$_2$B(Mes)X (Mes = C$_6$H$_2$Me$_3$-2,4,6)[7b,c,22] and are enforced largely to minimize steric interactions between the (η^5-C$_5$R$_5$) and aryl substituents. The steric bulk of the supermesityl substituent is presumably also responsible for the relatively long Fe−Ga bonds [2.346(1) and 2.372(2) Å for **2** and **3a**, respectively], with that for **2**, for example, being significantly longer that those reported for CpFe(CO)$_2$GaCl$_2$·thf and [CpFe(CO)$_2$GaCl$_2$]$_2$·dioxane [2.317(1) Å for both],[24] despite the reduction in coordination number at gallium from four to three. Differences *between* the structures of **2** and **3a** are presumably also primarily influenced by sterics, with the opening out of the Fe−Ga−C$_{\text{ipso}}$ angle [146.7(2)° vs 139.2(1)°] and lengthening of the Fe−Ga bond reflecting the greater size of the Cp* substituent. Interestingly, there is also a pronounced lengthening of the Ga−Cl bond [2.358(2) vs 2.272(1) Å], which, with subsequent halide abstraction chemistry in mind, may be indicative of a thermodynamically more attractive target bond.

The molecular structures of the halodiyl complexes [Cp*Fe(CO)$_2$]$_2$GaI (**6b**), [Cp*Fe(CO)$_2$]$_2$InI (**7b**), and {[CpFe(CO)$_2$]$_2$InI}$_2$ (**15**) are depicted in Figure 2. **6b** and **7b** [together with the related species **6a** (reported in our preliminary communication[9]) and **7a** (included in the Supporting Information)] represent the first structurally characterized neutral complexes containing three-coordinate bridging halogallanediyl or -indanediyl ligands [sum of angles = 359.96(2)° and 359.89(2)° for **6b** and **7b**, respectively].[12,29] As such, these compounds represent potential precursors for the synthesis of cationic trimetallic systems via halide abstraction.[9] Three-coordinate gallium centers of the type seen in **6b** have previously been observed only with bulky gallylene substituents such as Mes, ^{t}Bu, or CpFe(CO)$_2$, and the smaller size of the iodide ligand is presumably responsible for the shorter Fe−Ga bonds and wider Fe−Ga−Fe angle in **6b** {2.354 Å (mean) and 140.14(2)° for **6b** vs 2.432(2) Å, 124.42(7)°; 2.411 Å (mean), 122.4(1)°; 2.444 Å (mean), 120.0° (mean) for [Cp*Fe(CO)$_2$]$_2$GaMes, [CpFe(CO)$_2$]$_2$Ga^{t}Bu, and [CpFe(CO)$_2$]$_3$Ga, respectively}.[13]

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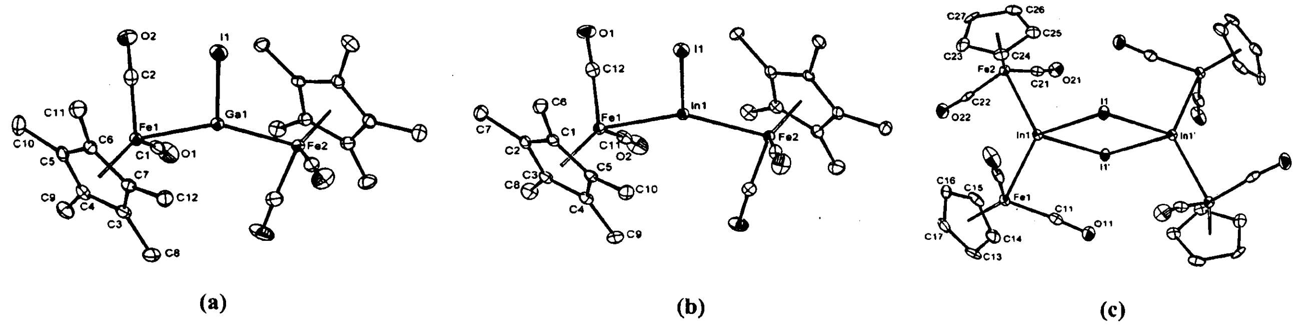
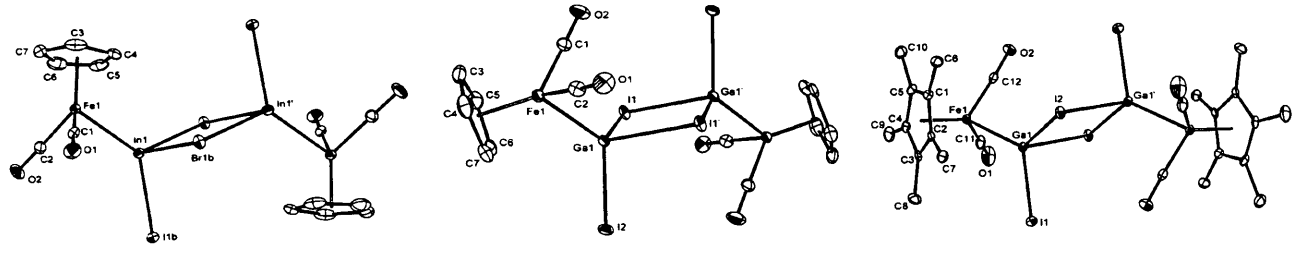
(29) For a related system containing an M−In(R)−halide unit in which the halide ligand bridges to a second group 13 center see: Steinke, T.; Gemel, C.; Cokoja, M.; Winter, M.; Fischer, R. A. *Chem. Commun.* **2003**, 1066.



(a) (b) (c)

Figure 2. Structures of (a) $[Cp^*Fe(CO)_2]_2GaI$, **6b**; (b) $[Cp^*Fe(CO)_2]_2InI$, **7b**; and (c) $\{[CpFe(CO)_2]_2InI\}_2$, **15**. Hydrogen atoms have been omitted for clarity and ORTEP ellipsoids set at the 50% probability level. Important bond lengths (Å) and angles (deg): (for **6b**) Fe(1)–Ga(1) 2.357(1), Fe(2)–Ga(1) 2.351(1), Fe(1)–C(1) 1.749(4), Fe(1)–Cp* centroid 1.732(2), Ga(1)–I(1) 2.701(1), Fe(1)–Ga(1)–Fe(2) 140.14(2), Fe(1)–Ga(1)–I(1) 109.01(2); (for **7b**) Fe(1)–In(1) 2.513(1), Fe(2)–In(1) 2.519(1), Fe(1)–C(11) 1.754(5), Fe(1)–Cp* centroid 1.726(5), In(1)–I(1) 2.854(4), Fe(1)–In(1)–Fe(2) 141.98(2), Fe(1)–In(1)–I(1) 110.30(2), Fe(2)–In(1)–I(1) 107.61(2); (for **15**) Fe(1)–In(1) 2.549(1), Fe(2)–In(1) 2.554(1), Fe(1)–C(11) 1.755(8), Fe(1)–Cp centroid 1.723(6), In(1)–I(1) 3.081(1), In(1)–I(1′) 2.932(1), Fe(1)–In(1)–Fe(2) 130.36(3), Fe(1)–In(1)–I(1) 102.15(3), Fe(2)–In(1)–I(1) 106.47(3), I(1)–In(1)–I(1′) 86.59(2).



(a) (b) (c)

Figure 3. Structures of (a) $[CpFe(CO)_2In(I)Br]_2$, **9**; (b) $[CpFe(CO)_2GaI_2]_2$, **11**; and (c) $[Cp^*Fe(CO)_2GaI_2]_2$, **12**. Hydrogen atoms have been omitted for clarity and ORTEP ellipsoids set at the 50% probability level. Important bond lengths (Å) and angles (deg): (for **9**) Fe(1)–In(1) 2.480(1), Fe(1)–C(1) 1.770(9), Fe(1)–Cp centroid 1.730(8), In(1)–Br(1b) 2.974(10), In(1)–Br(1b′) 2.623(10), In(1)–I(1b) 2.704(3), Fe(1)–In(1)–I(1b) 130.71(6), Br(1b)–In(1)–Br(1b′) 82.7(3); (for **11**) Fe(1)–Ga(1) 2.321(1), Fe(1)–C(1) 1.757(8), Fe(1)–Cp centroid 1.717(8), Ga(1)–I(1) 2.799(1), Ga(1)–I(1′) 2.731(1), Ga(1)–I(2) 2.557(1), Fe(1)–Ga(1)–I(2) 126.48(4), I(1)–Ga(1)–I(1′) 91.59(2); (for **12**) Fe(1)–Ga(1) 2.314(1), Fe(1)–C(11) 1.746(6), Fe(1)–Cp* centroid 1.725(4), Ga(1)–I(1) 2.585(1), Ga(1)–I(2) 2.756(1), Ga(1)–I(2′) 2.789(1), Fe(1)–Ga(1)–I(1) 124.72(3), I(2)–Ga(1)–I(2′) 92.01(2).

In the cases of both **6a** and **7b**, the trigonal planar ligand geometries contrast with those observed for the corresponding complexes containing the less bulky (η^5-C_5H_5) ligand.[9] Thus, $[CpFe(CO)_2]_2GaCl$ is polymeric (featuring bridging Ga–Cl–Ga units)[25] and readily coordinates external bases such as thf, dioxane, or chloride.[24,31] As might be expected given the decreased coordination number at gallium in **6a**, the Fe–Ga distances are shorter and the Fe–Ga–Fe angle wider than those found in four-coordinate complexes {e.g., 2.365(1) Å, 135.58(4)°; 2.390 Å (mean), 129.51(4)°; 2.430 Å (mean), 127.81(4)° for $[CpFe(CO)_2]_2GaCl$, $[CpFe(CO)_2]_2GaCl{\cdot}thf$, $[CpFe(CO)_2]_2GaCl_2^-$, respectively}.[9,24,25,29] Similar steric influences are presumably responsible for the analogous differences between **7b** and **15** [d(Fe–In) = 2.513(1), 2.549(1) Å, ∠Fe–In–Fe = 141.98(2)°, 130.36(3)°, respectively], with the four-coordinate halide-bridged structure of the latter mirroring that of the corresponding chloride $\{[CpFe(CO)_2]_2InCl\}_2$.[15f]

The dimeric, halide-bridged structures of $[CpFe(CO)_2E(I)Br]_2$ (**8**: E = Ga; **9**: E = In) and $[(\eta^5$-$C_5R_5)Fe(CO)_2GaI_2]_2$ (**11**: R = H; **12**: R = Me) have been confirmed crystallographically (Figure 3). Although a similar $L_nME(X)(\mu$-$X)_2E(X)ML_n$ motif exists in the species $[CpFe(CO)_2GaCl_2]_2(GaCl_3)_2$, reported by Barron and co-workers,[25] complexes **8**, **9**, **11**, and **12** represent the first structurally characterized neutral base-free dihalogallyl or -indyl species to be reported.[32,33] Not unsurprisingly, these dimeric structures contrast with that reported by Braunschweig and co-workers for the related dihaloboryl system $CpFe(CO)_2BCl_2$, which is monomeric and features a trigonal planar group 13 center.[34] The disparate terminal and bridging Ga–X distances [e.g., 2.585(1) and 2.756(1) Å for **12** (X = I)] and narrow $Ga(\mu$-$X)_2$ angles [e.g., 92.01(2)° for **12**] are reminiscent of the geometries found for related derivatives of the type $Y(X)Ga(\mu$-$X)_2Ga(X)Y$ [e.g., 2.714 (mean), 2.490(1) Å and 92.78(2)° for $(Cp^*GaI_2)_2$].[35]

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[31] Ueno, W.; Watanabe, T.; Ogino, H. *Organometallics* **2000**, *19*, 5679.

[32] For examples of Lewis base adducts of the type $CpFe(CO)_2GaX_2{\cdot}L$, see for example, ref 24, and: Fischer, R. A.; Miehr, A.; Priermeier, T. *Chem. Ber.* **1995**, *128*, 831.

[33] For a report of the synthesis (but not the crystal structure) of a compound of empirical composition $Cp^*Fe(CO)_2GaCl_2$ see ref 8b and: Ueno, K.; Watanabe, T.; Tobita, H.; Ogino, H. *Organometallics* **2003**, *22*, 4375.

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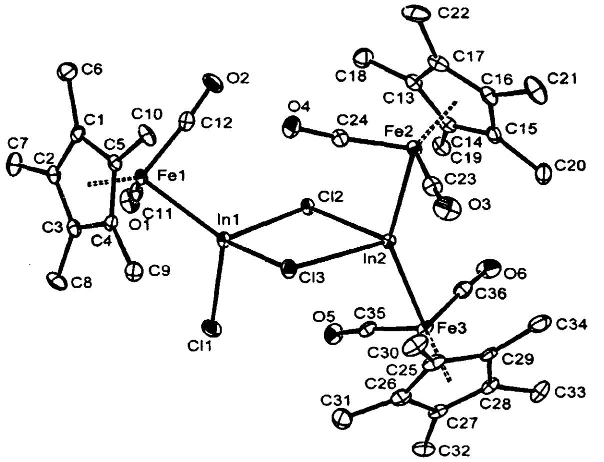

Figure 4. Structure of [Cp*Fe(CO)$_2$]$_2$In(μ-Cl)$_2$InCl[Fe(CO)$_2$Cp*], **13**. Hydrogen atoms have been omitted for clarity and ORTEP ellipsoids set at the 50% probability level. Important bond lengths (Å) and angles (deg): Fe(1)−In(1) 2.488(1), Fe(2)−In(2) 2.546(1), Fe(3)−In(2) 2.540(1), In(1)−Cl(1) 2.403(2), In(1)−Cl(2) 2.527(2), In(1)−Cl(3) 2.503(2), In(2)−Cl(2) 2.754(2), In(2)−Cl(3) 2.782(2), Cl(2)−In(1)−Cl(3) 89.04(5), Cl(2)−In(2)−Cl(3) 79.15(5).

An interesting variation on the theme of dinuclear halide-bridged complexes is seen in the structure of [Cp*Fe(CO)$_2$]$_2$In(μ-Cl)$_2$InCl[Fe(CO)$_2$Cp*], **13**. This effectively represents a chloride-bridged 1:1 adduct between [Cp*Fe(CO)]$_2$InCl and Cp*Fe(CO)$_2$InCl$_2$ fragments and features a highly asymmetric In$_2$Cl$_2$ bridging unit. Unusually **13** shows the first indication of quaternization via a donor/acceptor interaction at a group 13 center bearing two bulky [Cp*Fe(CO)]$_2$ fragments. Although this structural motif is common for less bulky organometallic fragments (cf. the chloride-bridged structure of [{CpFe(CO)$_2$}$_2$InCl]$_2$[15f]), complexes of the type [Cp*Fe(CO)]$_2$EX examined in this study have typically shown little or no tendency toward coordination of external bases at E. As might be expected, given the differing steric requirements of the peripheral substituents, the bridging In−Cl bond lengths and Cl−In−Cl angle associated with In(2) are significantly different than those associated with In(1) [2.781(2), 2.754(2) Å, 79.14(5)° vs 2.503(2), 2.527(2) Å, 89.01(5)°].

The structure of CpFe(CO)$_2$GaI$_2$(μ-I)Fe(CO)$_2$Cp, **10**, an intermediate in the reaction pathway from CpFe(CO)$_2$I and GaI to [CpFe(CO)$_2$GaI$_2$]$_2$ (**11**), is shown in Figure 5 and consistent with its description as a donor/acceptor adduct between CpFe(CO)$_2$I and CpFe(CO)$_2$GaI$_2$. Thus the bridging Ga−I linkage is significantly longer than the terminal Ga−I bonds [2.788(1) vs 2.596(1) and 2.605(1) Å]. Somewhat surprisingly, however, the Fe−I distance [2.589(1) Å] is actually slightly *shorter* than that found in "free" CpFe(CO)$_2$I [2.607 Å (mean)].[36]

Conclusions

Transition metal complexes containing three-coordinate halogallium and -indium ligands represent the key precursors to unsaturated cationic species of the type [L$_n$M(EX)]$^+$ via halide abstraction chemistry. The application of two routes to these systems has been demonstrated: (i) simple salt elimination using organometallic anions and (ii) insertion chemistry followed, where necessary, by halide substitution. The latter route, although potentially more powerful, in terms of the range of complexes accessible, lacks the convenience inherent in the one-pot salt elimination methodology. Crystallographic studies have confirmed the presence of the target trigonal planar ligand systems both in gallyl/indyl complexes of the type L$_n$M-E(Aryl)X and in halodiyl systems of the type (L$_n$M)$_2$EX. Furthermore, the crucial role of steric factors in preventing halide-bridged oligomerization has been emphasized, e.g., by comparison of [(η^5-C$_5$R$_5$)Fe(CO)$_2$]$_2$InI (R = H, Me). Further studies utilizing these three-coordinate systems in the synthesis of unsaturated transition metal/group 13 cations are reported in a subsequent paper.[37]

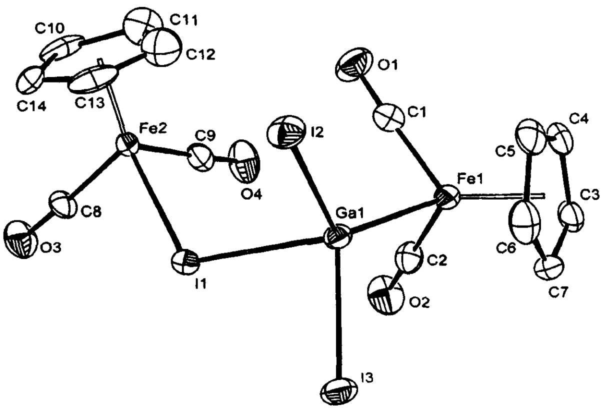

Figure 5. Structure of (a) CpFe(CO)$_2$GaI$_2$(μ-I)Fe(CO)$_2$Cp, **10**. Hydrogen atoms have been omitted for clarity and ORTEP ellipsoids set at the 50% probability level. Important bond lengths (Å) and angles (deg): Fe(1)−Ga(1) 2.331(2), Fe(1)−C(1) 1.740(11), Fe(1)−Cp centroid 1.726(9), Ga(1)−I(1) 2.788(1), Ga(1)−I(2) 2.596(1), Ga(1)−I(3) 2.605(1), Fe(2)−I(1) 2.589(1), Fe(2)−C(8) 1.760(8), Fe(2)−Cp centroid 1.727(8), Fe(1)−I(1)−Fe(2) 116.01(4), I(2)−Ga(1)−I(3) 106.60(4), Fe(1)−Ga(1)−I(2) 117.95(5), Fe(1)−Ga(1)−I(3) 117.98(5).

Acknowledgment. We would like to acknowledge the support of the EPSRC for funding this project and the EPSRC National Mass Spectrometry Service Centre, University of Wales Swansea.

Supporting Information Available: Complete details of the crystal structures of compounds **2**, **3a**, **5−16**, [tmpH$_2$]$^+$[CpFe(CO)$_2$GaBr$_3$]$^-$, and [CpFe(CO)$_3$]$^+$[CpFe(CO)$_2$Ga(I)Br$_2$]$^-$ are included. NMR spectra for all compounds have also been included as evidence for bulk purity. This material is available free of charge via the Internet at http://pubs.acs.org.

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Halide Abstraction as a Route to Cationic Transition-Metal Complexes Containing Two-Coordinate Gallium and Indium Ligand Systems

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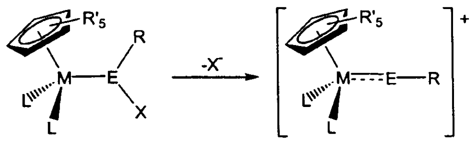
Received July 26, 2005

Halide abstraction chemistry offers a viable synthetic route to the cationic two-coordinate complexes $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}E)]^+$ (**7**, E = Ga; **8**, E = In) featuring linear bridging gallium or indium atoms. Structural, spectroscopic, and computational studies undertaken on **7** are consistent with appreciable Fe−Ga π-bonding character; in contrast, the indium-bridged complex **8** is shown to feature a much smaller π component to the metal−ligand interaction. Analogous reactions utilizing the supermesityl-substituted gallyl or indyl precursors of the type $(\eta^5\text{-}C_5R_5)Fe(CO)_2E(Mes^*)X$, on the other hand, lead to the synthesis of halide-bridged species of the type $[\{(\eta^5\text{-}C_5R_5)Fe(CO)_2E(Mes^*)\}_2(\mu\text{-}X)]^+$, presumably by trapping of the highly electrophilic putative cationic diyl complex $[(\eta^5\text{-}C_5R_5)Fe(CO)_2E(Mes^*)]^+$.

Introduction

Compounds offering the potential for multiple bonding involving the heavier group 13 elements have attracted considerable attention in recent years, with studies reporting examples of both homo- and heteronuclear multiple bonds having appeared in the literature.[1] Within this sphere, the transition-metal diyl complexes $L_nM(EX)$ have been the subject of considerable debate,[2,3] primarily concerning the nature of the interaction between the group 13 and transition-metal centers. The description of superficially similar complexes as being bound via multiple bonds (e.g. $L_nM{=}EX$ or $L_nM{\equiv}EX$) or via donor/acceptor interactions ($L_nM{\leftarrow}EX$) reflects not only the fundamental questions of structure and bonding posed by such systems but also the lack of definitive experimental verification of potential bonding models.[4]

Scheme 1. Halide Abstraction Methodology for Cationic Transition-Metal Complexes Containing Two-Coordinate Group 13 Ligands (E = Group 13 Element; R = Bulky Substituent; X = Halide; L = Generic Ligand Coordinated to Transition Metal M)



I

In an attempt to broaden the scope of synthetic methodologies available for unsaturated group 13 systems, we have been examining the use of halide abstraction chemistry to generate cationic derivatives (Scheme 1).[5] A series of preliminary computational analyses has suggested that the positive charge in cationic terminal diyl species, $[L_nM(EX)]^+$, resides primarily at the group 13 center (e.g. Mulliken charges of +0.438, +0.680, and +0.309 for $[Cp^*Fe(CO)_2E(Mes)]^+$; E = B, Al, Ga) and that M→E back-bonding may

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† Née Coombs.

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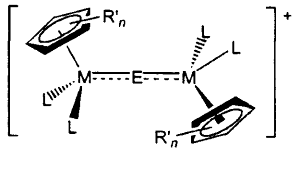
10.1021/om0506318 CCC: $30.25

Chart 1. Cationic Trimetallic Systems Featuring Naked Group 13 Atoms as Bridging Ligands (E = Group 13 Element; L = Generic Ligand Coordinated to Transition Metal M)



II

contribute appreciably to the overall metal−ligand interaction (e.g., a 38% π contribution to the FeB bonding density in $[Cp^*Fe(CO)_2B(Mes)]^+$).[6] Hence, the Fe=B double bond in $[Cp^*Fe(CO)_2B(Mes)]^+$ can be described simplistically as being comprised of B→Fe σ-donor and Fe→B π-acceptor components. Recently we have been seeking to extend this synthetic approach from boron to the heavier group 13 elements and from isolated metal−ligand bonds (i.e. **I**) to delocalized trimetallic systems featuring naked group 13 atoms as ligands (i.e. **II**; Chart 1).[7]

Herein we report an extended investigation into the use of halide abstraction chemistry in heavier group 13 systems, leading to the synthesis of cationic derivatives containing gallium and indium donors. This has allowed for comparative spectroscopic, structural, and computational probes of M−E bond character as a function of the element E, thereby probing the controversial subject of multiple bonding involving the heavier group 13 elements. In addition, preliminary studies of the fundamental reactivity of the trimetallic systems $[L_nM(\mu\text{-}E)ML_n]^+$ (E = Ga, In) are reported.

Experimental Section

(i) General Considerations. All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk line or drybox techniques. Solvents were predried over sodium wire (hexanes, toluene, thf) or molecular sieves (dichloromethane) and purged with nitrogen prior to distillation from the appropriate drying agent (hexanes, potassium; toluene and thf, sodium; dichloromethane, CaH_2). Benzene-d_6 and dichloromethane-d_2 (both Goss) were degassed and dried over the appropriate drying agent (potassium or molecular sieves) prior to use. $Na[BPh_4]$, $[^nBu_4N]I$, and [PPN]Cl were dried in vacuo prior to use; the compounds $(\eta^5\text{-}C_5R_5)Fe(CO)_2E(Mes^*)X$ (Mes* = supermesityl = $C_6H_2{}^tBu_3$-2,4,6; **1**, E = Ga, R = H, X = Cl; **2**, E = Ga, R = Me, X = Cl; **3**, E = In, R = H, X = Br), $[Cp^*Fe(CO)_2]_2EX$ (**4**, E = Ga, X = Cl; **5**, E = In, X = Br; **6**, E = In, X = I), and $Na[BAr^f_4]$ ($Ar^f = C_6H_3(CF_3)_2$-3,5) were prepared by literature methods.[8,9]

NMR spectra were measured on a Bruker AM-400 or JEOL 300 Eclipse Plus FT-NMR spectrometer. Residual signals of the solvent were used for reference for ^{1}H and ^{13}C NMR, while a sealed tube containing a solution of $[^nBu_4N][B_3H_8]$ in $CDCl_3$ was used as an external reference for ^{11}B NMR and $CFCl_3$ was used as a reference for ^{19}F NMR. Infrared spectra were measured for each compound either pressed into a disk with excess dry KBr or as a solution in the appropriate solvent, on a Nicolet 500 FT-IR spectrometer. Mass spectra were measured by the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea, Wales. Perfluorotributylamine was used as the standard for high-resolution EI mass spectra. Despite repeated attempts, satisfactory elementary microanalyses for the new cationic gallium and indium complexes were frustrated by their extreme air and moisture sensitivity. Characterization of the new compounds is therefore based upon multinuclear NMR, IR, and mass spectrometry data (including accurate mass measurement), supplemented by single-crystal X-ray diffraction studies in the cases of **7**, **8**, **10**, and **14**. In all cases the purity of the bulk material was established by multinuclear NMR to be >95% (see the Supporting Information). Abbreviations: br = broad, s = singlet, q = quartet, m = multiplet.

(ii) Syntheses. $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}Ga)][BAr^f_4]$ (7). To a suspension of $Na[BAr^f_4]$ (0.067 g, 0.075 mmol) in dichloromethane (10 mL) at −78 °C was added a solution of **4** (0.045 g, 0.075 mmol) in dichloromethane (10 mL), and the reaction mixture was warmed to 20 °C over 30 min. Further stirring for 20 min, filtration, and removal of volatiles in vacuo yielded **7** as a golden yellow powder (0.050 g, 46%). X-ray-quality crystals were grown by layering a dichloromethane solution with hexanes at −30 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.93 (s, 30H, Cp*), 7.54 (s, 4H, para CH of $BAr^f_4{}^-$), 7.70 (s, 8H, ortho CH of $BAr^f_4{}^-$). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 10.3 (CH_3 of Cp*), 97.5 (quaternary of Cp*), 117.5 (para CH of $BAr^f_4{}^-$), 122.8 (q, $^1J_{CF}$ = 273 Hz, CF_3 of $BAr^f_4{}^-$), 128.8 (q, $^2J_{CF}$ = 34 Hz, meta C of $BAr^f_4{}^-$), 134.8 (ortho CH of $BAr^f_4{}^-$), 160.8 (q, $^1J_{CB}$= 53 Hz, ipso C of $BAr^f_4{}^-$), 211.4 (CO). ^{19}F NMR (283 MHz, CD_2Cl_2): δ −62.8 (CF_3). ^{11}B NMR (96 MHz, CD_2Cl_2): δ −7.6 ($BAr^f_4{}^-$). IR (CH_2Cl_2): ν(CO) 2016, 1994, 1963 cm^{-1}. MS: ES−, *m/z* 863 (100%) $[BAr^f_4]^-$; ES+, *m/z* 563 (5%) $[M]^+$, correct isotope distribution for 2 Fe and 1 Ga atoms. Exact mass: calcd for $[M]^+$ 563.0093, found 563.0092.

$[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}In)][BAr^f_4]$ (8). To a suspension of $Na[BAr^f_4]$ (0.057 g, 0.064 mmol) in dichloromethane (4 mL) at −78 °C was added a solution of **5** (0.044 g, 0.064 mmol) in dichloromethane (4 mL), and the reaction mixture was warmed to 20 °C over 30 min. Further stirring for 90 min, filtration, and layering with hexanes and storage at −30 °C yielded **8** as orange crystals suitable for X-ray diffraction (0.060 g, 64%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.85 (s, 30H, Cp*), 7.44 (s, 4H, para CH of $BAr^f_4{}^-$), 7.64 (s, 8H, ortho CH of $BAr^f_4{}^-$). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 10.4 (CH_3 of Cp*), 96.5 (quaternary of Cp*), 117.8 (para CH of $BAr^f_4{}^-$), 124.6 (q, $^1J_{CF}$ = 272 Hz, CF_3 of $BAr^f_4{}^-$), 128.9 (q, $^2J_{CF}$ = 35 Hz, meta C of $BAr^f_4{}^-$), 134.8 (ortho CH of $BAr^f_4{}^-$), 161.8 (q, $^1J_{CB}$ = 50 Hz, ipso C of $BAr^f_4{}^-$), 211.9 (CO). ^{19}F NMR (283 MHz, CD_2Cl_2): δ −62.7 (CF_3). ^{11}B NMR (96 MHz, CD_2Cl_2): δ −7.6 ($BAr^f_4{}^-$). IR (CD_2Cl_2): ν(CO) 2005, 1983, 1951 cm^{-1}. MS: ES−, *m/z* 863 (100%) $[BAr^f_4]^-$; ES+, *m/z* 609 (6%) $[M]^+$, correct isotope distribution for 2 Fe and 1 In atoms, significant fragment ions at *m/z* 581 (weak) $[M - CO]^+$, 553 (5%) $[M - 2CO]^+$. Exact mass: calcd for $[M]^+$ 608.9876, found 608.9884.

Reaction of $[Cp^*Fe(CO)_2]_2InI$ (6) with $Na[BAr^f_4]$: Isolation of $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}I)][BAr^f_4]$ (9). To a suspension of $Na[BAr^f_4]$ (0.111 g, 0.13 mmol) in dichloromethane (6 mL) at −78 °C was added a solution of **6** (0.092 g, 0.13 mmol) in dichloromethane (8 mL), and the reaction mixture was warmed to 20 °C over 30 min. Further stirring for 3 h, filtration, and layering with hexanes yielded orange crystals of **9** (0.028 g, 15%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.84 (s, 30H, Cp*), 7.48 (s, 4H, para CH of $BAr^f_4{}^-$), 7.64 (s, 8H, ortho CH of $BAr^f_4{}^-$). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 10.4 (CH_3 of Cp*), 96.1 (quaternary of Cp*), 117.5 (para CH of $BAr^f_4{}^-$), 124.6 (q, $^1J_{CF}$ = 274 Hz, CF_3 of $BAr^f_4{}^-$), 128.9 (q, $^2J_{CF}$ = 31 Hz, meta C of $BAr^f_4{}^-$), 134.8 (ortho CH of $BAr^f_4{}^-$), 161.8 (q, $^1J_{CB}$ = 49 Hz, ipso C of $BAr^f_4{}^-$), 212.8 (CO). ^{19}F NMR (283 MHz, CD_2Cl_2): δ

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[6] Aldridge, S.; Rossin, A.; Coombs, D. L.; Willock, D. J. *Dalton Trans.* **2004**, 2649.

[7] For a preliminary report of part of this work see: Bunn, N. R.; Aldridge, S.; Coombs, D. L.; Rossin, A.; Willock, D. J.; Jones, C. Ooi., L.-L. *Chem. Commun.* **2004**, 1732.

[8] Bunn, N. R.; Aldridge, S.; Kays, D. L.; Coombs, N. D.; Day, J. K.; Ooi, L.-L., Coles, S. J.; Hursthouse, M. B. *Organometallics* **2005**, *24*, 5879.

[9] Reger, D. L.; Wright, T. D.; Little, C. A.; Lamba, J. J. S.; Smith, M. D. *Inorg. Chem.* **2001**, *40*, 3810.

−62.8 (CF_3). ^{11}B NMR (96 MHz, CD_2Cl_2): δ −7.6. IR (CH_2Cl_2): ν(CO) 2003, 1984, 1952 cm^{-1}. MS: ES−, 863 (100%) $[BAr^f_4]^-$; ES+, 621 (50%) $[M]^+$, correct isotope distribution for 2 Fe and 1 I atoms, significant fragment ions at *m/z* 593 (weak) $[M - CO]^+$, 565 (20%) $[M - 2CO]^+$, 537 (45%) $[M - 3CO]^+$, 509 (5%) $[M - 4CO]^+$. Exact mass: calcd for $[M]^+$ 620.9882, found 620.9872.

Reaction of $[Cp^*Fe(CO)_2]_2InI$ (6) with $Na[BPh_4]$. To a suspension of $Na[BPh_4]$ (0.074 g, 0.22 mmol) in dichloromethane (10 mL) at −78 °C was added a solution of **6** (0.080 g, 0.11 mmol) in dichloromethane (10 mL), and the reaction mixture was warmed slowly to 20 °C. Monitoring the reaction mixture by IR spectroscopy over a period of 72 h led to the gradual disappearance of the peaks due to the starting material (1969, 1957, and 1922 cm^{-1}) and the growth of bands at 2016, 1995, 1970, and 1940 cm^{-1}. Monitoring by ^{11}B NMR spectroscopy also revealed the growth of a strong broad signal at δ_B 67.0. Filtration of the supernatant solution, removal of volatiles in vacuo, and recrystallization from hexanes at −30 °C led to the formation of crops of colorless and dark red microcrystalline material, which were identified as BPh_3 (δ_B 67.0) and a mixture of $Cp^*Fe(CO)_2I$ (ν(CO) 2016 and 1970 cm^{-1}) and $Cp^*Fe(CO)_2Ph$ (ν(CO) 1995 and 1940 cm^{-1}), respectively, by comparison of multinuclear NMR, IR, and mass spectrometric data with those reported previously.[10] A similar procedure was adopted to monitor the reaction of $[Cp^*Fe(CO)_2]_2GaCl$ (**4**) with $Na[BPh_4]$; in this case both BPh_3 and $Cp^*Fe(CO)_2Ph$ were isolated and identified by comparison with literature data.[10]

Reactions of $(\eta^5\text{-}C_5R_5)Fe(CO)_2E(Mes^*)X$ (1, R = H, E = Ga, X = Cl; 2, R = Me, E = Ga, X = Cl; 3, R = H, E = In, X = Br) with $Na[BAr^f_4]$: Syntheses of $[\{(\eta^5\text{-}C_5R_5)Fe(CO)_2E(Mes^*)\}_2(\mu\text{-}X)][BAr^f_4]$ (10, R = H, E = Ga, X = Cl; 11, R = Me, E = Ga, X = Cl; 12, R = H, E = In, X = Br). The three reactions were carried out in a similar manner, exemplified for **1**. To a suspension of $Na[BAr^f_4]$ (0.042 g, 0.047 mmol) in dichloromethane-d_2 (1 mL) at −78 °C was added dropwise a solution of $CpFe(CO)_2Ga(Mes^*)Cl$ (**1**; 0.025 g, 0.047 mmol) in dichloromethane-d_2 (5 mL), and the reaction mixture was warmed to 20 °C over 30 min. At this point, the reaction was judged to be complete by ^{1}H NMR spectroscopy; filtration and layering with hexanes led to the isolation of **10** as crystals suitable for X-ray diffraction (yield: 0.021 g, 24%). **11** and **12** were isolated as pale yellow microcrystalline materials in yields of 31 and 28%, respectively.

Data for **10** are as follows. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.25 (s, 9H, para ^{t}Bu), 1.46 (s, 18H, ortho ^{t}Bu), 4.88 (s, Cp), 7.34 (s, 2H, aryl CH of Mes*), 7.55 (s, 4H, para CH of $BAr^f_4{}^-$), 7.71 (s, 8H, ortho CH of $BAr^f_4{}^-$). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 30.9 (CH_3 of para ^{t}Bu), 34.0 (CH_3 of ortho ^{t}Bu), 34.7 (quaternary of para ^{t}Bu), 38.2 (quaternary of ortho ^{t}Bu), 83.5 (Cp), 117.4 (para CH of $BAr^f_4{}^-$), 119.4 (meta CH of Mes*), 122.9 (q, $^1J_{CF}$ = 273 Hz, CF_3 of $BAr^f_4{}^-$), 128.8 (q, $^2J_{CF}$ = 31 Hz, meta C of $BAr^f_4{}^-$), 134.9 (ortho CH of BAr^f_4), 154.9 (para C of Mes*), 155.0 (ortho C of Mes*), 212.7 (CO), ipso carbons undetected. ^{11}B NMR (96 MHz, CD_2Cl_2): δ −7.6 ($BAr^f_4{}^-$). ^{19}F NMR (283 MHz, CD_2Cl_2): δ −62.7 (CF_3). IR (CD_2Cl_2): ν(CO) 2016, 2002, 1972, 1954 cm^{-1}. MS (EI): *m/z* 963.7 (5%) $[M - 2CO]^+$, correct isotope distribution for 2 Fe, 2Ga and 1 Cl atoms, significant fragment ions at *m/z* 527.1 (5%) $[CpFe(CO)_2Ga(Mes^*)Cl]^+$, 491.1 (20%) $[CpFe(CO)_2Ga(Mes^*)]^+$.

Data for **11** are as follows. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.25 (s, 18H, para ^{t}Bu), 1.42 (s, 36H, ortho ^{t}Bu), 1.76 (s, 30H, Cp*), 7.30 (s, 4H, aryl CH of Mes*), 7.50 (s, 4H, para CH of $BAr^f_4{}^-$), 7.66 (s, 8H, ortho CH of $BAr^f_4{}^-$). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 10.0 (CH_3 of Cp*), 30.9 (CH_3 of para ^{t}Bu), 33.9 (CH_3 of ortho ^{t}Bu), 34.7 (quaternary of para ^{t}Bu), 38.5 (quaternary of ortho ^{t}Bu), 95.5 (quaternary of Cp*), 117.5 (para CH of $BAr^f_4{}^-$), 123.4 (meta CH of Mes*), 124.6 (q, $^1J_{CF}$ = 272 Hz, CF_3 of $BAr^f_4{}^-$), 128.9 (q, $^2J_{CF}$ = 31 Hz, meta C of $BAr^f_4{}^-$), 134.9 (ortho CH of $BAr^f_4{}^-$), 137.9 (ipso C of Mes*), 151.6 (para C of Mes*), 155.4 (ortho C of Mes*), 161.8 (q, $^1J_{CB}$ = 50 Hz, ipso C of $BAr^f_4{}^-$), 214.5 (CO). ^{11}B NMR (96 MHz, CD_2Cl_2): δ −7.6 ($BAr^f_4{}^-$). ^{19}F NMR (283 MHz, CD_2Cl_2): δ −62.8 (CF_3). ν(CO) 1996, 1986, 1954, 1932 cm^{-1}. MS (EI): *m/z* 1131.1 (weak) $[M - CO]^+$, correct isotope distribution for 2 Fe, 2Ga and 1 Cl atoms, significant fragment ions at *m/z* 723.0 (25%) $[Cp^*Fe(CO)_2GaAr^f_2Cl - 2CO]^+$, 650.1 (100%) $[BAr^f_3]^+$, 631.1 (80%) $[BAr^f_3 - F]^+$.

Data for **12** are as follows. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.18 (s, 18H, para ^{t}Bu), 1.32 (s, 36H, ortho ^{t}Bu), 4.81 (s, 10H, Cp), 7.29 (s, 4H, aryl CH of Mes*), 7.37 (s, 4H, para CH of $BAr^f_4{}^-$), 7.57 (s, 8H, ortho CH of $BAr^f_4{}^-$). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 31.0 (CH_3 of para ^{t}Bu), 33.6 (CH_3 of ortho ^{t}Bu), 34.9 (quaternary of para ^{t}Bu), 37.7 (quaternary of ortho ^{t}Bu), 82.5 (Cp), 117.4 (para CH of $BAr^f_4{}^-$), 122.2 (meta CH of Mes*), 123.5 (q, $^1J_{CF}$ = 273 Hz, CF_3 of $BAr^f_4{}^-$), 128.7 (q, $^2J_{CF}$ = 29 Hz, meta C of $BAr^f_4{}^-$), 134.8 (ortho CH of $BAr^f_4{}^-$), 151.2 (para C of Mes*), 155.3 (ortho C of Mes*), 161.5 (q, $^1J_{CB}$ = 49 Hz, ipso C of $BAr^f_4{}^-$), 212.4 (CO), ipso carbon of Mes* not detected. ^{11}B NMR (96 MHz, CD_2Cl_2): δ −7.6 ($BAr^f_4{}^-$). ^{19}F NMR (283 MHz, CD_2Cl_2): δ_F −62.7 (CF_3). IR (CD_2Cl_2): ν(CO) 2013, 1977, 1968 cm^{-1}. MS (EI): *m/z* 1140.8 (5%) $[M - Me]^+$, correct isotope distribution for 2 Fe, 2 In, and 1 Br atoms, significant fragment ions at *m/z* 1127.8 $[M - 2CO]^+$, 650 (100%) $[BAr^f_3]^+$, 631 (80%) $[BAr^f_3 - F]^+$.

Reaction of 7 with [PPN]Cl: Synthesis of $[Cp^*Fe(CO)_2]_2GaCl$ (4). To a solution of [PPN]Cl (0.020 mg, 0.035 mmol) in dichloromethane-d_2 (1 mL) was added a solution of **7** (0.050 g, 0.035 mmol) in dichloromethane-d_2 (3 mL) at room temperature. The reaction mixture was sonicated for 1 h, after which time ^{1}H NMR spectroscopy revealed complete conversion to **4** (quantitative conversion by NMR). Further comparison of multinuclear NMR and IR data (for the isolated compound) with those obtained for an authentic sample of **4** confirmed the identity of **4** as the sole organometallic product.[7,8]

Reaction of 8 with $[^nBu_4N]I$: Synthesis of $[Cp^*Fe(CO)_2]_2InI$ (6). To a solution of $[^nBu_4N]I$ (0.010 g, 0.03 mmol) in dichloromethane-d_2 (1 mL) was added a solution of **8** (0.021 g, 0.01 mmol) in dichloromethane-d_2 (2 mL) at room temperature. The reaction mixture was sonicated for 1 h, after which time ^{1}H NMR spectroscopy revealed complete conversion to **6** (quantitative conversion by NMR). Further comparison of multinuclear NMR and IR data (for the isolated compound) with those obtained for an authentic sample confirmed the identity of **6** as the sole organometallic product.[8]

Reactions of 7 and 8 with thf: Syntheses of $[\{Cp^*Fe(CO)_2\}_2\{\mu\text{-}E(thf)\}][BAr^f_4]$ (13, E = Ga; 14, E = In). The two reactions were carried out in a similar manner, exemplified for **7**. To a solution of **7** in dichloromethane (12 mL), prepared in situ from $Na[BAr^f_4]$ (0.059 g, 0.067 mmol) and $[Cp^*Fe(CO)_2]_2GaCl$ (**4**; 0.040 g, 0.067 mmol) at −78 °C, was added thf (2 mL), and the reaction mixture warmed to 20 °C over 30 min. After the mixture was stirred for a further 1 h at 20 °C, the reaction was judged to be complete by IR spectroscopy; filtration and cooling to −30 °C led to the isolation of $[\{Cp^*Fe(CO)_2\}_2\{\mu\text{-}Ga(thf)\}][BAr^f_4]$ (**13**) as a pale yellow microcrystalline solid (yield: 0.035 g, 35%). **14** was isolated in a similar manner as single crystals suitable for X-ray diffraction (0.030 g, 41%).

Data for **13** are as follows. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.80 (br m, 4H, CH_2 of thf), 1.86 (s, 30H, Cp*), 3.65 (br m, 4H, CH_2 of thf), 7.48 (s, 4H, para CH of $BAr^f_4{}^-$), 7.65 (s, 8H, ortho CH of $BAr^f_4{}^-$). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 10.2 (CH_3 of Cp*), 25.5 (CH_2 of thf), 69.0 (CH_2 of thf), 97.4 (quaternary of Cp*), 117.6 (para CH of $BAr^f_4{}^-$), 122.8 (q, $^1J_{CF}$ = 273 Hz, CF_3 of $BAr^f_4{}^-$), 129.1 (q, $^2J_{CF}$ = 34 Hz, meta C of $BAr^f_4{}^-$), 134.9 (ortho

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[10] (a) Akita, M.; Terada, M.; Tanaka, M.; Morooka, Y. *J. Organomet. Chem.* **1996**, *510*, 255. (b) Odom, J. D.; Moore, T. F.; Goetze, R.; Nöth, H.; Wrackmeyer, B. *J. Organomet. Chem.* **1979**, *173*, 15. (c) Jacobsen, S. E.; Wojcicki, A. *J. Am. Chem. Soc.* **1973**, *95*, 6962.

Table 1. Details of Data Collection, Structure Solution, and Refinement for Compounds 8, 10, and 14

	8	10	14
empirical formula	$C_{56}H_{42}BF_{24}Fe_2InO_4$	$C_{82}H_{80}BClF_{24}Fe_2Ga_2O_4$	$C_{60}H_{50}BF_{24}Fe_2InO_5$
formula wt	1472.23	1882.86	1554.33
temp (K)	150(2)	150(2)	150(2)
CCDC deposit no.	276094	276095	276096
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$
unit cell dimens			
a (Å)	14.533(1)	13.744(3)	16.0540(3)
b (Å)	14.644(1)	14.521(3)	16.2940(3)
c (Å)	16.268(1)	21.345(4)	24.2520(6)
α (deg)	65.829(3)	99.44(3)	90
β (deg)	68.927(3)	97.12(3)	90
γ (deg)	74.823(3)	95.59(3)	90
V (Å³)	2920.5(4)	4139.6(14)	6343.9(2)
calcd density (Mg m⁻³)	1.674	1.511	1.617
Z	2	2	4
abs coeff (mm⁻¹)	1.003	1.122	0.929
F(000)	1464	1912	3088
cryst size (mm³)	0.05 × 0.28 × 0.35	0.15 × 0.20 × 0.25	0.10 × 0.15 × 0.23
θ range (deg)	3.53–26.37	1.50–26.03	3.55–26.37
index ranges			
h	−17 to +18	−16 to +16	−20 to +20
k	−16 to +18	−17 to +17	−20 to +20
l	−16 to +20	−26 to +26	−29 to +30
no. of rflns collected	28 114	52 550	26 498
no. of indep rflns	9917 (*R*(int) = 0.1035)	15 346 (*R*(int) = 0.0668)	12 739 (*R*(int) = 0.0692)
completeness to θ_{max} (%)	86.9	94.0	99.5
abs cor	semiempirical from equivs	Sortav	semiempirical from equivs
max and min transmissn	0.952 and 0.720	0.879 and 0.780	0.913 and 0.815
refinement method		full-matrix least squares (F^2)	
no. of data/restraints/params	9917/30/788	15346/18/1090	12739/150/857
goodness of fit on F^2	1.019	1.023	1.023
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0944, wR2 = 0.1918	R1 = 0.0512, wR2 = 0.1059	R1 = 0.0821, wR2 = 0.1815
R indices (all data)	R1 = 0.1812, wR2 = 0.2314	R1 = 0.0807, wR2 = 0.1175	R1 = 0.1226, wR2 = 0.2068
largest diff. peak and hole (e Å⁻³)	1.828 and −1.026	0.723 and −0.557	1.154 and −1.007

CH of $BAr^f_4{}^-$), 160.8 (q, $^1J_{CB}$= 53 Hz, ipso C of $BAr^f_4{}^-$), 211.6 (CO). ^{11}B NMR (96 MHz, CD_2Cl_2): δ −7.6 ($BAr^f_4{}^-$). ^{19}F NMR (283 MHz, CD_2Cl_2): δ − 62.8 (CF_3). IR (CH_2Cl_2/thf): ν(CO) 1978, 1962, 1927 cm⁻¹. MS: ES+, *m/z* 635.7 (weak) [M]⁺, correct isotope distribution for 2Fe and 1 Ga atoms, significant fragment ions at *m/z* 563 (45%) [M − thf]⁺, 535 (10%) [M − thf − CO]⁺, 507 (5%) [M − thf − 2CO]⁺. Exact mass: calcd for [M − thf]⁺ 563.0093, found 563.0095.

Data for **14** are as follows. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.69 (br m, 4H, CH_2 of thf), 1.86 (s, 30H, Cp*), 3.63 (br m, 4H, CH_2 of thf), 7.48 (s, 4H, para CH of $BAr^f_4{}^-$), 7.64 (s, 8H, ortho CH of $BAr^f_4{}^-$). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 10.5 (CH_3 of Cp*), 27.3 (CH_2 of thf), 59.1 (CH_2 of thf), 96.5 (quaternary of Cp*), 117.4 (para CH of $BAr^f_4{}^-$), 124.6 (q, $^1J_{CF}$ = 273 Hz, CF_3 of $BAr^f_4{}^-$), 128.9 (q, $^2J_{CF}$ = 34 Hz, meta C of $BAr^f_4{}^-$), 134.8 (ortho CH of $BAr^f_4{}^-$), ipso C of $BAr^f_4{}^-$ and CO signals not observed. IR (thf): ν(CO) 1974, 1958, 1922 cm⁻¹. MS (EI): *m/z* 609.0 (75%) [M − thf]⁺, correct isotope distribution for 2 Fe and 1 In atoms. Exact mass: calcd for [M − thf]⁺ 608.9876, found 608.9874.

(iii) Crystallographic and Computational Methods. Data for compounds **7**, **8**, **10**, and **14** were collected on an Enraf-Nonius Kappa CCD diffractometer; data collection and cell refinement were carried out using DENZO and COLLECT and structure solution and refinement using SIR-92, SHELXS-97, and SHELXL-97; absorption corrections were performed using SORTAV.[11] With the exception of compound **7**, the structure of which was communicated previously,[7] the details of each data collection, structure solution, and refinement can be found in Table 1. Relevant bond lengths and angles are included in the figure captions, and complete details of each structure have been deposited with the CCDC (numbers as listed in Table 1). In addition, complete details for each structure (including CIF files) have been included in the Supporting Information. The quality of the diffraction data for compound **8** is less than optimal, although the final structure (R1 = 9.44%) is sufficient to corroborate the inferences made on the basis of spectroscopic measurements and to confirm the linear, two-coordinate geometry at indium.

The computational approaches utilized both for geometry optimization processes and for the calculation of σ and π contributions to bonding densities were as reported previously for analogous investigations of transition-metal diyl and boryl complexes.[6,12]

Results and Discussion

(i) Synthetic and Reaction Chemistry of Cationic Derivatives. Halide abstraction chemistry has been examined for a range of three-coordinate halogallium and -indium substrates (Chart 2), with a view to probing this route for the synthesis of cationic diyl and metalladiyl complexes. The success of this methodology in delivering tractable cationic derivatives containing gallium or indium donors can readily be demonstrated but is dependent both on the nature of the precursor complex and on the halide abstraction agent. Thus, $Na[BAr^f_4]$ reacts readily with the three-coordinate bridg-

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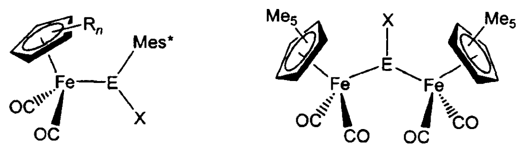
(11) (a) Otwinowski, Z.; Minor, W. In *Methods in Enzymology*; Carter, C. W., Sweet, R. M., Eds.; Academic Press: New York, 1996; Vol. 276, p 307. (b) COLLECT: Data Collection Software; Nonius BV, Delft, The Netherlands, 1999. (c) SIR-92: Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343. (d) Sheldrick, G. M. SHELX97: Programs for Crystal Structure Analysis (Release 97-2); University of Göttingen, Göttingen, Germany, 1998. (e) SORTAV: Blessing, R. H. *Acta Crystallogr. Sect. A* **1995**, *51*, 33.

(12) Dickinson, A. A.; Willock, D. J.; Calder, R. J.; Aldridge, S. *Organometallics* **2002**, *21*, 1146.

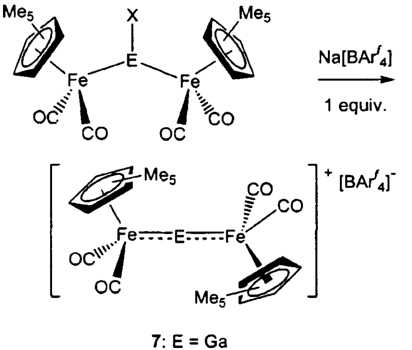
Chart 2 Precursor Systems for Halide Abstraction Chemistry Examined in This Study



1: E = Ga, R_n = H_5, X = Cl
2: E = Ga, R_n = Me_5, X = Cl
3: E = In, R_n = H_5, X = Br

4: E = Ga, X = Cl
5: E = In, X = Br
6: E = In, X = I

Scheme 2. Halide Abstraction Generating Cationic Trimetallic Systems

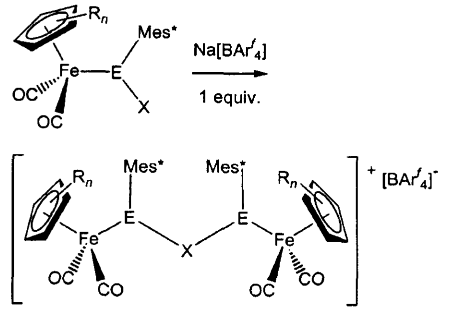


7: E = Ga
8: E = In

ing halogallane- and haloindanediyl complexes [Cp*Fe-$(CO)_2]_2$EX (**4**, E = Ga, X = Cl; **5**, E = In, X = Br; **6**, E = In, X = I). In the cases of **4** and **5** this reaction proceeds in dichloromethane over a period of ca. 2 h to give the expected cationic complexes $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}E)]^+$ (**7**, E = Ga; **8**, E = In) and sodium chloride/iodide (Scheme 2). The composition of the product in each case is implied by ^1H NMR and IR monitoring of the reaction, the former being consistent with a 2:1 ratio of Cp* and $[BAr^f_4]^-$ components and the latter revealing the shifts to higher wavenumber expected on formation of a cationic complex (2016, 1994, 1963 vs 1960, 1925, 1910 cm^{-1} for **7** and **4**, respectively; 2005, 1983, 1951 vs 1979, 1946, 1925 cm^{-1} for **8** and **5**, respectively). In both cases, the structures of **7** and **8** have been confirmed crystallographically and are consistent with base-free cationic two-coordinate group 13 systems (vide infra).

In the case of the reaction of the iodo-substituted indanediyl precursor **6**, an entirely different cationic organometallic product is isolated. Whereas abstraction chemistry with bromoindanediyl **5** proceeds as expected (to give **8**), the corresponding reaction with **6** leads to the formation of $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}I)]^+[BAr^f_4]^-$ (**9**) in 15% isolated yield. **9** has been characterized by multinuclear NMR, IR, and mass spectrometry (including exact mass determination), and although the precise mechanism for its formation is not clear, indium metal is deposited during the reaction, and IR monitoring reveals that Cp*Fe$(CO)_2$I is an intermediate on the overall reaction pathway. In addition to the nature of the halide substituent, the identity of the abstraction agent is also vital to the course of subsequent reaction chemistry. Thus, the reaction of $[Cp^*Fe(CO)_2]_2$GaCl (**4**) with Na[BPh_4] leads to the formation of Cp*Fe$(CO)_2$Ph and BPh_3. Similarly, the course of the reaction of $[Cp^*Fe(CO)_2]_2$InI (**6**) with Na[BPh_4] is also consistent with the more reactive nature of the $[BPh_4]^-$ anion (compared to $[BAr^f_4]^-$). Thus, here too the presence of both BPh_3 and Cp*Fe$(CO)_2$Ph among the reaction products is indicative of abstraction of a phenyl group from the tetraphenylborate counterion.[13] Similar reactivity has been observed previously with highly electrophilic group 13 complexes of iron.[5] Consequently, Na[BAr^f_4] has generally been preferred for halide abstraction chemistry, with reactions employing sources of the similarly weakly coordinating $[CB_{11}H_6Br_6]^-$ anion typically proceding at a significantly slower rate.

Scheme 3. Halide Abstraction from Asymmetric (Supermesityl)halogallyl and -indyl Complexes: Syntheses of Halide-Bridged Dinuclear Species



10: E = Ga, R_n = H_5, X = Cl
11: E = Ga, R_n = Me_5, X = Cl
12: E = In, R_n = H_5, X = Br

Similar abstraction methodology can be applied to the (aryl)halogallyl and -indyl precursors **1**−**3**. Given the success of this approach in the synthesis of a cationic aryl-substituted boranediyl complex featuring an isolated Fe=B double bond,[5] we were encouraged to examine the corresponding reactivity of analogous gallium and indium precursors. Complexes **1**−**3**, containing the extremely bulky supermesityl substituent, are readily accessible either by direct reaction of $[(\eta^5\text{-}C_5R_5)Fe(CO)_2]^-$ with Mes*EX_2 or (in the case of gallium) via a two-step process involving insertion of "GaI" into a M−X bond, followed by gallium-centered substitution (e.g. by Li[Mes*]) in the intermediate dihalogallyl $[L_nMGa(I)X]_2$.[7,8]

The reactions of Cp-substituted complexes **1** and **3** with Na$[BAr^f]_4$ proceed in a very similar fashion. Irrespective of reaction stoichiometry, time scale, or order of reagent addition, reaction of **1** with Na[BAr^f_4] in dichloromethane yields the chloride-bridged dinuclear species $[\{CpFe(CO)_2Ga(Mes^*)\}_2(\mu\text{-}Cl)]^+[BAr^f_4]^-$ (**10**; Scheme 3). **10** presumably results from trapping of the highly electrophilic first-formed intermediate species $[CpFe(CO)_2Ga(Mes^*)]^+$ by a second equivalent of the chlorogallyl starting material **1**. The formulation of **10** is implied by ^1H NMR monitoring of the reaction in dichloromethane-d_2, which reveals a 2:1 ratio of Cp* and $[BAr^f_4]^-$ moieties. In addition, IR data shows the expected shifts to higher wavenumber in the carbonyl stretching bands (2016, 2002, 1972, 1954 vs 1999, 1952 cm^{-1} for **10** and **1**, respectively), and the structure of **10** was subsequently confirmed crystallographically. In a similar fashion, the reaction of the analogous bromoindyl complex CpFe$(CO)_2$In(Mes*)Br (**3**) with Na[BAr^f_4] generates $[\{CpFe(CO)_2In(Mes^*)\}_2(\mu\text{-}Br)]^+[BAr^f_4]^-$

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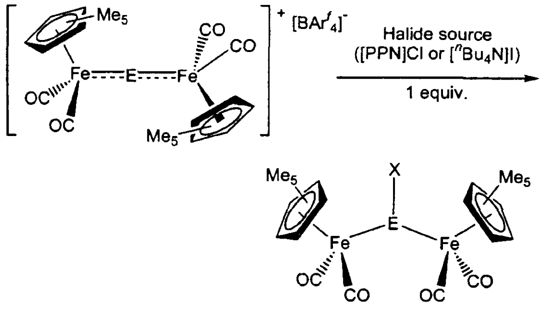
[13] Choukroun, R.; Douziech, B.; Pan, C.; Dahan, F.; Cassoux, P. *Organometallics* **1995**, *14*, 4471.

Scheme 4. Reaction of Cationic Trimetallic Systems 7 and 8 with Sources of Halide Ions



4: E = Ga, X = Cl
6: E = In, X = I

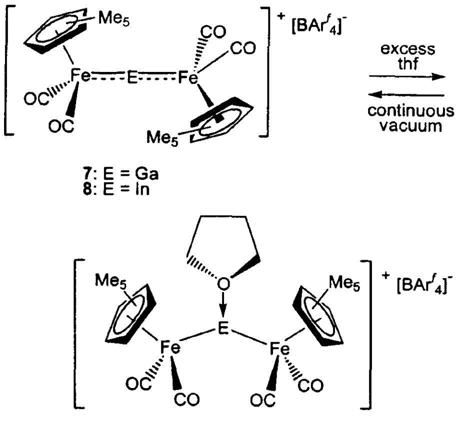
(**12**), which has been characterized by multinuclear NMR, IR, and mass spectrometry and which, by analogy with **10**, would be expected to have an In–Br–In bridged structure formed by trapping of the putative $[CpFe(CO)_2In(Mes^*)]^+$ by a further 1 equiv of **3**.

Given the extremely facile trapping of the putative diyl complexes $[CpFe(CO)_2E(Mes^*)]^+$ implied by the formation of **10** and **12**, a potential route to tractable mononuclear cationic systems involves the use of more sterically bulky and/or more electron releasing substituents at the metal center. The reactivity of $Cp^*Fe(CO)_2Ga(Mes^*)Cl$ (**2**) toward $Na[BAr^f_4]$ was therefore investigated. Despite the increased steric requirements of the Cp* ligand, however, the product isolated from this reaction (under a range of different conditions) is the analogous dinuclear compound $[\{Cp^*Fe(CO)_2Ga(Mes^*)\}_2(\mu\text{-}Cl)]^+[BAr^f_4]^-$ (**11**). **11** has been characterized by multinuclear NMR, IR, and mass spectrometry, with the similarity in the *pattern* of carbonyl stretches compared to that of **10** (1996, 1986, 1954, 1932 vs 2016, 2002, 1972, 1954 cm^{-1} for **11** and **10**, respectively) and the 2:1 integrated ratio of the Cp* and $[BAr^f_4]^-$ signals in the ^1H NMR spectrum providing compelling evidence for a chloride-bridged structure analogous to **10**.

The fundamental reactivity of group 13 diyl and related complexes remains an area which has received relatively little attention,[3f,g] despite obvious parallels with carbenes, silylenes, and their heavier homologues,[14] and the range of interesting and useful reactivity in which these group 14 systems have been implicated. Initial studies of the reactivity of the prototype cationic boranediyl system $[Cp^*Fe(CO)_2B(Mes)]^+$ imply dominant electrophilic character, with anionic and/or neutral nucleophiles displaying a mixture of boron- and iron-centered reactivity.[5] A preliminary survey of the reactivities of two-coordinate metalladiyls **7** and **8** toward neutral and anionic two-electron donors implies that the group 13 center in each is somewhat less electrophilic than that in $[Cp^*Fe(CO)_2B(Mes)]^+$.

Both **7** and **8** react rapidly with sources of halide ions in dichloromethane solution (Scheme 4) to generate the (structurally characterized) bridging halogallane- and haloindanediyl complexes $[Cp^*Fe(CO)_2]_2EX$ (**4**, E = Ga, X = Cl; **6**, E = In, X = I) in a fashion similar to the boron-centered halide addition chemistry observed for $[Cp^*Fe(CO)_2B(Mes)]^+$. However, whereas the latter compound is sufficiently Lewis acidic to abstract fluoride from $[BF_4]^-$ and generate $Cp^*Fe(CO)_2B(Mes)F$,[5b] the gallium-centered cation **7**, for example, is unreactive toward sources of $[BF_4]^-$ under similar conditions.

Scheme 5. Reversible Addition of Tetrahydrofuran to the Group 13 Center in 7 or 8



13: E = Ga
14: E = In

The reactivity of **7** and **8** toward *neutral* two-electron donors is also reflective of moderate Lewis acid character. Thus, in the presence of tetrahydrofuran, both cationic trimetallic species coordinate a single molecule of thf to generate the 1:1 adducts $[\{Cp^*Fe(CO)_2\}_2\{\mu\text{-}E(thf)\}]^+[BAr^f]^-$ (**13**, E = Ga; **14**, E = In; Scheme 5), which can be isolated as pale yellow solids. In each case the 1:1 stoichiometry is implied by integration of the ^1H NMR signals due to thf and Cp* moieties, and coordination of the oxygen donor at the group 13 center is consistent with the significant shifts to lower wavenumber in the CO stretching bands (1978, 1962, 1927 and 2016, 1994, 1963 cm^{-1} for **13** and **7**, respectively; 1974, 1958, 1922 and 2005, 1983, 1951 cm^{-1} for **14** and **8**, respectively). Furthermore, in the case of **14**, the structure of the adduct has been confirmed crystallographically (vide infra).

The isolation of the Lewis base stabilized derivatives **13** and **14** contrasts markedly with the behavior of the cationic boranediyl complex $[Cp^*Fe(CO)_2B(Mes)]^+$, which reacts rapidly in the presence of neutral two-electron donors with rupture of the metal–group 13 linkage.[5b] Interestingly, the coordination of the thf donor in **13** and **14** appears to be reversible. Thus, upon prolonged exposure to continuous vacuum (10^{-4} Torr), spectroscopic data for both compounds are consistent with loss of coordinated thf. Monitoring of this process by IR and ^1H NMR spectroscopy reveals that, in the case of **13**, a mixture of the donor-stabilized complex and the "naked" two-coordinate species **7** is obtained. In the case of **14** complete loss of thf is observed over a period of 6 h, leading to the regeneration of $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}In)]^+[BAr^f_4]^-$ (**8**). Such behavior is consistent with a relatively weak Lewis acid/base interaction in each case, with the apparently greater ease of removal of the indium-bound thf ligand being consistent with previous reports of the

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(14) See, for example: (a) Nugent, W. A.; Mayer, J. M. *Metal Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988. (b) Glaser, P. B.; Wanandi, P. W.; Tilley, T. D. *Organometallics* **2004**, *23*, 693 and references therein. For a review of related germylene and stannylene chemistry, see: (c) Petz, W. *Chem. Rev.* **1986**, *86*, 1019.

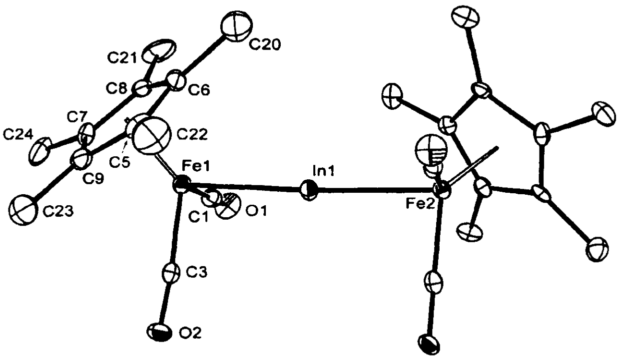

Figure 1. Structure of the cationic component of $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}In)]^+[BAr^f{}_4]^-$ (**8**). Hydrogen atoms have been omitted for clarity and ORTEP ellipsoids set at the 50% probability level. Important bond lengths (Å) and angles (deg): Fe(1)–In(1) = 2.460(2), Fe(2)–In(1) = 2.469(2), Fe(1)–Cp* centroid = 1.725(10), Fe(1)–C(1) = 1.757(13); Fe(1)–In(1)–Fe(2) = 175.32(6), Cp* centroid–Fe(1)–Fe(2)–Cp* centroid = 86.8(3).

thermodynamics of oxygen donor coordination to gallium- and indium-based Lewis acids.[15]

(ii) Spectroscopic, Structural and Computational Studies. Single-crystal X-ray diffraction studies were undertaken on compounds **7**, **8**, **10**, and **14**. With the exception of compound **7**, the structure of which has been communicated previously,[7] details of the data collection, structure solution, and refinement parameters for each compound are given in Table 1; relevant bond lengths and angles are included in the figure captions. Complete details of all structures are given in the Supporting Information and have been deposited with the Cambridge Structural Database.

Compounds **7** and **8** (Figure 1 and Table 1) represent extremely rare examples of structurally characterized species containing two-coordinate cationic gallium or indium centers. Previously reported examples typically feature extremely bulky hydrocarbyl substituents (e.g. $[Ar_2Ga]^+$),[16] and **7** and **8** represent the first examples containing metal–group 13 element bonds. In each case the geometry of the cationic component features a linear trimetallic unit (e.g. ∠Fe(1)–Ga(1)–Fe(2) = 178.99(2)° for **7**) in which the central group 13 atom engages in no significant intra- or intermolecular secondary interactions, for example with the $[BAr^f{}_4]^-$ anion. To our knowledge, the only other example of an isolated transition-metal complex featuring a "naked" bridging gallium or indium center is the neutral species $[Cp^*Fe(dppe)](\mu\text{-}Ga)[Fe(CO)_4]$, reported by Ueno and co-workers in 2003.[17–20] Like **7** and **8**, this complex also features a near-linear coordination geometry at the group 13 center (176.01(4)°),[17] in marked contrast to the bent frameworks typically found for base-stabilized analogues such as $[\{CpFe(CO)_2\}_2\{\mu\text{-}Ga(bipy)\}]^+$ and $[Cp^*Fe(CO)_2]\{\mu\text{-}Ga(bipy)\}[Fe(CO)_4]$ (132.81(5) and 136.68(2)°, respectively).[17,21]

Of significant interest are the Fe–E bond lengths for **7** and **8** (2.266(1), 2.272(1) and 2.460(2), 2.469(2) Å, respectively). These can be compared to the analogous bond lengths found for the bridging halogallane- and haloindanediyl precursors $[Cp^*Fe(CO)_2]_2EX$ (2.352(1) and 2.513(3), 2.509(3) Å for **4** (E = Ga, X = Cl) and **5** (E = In, X = Br), respectively[7,8]) and for three- or four-coordinate base-stabilized cationic systems (e.g. 2.397(2), 2.404(1) and 2.494(2), 2.498(2) Å for $[\{CpFe(CO)_2\}_2\{\mu\text{-}Ga(bipy)\}]^+$ and $[\{Cp^*Fe(CO)_2\}_2\{\mu\text{-}In(thf)\}]^+$, respectively (vide infra)).[21] In the case of gallium compound **7**, the shortening with respect to the single bonds found in **4** (ca. 3.5%) places the Fe–Ga distance in the region of values previously reported for two-coordinate gallium-containing systems.[4,17] Thus, the Fe–Ga bond lengths reported for $[Cp^*Fe(dppe)](\mu\text{-}Ga)[Fe(CO)_4]$ are 2.248(1) and 2.293(1) Å,[17] with the former distance (for the Cp*Fe(dppe)Ga unit) being described as indicative of "significantly unsaturated character". Clearly the Fe–Ga bond shortening observed on halide abstraction from **4** (to give **7**) is consistent with both steric and electronic factors: i.e., with a reduction in the coordination number at gallium and/or with an increase in the extent of Fe→Ga back-bonding. The extent of bond shortening accompanying the halide abstraction process is significantly less in the case of indium complex **8** (<2% with respect to **6**). This observation is also consistent with both underlying steric and electronic factors: i.e., both the extent of Fe→E back-bonding and the relief of steric strain are likely to be less pronounced in the case of **8**, due to the longer Fe–E linkages. A further point of interest concerning the structures of cations **7** and **8** is the relative alignment of the two $[Cp^*Fe(CO)_2]$ fragments. In each case the Cp* centroid–Fe(1)–Fe(2)–Cp* centroid torsion angle is close to 90° (e.g. 84.6(1)° for **7**). Given the presence of two formally vacant mutually perpendicular p orbitals at the group 13 center, such an alignment allows in principle for optimal π back-bonding from the HOMO of each of the two $[Cp^*Fe(CO)_2]^+$ fragments.[22]

Of significant interest from a comparative viewpoint are the metalloheterocumulene complexes of the type $[(\eta^5\text{-}C_5R_5)Mn(CO)_2]_2(\mu\text{-}E)$ (E = Ge, Sn), reported by a number of groups, including those of Hüttner and Herrman.[23] Indeed, the Ge and Sn compounds of this type, which have been described as featuring Mn=E double bonds, are formally isoelectronic with the cationic components of **7** and **8**, respectively. Furthermore, the structural parameters for the crystallographically characterized species $[Cp^*Mn(CO)_2]_2(\mu\text{-}Ge)$ are remarkably

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[15] See, for example: (a) Tuck, D. G. In *Chemistry of Aluminium, Gallium, Indium and Thallium*; Downs, A. J., Ed.; Blackie Academic and Professional: London, 1993; Chapter 8. (b) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: Oxford, U.K., 1984; Chapter 7.

[16] (a) Hausen, H. D.; Mertz, K.; Weidlein, J.; Schwarz, W. *J. Organomet. Chem.* **1975**, *93*, 291. (b) Gahlmann, F.; Neumuller, B. *Z. Anorg. Allg. Chem.* **1994**, *620*, 847. (c) Wehmschulte, R. J.; Steele, J. M.; Young, J. D.; Khan, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 1470.

[17] Ueno, K.; Watanabe, T.; Tobita, H.; Ogino, H. *Organometallics* **2003**, *22*, 4375.

[18] For an example of a metal cluster containing near linear M–Ga–M units, see: Scheer, M.; Kaupp, M.; Virovets, A. V.; Konchenko, S. N. *Angew. Chem., Int. Ed.* **2003**, *42*, 5083.

[19] For a related boron-containing system, see: Braunschweig, H.; Radacki, K.; Scheschkewitz, D.; Whittell, G. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 1658.

[20] For cationic compounds containing two-coordinate thallium see, for example: (a) Balch, A. L.; Nagle, J. K.; Olmstead, M. M.; Reedy, P. E. *J. Am. Chem. Soc.* **1987**, *109*, 4123. (b) Jeffery, J. C.; Jelliss, P. A.; Liao, Y.-H.; Stone, F. G. A. *J. Organomet. Chem.* **1998**, *551*, 27. (c) Catalano, V. J.; Bennett, B. L.; Kar, H. M.; Noll, B. C. *J. Am. Chem. Soc.* **1999**, *121*, 10235. (d) Catalano, V. J.; Bennett, B. L.; Yson, R. L.; Noll, B. C. *J. Am. Chem. Soc.* **2000**, *122*, 10056.

[21] Ueno, K, Watanabe, T, Ogino, H. *Organometallics* **2000**, *19*, 5679.

[22] Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. *J. Am. Chem. Soc.* **1979**, *101*, 585.

Table 2. Calculated and Crystallographically Determined Structural Parameters for the Cationic Components of $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}E)]^+[BAr^f_4]^-$ (7, E = Ga; 8, E = In)

compd	Fe−E dist (Å)	Fe−E−Fe angle (deg)	Ct−Fe−Fe−Ct torsion angle (deg)	σ:π break-down	E_{rel} (kcal mol^{-1})[a]
7 (exptl)	2.266(1), 2.272(1)	178.99(2)	84.6(1)		
7 (calcd)	2.338, 2.337	177.93	86.5	61:38	0
8 (exptl)	2.460(2), 2.469(2)	175.32(6)	86.8(3)		
8 (calcd)	2.463,2.463	179.40	161.8	74:26	0
8 (calcd)	2.469, 2.469	179.87	82.8	74:26	+1.78

[a] Calculated energy relative to minimum energy conformation.

similar to those for **7** (d(Mn−Ge) = 2.18(2) Å; ∠Mn−Ge−Mn = 179(1)°; centroid−Mn−Mn−centroid torsion angle 83(3)°).[23b]

In an attempt to determine whether these structural observations (i.e. the shortening in Fe−E bond lengths on halide abstraction, the orthogonal alignment of $[Cp^*Fe(CO)_2]^+$ fragments, and the close relationship of the structures of $[Cp^*Mn(CO)_2]_2(\mu\text{-Ge})$ and **7**) are related to any Fe−E multiple-bond character, and to relate any trends in bonding to the nature of the group 13 element E, DFT analyses were carried out on compounds **7** and **8** using methods described previously.[6,12]

DFT calculations were carried out at the BLYP/TZP level, and salient parameters relating to the fully optimized geometries of $[\{Cp^*Fe(CO)_2\}_2E]^+$ (E = Ga, In) are detailed in Table 2. In the case of $[\{Cp^*Fe(CO)_2\}_2Ga]^+$, the agreement between calculated and experimentally derived geometric parameters is very good, with the near-linear Fe−Ga−Fe trimetallic framework and near-orthogonal alignment of the $[Cp^*Fe(CO)_2]$ fragments being accurately reproduced computationally. The 2−3% overestimate in the calculated Fe−Ga bond lengths mirrors that found for related diyl systems and has been ascribed to solid-state effects, leading to the shortening of donor/acceptor bonds accompanied by a general overestimate in bond lengths by generalized gradient approximation (GGA) methods.[6,12,24] In the case of $[\{Cp^*Fe(CO)_2\}_2In]^+$, the minimum energy conformation calculated by DFT corresponds to a centroid−Fe−Fe−centroid torsion angle of 161.8°, in contrast to the experimentally determined value of 86.3(3)°. Closer inspection, however, reveals that there is a very shallow potential energy surface for rotation about this axis (see the Supporting Information for a complete rotational profile) and that the energy difference between the minimum energy conformer and that corresponding to the approximately orthogonal alignment found in the solid state is very small (e.g. ΔE = 1.78 kcal mol^{-1} between rotamers, corresponding to torsion angles of 161.8 and 82.4°). σ and π contributions to the overall Fe−In bonding density have therefore been calculated for both of these conformations.

A bond population analysis for $[\{Cp^*Fe(CO)_2\}_2Ga]^+$ carried out using a widely precedented method reveals a 61:38 σ:π breakdown of the covalent Fe−Ga interaction,[6,12] which can be put in context by comparison with a ratio of 86:14 for the formal Fe−Ga single bond in the model compound $CpFe(CO)_2GaCl_2$.[6,25] Using the same approach, corresponding values of 62:38 have been calculated for the iron to boron linkage in $[Cp^*Fe(CO)_2(BMes)]^+$. Further evidence for a significant Fe−Ga π component in $[\{Cp^*Fe(CO)_2\}_2Ga]^+$ is provided by the orbitals HOMO-3 to HOMO-6, each of which features in-phase contributions from gallium- and iron-centered π symmetry orbitals (Ga $4p_x$ and $4p_y$; Fe $3d_{xz}$ and $3d_{yz}$). Similar analyses for the indium-centered cation $[\{Cp^*Fe(CO)_2\}_2In]^+$ are consistent with a significantly smaller π contribution to the metal−group 13 element bond. Thus, the σ:π breakdown in this case is 74:26 (for both conformations corresponding to torsion angles of 82.4 and 161.8°); these values can be compared to an 11% calculated π contribution for the formal Fe−In single bond in the model compound $CpFe(CO)_2InCl_2$.[25] The significantly smaller π contribution for E = In than for E = Ga is as expected on the well-precedented basis of diminished π orbital overlap for the heavier main-group elements.[26] In addition, although the barrier to rotation about the Fe−In−Fe axis is not a direct measure of π bond strength (rather the difference in π contributions between 0 and 90° orientations), the relatively flat potential function for rotation about his bond is consistent with the similar (and relatively low) π contributions calculated for both conformations.

An X-ray diffraction study has also been carried out on the thf-stabilized complex $[\{Cp^*Fe(CO)_2\}_2\{\mu\text{-In}(thf)\}]^+[BAr^f_4]^-$ (**14**), with the results being displayed in Figure 2 and Table 1. This is consistent with the 1:1 stoichiometry and indium-coordinated thf donor implied by spectroscopic data. The indium center is trigonal planar (sum of angles at indium 360.0(3)°), and the approximately orthogonal alignment of Fe_2In and OC_2 planes (torsion Fe(1)−In(1)−O(5)−C(57) = 80.0(4)°) is presumably enforced on steric grounds. As expected, given the relatively small π component determined for the Fe−In bonds in base-free **8**, there is only a relatively minor lengthening of these linkages on coordination of the thf molecule (2.498(2), 2.494(2) vs 2.460(2), 2.469(2) Å for **14** and **8**, respectively). **14** represents only the second structurally characterized cationic three-coordinate indium species and the first containing bonds to a transition metal,[27] although related N-donor-stabilized gallium complexes of the type $[(L_nM)_2GaD_2]^+$ have previously been reported.[21,28] The Fe−In−Fe angle (156.72(6)°) is somewhat wider than that found in $[\{CpFe(CO)_2\}_2\{\mu\text{-Ga(bipy)}\}]^+$, presumably reflecting not only the longer Fe-E bonds for E = In but also the lower coordination number at the group 13 center in **14** (i.e.

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(23) For examples of metalloheterocumulene complexes of the type $L_nM{=}E{=}ML_n$ (E = Ge, Sn), see: (a) Gäde, W.; Weiss, E. *J. Organomet. Chem.* **1981**, *213*, 451. (b) Korp, J. D.; Bernai, I.; Horlein, R.; Serrano, R.; Herrmann, W. A. *Chem. Ber.* **1985**, *118*, 340. (c) Herrman, W. A.; Kneuper, H. J.; Herdtweck, E. *Chem. Ber.* **1989**, *122*, 437. (d) Ettel, F.; Hüttner, G.; Imhof, W. *J. Organomet. Chem.* **1990**, *397*, 299. (e) Ettel, F.; Hüttner, G.; Zsolnai, L.; Emmerich, C. *J. Organomet. Chem.* **1991**, *414*, 71.

(24) See, for example: (a) McCullough, E. A., Jr.; Aprà, E.; Nichols, J. *J. Phys. Chem. A* **1997**, *101*, 2502. (b) MacDonald, C. A. B.; Cowley, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 12113. (c) Uddin, J.; Boehme, C.; Frenking, G. *Organometallics* **2000**, *19*, 571. (d) Giju, K. T.; Bickelhaupt, M.; Frenking, G. *Inorg. Chem.* **2000**, *39*, 4776. (e) Uddin, J. Frenking, G. *J. Am. Chem. Soc.* **2001**, *123*, 1683.

(25) Dickinson, A. A. Ph.D. Thesis, Cardiff University, 2003.

(26) See, for example, Massey, A. G. *Main Group Chemistry*; Wiley: London, 2000; pp 51−59.

(27) Delpech, F.; Guzei, I. A.; Jordan, R. F. *Organometallics* **2002**, *21*, 1167.

(28) Ueno, K.; Watanabe, T.; Ogino, H. *Appl. Organomet. Chem.* **2003**, *17*, 403.

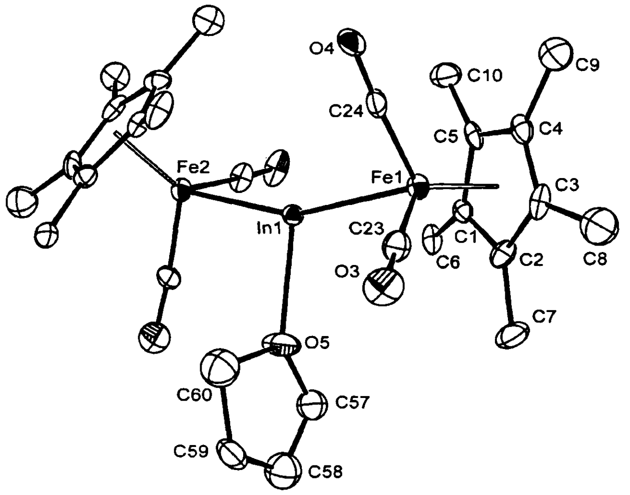

Figure 2. Structure of the cationic component of $[\{Cp^*Fe(CO)_2\}_2\{\mu\text{-}In(thf)\}]^+[BAr^f_4]^-$ (**14**). Hydrogen atoms have been omitted for clarity and ORTEP ellipsoids set at the 50% probability level. Important bond lengths (Å) and angles (deg): Fe(1)–In(1) = 2.498(2), Fe(2)–In(1) = 2.494(2), Fe(1)–Cp* centroid = 1.729(12), Fe(1)–C(23) = 1.748(13); Fe(1)–In(1)–Fe(2) = 156.72(6), Fe(1)–In(1)–O(5) = 100.1(3), Fe(2)–In(1)–O(5) = 103.2(3), Fe(1)–In(1)–O(5)–C(57) = 80.0(4).

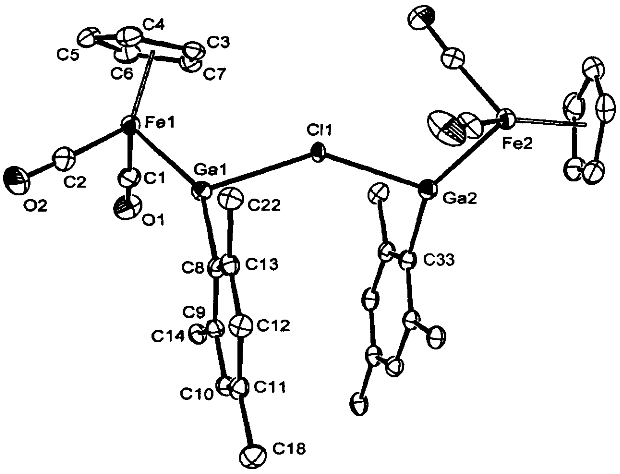

Figure 3. Structure of the cationic component of $[\{CpFe(CO)_2Ga(Mes^*)\}_2(\mu\text{-}Cl)]^+[BAr^f_4]^-$ (**10**). Hydrogen atoms and ^tBu methyl groups have been omitted for clarity and ORTEP ellipsoids set at the 50% probability level. Important bond lengths (Å) and angles (deg): Fe(1)–Ga(1) = 2.333(1), Fe(2)–Ga(2) = 2.328(1), Fe(1)–Cp* centroid = 1.724(4), Fe(1)–C(1) = 1.755(4), Ga(1)–Cl(1) = 2.552(1), Ga(2)–Cl(1) = 2.476(1); Fe(1)–Ga(1)–C(8) = 149.07(8), Fe(2)–Ga(2)–C(33) = 150.50(9), Ga(1)–Cl(1)–Ga(2) = 142.16(3).

3 vs 4).[21] Furthermore, this angle is significantly wider than that found in the charge-neutral bridging haloindanediyl complexes $[Cp^*Fe(CO)_2]_2InX$ (141.46(1), 141.98(2)° for **5** (E = Br) and **6** (E = I), respectively), despite the greater steric demands of thf (cf. Br^- or I^-).[7,8] This phenomenon has previously been observed for a range of group 13 adducts. Thus, for example, the Cl–Ga–Cl angles in $GaCl_3{\cdot}thf$ (113.07° (mean)) are significantly wider than those in the corresponding Cl^- adduct (109.5° (mean)).[29]

An X-ray diffraction study has also confirmed the chloride-bridged structure of $[\{CpFe(CO)_2Ga(Mes^*)\}_2(\mu\text{-}Cl)]^+[BAr^f_4]^-$ (**10**; see Figure 3 and Table 1). The synthesis of **10** is viewed as being due to the trapping of the putative cationic gallanediyl $[CpFe(CO)_2Ga(Mes^*)]^+$ by a second equivalent of the precursor $CpFe(CO)_2Ga(Mes^*)Cl$ (**1**). Thus, the structure of **10** can be viewed as a base-stabilized gallanediyl complex, in which the gallium-coordinated donor is the bridging chloride ligand. In common with other base-stabilized diyl complexes, the metal–group 13 distance is more akin to that expected for related single bonds rather than for unsaturated species (e.g. 2.333(1), 2,328(1) and 2.346(1) Å for **10** and **1**, respectively).[7,8] By comparison, an Fe–Ga distance of 2.416(3) Å has been reported by Fischer and co-workers for base-stabilized $(OC)_4FeGaMe(tmpa)$ (tmpa = $Me_2NCH_2CH_2CH_2NMe_2$), compared with 2.225(1) Å for two-coordinate $(OC)_4FeGaAr$ (Ar = $2,6\text{-}(2,4,6\text{-}^iPr_3C_6H_2)_2C_6H_3$).[4,30] In contrast, the structural effects of the abstraction and Ga–Cl–Ga bridge formation processes are much more pronounced on the Ga–Cl bonds and on the Fe–Ga–C_{ipso} angles. Thus, the bridging nature of the remaining chloride substituent is reflected in markedly longer Ga–Cl bond lengths (2.476(1), 2.552(1) and 2.272(1) Å for **10** and **1**, respectively), which in turn allows for significant opening out of the Fe–Ga–C_{ipso} angle (149.07(8), 150.50(9) and 139.18(10)° for **10** and **1**, respectively).

Conclusions

Halide abstraction chemistry has been demonstrated to offer a viable synthetic route to cationic two-coordinate complexes featuring the heavier group 13 elements gallium and indium as donor atoms. Thus, the linear trimetallic species $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}E)]^+$ (**7**, E = Ga; **8**, E = In) featuring naked bridging gallium or indium atoms can be synthesized by the reaction of the corresponding chloro- or bromo-substituted bridging diyl complexes with $Na[BAr^f_4]$. Analogous reactions utilizing the supermesityl-substituted gallyl or indyl precursors of the type $(\eta^5\text{-}C_5R_5)Fe(CO)_2E(Mes^*)X$, on the other hand, lead to the synthesis of halide-bridged species of the type $[\{(\eta^5\text{-}C_5R_5)Fe(CO)_2E(Mes^*)\}_2(\mu\text{-}X)]^+$, presumably by trapping of the highly electrophilic putative cationic diyl complex $[(\eta^5\text{-}C_5R_5)Fe(CO)_2E(Mes^*)]^+$. Ongoing further attempts to modify these systems, e.g. by the introduction of bulky, strongly σ-basic phosphine ligands at the group 8 metal center, are aimed at the isolation of such cationic gallane- and indanediyl systems.

Preliminary studies have shown complexes **7** and **8** to be reactive toward both anionic and neutral nucleophiles, although the reversible coordination of thf is indicative of surprisingly weak Lewis acidic behavior. Structural, spectroscopic, and computational studies performed for **7** are consistent with appreciable Fe–Ga π-bonding character, as proposed for the only other previously reported example of a trimetallic system featuring a naked bridging gallium atom. The analogous

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indium-bridged complex **8**, in contrast, is shown both by structural and quantum chemistry methods to feature a much smaller π component to the metal–ligand interaction.

Acknowledgment. We acknowledge the support of the EPSRC for funding this project and the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea, Wales.

Supporting Information Available: Complete details of the crystal structures of compounds **7**, **8**, **10**, and **14**, details of the DFT derived (fully optimized) geometries of the cations $[\{Cp^*Fe(CO)_2\}_2E]^+$ (E = Ga, In), and NMR spectra for all compounds (as evidence for bulk purity). This material is available free of charge via the Internet at http://pubs.acs.org. Crystal data for **7**, **8**, **10**, and **14** have also been deposited with the Cambridge Structural Database.

OM0506318