Co-ordination and Organometallic Chemistry of Facially Capping Tridentate Macrocycle [12]-ane-$P_3(^iPr)_3$

by

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To all of you, thank you so much

DECLARATION

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Abstract

The co-ordination chemistry of metal-phosphine complexes has developed dramatically since its appearance in 1857 by Hofman[1] and now it is one of the major areas in inorganic chemistry. The architecture of phosphine ligands to stabilise unusual complexes and oxidation states is the major contribution for the increasing interest in the chemistry of metal-phosphorous compounds. However, due to the difficulties in their synthesis, phosphorous-based macrocycle systems are rare in comparison to the other systems of analogous nitrogen-based macrocyles. This thesis concerns the detailed study of the chemistry of triphosphamacrocycle ligands with metals of iron, ruthenium, nickel and copper sub-groups. Specifically Fe(II), Ru(II), Ni(II), Ni(I), Ni(0) and Cu(I)X where X is Cl, Br and I complexes of 1,5,9-triphosphacyclododecane ligands; their syntheses, characterisation and structural analysis have been studied.

In *Chapter* **1**, the background of this project is explained.

The radical-initiated template coupling of three facially co-ordinated allylphosphine ligands on a neutral $(CO)_3Mo(0)$ template leads to the co-ordinated tri-secondary macrocycle, [12]-ane-P_3H_3. The synthesis of tertiary derivatives is two-fold, one involving the deprotonation fallowed by alkylation at co-ordinated phosphorus by alkyl halide, in this study the use of Na-dimsyl as a deprotonating agent is documented. The macrocycle {[12]-ane-$P_3(^iPr)_3$} is liberated by the oxidation of the template complex stereospecifically as the *syn-syn* isomer in high yield and its co-ordination chemistry with Fe(II) and Ru(II) is detailed in *chapter* **2**.

In *Chapter* **3**, co-ordination studies of triphosphacyclododecane ligand with various oxidation states of nickel compounds has led to a range of novel macrocycle complexes, and they are characterised by multinuclear NMR and infrared spectroscopy.

In *Chapter* **4**, the preparation of novel Cu(I) complexes, which contain the macrocycle ligand is reported and described the very first X-Ray crystal structure of Cu(I) bimetallic species.

CONTENTS

Chapter 1:

Introduction

1.1. Phosphine Ligands

The extent of the known transition metal complexes containing phosphine ligands is enormous,[2] including numerous examples with mono-, bi-dentate or polydentate chelating phosphine ligands, and the diversity of the phosphorus substituent further increases the variety of these ligands and their complexes.[2]

Some representatives are shown in Figure 1.1 and these ligands have a variety of steric and electronic properties. As examples of these features, PH_3 (**1.1**) is the smallest known phosphine whilst PCy_3 (**1.3**) is one of the largest. As well as manipulating steric properties, variations in substituents also influence the electronic properties e.g. PF_3 (**1.2**) has electron-withdrawing substituents and acts as a strong π acid.

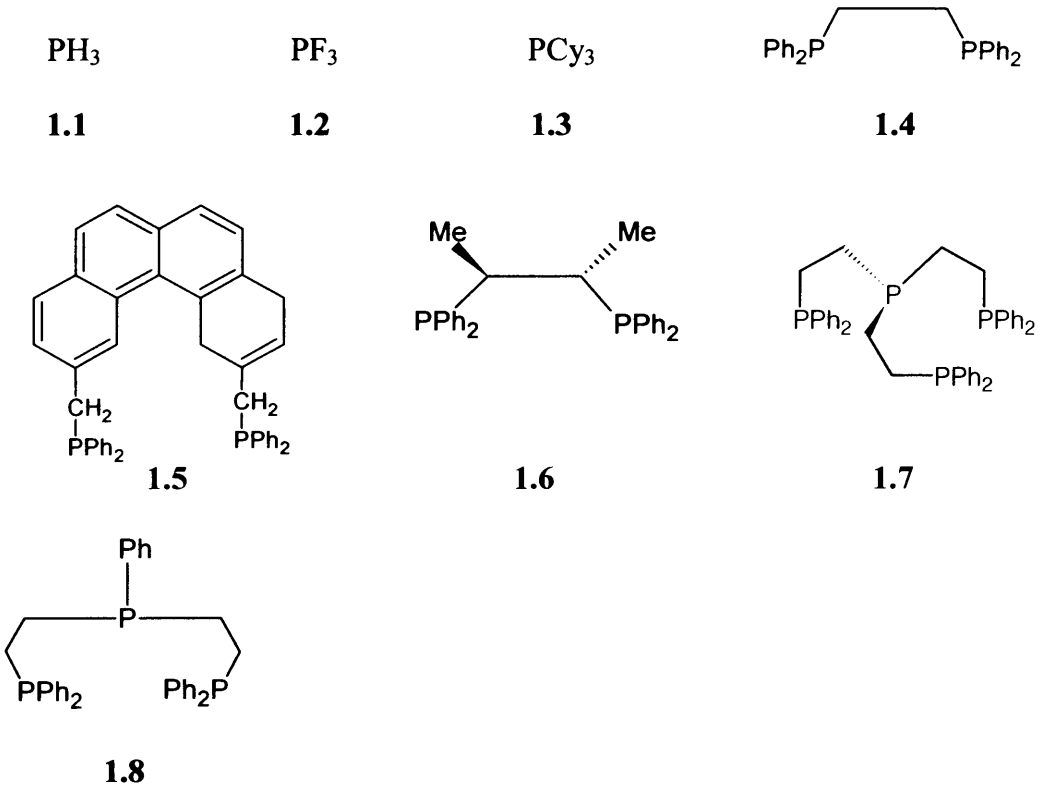


Figure 1.1 Some selected examples of phosphine ligands

Chelating phosphines **1.4** and **1.5** are also extensively studied and chiral phosphines **1.6** and **1.7** are important in asymmetric catalysis. Multidentate phosphines such as **1.7** and

1.8 are less well known and have seldom been used due to the unavailability of vacant *cis* coordination sites on metal complexes containing these ligands.

1.1.1. Remarkable Nature of Phosphines Ligands.

Most commonly group 15 donor atoms in their ligands have the oxidation state of +3 with a pyramidal structure. In addition to that they all bear a lone pair which can be donated to a metal centre forming a σ-coordinate bond.

Figure 1. 2 A representation of the frontier-orbital σ-bonding in metal-phosphine complexes

1.1.1.1. Electronic Nature

Having empty orbitals of π symmetry, phosphine can interact with the occupied metal t_{2g} orbitals (Figure 1.3a). Alternatively the σ bonds which bind the substituents to phosphorus have vacant σ* antibonding orbitals which can also interact with metal π-orbitals (Figure 1.3b). This σ dative/π retrodative capacity of phosphine ligands may be fine tuned to allow control over the electronic nature of the metal centre.[3] Consequently, alkyl phosphines are less π-acidic than aryl phosphines with more electronegative substituents. [3, 4]

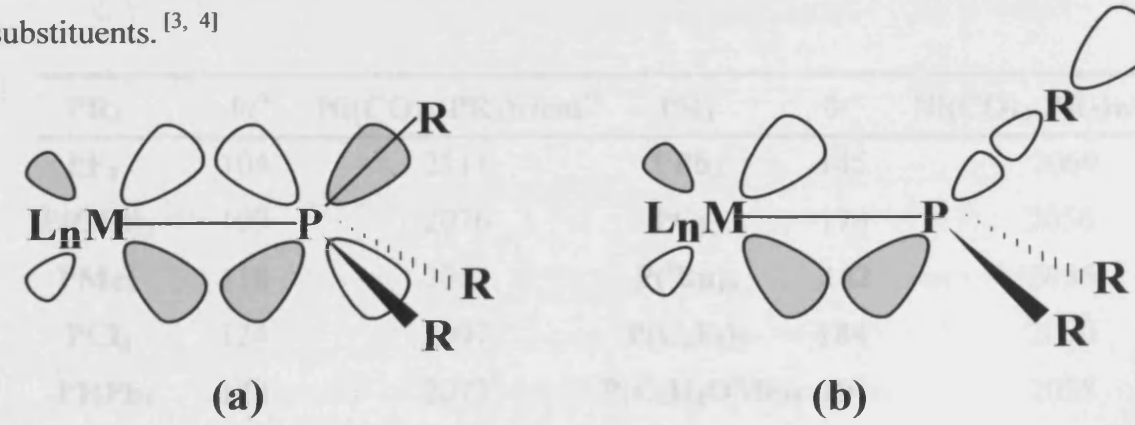


Figure 1. 3 Retrodonation of phosphines

1.1.1.2. Steric Nature

The second important variable of phosphine ligands is the steric profile. An approximate measure of this phenomenon is explained by the Tollman cone angle (θ).[3]

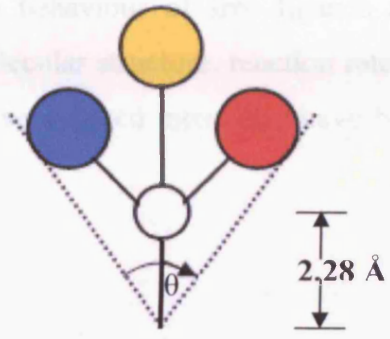


Figure 1. 4 Schematic representation of phosphine ligand cone angle (θ)

Tolman's cone angle is related to Ni-P bond lengths, as his original study was based upon tetrahedral phosphino-nickel systems. The angle is explained by considering the cone, which is defined by the van der Waals surface generated by a phosphine bound central metal atom which freely rotates around the metal-P bond. [5, 6]

Table 1.1 Steric (θ) and electronic (ν/cm^{-1}) properties of phosphine ligands in $Ni(CO)_3(PR_3)$

PR_3	θ/°	$Ni(CO)_3(PR_3)$ν/cm^{-1}	PR_3	θ/°	$Ni(CO)_3(PR_3)$ν/cm^{-1}
PF_3	104	2111	PPh_3	145	2069
$P(OEt)_3$	109	2076	PCy_3	170	2056
PMe_3	118	2064	$P(^tBu)_3$	182	2056
PCl_3	124	2097	$P(C_6F_5)_3$	184	2090
$PHPh_2$	128	2073	$P(C_6H_4OMe)_3$	194	2058

The data in table 1 lists the influence of phosphine substituents upon ν(C-O) in the IR spectra of a series of nickel carbonyl phosphine complexes where Tolman quantified the electronic influence of substituents indirectly. The IR data shows a clear trend as a function of electron negativity of the substituents.

It has long been recognized that changing substituents on phosphorus ligands can cause marked changes in the behaviour of free ligands and of their transition metal complexes. As an example molecular structure, reaction rate, equilibrium constants, NMR chemical shifts and even relative infrared intensities have been correlated with the ligand cone angle.[7]

1.2. Chelating Ligands

Ligands that have the ability to form more than one bond to a single metal atom can be defined as polydentate, and when such metallacyclic complexes are produced the resulting ligand-metal fragment is termed as chelate. These complexes are thermodynamically more stable and kinetically less reactive towards the dissociation of the ligands than are analogous compounds containing mono-dentate ligands of a similar fashion. This entropically favoured phenomenon is defined as a "*Chelate Effect*" and it is illustrated by the formation constant (**β**) of the following selected examples in Scheme 1.1.

$$Cd^{2+}(aq) + 4MeNH_2(aq) \rightleftharpoons [Cd(MeCH_3)_4]^{2+}(aq) \qquad \log \beta = 6.55$$

$$Cd^{2+}(aq) + 2en(aq) \rightleftharpoons [Cd(en)_2]^{2+}(aq) \qquad \log \beta = 10.6$$

$$Ni^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq) \qquad \log \beta = 8.61$$

$$Ni^{2+}(aq) + 3en(aq) \rightleftharpoons [Ni(en)_3]^{2+}(aq) \qquad \log \beta = 18.28$$

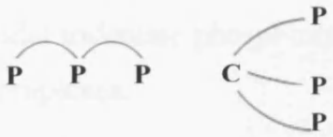
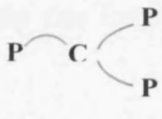
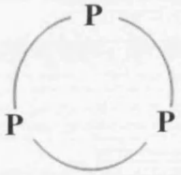
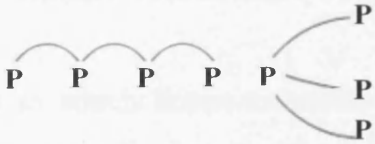
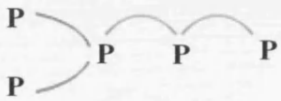
Scheme 1.1: Reaction illustrating the chelate effect[8]

1.2.1. Multidentate Phosphines

Bi-dentate phosphines are well known and in addition to the simple kinetic stabilization through the chelate effect, the ring size of the chelate formed between transition metal and bi-dentate phosphine is becoming recognised as a key factor in catalyst design.

Although the possible arrangement of phosphorus atoms in a ligand increase rapidly as the number of donor atoms increases, there are only a limited number of ligand types that have been obtained.[9]

Table 1.2 Major types of polydentate phosphine ligands

	Linear	Tripodal	Branched	Macrocylic
Tridentate	 9a	9b	 9c	
Tetradentate	 9d	9e	 9f	
Pentadentate	 9g		 9h	
Hexadentate			 9i	

1.2.1.1. Structural Aspects of Transition Metal Complexes of Polydentate Phosphine

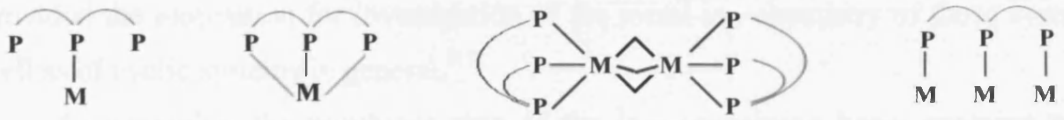
Polydentate phosphine ligands can be used to modify the coordination stereochemistry of phosphine-metal complexes by carefully selecting parameters such as the number of phosphorus atoms, the length of the connecting chain between phosphorus atoms and the sterically demanding substituent groups.[9] A number of possible coordination modes may be available for a given type of phosphine ligand but in practice only a few modes are observed.[10]

1.2.1.1.1. Tridentate Phosphines

With the exception of macrocyclic ligands discussed later, known tridentate phosphines can be categorised into two different classes. They include linear tridentate phosphines and tripodal tridentate phosphines and they can form mononuclear, bi-nuclear or even tri-nuclear complexes.

1.2.1.1.1.1. Linear Tridentate Phosphines

The ways in which linear tridentate phosphines ligands coordinate to transition metal centres depend on the choice of the metal centre and the other ligands surrounding the metal centre. More importantly, the substituent groups on the donor atoms may influence the observed coordination mode.

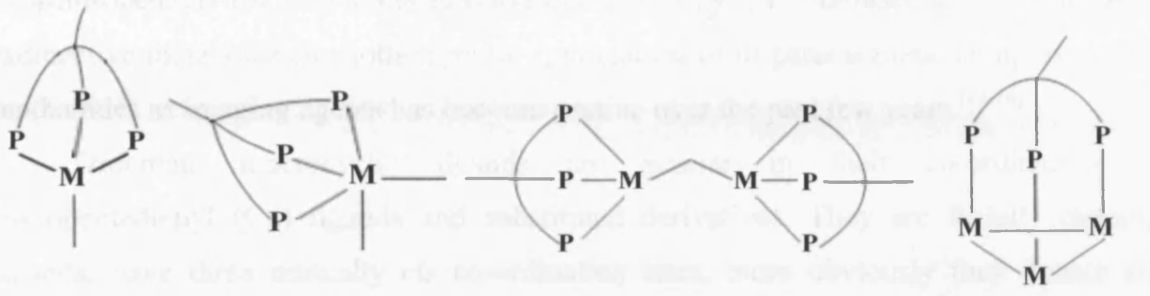


Mononuclear complex **Binuclear complex** **Trinuclear complex**

Figure 1. 5 Possible coordination modes of linear tripodal phosphines[9a, 9b, 9c]

1.2.1.1.1.2. Tripodal Tridentate Phosphines

Tripodal tridentate phosphines can form stable complexes with most d-block metals in a variety of stereochemistries.



Mononuclear complex **Binuclear complex** **Trinuclear complex**

Figure 1. 6 Possible coordination modes of tripodal tridentate phosphines[9d, 9e, 9f]

1.2.2. Macrocycles: What is different about macrocyclic ligand complexes?

The understanding of metal ion chemistry of macrocyclic ligands has important implications for a range of chemical and biological areas.[11] Macrocyclic ligands are poly-dentate ligands containing their donor atoms either incorporated in or less commonly attached to cyclic backbone. These ligands contain at least three donor atoms and the macrocyclic ring should consist of minimum of a nine atoms.[11]

The fact that macrocylic ligand complexes are involved in a number of fundamental biological systems has long been recognised.[11] The importance of such complexes to the mechanism of photosynthesis, or the transport of oxygen in respiratory systems, has provided the motivation for investigation of the metal ion chemistry of these systems as well as of cyclic systems in general.[11]

As examples, the porphyrin ring of the iron-containing haem proteins and the related chlorin complex of magnesium in chlorophyll, together with the corrin ring of vitamin B_{12} have all been studied for many years. So it is obvious that macrocyclic

ligands are widespread in biology and it is no exaggeration to state that life could not exist in the absence of such molecules.

In addition to the biological advantages, the clinical use of macrocycle ligands [(S)-2-(4-nitrobenzyl)-1,4,7,10-tetraazacyclodocecne-*N,N',N'',N'''*-tetraacetic acid] to bind radioactive metals for chemotherapeutic applications or of paramagnetic complexes with lanthanides as imaging agents has become routine over the past few years.[12-14]

Tridentate macrocyclic ligands are similar in their co-ordination to cyclopentadienyl (Cp) ligands and substituted derivatives. They are facially capping ligands, have three mutually *cis* co-ordination sites, more obviously they donate six electrons to the metal centre and due to the chelating nature of the macrocyclic ligand the remaining co-ordinated ligands are situated trans to the macrocycle or Cp ligand and geometry as also mutually *cis*.

Finally, macrocyclic chemistry is fun! The structures of these molecules are unusual and interesting, very often unexpected results are encountered, and when the synthetic routes have been optimized remarkable large molecules may be prepared in high yield from the most unlikely small molecule precursors.

Since early 1960, an enormous number of other synthetic macrocyles has been prepared and this has resulted in a great increase in interest in all aspects of the chemistry of macrocyclic systems.

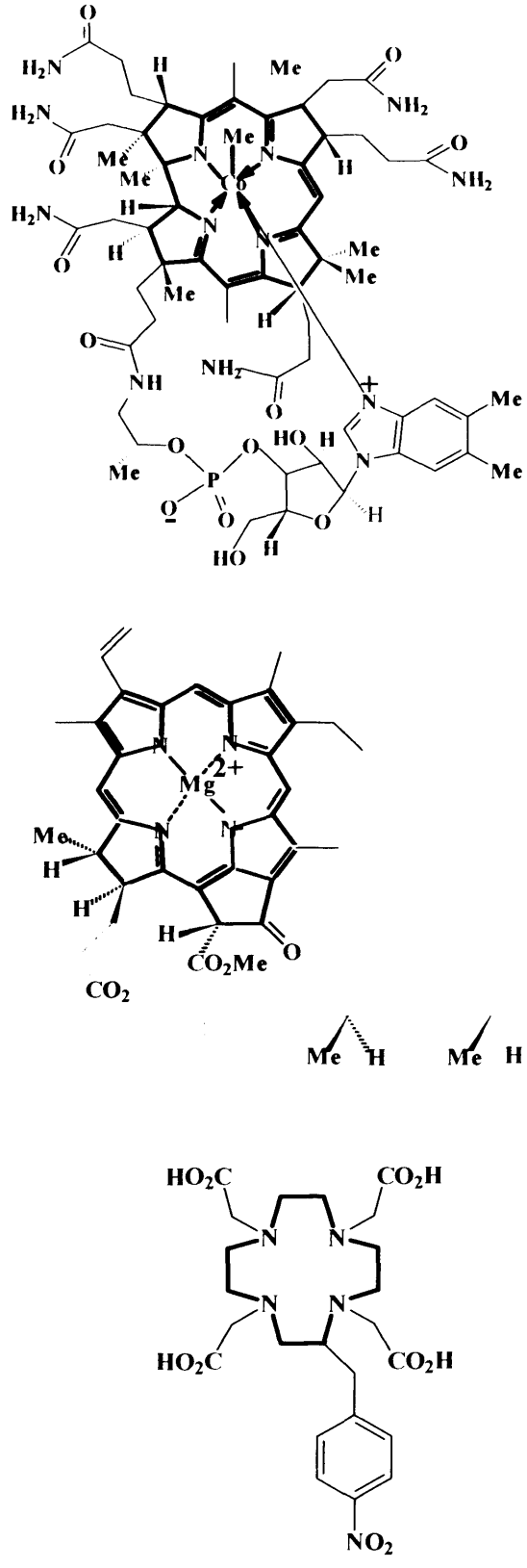
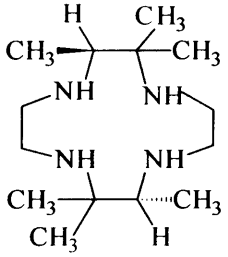


Figure 1. 7 structures of vitamin B_{12} (a), chlorophyll (b) and (*S*)-2-(4-nitrobenzyl)-DOTA (c)

1.2.2.1. The Macrocyclic Co-ordination Effect

The chelate effect has long been known in co-ordination chemistry to lead to an increase in stability of complexes.[15] The extension of the chelating effect can be identified as the macrocyclic effect which can be stated that complexes of macrocyclic ligands are more stable than those with linear polydentate ligands of similar strength. This phenomenon is demonstrated in Table 1.3 of complexes of tetramines with copper(II).

Table 1.3 Stability constant (K) for the 1:1 complexes of tetramine Copper(II)

Ligand	log K
$N[(CH_2)_3NH_2]_3$	13.1
$NH_2(CH_2)_3NH(CH_2)_3NH(CH_2)_3NH_2$	17.8
$N[(CH_2)_2NH_2]_3$	18.8
$NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$	20.1
$NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$	23.9
	28.0

In addition to the chelate effect, the stability of a macrocyclic complex is controlled by entropy effect, change of enthalpy and the ring size of the macrocycle.[16] As a result of enhanced thermodynamic stability of macrocyclic complexes it is obvious that these complexes are kinetically stable with respect to the liberation of the free ligand from the

central metal atom. However, although rare, the liberation of the macrocycle from the metal centre by applying extremely severe conditions has been reported.

1.3. Synthetic Aspect of Phosphorus Macrocycles

Despite the fact that the first phosphorus containing macrocycles $[(PNCl_2)_n$ n= 5,6,7] were prepared in 1897 by Stokes,[17] intensive studies in this field emerged after the discovery of the complex forming properties of crown ethers by Pedersen in 1967.[18,19] However, the appearance of P_3 macrocycle is limited, predominantly due to the experimental difficulties such as multistep procedures, low yield and the instability of the final products.[19] In particular, primary and secondary phosphines are inherently toxic, air sensitive, volatile and extremely malodorous.

There are two general and different synthetic strategies for the formation of macrocyclic donor ligands, specifically solution phase cycloaddition reaction and metal template methods.[19, 20]

1.3.1. Cycloaddition Reactions

Although the large ring compounds may be prepared, in principle, from any number of components, in the majority of the cases, the final reaction step involves the cyclization process in which two ends of a chain, bearing mutually reactive functionalities, come together to create the ring forming bond.[21] (Figure 1.8)

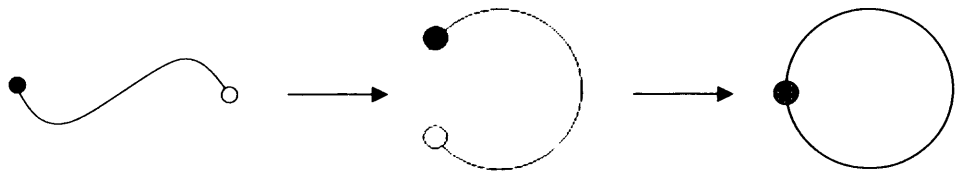


Figure 1. 8 A schematic view of the cyclization step involved in macrocycle synthesis

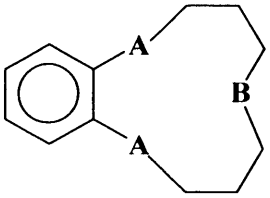
However there are drawbacks in this pathway. Specifically, it is relatively unlikely that a reactive group will meet the reaction partner at the other end of its own molecule- it is far more likely that it will meet the reactive functionality of the second molecule.

The result of this entropic constraint is that the formation of oligomer and polymer species will be a significant alternative and deleterious pathway to the desired macrocylization reaction.[21]

The widely adopted method that avoids this problem involves the application of high dilution reaction conditions, as a result of that the probability of a specific molecule meeting another molecule causing an intermolecular reaction to occur reduces dramatically due the reduction of concentration. Such intermolecular reactions are involved in the oligomerisation or polymerisation side reactions, clearly intramolecular reactions are required for the formation of a macrocycle. So, the more dilute the solution, the better the ratio of macrocycle to polymer.

It is also paramount that the reactants are mixed very slowly and special apparatus is required which allows very slow, consecutive, addition of reactants to the reaction medium over several hours or days.

Kyba and Ciampolini are the early contributors to this field regarding phosphorus macrocycles and Kyba managed to synthesise various 11 and 14-membered macrocycles [22-25] with phosphorus donor atoms along with oxygen, nitrogen and sulphur donors and Ciampolini was successful in obtaining 18-membered macrocycles[26-28] with four phosphorus atoms and two other donors including oxygen, nitrogen and sulphur.

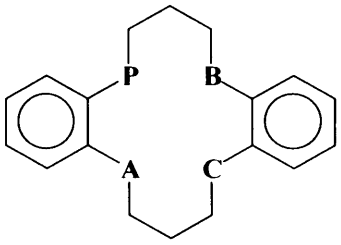


1.9

[11]-ane-A_2B

A= P, S, AS

B= N, O, S, P, As



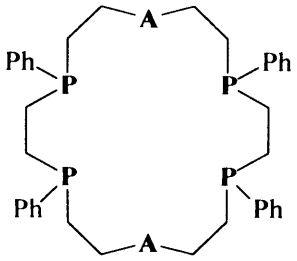
1.10

[14]-ane-PABC

A= P, S

B= N, O, S, P, As

C= N, O, S, P, As



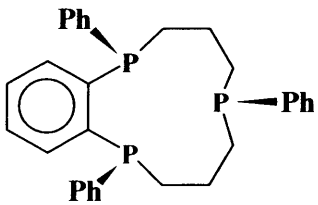
1.11

[18]-ane-P_4A_2

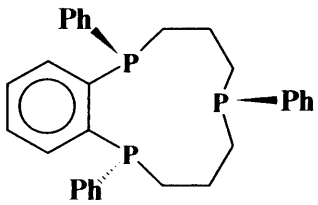
A=N, O, S

Figure 1. 9 Various types of phosphorus containing macrocycles synthesized by cycloaddition reaction

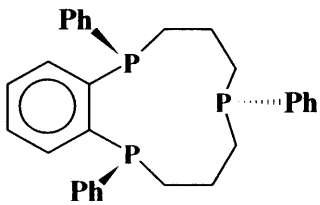
In all of these examples, there is no stereochemical control during the synthesis process and various stereoisomers were observed resulting in low yields of the individual isomers.



1.12
syn, syn



1.13
syn, anti



1.14
syn, anti

Figure 1. 10 Possible geometrical arrangement of [11]-ane-$P_3(Ph)_3$

Therefore, it is obvious that to achieve a high yield of the macrocyclic complexes at high concentration a way to position reaction sites in such a way that they happily undergo cyclisation is essential. Transition metals with their ability to gather and dispose of ligands with a given predictable geometry can induce a "Template effect".

1.3.2. Template Method

This is a widely used strategy as it overcomes the problems in high dilution method. In essence, the method involves the incorporation of additional donor atoms in to the chain and performing the cyclisation reaction in the presence of a metal ion which can coordinate to these. The idea is that the metal ion will coordinate to the donor atoms and pre-organize the various intermediates in the conformation required to give the desired cyclic products. This effect is summarised schematically in Figure 1.11.

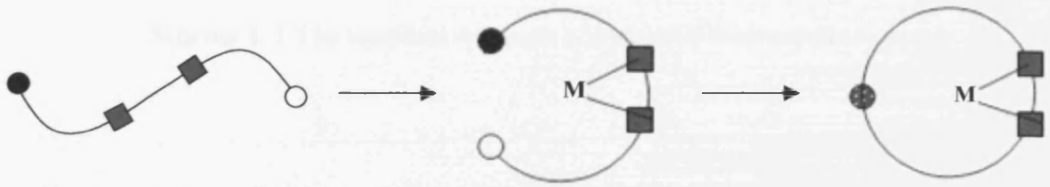
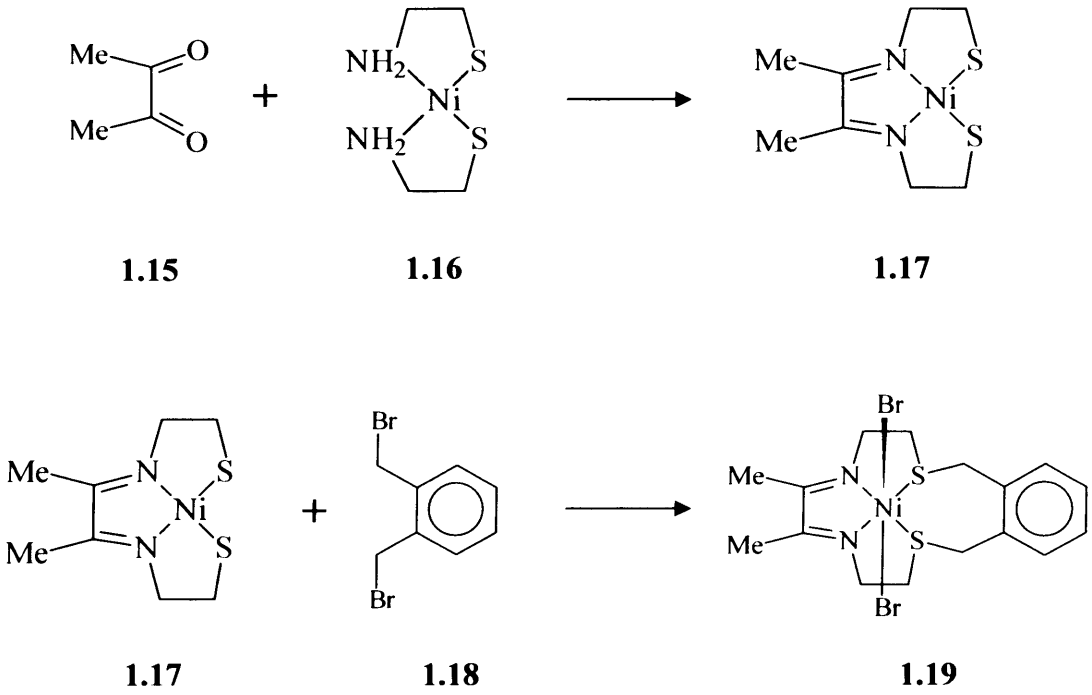


Figure 1. 11 A schematic view of the cyclisation step involved in a template macrocycle synthesis

According to the available information the very first deliberate template reaction was demonstrated by N. F. Curtis in 1960[29] and further extended by M. C. Thompson. This novel attempt illustrates some important features. Firstly, the metal ion remains coordinated and a nickel(II) complex of the N_2S_2 macrocycle is obtained. Secondly, the ring forming reaction steps are usually similar to those used in metal free

syntheses- in this case nucleophilic displacement of halide leaving group on an external electrophile(benzylic halide) by a coordinated deprotonated donor atom was adopted. Thirdly, and in this case most importantly, it is impossible to perform this reaction in the absence of the metal ion as the required reactants can not be isolated.[30]



Scheme 1. 1 The template synthesis of nickel(II) macrocyclic complex

The central metal ion is paramount in this reaction because it pre-organizes the two thiolate groups so that they are correctly oriented for the reaction with the electrophilic 1,2-bis(bromomethyl)benzene to give the macrocyclic ligand. One of the more subtle effects of the metal ion is to reduce the reactivity, and hence increase the selectivity of the thiolate groups.

Even though there are many advantages of template assisted methods there are some disadvantages as well.

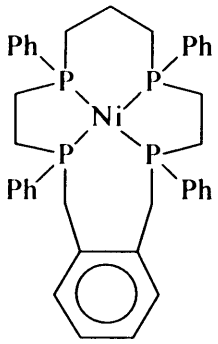
1.3.2.1. Advantages of Template Assisted Syntheses

1) Good yield
2) Mild reaction conditions
3) High dilution methods are not necessary
4) High degree of stereo and conformational control of the reaction

1.3.2.2. Disadvantages of Template Assisted Syntheses

1) Not all metal ions will act as a template for the desired reaction
2) Difficult to obtain the free macrocycle from the metal template as a consequence of macrocyclic coordination effect in some cases
3) The conditions required to remove the metal ion from macrocyclic complex can often lead to fragmentation of the fragile ligand system

There are few groups across the world involved in synthesising phosphorus containing macrocyclic ligand systems and most of these reported systems that are tetra dentate macrocycles with a square planar metal such as Ni^{2+}.



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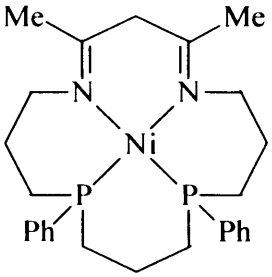

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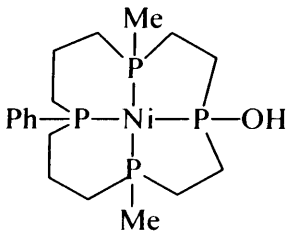

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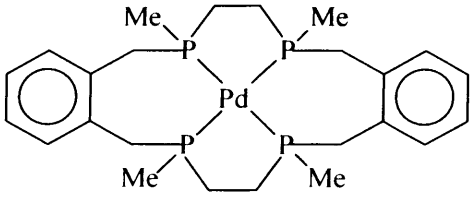
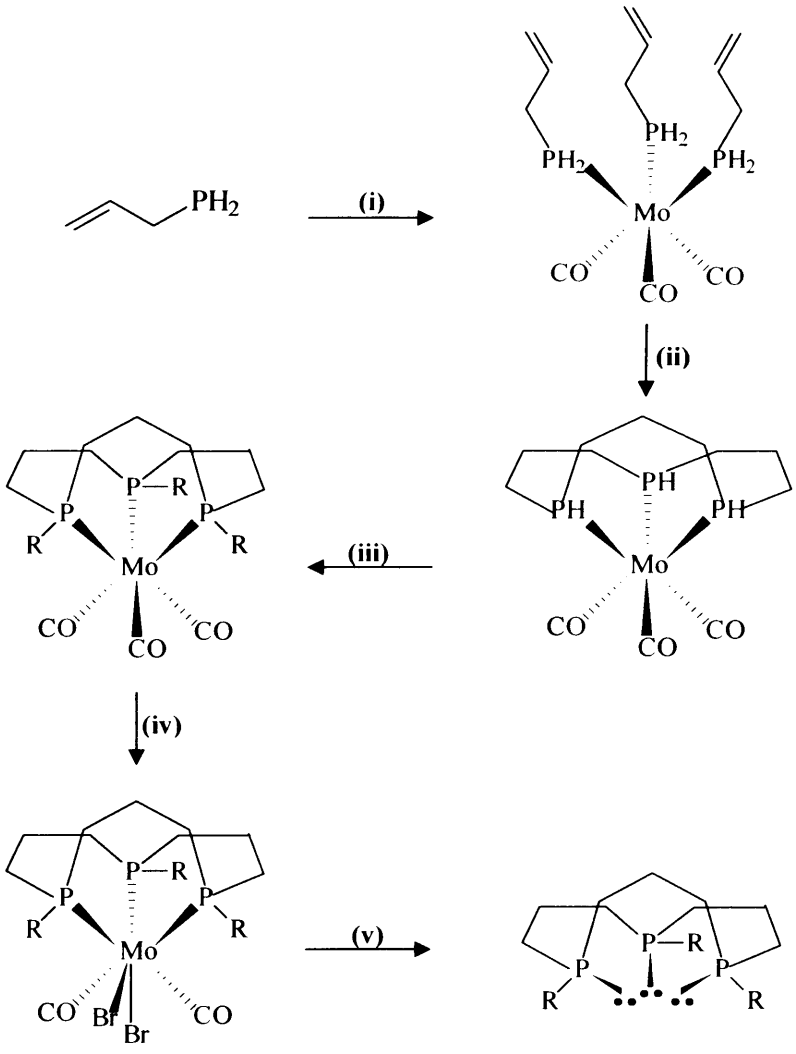


1.23

Figure 1.12 Examples of complexes with phosphorus containing macrocycles[31-33]

Despite the presence of numerous examples of cyclic polyphosphine ligands, few examples of tridentate phosphorus macrocycles have been reported.[34] In 1982 Norman and co-workers reported the first synthesis of a metal complex containing P_3 macrocycle known as [12]-ane-P_3H_3[34] with only an aliphatic backbone. The ligand was synthesized stereospecifically on a group 6 metal template.

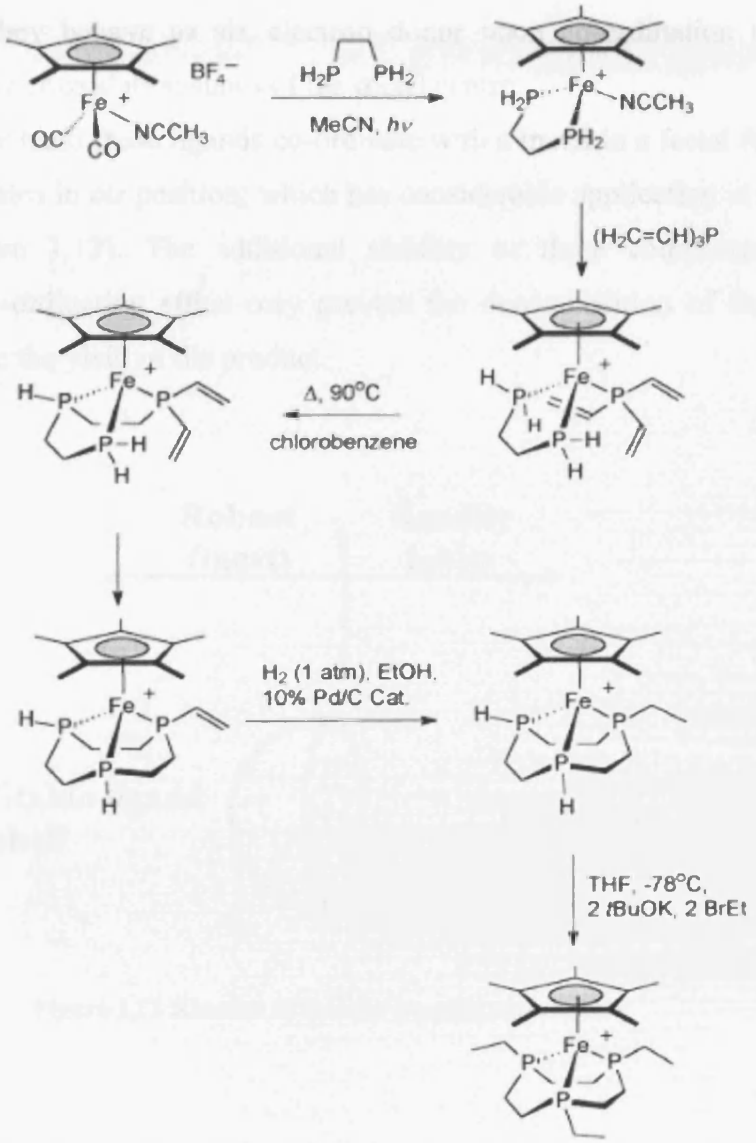
However, Norman was not successful in functionalizing phosphorus in the macrocycle, or the macrocycle liberation from the metal template. Subsequently, Edwards and co-workers reported the very first paper for functionalisation phosphorus in the system. [35, 36] Later on, the isopropyl substituted tertiary macrocycle was synthesized on a molybdenum metal centre and the free macrocycle successfully liberated. (Scheme 1.2).[37]



Scheme 1.2 The template synthesis of [12]-ane-P_3R_3 and the liberation of free macrocycle [38]

(i) $(CH_3CN)_3Mo(CO)_3$, PhMe; (ii) AIBN, PhMe, 80 ^{0}C; (iii) 3BuLi, 3RX; (iv) Br, CH_2Cl_2; (v) NaOH, EtOH

In addition to the 12-membered P_3 macrocycles Edwards and co-workers have managed to produce the first 9-membered P_3 macrocycles on an iron template (Scheme 1.3).[39] They were also successful in functionalizing the secondary 9-membered P_3 macrocycle, but they were unable to liberate the free ligand.



Scheme 1.3 The template synthesis of 9-membered P3 macrocycle

1.4. Aims of the thesis

Phosphorus ligands are known to readily form complexes with late transition metals. Particularly, monodentate and bidentate phosphine ligands have studied intensively. Tridentate phosphorus macrocyclic ligands are potentially interesting ligands since they behave as six electron donor upon co-ordination to metals and stabilised the lower oxidation states of the metal centre.

On the other hand these ligands co-ordinate with a metal in a facial fashion leaving the remaining sites in *cis* position; which has considerable application in homogeneous catalysis (Figure 1.12). The additional stability of these complexes due to the macrocyclic co-ordination effect may prevent the decomposition of the catalyst and thereby enhance the yield of the product.

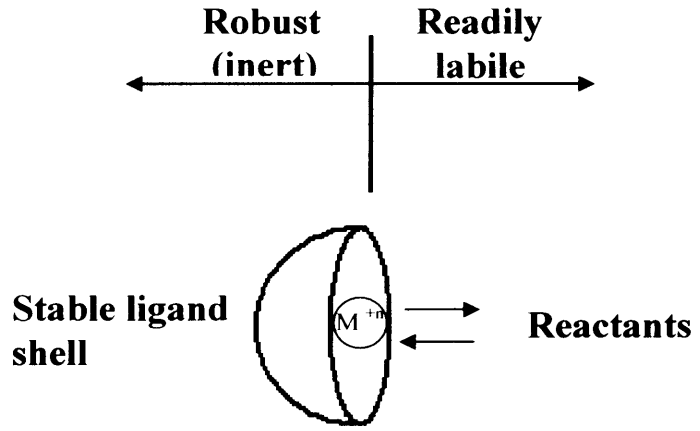


Figure 1.13 Kinetics of facially capping macrocycle

However due to the difficulties in the synthesis process of these macrocycles the co-ordination chemistry of them with the metal ions has been limited substantially. In this thesis we aim to investigate the co-ordination chemistry and organometallic

behaviour of 1,5,9-triisopropyl-1,5,9-triphosphacyclododecane with late transition metals including group 8, 10 and 11 metals.

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Chapter 2:

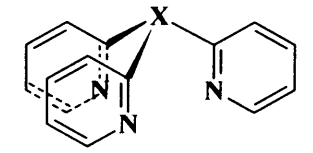
Ligand Synthesis and Coordination Chemistry of [12]-ane-$P_3(CH(CH_3)_2)_3$ with Group 8 metals Fe(II) and Ru(II)

2.1. Introduction

2.1.1. Tripodal phosphine ligands

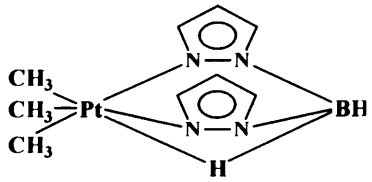
In general, tripodal ligands are commonly facially capping, tridentate chelate ligands which have received considerable attention in both coordination and organometallic chemistry.[1] There are only a few examples, however that have been reported for nitrogen, phosphorus and arsenic bridged pyridine donors.[1] The majority of examples of complexes of related rigid tridentate ligands are of polypyrazolylborate ligands.[2-4]

Although there are many reported tripodal ligands,[5-7] tripodal tridentate macrocyclic ligands containing phosphorus donor atom are extremely rare. The lack of this class of complexes is mainly due to the unavailability of suitable phosphorus precursors.



X = CH, COH, N, P, As

2.1



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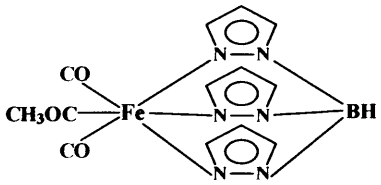

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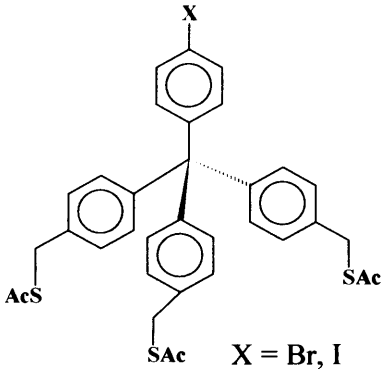
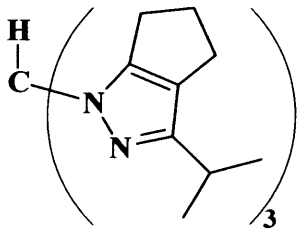


X = Br, I

2.4



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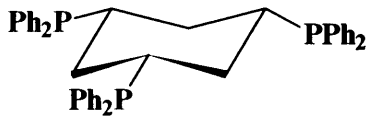


2.6

Figure 2.1: Examples of tripodal ligands with different donor atoms[1-7]

This chapter is focused on the synthesis of the macrocyclic phosphine, 1,5,9-triisopropyl-1,5,9-triphosphacyclododecane ([12]-ane-$P_3(^iPr)_3$) and coordination chemistry with group 8 metals Fe(II) and Ru(II).

Norman's synthesis of the parent trisecondary cyclic triphosphine was *via* a template coupling of the tris(allylphosphine)tricarbonyl molybdenum(0) complex.[8] As previously mentioned Edwards *et al* reported the functionalisation of this ligand [9, 10] although the liberation from the Mo(0) template remained inaccessible. Due to the d^6 octahedral high-field environment at the Mo centre, these complexes are remarkably inert. To disrupt this inertness oxidation of Mo was studied and enabled liberation and free macrocycle from oxidized Mo(II) template.[11]

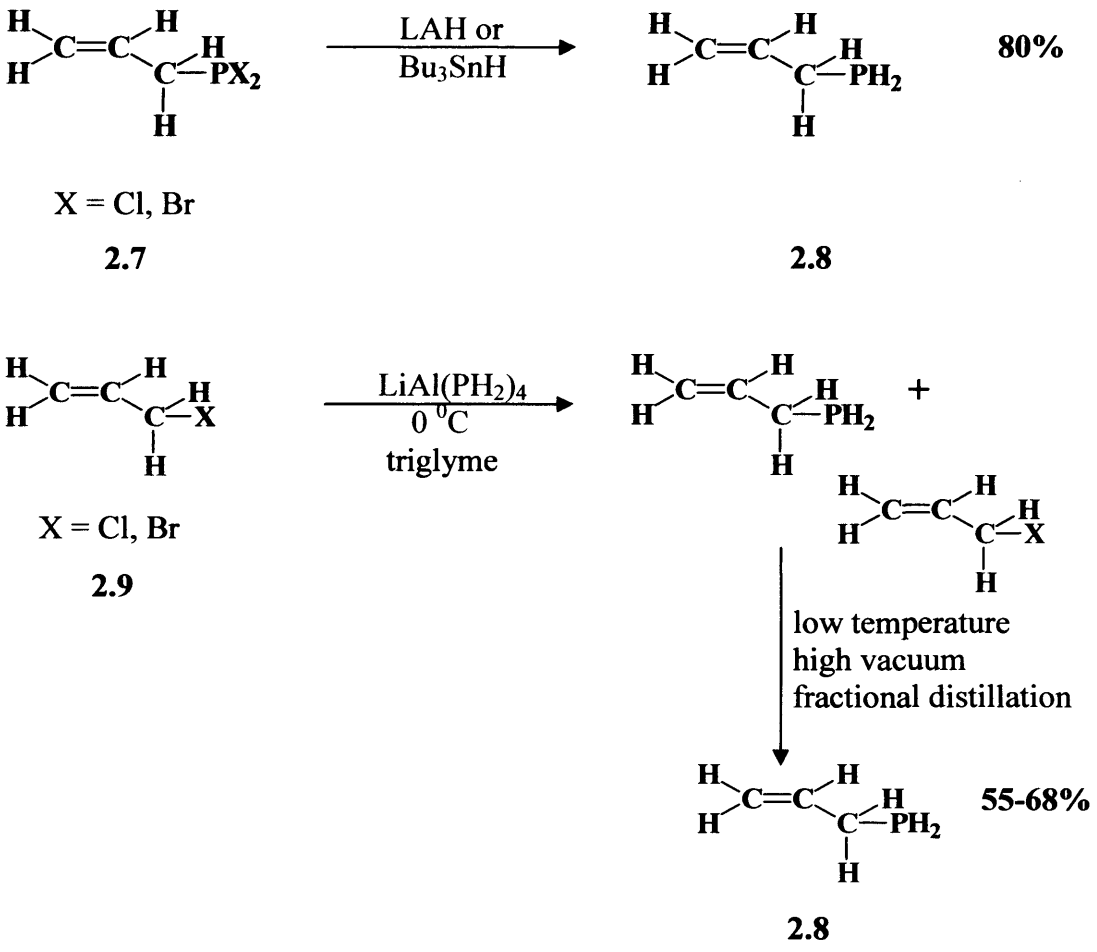
The original reported route to tricarbonyl[1,5,9-tris(isopropyl)-1,5,9-triphosphacyclododecane]-molybdenum(0) was by three consecutive addition of base followed by alkylating agent to the secondary macrocycle.[12] This may lead to progressive amount of decomposition products due to the extreme air sensitivity of alkali metal substituted phosphorus macrocycle and the total synthesis will relatively low yielding, limiting possible applications. Therefore a new reliable synthetic method for the conversion of secondary phosphorus macrocycles into a tertiary phosphorus macrocycle with less decomposition products is paramount and implemented in this work.

2.2. Results and Discussion

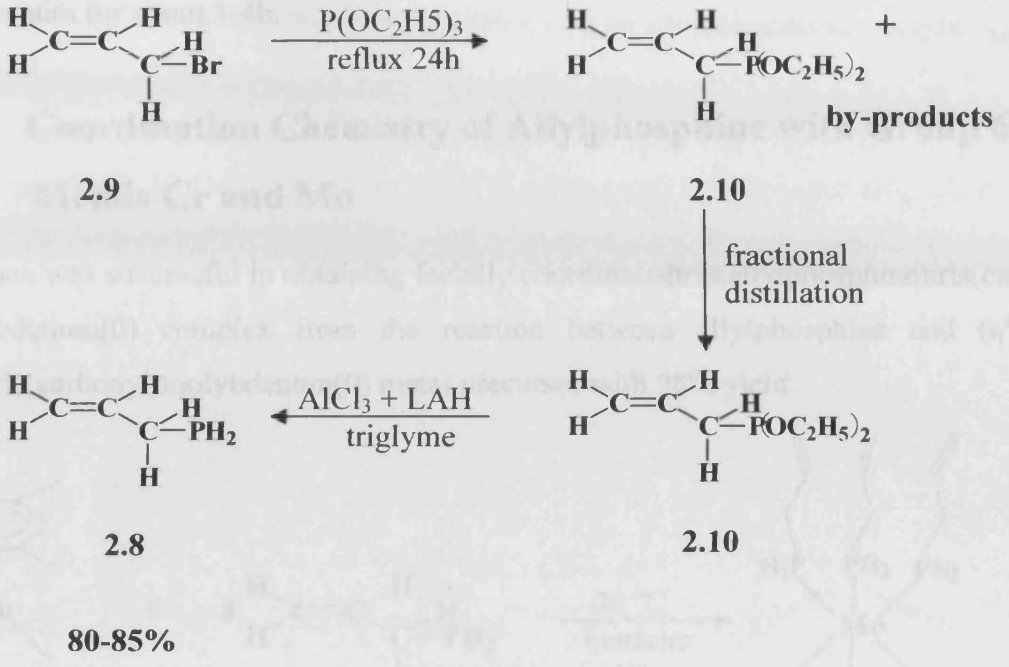
2.2.1. General route for the synthesis of allylphosphine

Aliphatic primary phosphines are generally poisonous, pyrophoric and malodorous. [13] This is assumed to be the reason that the structural and conformational properties and their coordination chemistry has been limited dramatically.

The following methods (Schemes 2.1 and 2.2) are among those reported in the literature to synthesise allylphosphines in good yield.



Scheme 2.1: Synthetic method for the preparation of allylphosphine.[14, 15]



Scheme 2.2: An efficient method for the preparation of allylphosphine

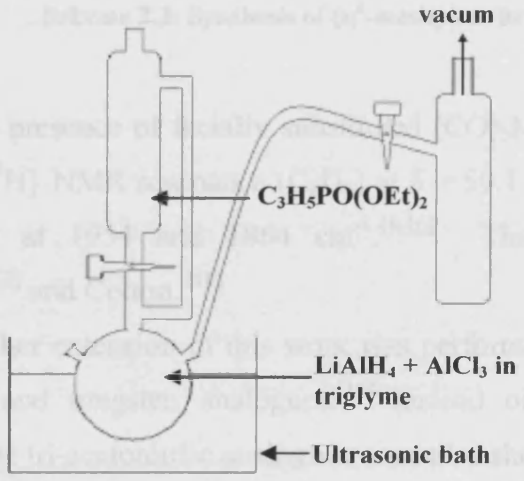


Figure 2.2: Apparatus for the synthesis of allylphosphine

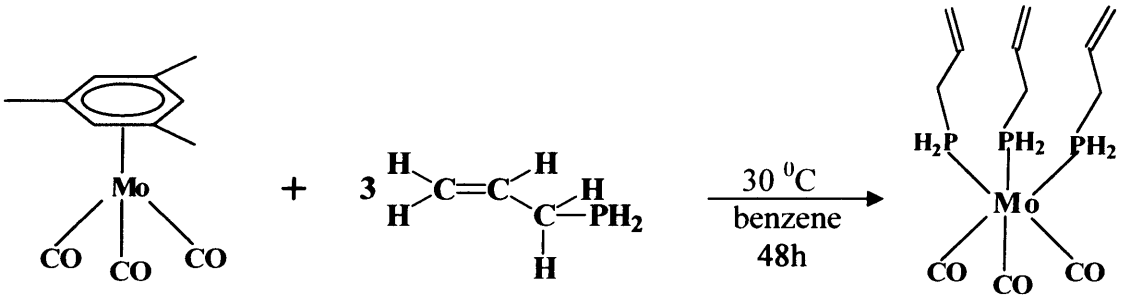
In a three necked flask $LiAlH_4$ in triglyme was cooled to -5 ^{0}C and $AlCl_3$ was slowly added over a 4h. The reducing mixture was allowed to warm to room temperature and stirred overnight. Triethylallyl phosphonate was added drop wise under Ar and after the addition the apparatus was kept in vacuum for 6h.

Allylphosphine was separated as a colourless liquid and the purity was determined by ^{1}H NMR and ^{31}P{^{1}H}NMR.

According to this method, the major difficulty associate with the synthesis is the presence of allyl bromide with allyl phosphine. This can be avoided by leaving the reaction mixture in vacuum for about 3-4h.

2.2.2. Coordination Chemistry of Allylphosphine with Group 6 Metals Cr and Mo

Norman was successful in obtaining facially coordinatedtris(allylphosphine)tris(carbonyl)molybdenum(0) complex from the reaction between allylphosphine and (η^6-mesitylene)tris(carbonyl)molybdenum(0) metal precursor with 98% yield.



2.11 **2.8** **2.12**

Scheme 2.3: Synthesis of (η^6-mesitylene)tris(carbonyl)molybdenum(0)

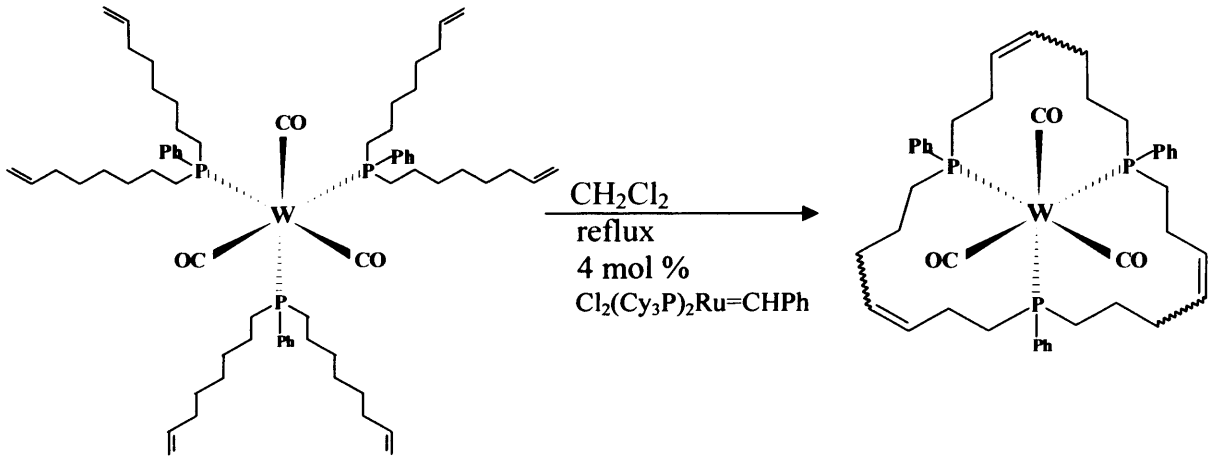
The presence of facially substituted $(CO)_3Mo(CH_2CHCH_2PH_2)_3$ is supported by a single $^{31}P\{^1H\}$ NMR resonance (C_6D_6) at δ = 59.1 ppm and the presence of two carbonyl absorptions at 1954 and 1864 cm^{-1}.[8-16] These results were supported by both Wilkinson[17] and Cotton. [18]

Further extension of this work was performed by Edwards *et al* and reported both chromium and tungsten analogues.[19] Instead of using mesitylene metal tricarbonyl precursor the tri-acetonitrile analogues were also shown to be successful.

	^{31}P NMR	CO stretch /cm^{-1}
fac-$[W(CO)_3(H_2PC_3H_5)_3]$	-80.1 (t)	1935, 1825
fac-$[Cr(CO)_3(H_2PC_3H_5)_3]$	-23.6(t)	1932, 1834

2.2.3. Cyclization of Metal Coordinated Phosphines

Cyclization of metal coordinated phosphines can be divided into two major sub groups. These can be identified as base catalysed and the free radical-catalysed addition of P-H bonds across the double bond of vinyl phosphines.[20, 21] In addition to this method, Gladysz reported large P_3 macrocycles by using Grubbs catalyst to achieve ring closing metathesis to form the cycle.[22]

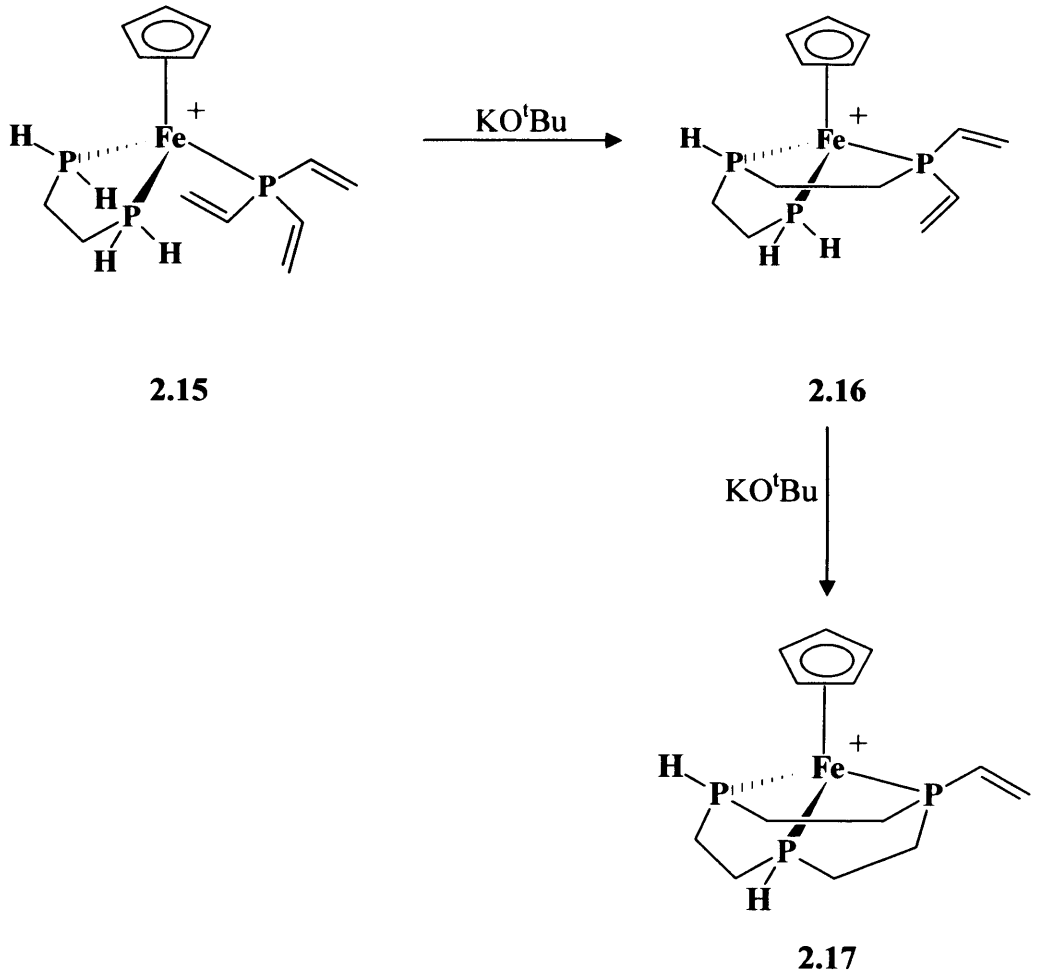


2.13 **2.14**

Scheme 2.4: Ring-closing macrocyclization reaction of large P_3 macrocycle

2.2.3.1. Base Promoted Cyclization

The ring closing reaction based on the internal nucleophilic attack is one of the most straightforward methods for the synthesis of cyclic products. Here, a strong base is used as an initiator for the cyclization process of the metal coordinated complex.



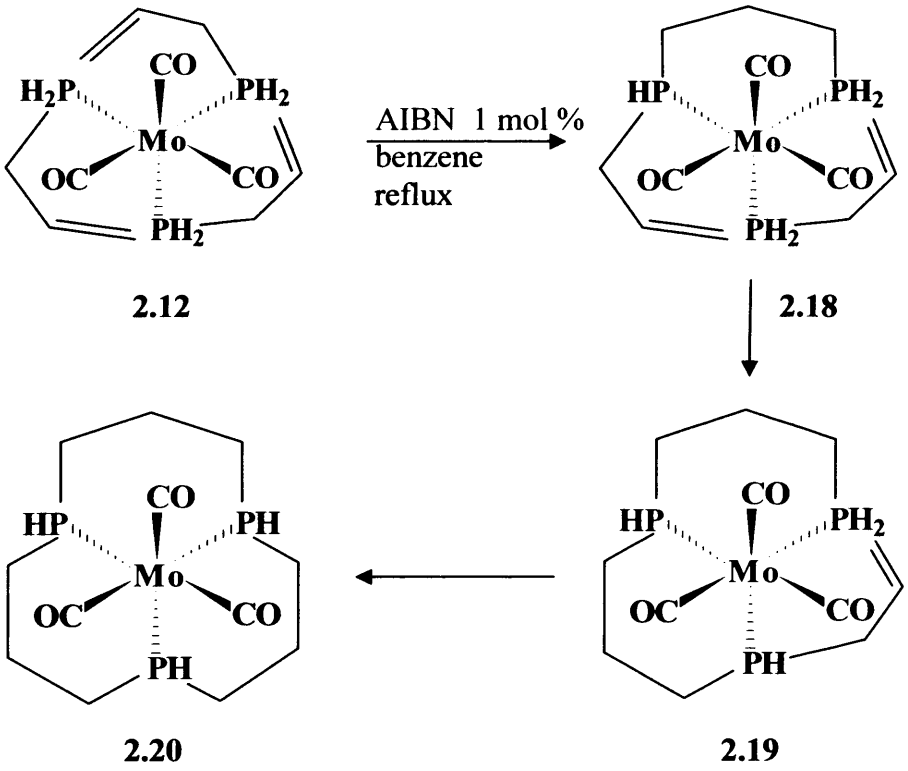
2.15 **2.16** **2.17**

Scheme 2.4: Ring-closing reaction performed by using a base

For the iron template synthesis of 9-membered P_3 macrocycles, the partial cyclization was observed even without added base. According to the $^{31}P\{^1H\}$ NMR data starting material and the intermediate were present after prolonged stirring at 80 ^0C without the addition of base. The final step was achieved only after the addition of a base such as KO^{t}Bu.[23]

2.2.3.2. Radical Promoted Cyclization

In contrast to the base promoted cyclization, in this method, cyclization is achieved following free radical initiation path. This is a stepwise cyclization process and well supported by the observation of Norman *et al.*[24]

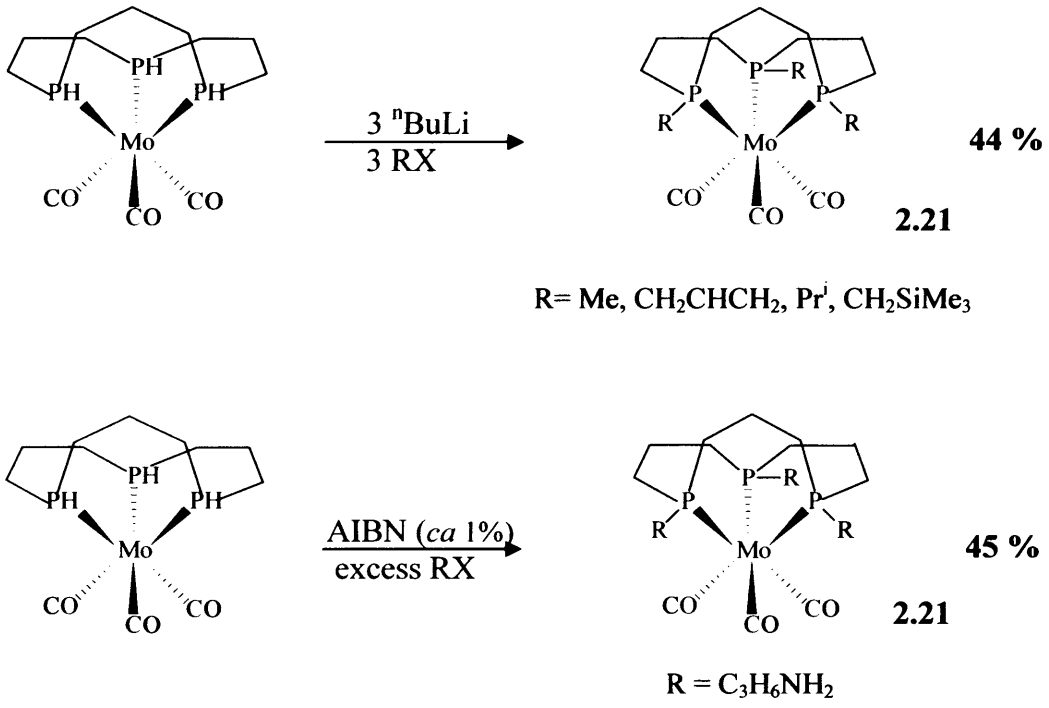


Scheme 2.5: Ring-closing reaction performed by using a catalyst

In order to perform the cyclization, Norman used AIBN as a catalyst for the above reaction and the presence of the species (**2.18**, **2.19** and **2.20**) was proved by the ^{31}P NMR analysis as a function of time.[24]

2.2.4. Synthesis of Tertiary Macrocyles

Conversion of the secondary phosphine macrocycle products into tertiary phosphine macrocycles is achieved in two different ways. They include either base catalysed addition or radical-catalysed addition of alkylating agent to the secondary macrocycle. Generally, both methods are deprotonation/alkylation stepwise cycles resulting in the clean formation of tritertiary macrocycle complexes in considerable yield. [25-28]



Scheme 2.6: Synthesis of tertiary phosphine macrocycles

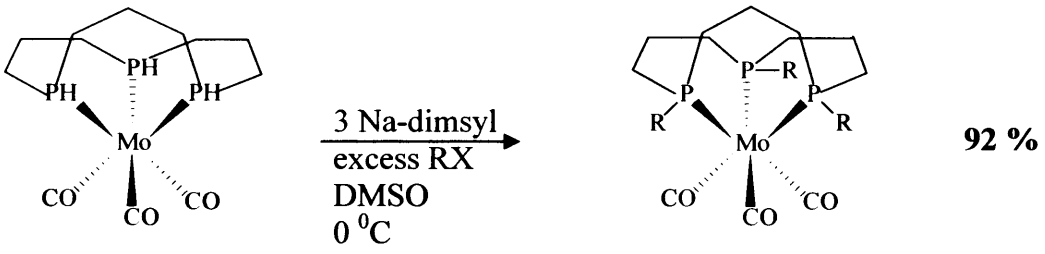
In this thesis, we discuss an innovation of the synthesis of tertiary phosphine macrocycles in high yield (92 %) by a one-pot process leading to a more reliable route to these P_3 macrocycles.

2.2.4.1. Synthesis of Na-dimsyl

In this approach Na-dimsyl is used as a base and it is synthesised by heating DMSO with NaH at about 50 ^{0}C. The product was presumably a mixture of $NaCH_2SOCH_3$ and NaH dissolved in DMSO which has a light green colour after filtration through a celite column. High temperature (more than 50 ^{0}C) will result in a very dark viscous material which can not be purified by filtration through a celite column.

2.2.4.1.1. Reaction of Secondary Phosphine Macrocycles with Na-dimsyl

This is straightforward technique by the addition of three equivalent amount of Na-dimsyl followed by the immediate addition of a slight excess amount of alkylating agent in DMSO to give rise to a tertiary phosphine macrocycle product.



2.20 **2.21**

Scheme 2.7: Synthesis of tertiary phosphine macrocycles using Na-dimsyl as a deprotonating agent.

The intermediate in the substitution (presumably $(CO)_3Mo\{[12]\text{-ane-}P_3Na_3\}$) was not be isolated due to its extreme air and moisture sensitivity. More importantly, delaying the immediate addition of alkylating agent results in a mixture of unidentified

dark products. The reaction may be monitored by $^{31}P\{^1H\}$ NMR spectroscopy, the isopropyl substituted tertiary macrocycle on molybdenum metal template appears δ ^{31}P at 12.1 ppm. (Figure 2.3)

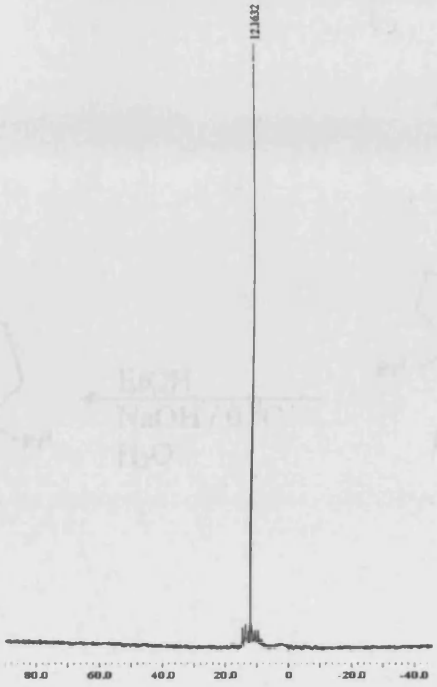
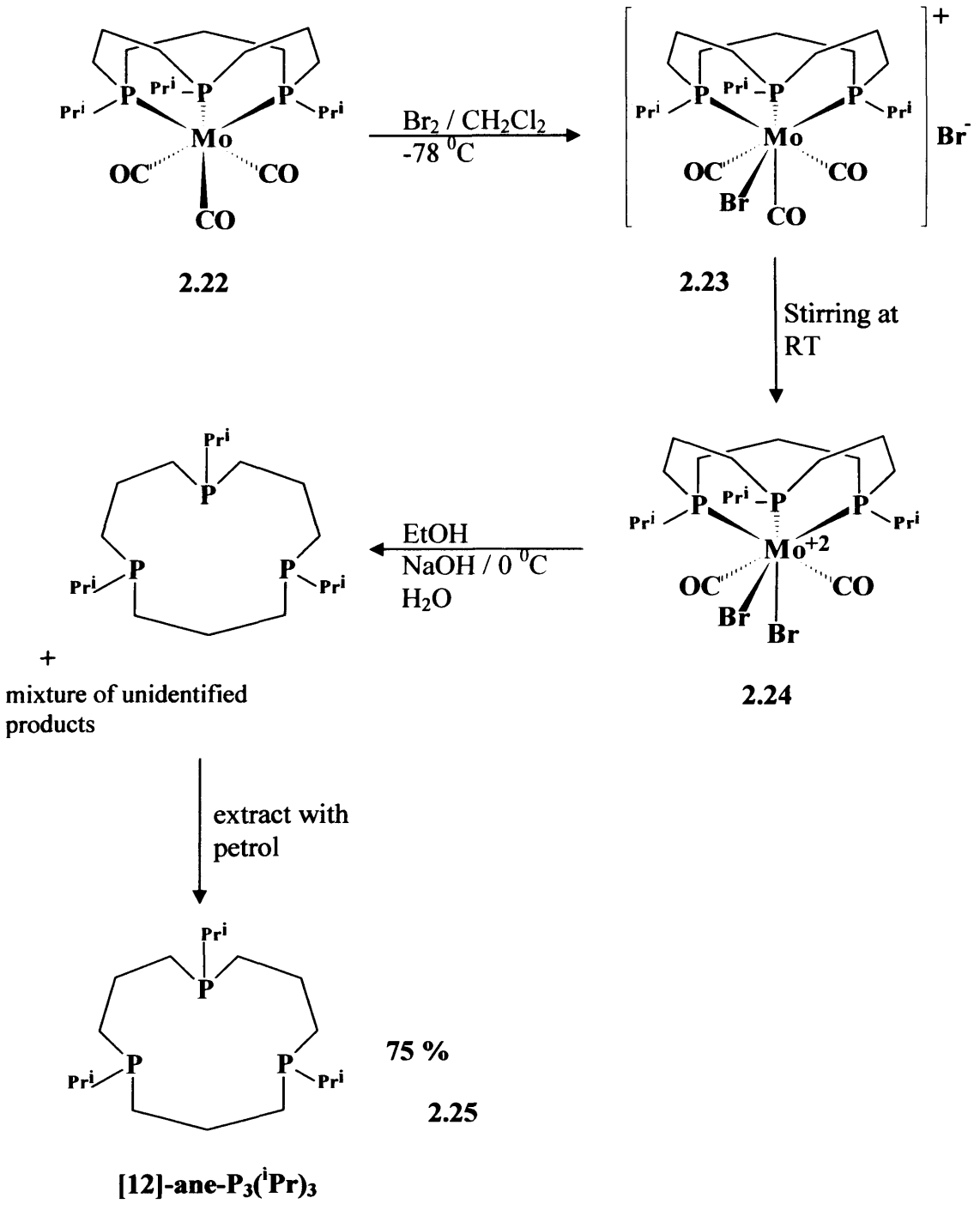


Figure 2.3: $^{31}P\{^1H\}$ NMR Spectrum of $[(CO)_3Mo([12]\text{-ane-}P_3(^iPr)_3]$

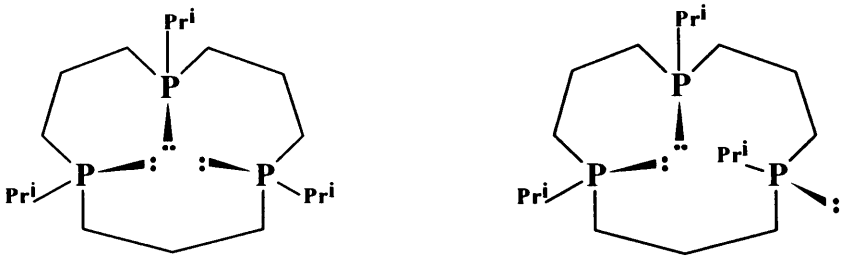
2.2.5. Liberation of the Macrocycle from Metal Template

Since Mo(0) template complexes tend to be kinetically inert (d^6, octahedral), direct liberation of the free macrocycle is difficult. A solution to this difficulty experienced with liberation attempts is to disrupt this kinetically inert state by oxidizing the metal centre. The reaction performed in this step may give rise initially to a salt of the metal complex **2.23** ($\{(CO)_3Mo\{[12]\text{-ane}P_3R_3\}Br\}Br$) in a formal oxidation state of +2 and prolong stirring will convert this salt into a seven coordinate species **2.24** ($(CO)_2Mo\{[12]\text{-ane}P_3R_3\}BrBr$).[29] This process is illustrated in the scheme 2.8 below.



Scheme 2.8: Liberation from the macrocycle from the metal template[29]

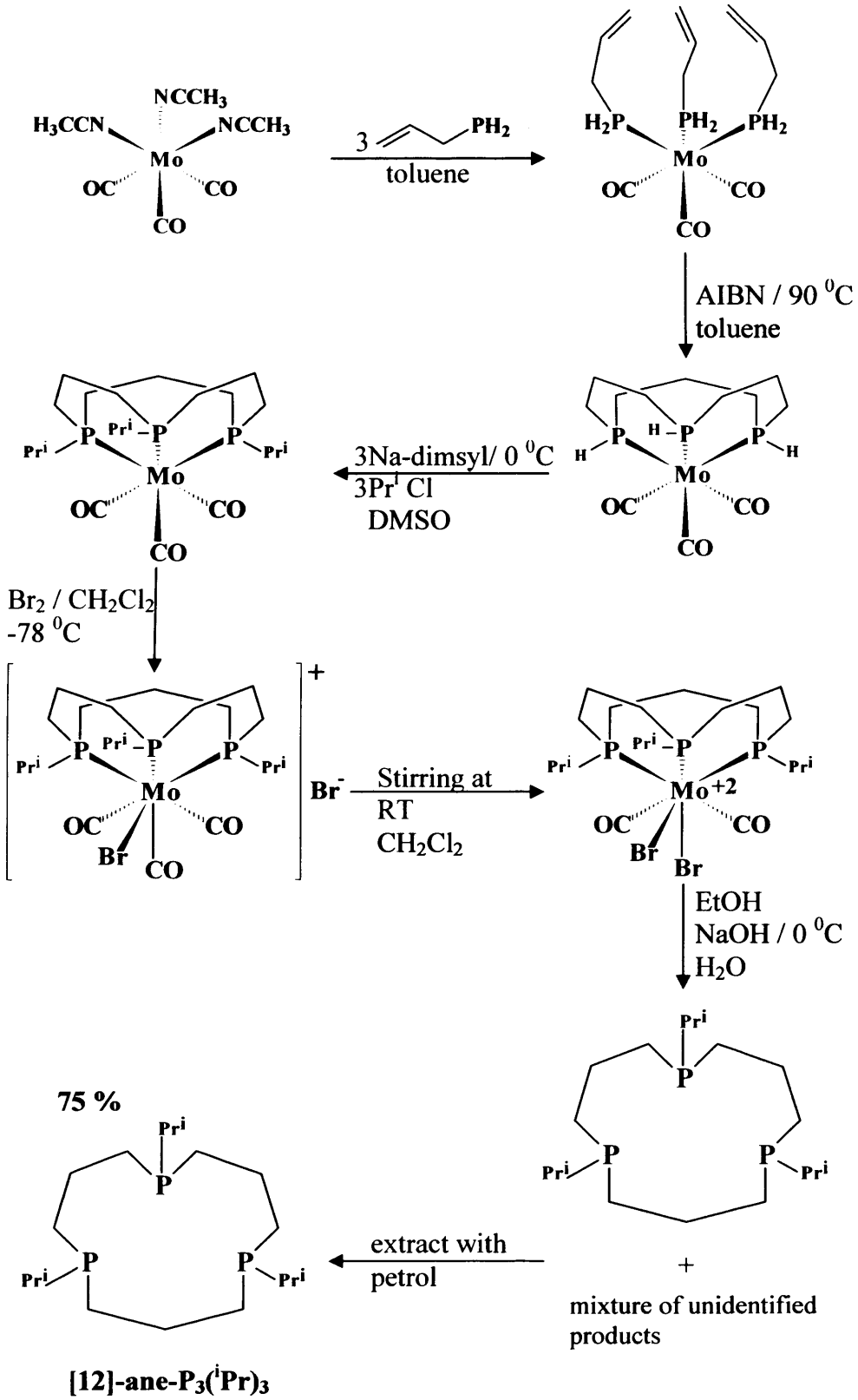
Theoretically, there are two possible geometric isomers of [12]-ane-$P_3(^iPr)_3$, however the NMR spectra indicate that the liberation is stereospecific for the syn-syn isomer since the syn-anti isomer requires an A_2B spin pattern in the ^{31}P NMR spectrum.[29]



syn-syn **syn-anti**

2.25 **2.26**

Figure 2.3: Possible geometrical isomers of [12]-ane-$P_3(^iPr)_3$



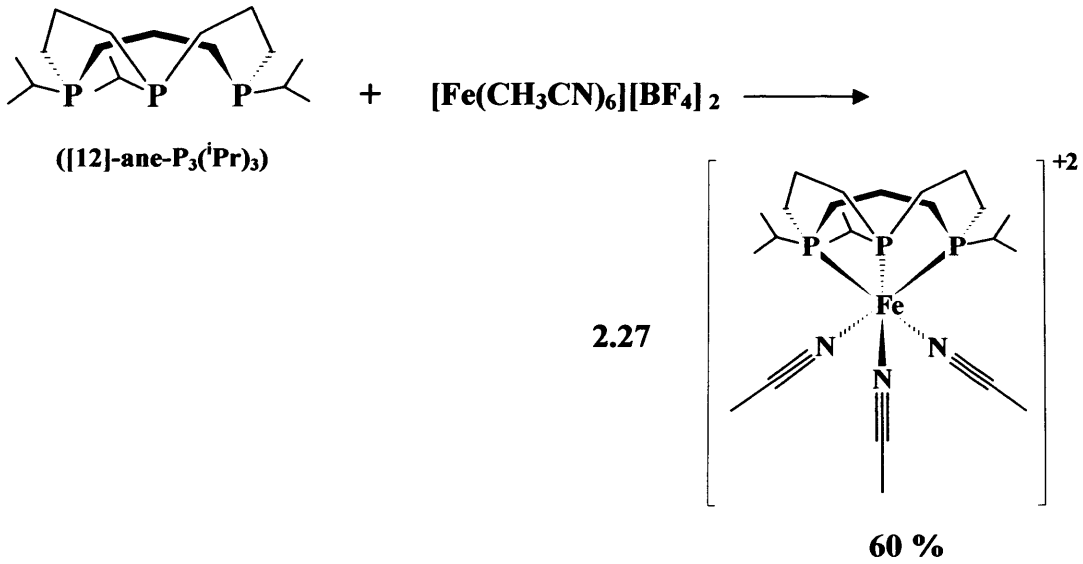
Scheme 2.9: Total synthesis of [12]-ane-$P_3(^iPr)_3$

2.2.6. Coordination Chemistry of [12]-ane-$P_3(^iPr)_3$ with Group 8 Metals Fe(II) and Ru(II)

The properties of facially capping triphosphorus macrocycles in the coordination chemistry of iron and ruthenium are of interest. There is a good precedent for complexes of these metals to be of value in catalytic applications (e.g. iron pentacarbonyl is an effective homogeneous catalyst for the hydrogenation of polyunsaturated fats[30]) as well as the biological application (e.g. it is the active centre of molecules responsible for oxygen and electron transport in metalloenzymes such as reductases, hydrogenases, etc. [31]).

Ruthenium can also be considered as a noble metallic element, and has its own expansive chemistry. It is well known to exist in a different oxidation states from (-II) to (VIII). Among these states (-II) is extremely rare but does occur: $[Ru(CO)_4]^{-2}$. Having the ability to have back bonding with ligands such as CO and phosphines Ru(II) $[RuCl_2(PPh_3)_3]$ and Ru(III) $[RuCl_3]$ states give rise to vast variety of complexes.

2.2.6.1. New Iron Chemistry



Scheme 2.10: Synthesis of tris(acetonitrile)-fac-(η3-1,5,9-triisopropyl-1,5,9-triphosphacyclododecane)iron(II)bis(tetrafluoroborate), 2.27

Scheme 2.10 indicates the reaction of [12]-ane-$P_3(^iPr)_3$ with hexa(acetonitrile)iron(II)bis(tetrafluoroborate) to give the half-sandwich compound, tris(acetonitrile)-fac-(η^3-1,5,9-triisopropyl-1,5,9,-triphosphacyclododecane)iron(II)bis(tetrafluoroborate), **2.27.** The reaction occurs in acetonitrile at room temperature instantaneously and quantitatively. There is no evidence of the formation of bis-macrocycle complex in the presence of excess [12]-ane-$P_3(^iPr)_3$.

The tris acetonitrile macrocycle complex, **2.27** is isolated as deep-orange crystals in good yield by crystallization from acetonitrile/diethyl ether and lacks solubility in most common solvents except acetonitrile and nitromethane. The $^{31}P\{^1H\}$ NMR spectrum of **2.27** shows a singlet at 35.8 ppm corresponding to the coordinated phosphine. The ^1H NMR and $^{13}C\{^1H\}$ NMR spectra consist of 5H resonances and 6C resonances of which four resonances are assignable to the four different proton and carbon environments relevant to the macrocycle similar to the spectra observed for the molybdenum (0) and (II) precursors. The ν(C-N) stretching frequencies in the IR spectrum of **2.27** are observed at 2253 cm^{-1} and 2350 cm^{-1} as expected for the complexes of this class. The structure of **2.27** is depicted in figure 2.4 and selected data are included in appendix which follows this chapter.

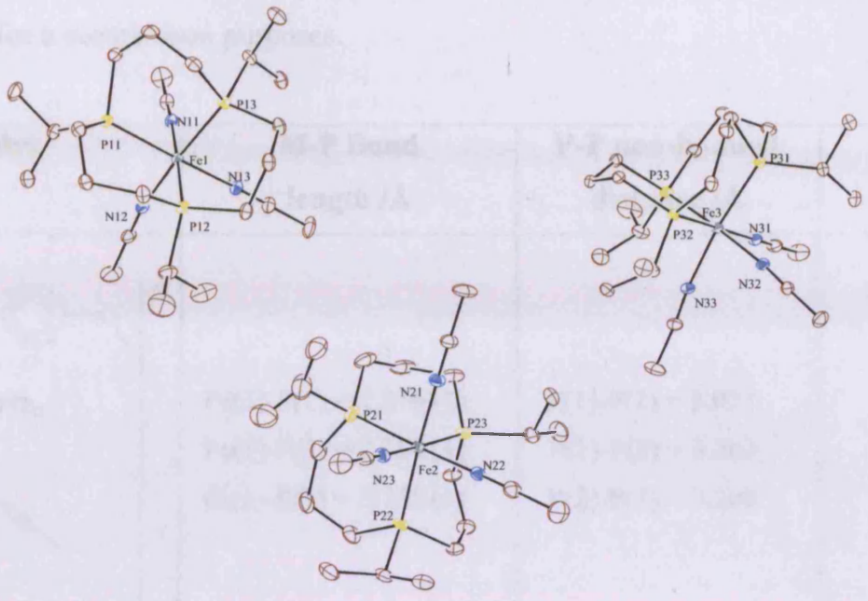


Figure 2.4: Molecular structure of the three crystallographically independent cations of tris(acetonitrile)-fac-(η^3-1,5,9-triisopropyl-1,5,9-triphosphacyclododecane)iron(II)bis(tetrafluoroborate), 2.27, the anions and the hydrogen atoms have been omitted for clarity.

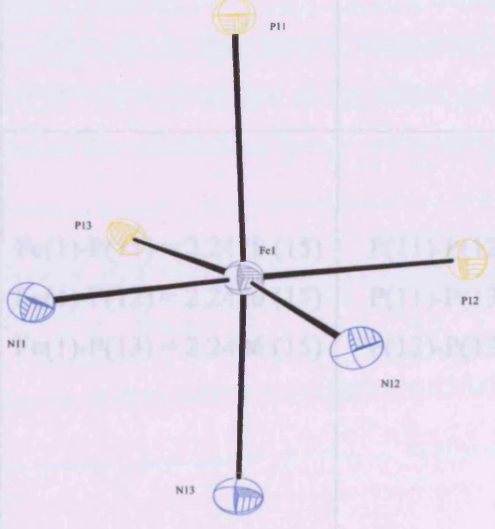


Figure 2.5: A view of the core geometry of 2.27 showing the atom numbering. Displacement ellipsoids are shown at the 30 % probability level.

Selected bond lengths of known triphosphorus tripodal ligands are included in the fallowing table for a comparison purposes.

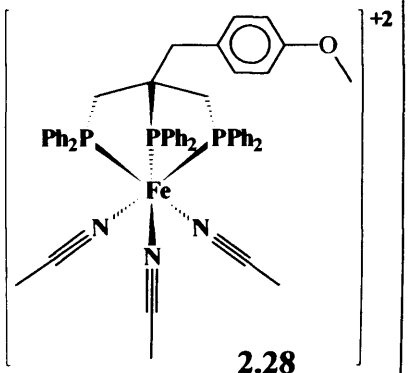
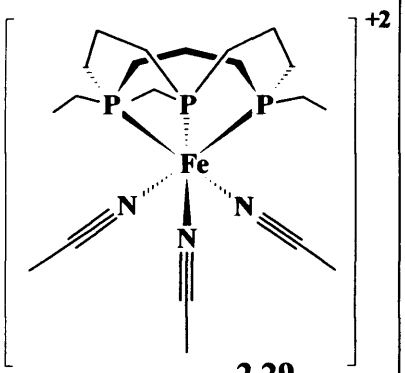
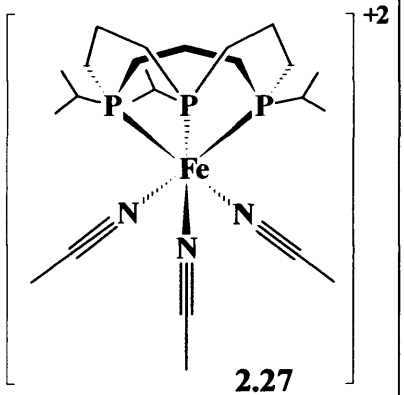
Complex	M-P Bond length /Å	P-P non-bonded distance /Å	Ref.
 2.28	Fe(1)-P(1) = 2.276 (1) Fe(1)-P(2) = 2.250 (1) Fe(1)-P(3) = 2.271 (1)	P(1)-P(2) = 3.074 P(1)-P(3) = 3.263 P(2)-P(3) = 3.208	32
 2.29	Fe(1)-P(1) = 2.217(2) Fe(1)-P(2) = 2.2257 (15) Fe(1)-P(3) = 2.224 (2)	P(1)-P(2) = 3.202 P(1)-P(3) = 3.176 P(2)-P(3) = 3.245	33
 2.27	Fe(1)-P(11) = 2.2478 (15) Fe(1)-P(12) = 2.2420 (15) Fe(1)-P(13) = 2.2406 (15)	P(11)-P(12) = 3.285 P(11)-P(13) = 3.205 P(12)-P(13) = 3.207	This work

Table 2.1: Selected interatomic distances (Å) of M-P and P-P interaction of complex 2.27 and other literature examples

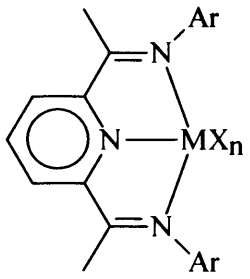
The data in table 2.1 clearly shows that the macrocycle ligand imposes different geometrical constraints on its Fe(II) complexes that does the related tripodal phosphine ligand. The tripodal complex has an average Fe-P bond length longer than that of macrocyclic complexes, indicating that either macrocycle ligand is more strongly coordinated than the tripodal analogue or that the large bulky phenyl groups in the tripodal phosphine complex restrict the approach of the phosphorus to the central metal centre.

On the other hand, in figure 2.5, the Fe(II) ion lies in the centre of the predominantly octahedral geometry and is coordinated in an identical manner to the ethyl analogue. All mutually trans donor atoms all form significantly less obtuse bond angles than the expected 180^0, P(11)-Fe(1)-N(13)(176.39^0(14)), P(12)-Fe(1)-N(11)(176.80^0(14)) and P(13)-Fe(1)-N(12)(173.52^0(14)); this is also manifested in narrow bite angles of the macrocyclic unit P(11)-Fe(1)-P(12)= 94.05^0(6), P(12)-Fe(1)-P(13)= 91.37^0(6) and P(11)-Fe(1)-P(13)= 91.12^0(6) which may be a controlling factor in the distortion from the regular octahedron.

Geometrically, there are no clear significant differences between the ethyl (**2.29**) and isopropyl (**2.27**) substituted macrocyclic complexes, but spacially there is a clear difference between them. The ethyl group substituted macrocyclic unit of the iron (II) complex is much closer to the metal atom than that of the isopropyl group substituted one. This may be due to the bulkiness of the substituent group preventing the closer approach to the metal centre.

The structure also indicates that the strong stereochemical preference of the d^6 configuration, presumably low spin, forces [12]-ane-$P_3(^iPr)_3$ to adopt an octahedral conformation.

Iron halide chemistry is well stabilised[34] and in 1999 V. C. Gibson reported highly active ethylene polymerization catalyst based on iron bearing 2,6-bis(imino)pyridyl ligands.[35]

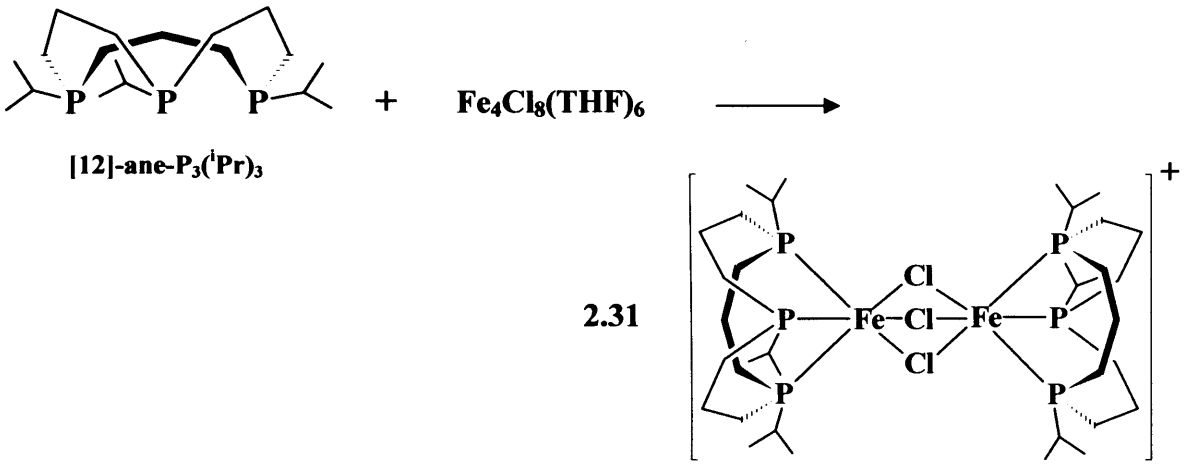


M = Fe
n = 2, 3

2.30

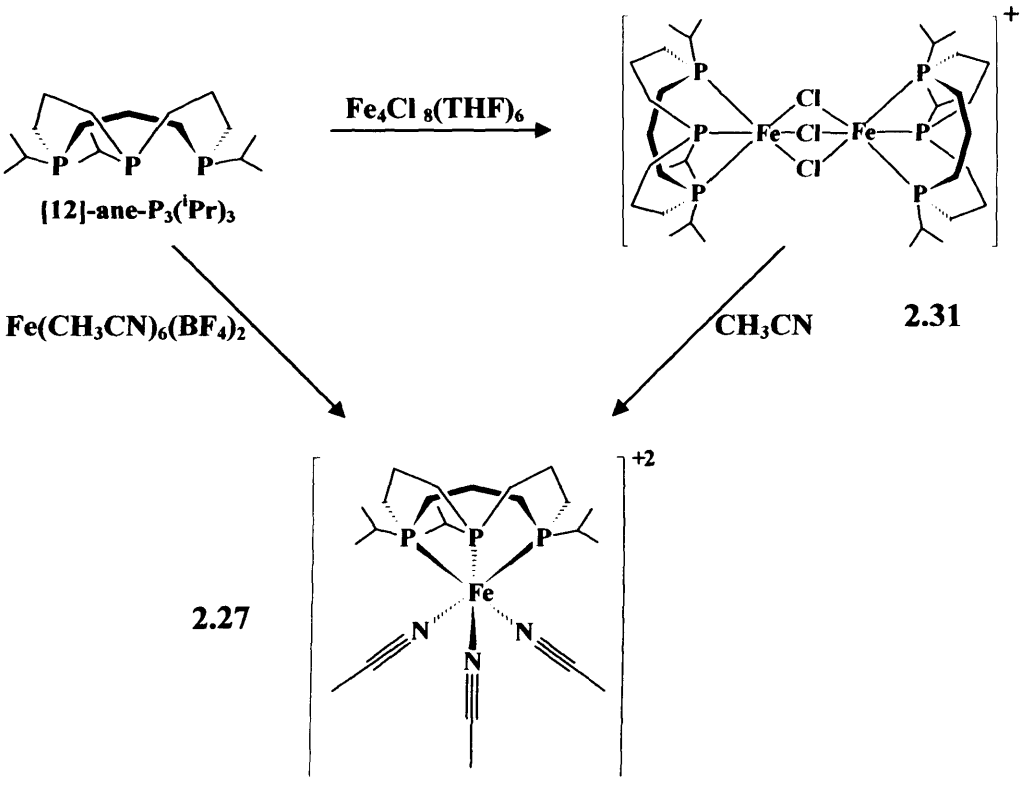
Figure 2.6 : A reported Iron based ethylene polymerization catalyst[35]

Based on this background, the investigation of the chemistry of iron halide with the triphosphorus macrocycle ligand is paramount since it has a similarity to the mentioned pyridyl ligand in coordination to the metal centre.



Scheme 2.11: Synthesis of tris(μ-chloro)bis-fac-(η^3 -1,5,9-triisopropyl-1,5,9-triphosphacyclododecane)bis(iron(II)) chloride, 2.31

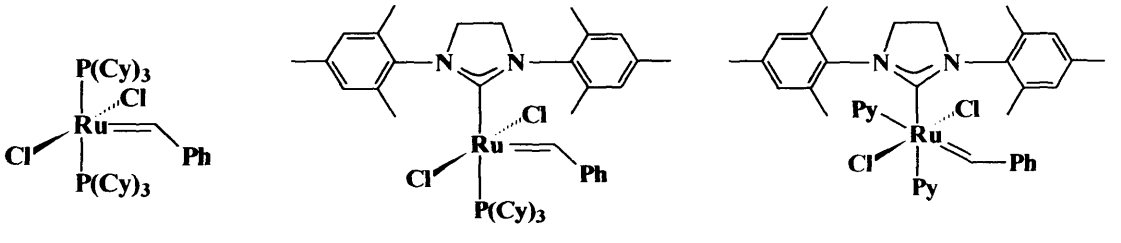
Addition of [12]-ane-$P_3(^iPr)_3$ to the suspension of tetra-metallic cluster, $Fe_4Cl_8(THF)_6$ in CH_2Cl_2 results in formation of the bimetallic species, **2.31**. The reaction is instantaneous and **2.31** is formed in purple colour. **2.31** shows a singlet in the $^{31}P\{^1H\}$ NMR spectrum at 37.1 ppm suggesting the coordination of the free ligand. In the presence of acetonitrile the colour changed to deep orange and the $^{31}P\{^1H\}$ NMR signal is shifted to 35.8 ppm indicating the presence of tri acetonitrile complex **2.27**. The attempt to isolate **2.31** as a pure compound is unsuccessful since it is not soluble in common solvents used except acetonitrile. This observation is summarised as follows.



Scheme 2-12

2.2.6.2. New Ruthenium Chemistry

Ruthenium has well established coordination and organometallic chemistry; in particular ruthenium-phosphine chemistry is thoroughly documented including well known Grubbs catalysts.[36]

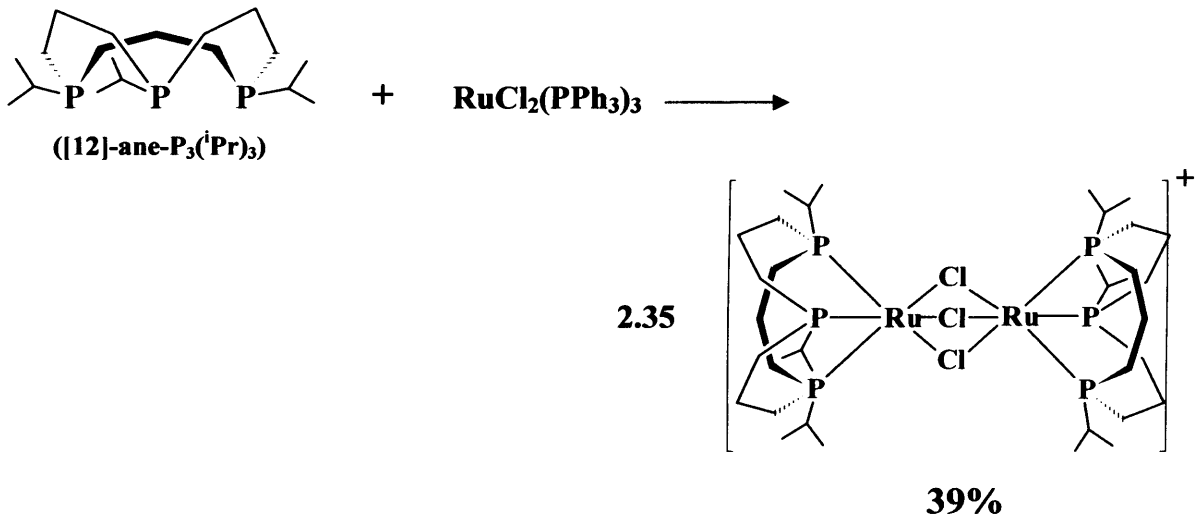


1st generation **2nd generation** **3rd generation**

2.32 **2.33** **2.34**

Figure 2.7: Some reported Ru(II) catalysts[36]

In fact ruthenium macrocyclic chemistry bearing a P_3 12-membered ring is poorly studied and therefore investigation of this area will be of interest in the study of reactivity (e.g. in catalysis) as the higher stability of the macrocyclic ligand complexes (in comparison to cyclic or monodentate analogues) may lead to more robust catalysts. This in turn should lead to higher longevity. In addition, the rigid facially capping (all *cis*) arrangement of P-ligands, which is not enforced for non-macrocyclic ligands, may lead to mechanistic differences and hence new reactivity.



Scheme 2-13: Synthesis of tris(μ-chloro)bis-fac-(η^3 -1,5,9-triisopropyl-1,5,9-triphosphacyclododecane)bis(ruthenium(II)) chloride, 2.35

The complex **2.35,** tris(μ-chloro)bis-fac-(η^3 -1,5,9-triisopropyl-1,5,9-triphosphacyclododecane)bis(ruthenium(II)) chloride is formed instantaneously upon the addition of [12]-ane-$P_3(^iPr)_3$ into a $RuCl_2(PPh_3)_3$ in CH_2Cl_2. This bi-metallic bridging complex is crystallized with CH_2Cl_2/petrol and gives white colour needle crystals with 39.3 % yield. Complex **2.35** gives a singlet for its $^{31}P\{^1H\}$ NMR at 35.2 ppm suggesting the coordination of free macrocyclic ligand to the metal centre.

The ^1H NMR and $^{13}C\{^1H\}$ NMR spectra consist of four resonances assignable to the four different proton and carbon environments relevant to the macrocycle similar to the spectra observed for the molybdenum (0) and (II) precursors.

The pioneering work of Geoffrey Wilkinson has provided the fruitful understanding of tertiary phosphine complexes of ruthenium(II).[37] In contrast to these reportedanalogous complexes of ruthenium bridges bearing phosphorus ligands are observed[38] only few structures have been crystallographically characterised.

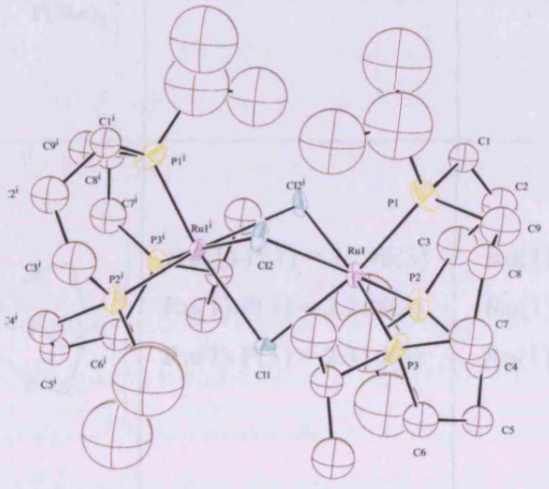


Figure 2.8: Molecular structure of tris(μ-chloro)bis-fac-(η^3 -1,5,9-triisopropyl-1,5,9-triphosphacyclododecane)bis(ruthenium(II)) chloride, 2.35 the anions and the hydrogen atoms have been omitted for clarity.

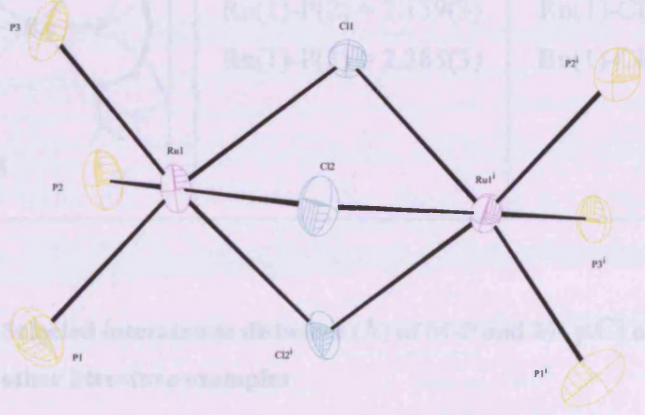


Figure 2.9: A view of the core geometry of 2.35 showing the atom numbering. Displacement ellipsoids are shown at the 30 % probability level.

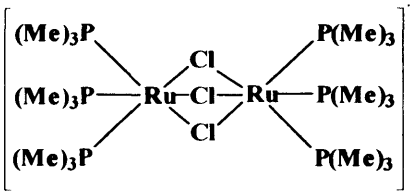
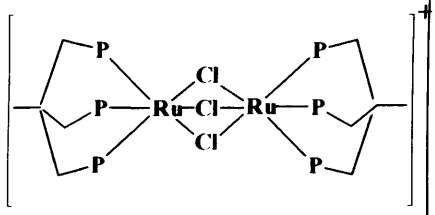
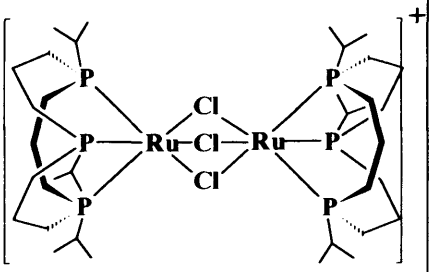
Complex	M-P Bond length /Å	P-μCl bond length /Å	Ref.
 **2.36**	Ru(1)-P(1) = 2.256(4) Ru(1)-P(2) = 2.255(4) Ru(1)-P(3) = 2.248(4)	Ru(1)-Cl(1) = 2.488(4) Ru(1)-Cl(2) = 2.463(4) Ru(1)-Cl(3) = 2.481(4)	37
 **2.37**	Ru(1)-P(1) = 2.296(3) Ru(1)-P(2) = 2.308(3) Ru(1)-P(3) = 2.310(3)	Ru(1)-Cl(1) = 2.488(3) Ru(1)-Cl(2) = 2.500(3) Ru(1)-Cl(3) = 2.494(3)	39
 **2.35**	Ru(1)-P(1) = 2.251(3) Ru(1)-P(2) = 2.159(3) Ru(1)-P(3) = 2.285(3)	Ru(1)-Cl(1) = 2.553(4) Ru(1)-Cl(2) = 2.509(4) Ru(1)-Cl(3) = 2.533(4)	This work

Table 2.2: Selected interatomic distances (Å) of M-P and M- μCl of complex 2.35 and other literature examples

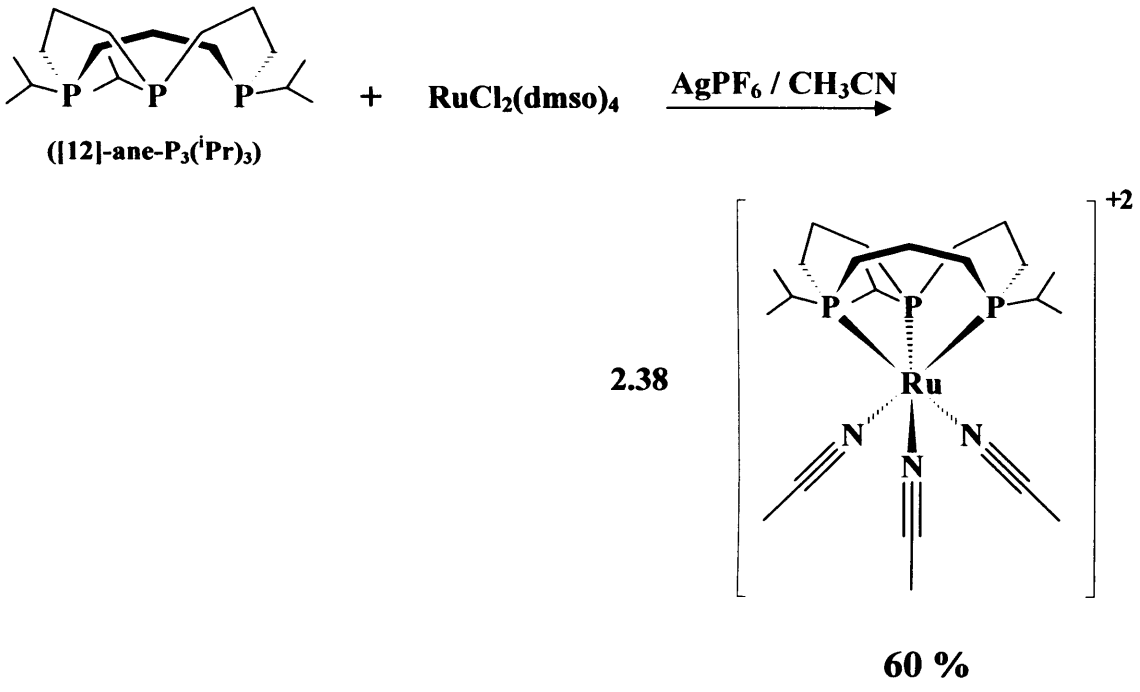
Edwards *et al* reported the synthesis of **2.35** in 1997 *via* a different route but was not successful in getting the crystallographic analysis.[40]

The bimetallic macrocyclic phosphine complex, **2.35** crystallizes in the monoclinic space group C2. The central metal atom ruthenium(II) ion has a slightly distorted octahedral coordination geometry.

The data in table 2.2 clearly explain that the similarities between the bimetallic Ru(II) species bridged with three chlorine atoms. All three complexes have average Ru-P bond lengths almost similar, indicating the identical nature in coordination to the metal centre. In contrast to the Ru-P bond distance, the complex **2.35** has slightly longer Ru-μCl bond.

On the other hand, in the figure 2.8 Ru(II) ion lies at the centre of the predominantly octahedral geometry and is coordinated in an identical manner to the ethyl group substituted bimetallic Fe(II) species. All mutually trans sets of donor atoms all from significantly obtuse bond angles than the expected 180^0, P(1)-Ru(1)-Cl(1)(170.14^0(11)), P(2)-Ru(1)-Cl(2) (169.77^0(11)) and P(3)-Ru(1)-Cl(3) (172.78^0(10)) The narrow bite angles of the macrocyclic unit P(1)-Ru(1)-P(2)= 91.38^0(9), P(2)-Ru(1)-P(3)= 92.68^0(10) and P(1)-Ru(1)-P(3)= 93.23^0(9) may be also another factor for the distortion from the regular octahedron since it provides more space for the chlorine groups to organise in the octahedral environment.

Again the structure also indicates that the strong stereochemical preference of the d^6 configuration, presumably low spin, forces [12]-ane-$P_3(^iPr)_3$ to adopt an octahedral conformation.



60 %

Scheme 2.14: Synthesis of tris(acetonitrile)-fac-(η3-1,5,9-triisopropyl-1,5,9-triphosphacyclododecane) ruthenium (II)bis(hexafluorophosphine), 2.38

The synthesis of tri acetonitrile macrocyclic ruthenium complex, **2.38** is achieved *via* two steps. The first step includes the addition of 1 equivalant of [12]-ane-$P_3(^iPr)_3$ into $RuCl_2(dmso)_4$ in dichloromethane at room temperature producing $LRuCl_2(dmso)$.[40] The product is isolated and the addition of two equivalent amount of $AgPF_6$ into it in acetonitrile at room temperature results **2.38**. The second step is instantaneous and **2.38** is isolated as a light purple colour product by vapour diffusion of petrol into acetonitrile.

The monometallic complex, **2.38** has been characterised by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectroscopy and the IR spectrum is prominent by the peak at 2253 cm^{-1} which can be assigned to acetonitrile C-N stretch.

The $^{31}P\{^1H\}$ NMR spectrum of **2.38** has a singlet at 27.3 ppm which is assigned to the coordinated phosphine and the counter ion hexafluorophosphine gives a spt at -143.1 ppm (J_{P-F} = 707 Hz) due to the coupling with fluorine. The ^1H NMR spectrum of **2.38** is almost identical to that of iron analogue, **2.27**.

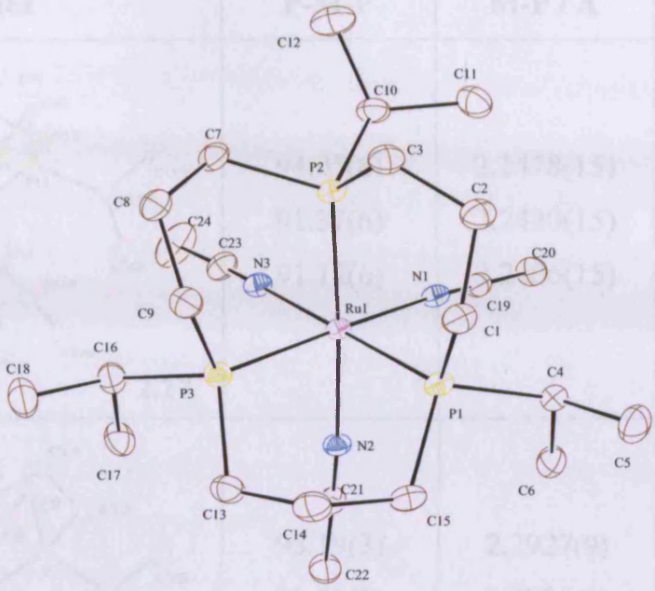


Figure 2.10: Molecular structure of tris(acetonitrile)-fac-(η3-1,5,9-triisopropyl-1,5,9-triphosphacyclododecane) ruthenium (II)bis(hexafluorophosphine), 2.38

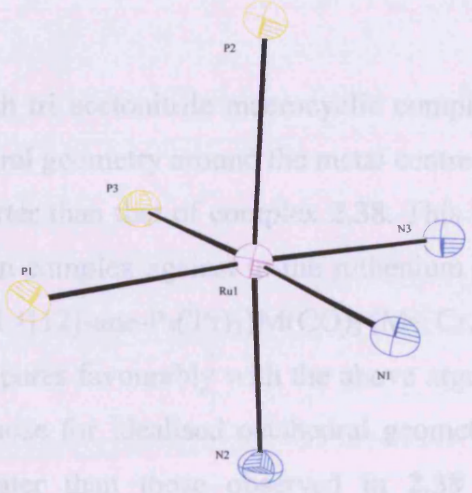
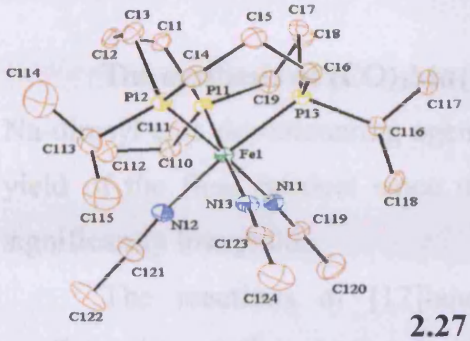
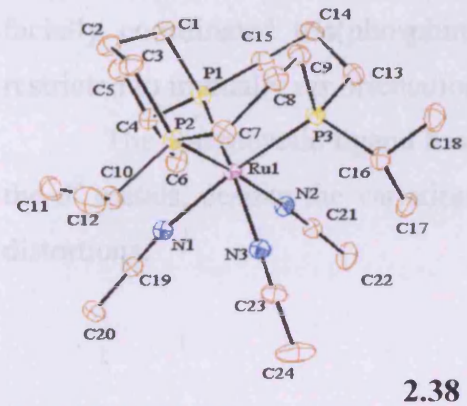


Figure 2.11: A view of the core geometry of 2.38 showing the atom numbering. Displacement ellipsoids are shown at the 30 % probability level.

Complex	P-M-P	M-P / Å	M-N/ Å
 **2.27**	94.05(6) 91.37(6) 91.12(6)	2.2478(15) 2.2420(15) 2.2406(15)	1.964(5) 1.967(5) 1.970(4)
 **2.38**	93.19(3) 90.58(3) 90.21(3)	2.2927(9) 2.2926(9) 2.2828(9)	2.118(3) 2.118(3) 2.121(3)

The structures of both tri acetonitrile macrocyclic complexes **2.27** and **2.38** have slightly distorted *fac*-octahedral geometry around the metal centre. The M-P bond length of complex **2.27** is slightly shorter than that of complex **2.38**. This relative shortening of the metal–ligand bond in the iron complex against to the ruthenium complex is expected and agrees well with the series of {[12]-ane-$P_3(^iPr)_3$}$M(CO)_3$ (M= Cr, Mo) complexes.[19] The M-N bond distance also compares favourably with the above argument and the interligand bond angles are closed to those for idealised octahedral geometry[average P-Fe-P angle $92.13(3)^0$] in **2.27** are greater than those observed in **2.38** [average P-Ru-P angle $91.26(6)^0$]. These minor differences reflect the relative size of the metal atoms, thus the size of this macrocyclic ligand appears to result in a slight expansion of the P-M-P angles around the smaller iron relative to those for ruthenium.

2.3. Conclusion

The synthesis of $(CO)_3Mo\{[12]\text{-ane-}P_3(^iPr)_3\}$ from $(CO)_3Mo\{[12]\text{-ane-}P_3H_3\}$ using Na-dimsyl as a deprotonating agent has proven a remarkable achievement in terms of the yield of the final product since most of the conventional bases such as ^{n}BuLi gives a significantly low yield.

The reactions of [12]-ane-$P_3(^iPr)_3$ with group 8 metals with the electronic configuration of d^6 including Fe(II) and Ru(II) precursor complexes rapidly give rise to facially coordinated tris(phosphine) complexes with the other coordinated ligands are restricted to mutually *cis* orientation environment.

The macrocyclic ligand has the ability to form halide and acetonitrile complexes of the d^6 metals, despite the variation in radii, which are comparatively free from structural distortions.

2.4 Experimental

2.4.1. General

Techniques and Instruments: All reactions were carried out in an atmosphere of dry argon. All solvents were dried by refluxing over standard drying agents. The compounds allylphosphine, *syn,syn*-1,5,9-triisopropyl-1,5,9-triphosphacyclododecane, [12]-ane-$P_3(^iPr)_3$ were prepared by a slight change of literature methods. **Caution:** The organophosphines and some of their complexes described are *highly malodorous* and likely *highly toxic*. Great care should be exercised in their handling. All other reagents were obtained from the Aldrich Chemical Company and, where appropriate, were degassed before use. NMR spectra were recorded on a Bruker DPX-500 instrument at 500 MHz (^1H), and 125.75MHz (^{13}C), Bruker DPX-400 instrument at 400 MHz and 100 MHz (^{13}C), Jeol Lamda Eclipse 300 at 121.65 MHz (^{31}P), 75.57 MHz (^{13}C). ^1H and ^{13}C chemical shifts are quoted in ppm relative to residual solvent peaks, and ^{31}P NMR chemical shifts quoted in ppm relative to 85% external H_3PO_4. The infra-red spectra were recorded on a Nicolet 500 FT-IR spectrometer and the samples were prepared under Ar atmosphere as a KBr disk. Mass spectra of all the samples have been measured by direct injection into a Water Low Resolution ZQ Mass Spectrometer fitted with ESCI source. Elemental analysis was performed by MedacLTD Analytical Service.

X-Ray Crystallography: data collections were carried out on a Bruker Kappa CCD diffractometer at 150(2) K with Mo $K\alpha$ irradiation (graphite monochromator). Empirical absorption corrections were performed using equivalent reflections. For the solution and refinement of the structures, the program package SHELXL 97 was employed. H atoms were placed into calculated positions and included in the last cycles of refinement. Crystal structure and refinement data are collected in **Appendix A** and supplementary CD.

2.4.2. Preparation of tris(acetonitrile)-*fac*-(η^3-1,5,9-triisopropyl-1,5,9-triphosphacyclododecane)iron(II) bis(tetrafluoroborate), 2.27:

$[Fe(CH_3CN)_6][BF_4]_2$ (205 mg, 4.30×10^{-4} mol) was dissolved in a acetonitrile (20 ml) To this was added [12]-ane-$P_3(^iPr)_3$ (150 mg, 4.30×10^{-4}mol) in 10 ml of acetonitrile to give an immediate orange colouration. The solution was stirred for 1 hour, and the solvent removed in *vacuo* leaving an oily residue, **2.27**, which was washed with petrol (3 × 30 ml). The resultant powder was then recrystallised from acetonitrile / diethyl ether to give X-ray quality crystals (182 mg, 2.59×10^{-4} mol, 60.4% yield). Analysis found (calculated): C, 40.81 (41.11); H, 6.74 (6.90), N, 5.76 (5.99). MS(ES), *m/z*: no assignable peaks. IR: ν(C-N) = 2253 cm^{-1} and 2350 cm^{-1} (KBr disc). NMR ($CDCl_3$): $^{31}P\{^1H\}$ NMR, δ (ppm): 35.83 (*s*, cation). ^1H NMR, δ (ppm): 1.85 (br *m*, PCH_2CH_2); 1.60 (*br m*, PC*H* and PCH_2); 1.10(dd, ^3J(PH) 13 and ^2J(HH) 6Hz,CH_3); 2.00 (*s*, CH_3CN). $^{13}C\{^1H\}$ NMR, δ (ppm): 3.9 (*s*, CH_3CN) 31.1 (*br, m*, PCH_2); 21.3 (*m*, PCH_2CH_2); 18.4 (*m,* PCH); 17.4 (*s*, CH_3); 129.8 (*s*, CH_3CN).

2.4.3. Preparation of tris(μ-chloro)bis-fac-(η^3-1,5,9-triisopropyl-1,5,9-triphosphacyclododecane)di-iron(II) chloride, 2.31:

$[Fe_4Cl_8(THF)_6]$ (158 mg, 19.8×10^{-5}mol) was suspended in CH_2Cl_2 (30 ml), and [12]-ane-$P_3(^iPr)_3$ (206 mg, 7.92×10^{-4}mol) in 10 ml of CH_2Cl_2 was syringed directly into this giving an immediate deep-purple homogeneous solution. After 2h of stirring, the solvent was removed *in vacuo*, and the residual **2.31** was washed with petrol (3 × 30 ml). Analytical data may suggest the presence of tris(μ-chloro)bis-fac-(η^3-1,5,9-triisopropyl-1,5,9-triphosphacyclododecane)di-iron(II) chloride complex. *Tris(μ-chloro)bis-fac-(η^3 1,5,9-triisopropyl-1,5,9-triphosphacyclododecane)di-iron(II) chloride,* **2.31:** NMR

($CDCl_3$): $^{31}P\{^1H\}$ NMR, δ (ppm): 38.8 (*s*, cation). ^1H NMR, δ (ppm): 1.55 (br *m*, PCH_2CH_2); 1.45 (*br m*, PC*H* and PCH_2); 1.10(br S, C*H*);

2.4.4. Preparation of tris(μ-chloro)bis-fac-(η^3 -1,5,9-triisopropyl-1,5,9-triphosphacyclododecane)bis(ruthenium(II)) chloride, 2.35:

A solution of [12]-ane-$P_3(^iPr)_3$ (39 mg, 0.10 mmol) in dichloromethane (15 cm^3) was added dropwise to a solution of $RuCl_2(PPh_3)_3$ (48 mg, 0.05 mmol) in dichloromethane (15 cm^3) and the resultant mixture stirred for 2h at room temperature. Evaporation to dryness *in vacuo* gave a yellow colour residue which was recrystallised from CH_2Cl_2/petrol to give **2.35** as light yellow colour crystals.(41 mg, 39.3%) Analysis found (calculated): C, 41.47 (41.54); H, 7.48 (7.50), MS(ES), *m/z*: 1004.14 [45%, (M^+-H)]. IR: ν(Ru-Cl) = 270 cm^{-1}(vw) and (KBr disc). NMR ($CDCl_3$): $^{31}P\{^1H\}$ NMR, δ (ppm): 35.24 (*s*, cation). ^1H NMR, δ (ppm): 1.75 (br m, PCH_2CH_2); 1.45 (br m, PC**H** and PCH_2); 1.05(br S, C**H**);. $^{13}C\{^1H\}$ NMR, δ (ppm): 31.5 (br, m, PCH_2); 21.5 (m, PCH_2CH_2); 18.5 (m, PCH); 17.5(s, CH_3).

2.4.5. Preparation of tris(acetonitrile)-fac-(η3-1,5,9-triisopropyl-1,5,9-triphosphacyclododecane)ruthenium(II) bis(hexafluorophosphine), 2.38:

A solution of [12]-ane-$P_3(^iPr)_3$ (0.10 mmol) in dichloromethane (15 cm^3) was added dropwise to a solution of $[RuCl_2(dmso)_4]$ (48 mg, 0.10 mmol) in dichloromethane (15 cm^3) and the resultant mixture stirred for 3 h at room temperature. The solvent was

removed, the product is isolated (43 mg, 0.072 mmol) and the addition of two equivalent amount of $AgPF_6$ (36 mg, 0.144 mmol) into it in acetonitrile (25 cm^3) at room temperature results **2.38**. The solvent was removed to give a light yellow solid which was recrystallised from acetonitrile/diethyl ether to give **2.38** as yellow crystals (64 mg, 0.06 mmol, 60.0 %). Analysis found (calculated): C, 33.39 (33.42); H, 5.59 (5.61), N, 4.72 (4.87). MS(ES), *m/z*: 286.60 [100%, $(M)^{+2}$]. IR: ν(C-N) = 2250 cm^{-1} and 2342 cm^{-1} (KBr disc). NMR ($CDCl_3$): $^{31}P\{^1H\}$ NMR, δ(ppm): 27.33 (*s*, cation). ^1H NMR, δ (ppm): 1.74 (br *m*, $PCH_2C\boldsymbol{H_2}$); 1.52 (*br m*, P***C*H** and $PC\boldsymbol{H_2}$); 1.01 (dd, ^3J(PH) 13 and ^2J(HH) 6Hz,CH_3); 1.90 (*s*, $C\boldsymbol{H_3}CN$). $^{13}C\{^1H\}$ NMR, δ (ppm): 3.2 (*s*, $\boldsymbol{C}H_3CN$) 30.5 (*br, m*, $P\boldsymbol{C}H_2$); 21.1 (*m*, $PCH_2\boldsymbol{C}H_2$); 17.4 (*m,* P***C*H**); 16.5 (*s*, $\boldsymbol{C}H_3$); 128.1 (*s*, $CH_3\boldsymbol{C}N$).

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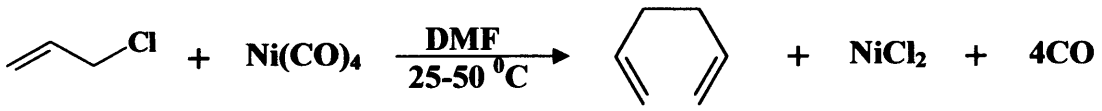
Chapter 3:

Coordination chemistry of [12]-ane-$P_3(CH(CH_3)_2)_3$ with group 10 metals Ni(II), Ni(I) and Ni(0)

3.1. Introduction

Swedish chemist Axel Fredrik Cronsted isolated nickel and classified it as a chemical element in 1751. It has subsequently been used in many applications in industrial and consumer products, including stainless steel, magnets, coinage, rechargeable batteries, electric guitar strings and special alloys. Due to its electronic configuration of [Ar] $3d^8$ $4s^2$ it can exist in many different oxidation states 0, +1, +2, +3 and +4. Among these states the most common oxidation state is +2. Ni(0) complexes are also well known, especially in organometallic systems, Ni(I) is less common.[1] In contrast with the other group 10 elements, tetracoordinate nickel (II) takes both tetrahedral and square planar geometries.

The discovery of nickel carbonyl by Mond and co-workers in 1890 led to a new era of transition metal carbonyls.[2] As a catalyst nickel carbonyl has many applications including polymerization of conjugated dienes,[3] the synthesis of cyclopentene-1,2-dione from diphenylcyclopropenone and ketenes[4] and conversion of allylhalide to biallyl can be mentioned.[5]

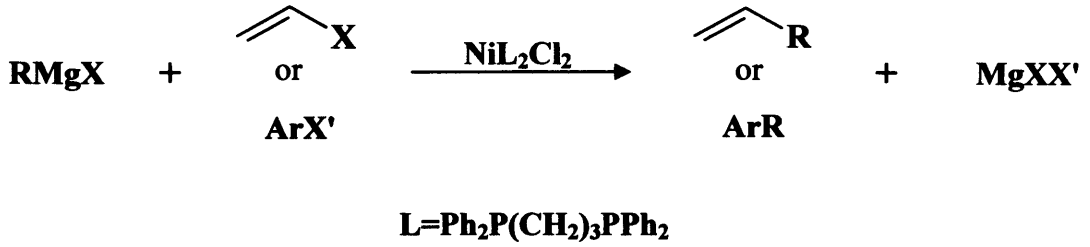


Scheme 3.1: Application of $Ni(CO)_4$ as a catalyst.

In addition to the $Ni(CO)_4$ as a catalyst, as early as 1924 Job and co-workers noticed that phenylmagnesium bromide absorbs ethylene in the presence of catalytic amount of nickel chloride.[6]

Scheme 3.2: Application of $NiCl_2$ as a catalyst.

Subsequently, Kumada *et al* developed this reaction for Grignard reagents with aryl and olefinic halide using nickel phosphine complex as a catalyst.[7-9]



Scheme 3.3: Application of nickel phosphine as a catalyst.

Apart from the above application, nickel has some biological importance as well. Enzymes known as CO dehydrogenase enzymes whose study is relatively recent, catalyse two organometallic reactions,[10] which include the well known water-gas-shift reaction and the carbonylation of methyltetrahydrofolate.[10] The enzyme contains two nickel-centered fragments, the first one is a cluster containing Fe and Ni, whereas the other one, is supposed to be responsible for CO oxidation.[11] The complexes based on nickel that serve as a model for this enzyme have been synthesised by Crabtree and Holm.[12]

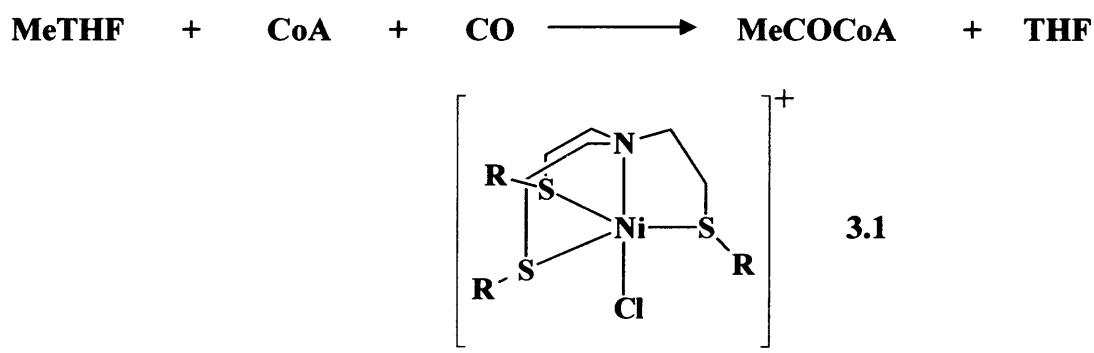
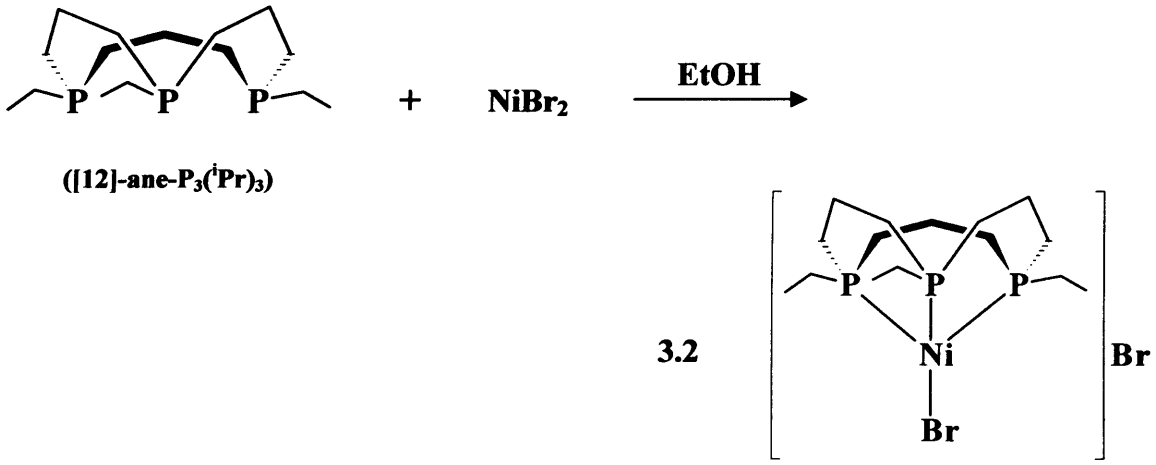


Figure 3.1: A Model enzyme for carbonylation of methyltetrahydrofolate [12]

As outline previously, nickel has many applications in a variety of fields, which has promoted the exploration of nickel coordination chemistry and numerous examples are reported. [13-17]

In contrast to the large body of reported complexes, there are few examples of nickel based macrocyclic polyphosphine complexes and there is only one with a macrocyclic triphosphine which is preliminary reported by Edwards and co-workers in 1998.[18]



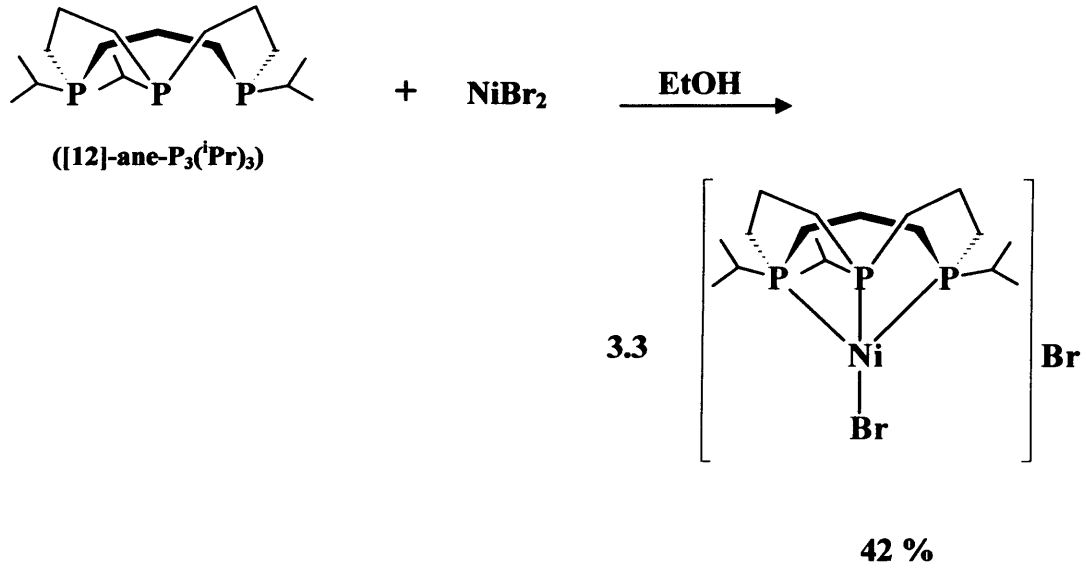
Scheme 3.4: Synthesis of bromo[*fac*-η^3 -*cis*-1, 5, 9-triethyl-1, 5, 9-triphosphacyclododecane]nickel(II) bromide[18], 3.2

Due to the lack of this class of organometallic complexes there is a great interest to study them and more importantly, their physical properties and reactivity.

In this chapter the reaction of 1, 5, 9-triisopropyl-1, 5, 9-triphosphacyclododecane ([12]-ane-$P_3(^iPr)_3$,) with $NiBr_2$ is discussed as Ni(II) complex. The product, {NiBr(η^3-[12]-

ane-$P_3(^iPr)_3$)}Br, **3.3** has been characterised and the crystal structure shows nickel atom in a pseudo tetrahedral environment. The Ni(I) complex, {Ni(CO)(η^3-L)}NO_3, **3.5** formed under reducing conditions from the reaction between $Ni(NO_3)_2$. $6H_2O$ and [12]-ane-$P_3(^iPr)_3$ will be discussed.

3.2 Results and discussion



Scheme 3.5: Synthesis of bromo[*fac*-η^3 -*cis*-1, 5, 9-triisopropyl-1, 5, 9-triphosphacyclododecane]nickel(II) bromide, 3.3

The reaction of [12]-ane-$P_3(^iPr)_3$ with $NiBr_2$ in EtOH instantly gives rise to a deep purple coloured solution from which purple crystals of **3.3** may be isolated and for which analytical data indicate the formula of $LNiBr_2$. **3.3** is also diamagnetic, giving rise to sharp NMR spectra and so presumably does not have a tetrahedral Ni(II) atom which would be expected to be paramagnetic. The $^{31}P\{^1H\}$ NMR spectrum of **3.3** clearly indicates the formation of a tertiary phosphine complex with a downfield resonance at δ 13.2 ppm due to the strong σ bond from phosphorus to metal atom. The co-ordination chemical shift ($\Delta^{31}P = \delta_{\text{co-ordinated P}} - \delta_{\text{unco-ordinated P}}$) relative to the free phosphine ligand is *ca* 33.0 ppm. The

sharp $^{31}P\{^1H\}$ NMR signal indicates that **3.3** is fluxional in solution, since the static distorted four coordinated geometry in the solid state structure would not have magnetically equivalent phosphorus atoms.

Analytical data is consistent with the crystal structure of **3.3** has a formula of {[12]-ane-$P_3(^iPr)_3$}$NiBr^+Br^-$. This result is also clearly compatible with the structure observed for the ethyl group substituted Ni-P_3 macrocycle.[18] In addition to these data the complex **3.3** has been fully characterised by ^1H, $^{13}C\{^1H\}$ NMR, and mass spectrometry.

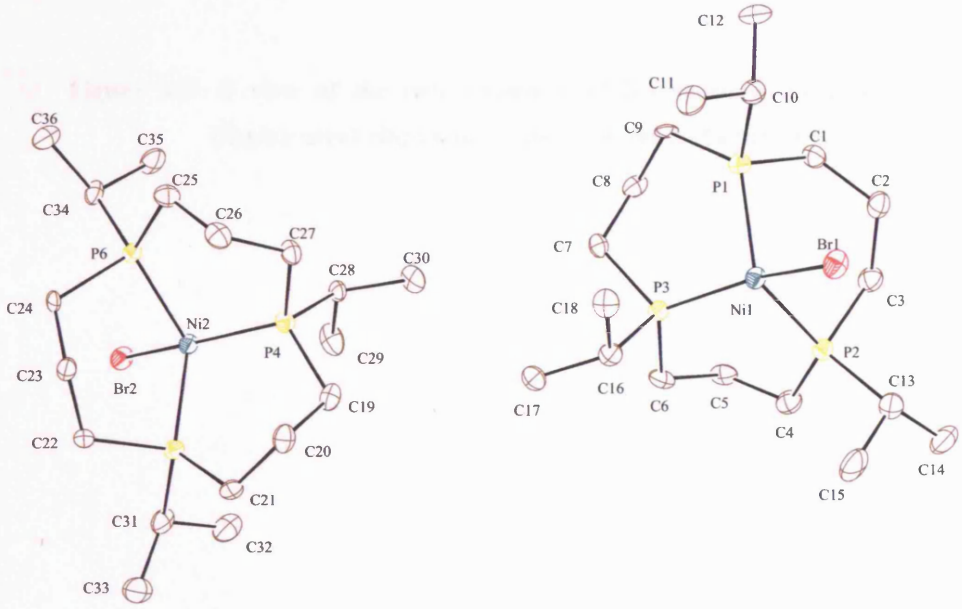
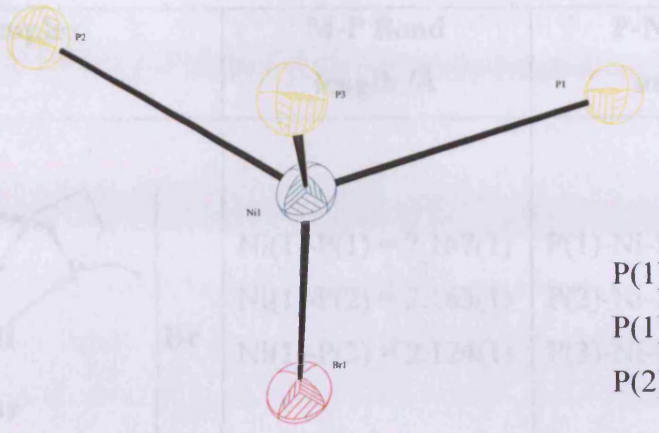


Figure 3.2: Molecular structure of bromo[*fac*-η^3 -*cis*-1, 5, 9-triisopropyl-1, 5, 9-triphosphacyclododecane]nickel(II) bromide, 3.3, the anions and the hydrogen atoms have been omitted for clarity.



P(1)-Ni(1)-P(2) = 126.61^0(10)

P(1)-Ni(1)-P(3) = 95.74 ^{0}(9)

P(2)-Ni(1)-P(3) = 96.22 ^{0}(9)

Figure 3.3: A view of the core geometry of 3.3 showing the atom numbering. Displacement ellipsoids are shown at the 30 % probability level.

Selected bond lengths of known triphosphorus tripodal ligands are included in the following table for comparison.

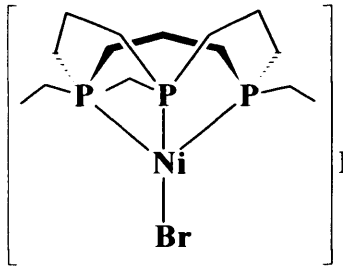
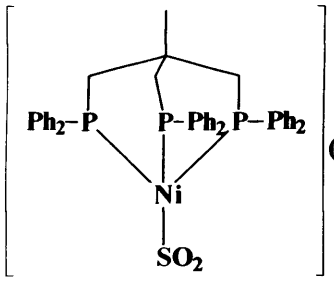
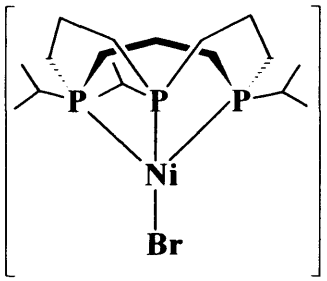
Complex	M-P Bond length /Å	P-Ni-R Bond angle/deg	Ref.
 **3.2**	Ni(1)-P(1) = 2.167(1) Ni(1)-P(2) = 2.163(1) Ni(1)-P(3) = 2.124(1)	P(1)-Ni-Br = 96.19(3) P(2)-Ni-Br = 94.52(3) P(3)-Ni-Br = 155.60(4)	18
 **3.4**	Ni(1)-P(1) = 2.225(3) Ni(1)-P(2) = 2.203(3) Ni(1)-P(3) = 2.188(3)	P(1)-Ni-S = 121.2(1) P(2)-Ni-S = 117.5(1) P(3)-Ni-S = 126.3(1)	19
 **3.3**	Ni(1)-P(1) = 2.175(2) Ni(1)-P(2) = 2.170(2) Ni(1)-P(3) = 2.131(2)	P(1)-Ni-Br = 96.58(7) P(2)-Ni-Br = 96.21(7) P(3)-Ni-Br = 152.23(8)	This work

Table 3.1: Selected interatomic distances (Å) of M-P and P-P interaction of complex 3.3 and other literature examples

The data in table 3.1 clearly illustrates that the geometrical constraints imposed by the macrocycle in comparison to related tripodal tridentate ligands. The tripodal tridentate ligand complex has an average Ni-P bond length longer than both the ethyl, **3.2** and isopropyl, **3.3** substituted macrocyclic complexes, indicating that either the macrocycle ligand is more strongly coordinated than the tripodal ligand or that the large bulky phenyl groups in the complex restrict the approach of the phosphorus to the central metal centre.

On the other hand, in both the ethyl, **3.2** and isopropyl, **3.3** substituted macrocyclic complexes, the metal ion lies at the centre of the significantly distorted tetrahedral geometry. The all mutually *cis* set of donor atoms form significantly more obtuse bond angles than the expected 109^0, P(1)-Ni(1)-Br(1)(96.58^0 (7)), P(2)-Ni(1)-Br(1)(96.21^0 (7)) and P(3)- Ni(1)-Br(1) (152.23^0 (8)) The remarkable differences in the angles between the macrocyclic P-atoms arises from the distortion from the regular tetrahedron. This is being presumably due to restricted freedom or flexibility in the macrocycle in comparison to the tripod. Both diamagnetic nature and the structural distortion due to the macrocyclic coordination effect of complex **3.3** can be explained by the following electron splitting diagram. However, other metals such as Cu(I) do not show this type of distortion with the P_3 macrocycle.

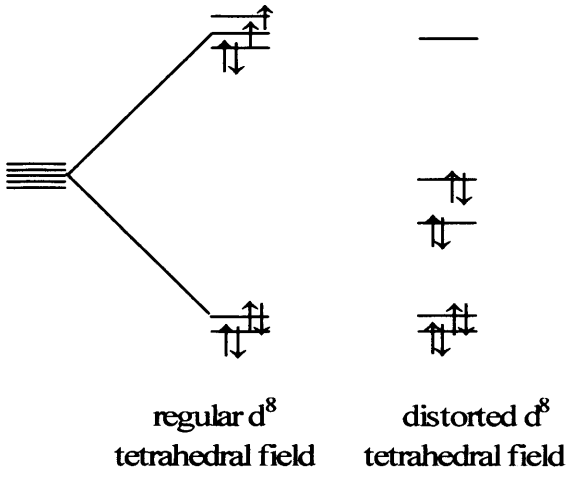


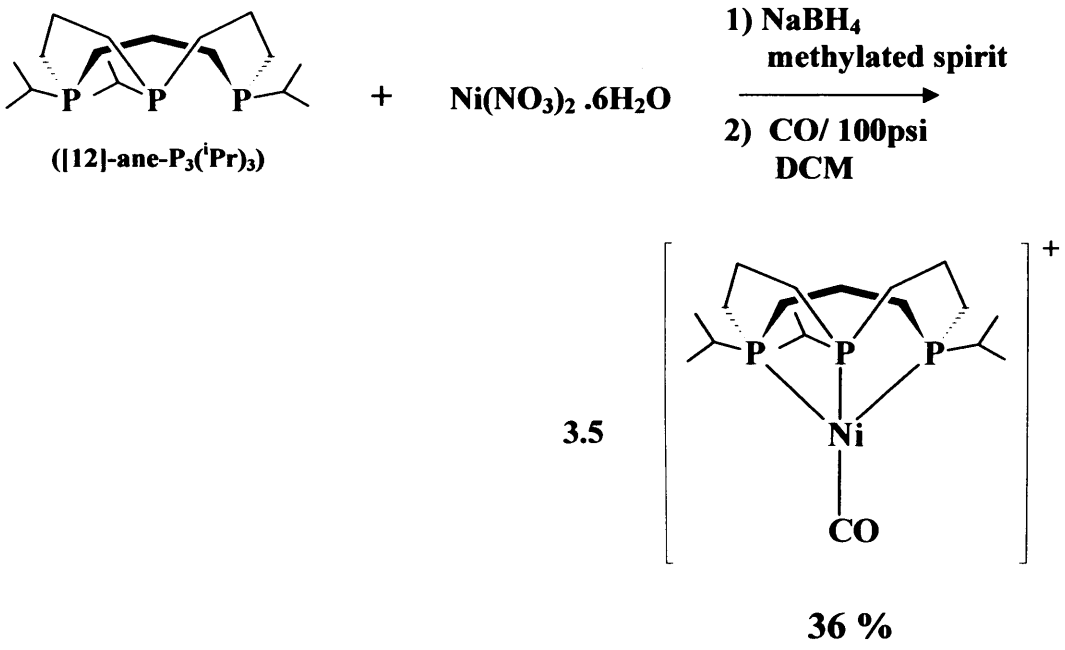
Figure 3.4: Predicted electron splitting of complex 3.3

Geometrically, there are no clear significant differences between the ethyl and isopropyl substituted macrocyclic complexes but there are peripheral differences between them. The ethyl group substituted macrocyclic unit of nickel complex, **3.2** is much closer to the metal atom than that of the isopropyl group substituted one, **3.3**. This may be due to the bulkiness of the substituent group preventing the closer approach to the metal centre.

Ni(1)-P(1)-C(10) = 121.4^0 (3)

Ni(1)-P(2)-C(13) = $121.1\ ^0$(3)

Ni(1)-P(3)-C(16) = $100.2\ ^0$(3)

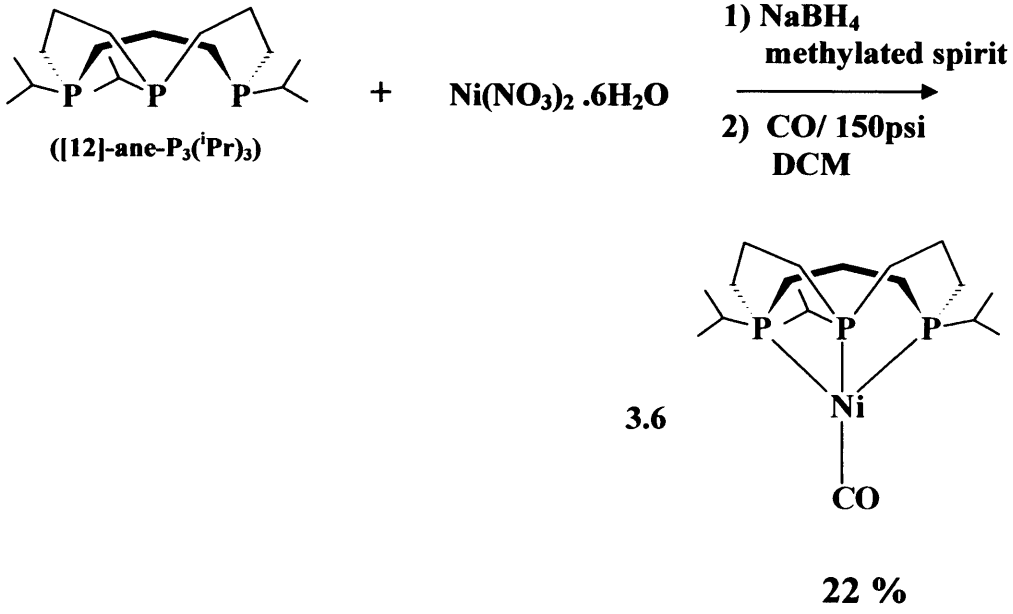


Scheme 3.6: Synthesis of mono(carbonyl)-*fac*-η^3 -*cis*-1, 5, 9-triisopropyl-1, 5, 9-triphosphacyclododecane]nickel(I)nitrate, 3.5

In an attempt to synthesise a Ni(I) complex of [12]-ane-$P_3(^iPr)_3$, the reduction of Ni(II) salts with sodium tetrahydroborate in aqueous alcohol solution, according to the method developed by Chatt and co-workers was studied.[23] Under these conditions, the reduction of $Ni(NO_3)_2 .6H_2O$ results in a solution that contains a species, which gives rise to a singlet in the $^{31}P\{^1H\}$ NMR spectrum in a position consistent with co-ordinated [12]-ane-$P_3(^iPr)_3$ (δ = 12.0 ppm). A diamagnetic complex could not be isolated from these solutions, however after the treatment of this solution with CO under mild condition, a new Ni(I) carbonyl complex {{[12]-ane-$P_3(^iPr)_3$}Ni(CO)}NO_3}, may be isolated as dark red needles with 36.0 % yield.

Elemental analytical data are consistent with the formation of (Ni^+). The IR spectrum of the KBr disk of **3.5** gives a sharp band due to ν_{CO} (1919 cm^{-1}) along with further bands which may be assigned to the ligand and NO_3^- absorptions.

Further reduction of **3.5** with CO with the same condition but pressure is at about 150 psi forms presumably the Ni(0) complex **3.6**.



Scheme 3.7: Synthesis of mono(carbonyl)-*fac*-η^3 -*cis*-1, 5, 9-triisopropyl-1, 5, 9-triphosphacyclododecane]nickel(0), 3.6

The Ni(0) complex **3.6** has been fully characterised by $^{31}P\{^1H\}$, ^1H, $^{13}C\{^1H\}$, IR, mass spectrometry, high resolution mass spectrometry and microanalysis and data are consistent the structure of **3.6** which is comparable with the unpublished data of the ethyl group substituted identical nickel complex, **3.9**.

Unfortunately, attempts to grow single crystals of this new nickel(0) complex were unsuccessful, regardless of the technique used.

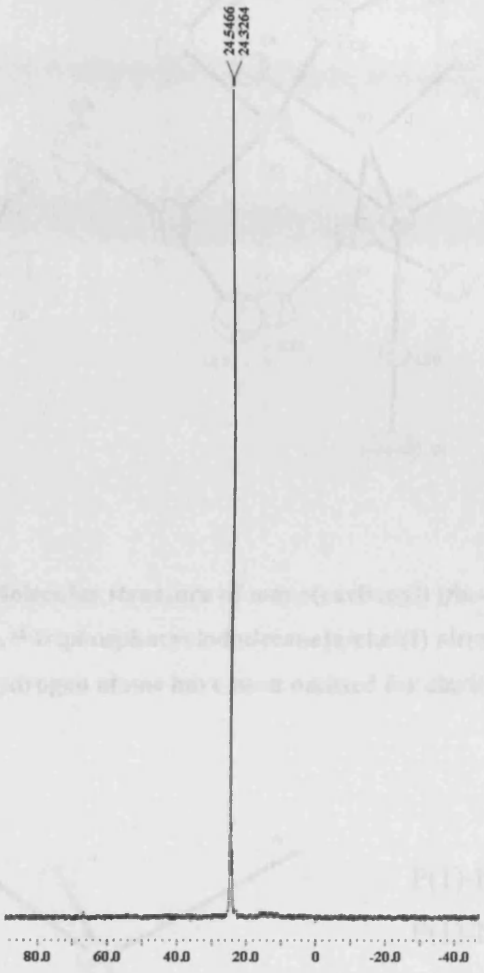


Figure 3.5: ^{31}P NMR Spectrum of LNi(CO)

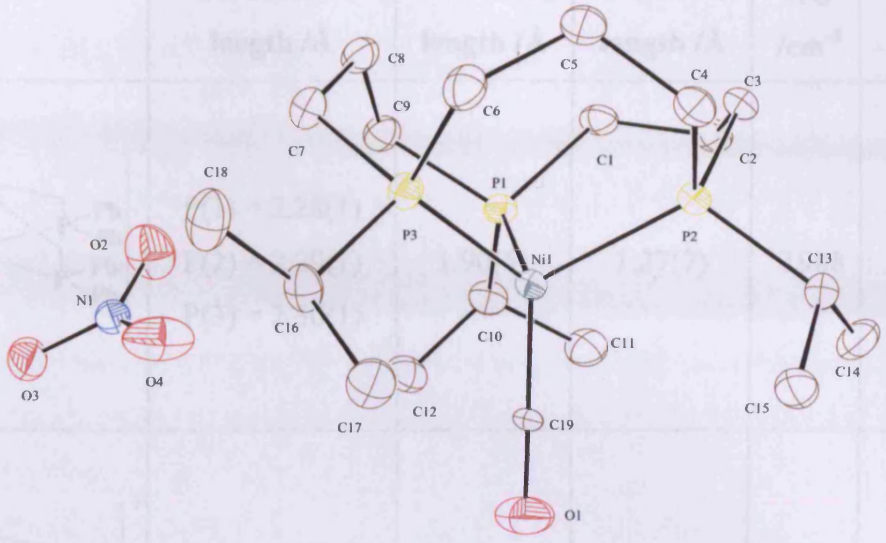
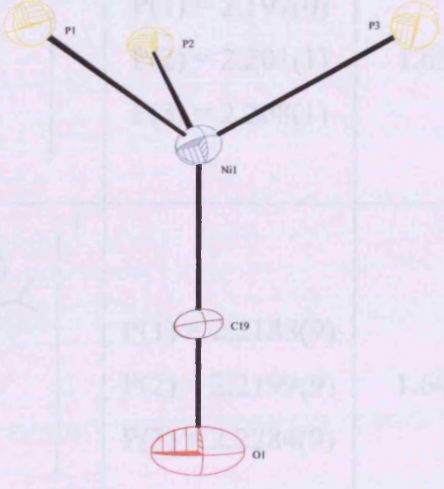


Figure 3.6: Molecular structure of mono(carbonyl) [*fac*-η^3 -*cis*-1, 5, 9-triisopropyl-1, 5, 9-triphosphacyclododecane]nickel(I) nitrate, 3.5, the anions and the hydrogen atoms have been omitted for clarity.



P(1)-Ni(1)-P(2) = 100.73 ^{0}(3)

P(1)-Ni(1)-P(3) = 100.01 ^{0}(3)

P(2)-Ni(1)-P(3) = 99.46 ^{0}(3)

C(19)-Ni(1)-P(1) = 116.41 ^{0}(11)

C(19)-Ni(1)-P(2) = 118.93 ^{0}(10)

C(19)-Ni(1)-P(3) = 117.91 ^{0}(11)

Figure 3.7: A view of the core geometry of 3.5 showing the atom numbering. Displacement ellipsoids are shown at the 30 % probability level.

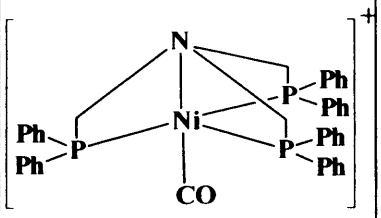
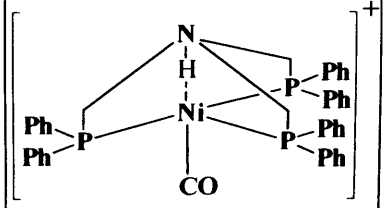
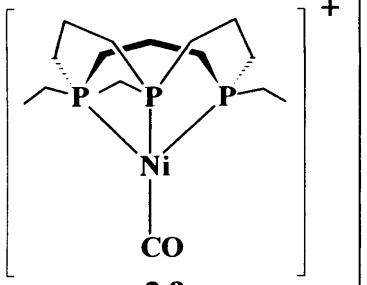
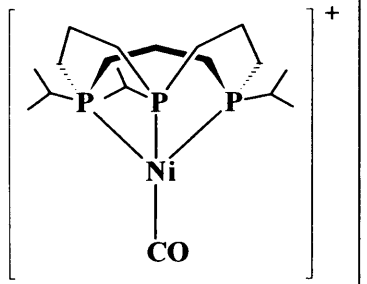
Complex	Ni-P bond length /Å	Ni-C bond length /Å	C-O bond length /Å	ν_{CO} /cm^{-1}	Ref:
 **3.7**	P(1) = 2.28(1) P(2) = 2.29(1) P(3) = 2.30(1)	1.90(5)	1.27(7)	1988	24
 **3.8**	P(1) = 2.222(3) P(2) = 2.223(3) P(3) = 2.220(3)	1.737(12)	1.154(1)	1990	25
 **3.9**	P(1) = 2.197(0) P(2) = 2.201(1) P(3) = 2.208(1)	1.63(2)	1.14(3)	1921	Unpub:
 **3.5**	P(1) = 2.2188(9) P(2) = 2.2199(9) P(3) = 2.2284(9)	1.64(4)	1.16 (5)	1919	This work

Table 3.2: Selected interatomic distances (Å) of M-P and M- μCl of complex 3.5 and other literature examples

An X –Ray diffraction study has been carried out for the paramagnetic complex **3.5** and this cationic nickel compound is presented in Figure 3.6. According to the literature, there are no nickel d^9 carbonyl complex with the metal centre coordinated to P_3 macrocyclic ligands although some tripodal ligand complexes of nickel d^9 have been reported.[24, 25] Even though there is no clear difference between the Ni-C and C-O bonds in the ethyl, **3.9** and isopropyl, **3.5** substituted nickel complexes, there is a significant difference between the Ni-P bonds. The Ni-P bond lengths of the isopropyl, **3.5** substituted complex are longer than that of ethyl, **3.9** substituted complex. This may be accounted for the bulkiness of the isopropyl groups which hinders the closer approach of the macrocyclic unit to the metal centre.

The data in table 3.2 clearly illustrate the geometrical constraints of the macrocycle ligand complex with the tripodal ligand, **3.7** and **3.8**. Again the tripodal tridentate ligand complex has average Ni-P bond lengths longer than **3.5** and the ethyl, **3.9** substituted analogue, indicating that either the macrocycle ligand is more strongly coordinated than the tripodal ligand or that the large bulky phenyl groups in the complex restrict the approach of the phosphorus to the central metal centre.

3.3. Conclusion

The reactions of [12]-ane-$P_3(^iPr)_3$ with Ni in the electronic configuration of d^8, Ni(II)) precursor complexes rapidly give rise to facially coordinated tris(phosphine) complexes.

The macrocyclic ligand has the ability to form halide and carbonyl complexes of the group 10 metals with the variation of radii and more importantly d^8 complex of nickel is an unusually distorted structure as a result of constraints imposed by the macrocyclic ligand.

Under the reducing conditions in the presence of CO, $Ni(NO_3)_2$ react with [12]-ane-$P_3(^iPr)_3$ to give a paramagnetic cationic Ni(I) complex $\{Ni(CO)(\eta^3\text{-}L)\}NO_3$ with the nickel atom again in a pseudo tetrahedral environment. Further reduction of $\{Ni(CO)(\eta^3\text{-}L)\}NO_3$ results in the formation of the Ni(0)complex {LNi(CO)}.

3.4 Experimental

3.4.1. General

Techniques and Instruments: All reactions were carried out in an atmosphere of dry argon. All solvents were dried by refluxing over standard drying agents. The compounds allylphosphine, *syn,syn*-1,5,9-triisopropyl-1,5,9-triphosphacyclododecane, [12]-ane-$P_3(^iPr)_3$ were prepared by a slight change of literature methods. **Caution:** The organophosphines and some of their complexes described are ***highly malodorous*** and likely ***highly toxic***. Great care should be exercised in their handling. All other reagents were obtained from the Aldrich Chemical Company and, where appropriate, were degassed before use. NMR spectra were recorded on a Bruker DPX-500 instrument at 500 MHz (^1H), and 125.75MHz (^{13}C), Bruker DPX-400 instrument at 400 MHz and 100 MHz (^{13}C), Jeol Lamda Eclipse 300 at 121.65 MHz (^{31}P), 75.57 MHz (^{13}C). ^1H and ^{13}C chemical shifts are quoted in ppm relative to residual solvent peaks, and ^{31}P NMR chemical shifts quoted in ppm relative to 85% external H_3PO_4. The infra-red spectra were recorded on a Nicolet 500 FT-IR spectrometer and the samples were prepared under Ar atmosphere as a KBr disk. Mass spectra of all the samples have been measured by direct injection into a Waters Low Resolution ZQ Mass Spectrometer fitted with ESCI source. Elemental analysis was performed by MedacLTD Analytical Service.

X-Ray Crystallography: data collections were carried out on a Bruker Kappa CCD diffractometer at 150(2) K with Mo $K\alpha$ irradiation (graphite monochromator). Empirical absorption corrections were performed using equivalent reflections. For the solution and refinement of the structures, the program package SHELXL 97 was employed. H atoms were placed into calculated positions and included in the last cycles of refinement. Crystal structure and refinement data are collected in **Appendix A** and supplementary CD.

3.4.2. Preparation of bromo[*fac*-η^3 -*cis*-1, 5, 9-triisopropyl-1, 5, 9-triphosphacyclododecane]nickel(II) bromide, 3.3:

$NiBr_2 .6H_2O$ (100 mg, 4.57×10^{-4} mol) was dissolved in ethanol (15 ml). To this was added [12]-ane-$P_3(^iPr)_3$ (159 mg, 4.57×10^{-4} mol) in 15 ml of ethanol to give an immediate dark black colouration. The solution was stirred for 4 h, and the solvent removed in *vacuo* leaving an oily residue, **5**, which was washed with petrol (3 × 20 ml). The resultant powder was then recrystallised from dichloromethane/ petrol to give X-ray quality purple crystals (108 mg, 1.92×10^{-4} mol 42.0% yield). Analysis found (calculated): C, 38.49 (38.14); H, 6.82 (6.93). MS(ES), *m/z*: 487.04 [100%, $(M)^+$]. IR: ν(Ni-Br) = 722.2 cm^{-1} (KBr disc). NMR ($CDCl_3$): $^{31}P\{^1H\}$ NMR, δ (ppm): 13.24(*s*, cation). ^1H NMR, δ (ppm): 1.80 (br *m*, PCH_2CH_2); 1.60-1.40 (*br m*, PC*H* and PCH_2); 1.10 (*br s*, CH). $^{13}C\{^1H\}$ NMR, δ (ppm): 30.31 (*br, m*, PCH_2); 22.04 (*m*, PCH_2CH_2); 20.75 (*m*, PCH); 19.38 (*s*, CH_3).

3.4.3. Preparation of mono(carbonyl)[*fac*-η^3 -*cis*-1, 5, 9-triisopropyl-1, 5, 9-triphosphacyclododecane]nickel(I)nitrate, 3.5:

$Ni(NO_3)_2.6H_2O$ (87 mg, 3×10^{-4} mol) was dissolved in methylated spirit (10 ml). To this was added [12]-ane-$P_3(^iPr)_3$ (104 mg, 3×10^{-4} mol) in 10 ml of methylated spirit to give immediate dark brown colouration. After 1 h of stirring $NaBH_4$ (12 mg, 3×10^{-4} mol) was dissolved in methylated spirit (15 ml) were added to the mixture containing L and $Ni(NO_3)_2.6H_2O$. The solution was stirred another 2 h and the solvent removed under *vacuum*. The dark brown solid was dissolved in CH_2Cl_2 (30 ml). The solution was filtered and transferred to a glass pressure reaction flask and the CO pressure of 100 psi was established. After overnight stirring at CO pressure of 100 psi a deep red colour solution was obtained.

The sample was concentrated under *vacuum* and washed with petrol (3 × 20 ml) The resultant powder was then recrystallised from dichloromethane/ petrol to give X-ray quality deep red colour crystals (53 mg, 1.08×10^{-4} mol 36.0% yield). Analysis found (calculated): C, 44.72 (45.91); H, 7.83 (7.91); N, 2.71 (2.82). MS(ES), *m/z*: no assignable peak. IR: ν(C-O) = 1919 cm^{-1} (KBr disc).

3.4.4. Preparation of mono(carbonyl)[fac-η^3 -cis-1, 5, 9-triisopropyl-1, 5, 9-triphosphacyclododecane]nickel(0) , 3.6:

The sample from the preparation of mono(carbonyl)[fac-η^3 -cis-1, 5, 9- triisopropyl-1, 5, 9- triphosphacyclododecane]nickel(I)nitrate, (152 mg, 3.08×10^{-4} mol)was dissolved in CH_2Cl_2 (50 ml)and placed in a glass pressure reaction flask and the CO pressure of 150 psi was established. After overnight stirring at CO pressure of 150 psi a deep red coloured solution was obtained. The sample was concentrated under *vacuum* and washed with petrol (3 × 20 ml) (29 mg, 0.68×10^{-4} mol 22.0% yield). Analysis found (calculated): C, 52.24 (52.44); H, 8.87 (9.03). MS(ES), *m/z*: 436.15[100%, $(M^+ + H)$]. IR: ν(C-O) = 1820 cm^{-1} (KBr disc). NMR ($CDCl_3$): $^{31}P\{^1H\}$ NMR, δ (ppm): 24.54. ^1H NMR, δ (ppm): 2.10 (br *s*, $PCH_2C\boldsymbol{H_2}$); 1.90-1.60 (*br m*, P***C*H** and $PC\boldsymbol{H_2}$); 1.00-1.20 (*br s*, CH). $^{13}C\{^1H\}$ NMR, δ (ppm): 29.93 (*br, m*, $P\boldsymbol{C}H_2$); 24.68 (*m*, $PCH_2\boldsymbol{C}H_2$); 20.78 (*m,* P***C*H**); 18.20 (*s*, $\boldsymbol{C}H_3$).

3.5. References

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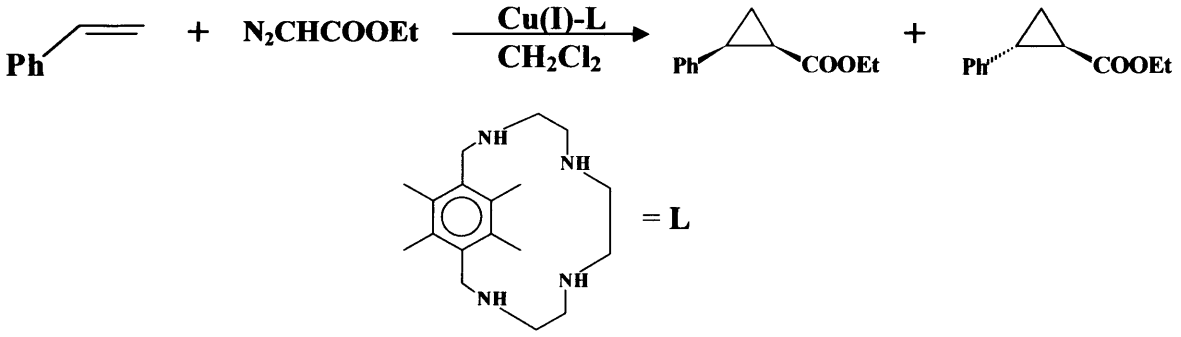
Chapter 4:

Coordination chemistry of [12]-ane-$P_3(CH(CH_3)_2)_3$ with group 11 metals Cu(I)X (X= Cl, Br, I)

4.1. Introduction

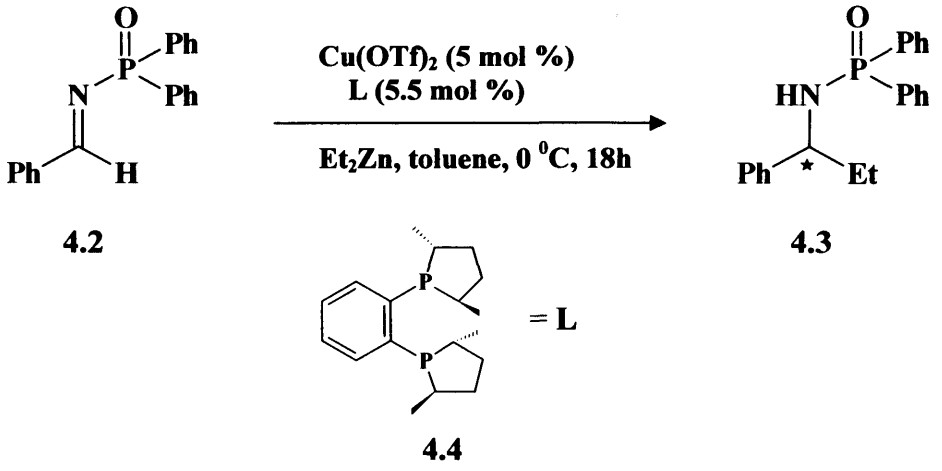
Being placed in group 11 of the periodic table copper has the electronic configuration of [Ar] $3d^{10}$ $4s^2$. Due to this electronic configuration it can exist in different oxidation states including +1, +2, +3 and +4. Among these states, Cu(II) becomes the most stable in aerobic environments and there are few Cu(III) complexes reported. Cu(I) state is also quite stable in solids.[1-3] Copper(I) compounds are known to be very active catalysts in the cyclopropanation of alkenes with diazo compounds[4, 5] and cyanation of aryl iodides[6] while copper(II)triflate/diphosphine complexes efficiently catalyze the enantioselective addition of dialkylzinc reagents to N-diphenylphosphinoylimines.[7-9]

Understanding and controlling the stability of Cu(III) organometallic complexes is an extremely important area in catalysis[10, 11] since access to it would enhance the availability of one of the fundamental steps of organometallic catalysis, i.e., the activation of R-X bonds through oxidative addition to Cu(I) center. (Scheme 4.3) Recently, the existence of a Cu(III) organometallic complex, (4.6) has been suggested in the C-X bond activation promoted by Cu(I) complexes, (4.5) containing (2-pyridyl)alkylamine-based ligands.[12]



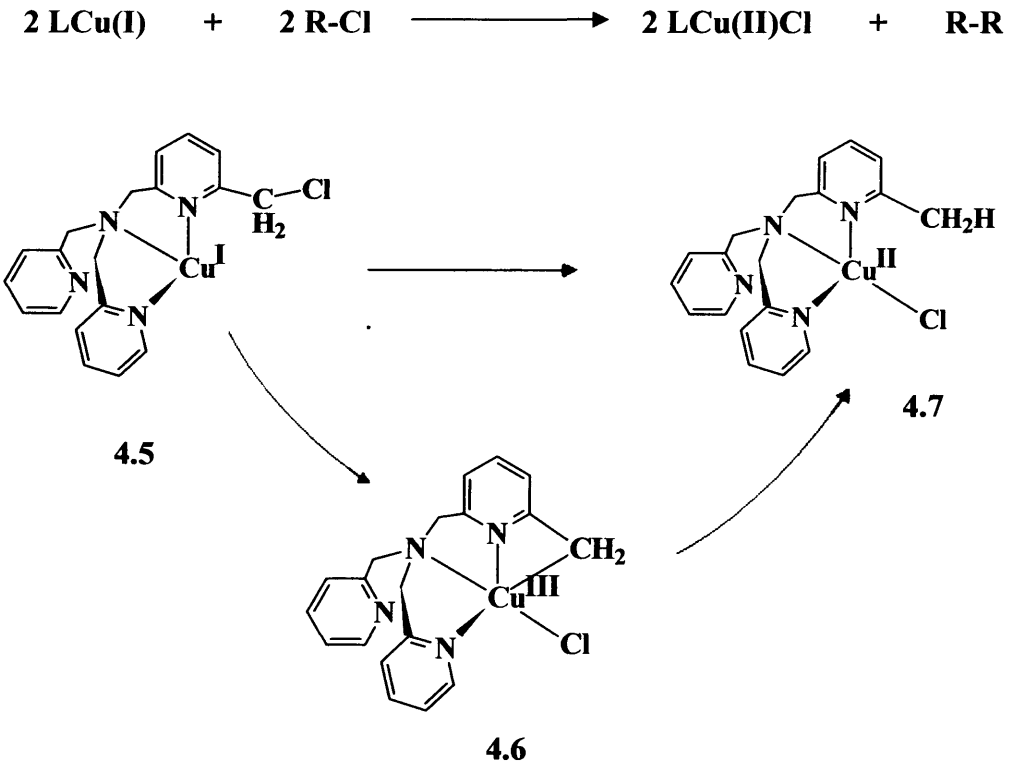
4.1

Scheme 4.1: Application of Cu(I) as a catalyst[4, 5]



4.2 4.3 4.4

Scheme 4.2: Application of Cu(II) as a catalyst[7-9]



4.5 4.6 4.7

Scheme 4.3: Dehalogenation of R-Cl via Cu(III) state[10, 11]

According to this mechanism, the first step is the intramolecular activation of the C-Cl bond to produce unstable Cu(III) complex, which possibly forms a dimmer from which the C-C coupling step occurs.

In addition to the application of copper as a commercial catalyst, it is paramount for the biological electron transfer processes in proteins such as plastocyanin[13-17] and Azurin.[18] The structure of Azurin shows a copper ion is in an elongated distorted trigonal bipyramidal coordination environment[18] but in plastocyanin it has an approximate tetrahedral environment[19, 20] which mediates the preferred pathway for biological ground state electron transfer.[21]

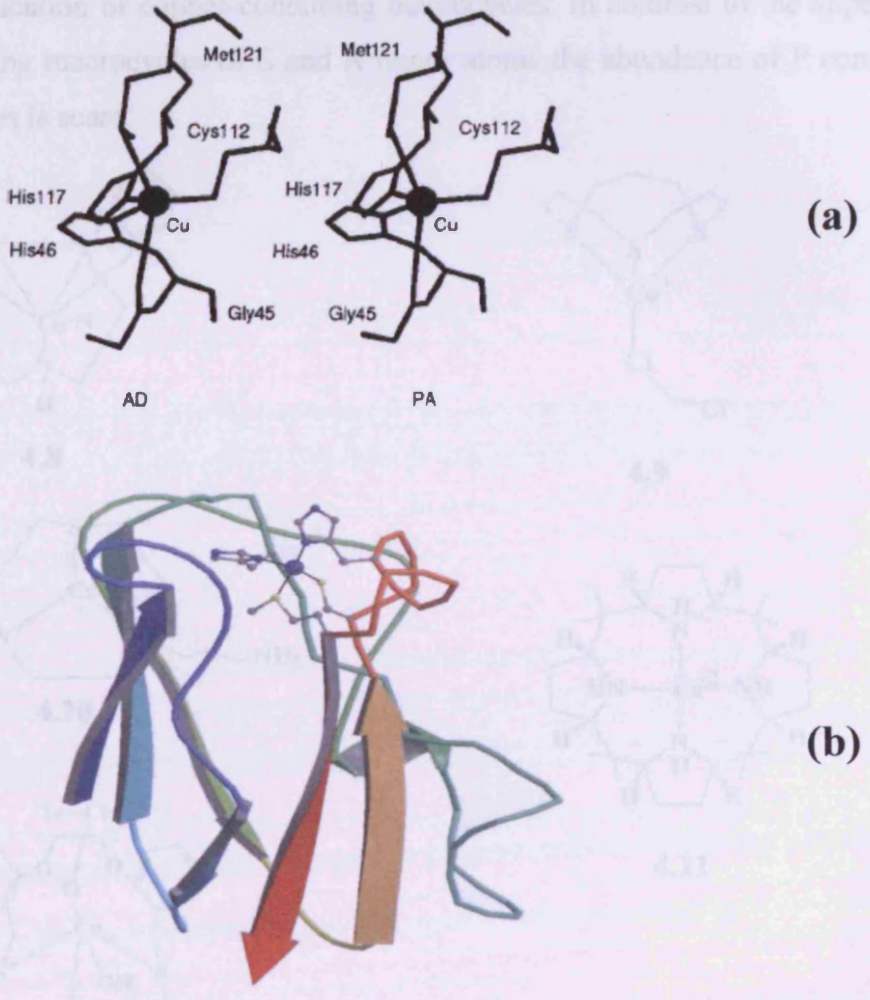
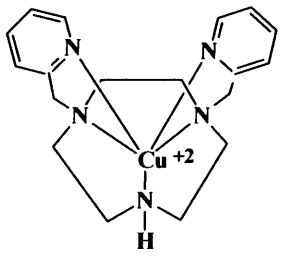
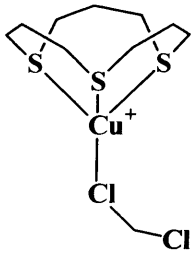


Figure 4.1: Copper binding proteins of Azurin (a) and plastocyanin (b)

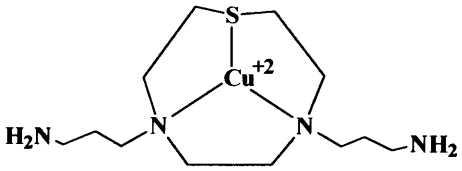
In our case, the rigid facially capping arrangement of the macrocycle will favour particular coordination geometries (eg. tetrahedral) and hence may also influence reactivity by stabilising specific oxidation states. It is obvious that copper is a versatile element and its coordination chemistry is extensive. There are good examples where ligand structure, both in the nature of the donor atoms and in shape (or geometrical) distortions (or constraints) influence the properties of copper complexes, particularly reactivity. This is the basis of the entatic effect in biology and the ability to manipulate shape and shape distortions provides the powerful controlling influence over reactivity for the design of applications. In the study of reactivity, many different ligand systems have been studied, including the application of copper-containing macrocycles. In contrast to the appearance of copper containing macrocycles of S and N donor atoms the abundance of P containing copper macrocycles is scare.



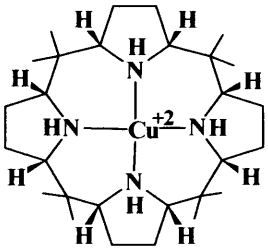
4.8



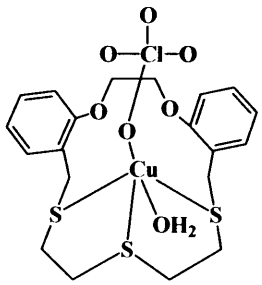
4.9



4.10



4.11



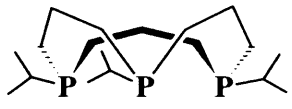
4.12

Figure 4.2: Examples of Cu based macrocyles [22-26]

Despite the abundance of Cu(II) and Cu(I) bearing macrocycle complexes with various donor atoms such as S and N there are no reported copper complexes of P_3 macrocycles.

In order to explore the potentially interesting chemistry of copper phosphine macrocycle complexes, we have studied the coordination chemistry of [12]-ane-$P_3(^iPr)_3$ ligand with copper(I). For Cu(I), a tetrahedral environment is common (due to its d^{10} electronic state), and phosphine complexes of Cu(I) are well known.[27, 28] Thus we can expect macrocyclic triphosphines such as [12]-ane-$P_3(^iPr)_3$ to facially coordinates tetrahedral Cu(I) and be good ligands for stabilizing the Cu(I) state.

4.2. Results and discussion

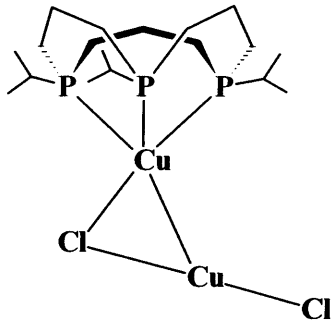


([12]-ane-$P_3(^iPr)_3$)

(4.13)

+ CuCl $\xrightarrow{CH_2Cl_2}$

(4.14)



92 %

Scheme 4.4: Synthesis of (μ-chloro) fac-(η^3 -1,5,9-triisopropyl-1,5,9-triphosphacyclododecane)copper(I) copper chloride, 8

The reaction of [12]-ane-$P_3(^iPr)_3$ (Scheme 4.4) with CuCl at room temperature in CH_2Cl_2 rapidly gives rise to a off white coloured solution from which crystals of **4.14** may be isolated in 92.0 % yield. Analytical data indicate the formula of {[12]-ane-$P_3(^iPr)_3$}Cu(μ-Cl)CuCl, (**4.14**) is also diamagnetic, although it gives rise to very broad NMR spectra. The ^{31}P $\{^1H\}$ NMR spectrum of **4.14** clearly indicates the formation of a tertiary phosphine complex with a resonance at δ -19.7 ppm due to the strong σ bond from phosphorus to the metal atom. The co-ordination chemical shift ($\Delta\ ^{31}P = \delta_{co\text{-}ordinated\ P} - \delta_{unco\text{-}ordinated\ P}$) relative to the free phosphine ligand is *ca* 0.0 ppm.

The ^{1}H NMR spectrum of **4.14** shows resonances attributable to α P***CH₂*** ring protons in the region of δ 1.80-1.60 ppm and those assigned to the ring β PCH_2***CH₂*** fall in the region δ 2.10-1.90 ppm. The protons of the isopropyl PCH appear in the region of δ 1.80-1.60 ppm and the methyl PCH***CH₃*** are observed at δ 1.00-1.20 ppm. In the ^{13} C{^{1}H} NMR spectra the carbon assigned to the ring α P***CH₂*** fall at δ 27.14 ppm and those due to ring β PCH_2***CH₂*** are at δ 24.85 ppm. The PCH carbon of the isopropyl group appears at 21.44 ppm and those due to PCH***CH₃*** are at 17.76 ppm. These assignments are confirmed by a standard 2D NMR experiment.

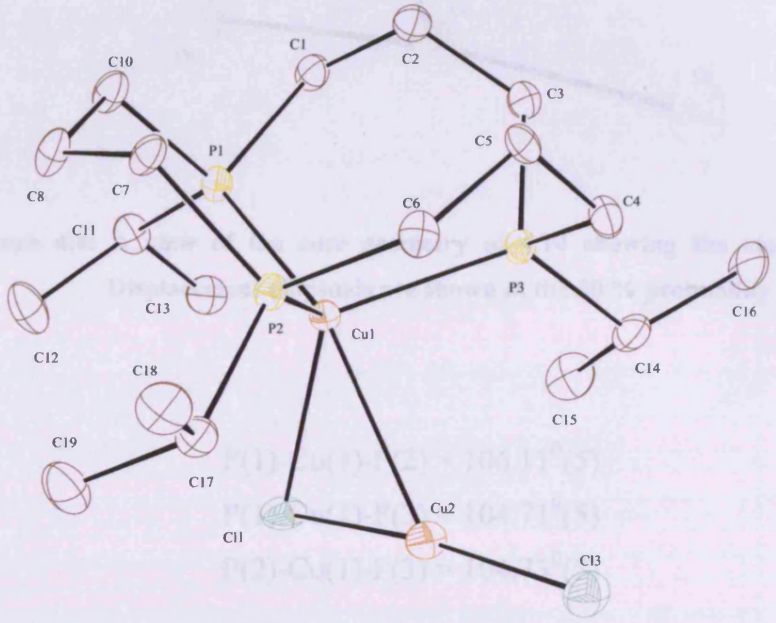


Figure 4.3: Molecular structure of (μ-chloro) fac-(η^3 -1,5,9-triisopropyl-1,5,9-triphosphacyclododecane)copper(I) copper chloride, 4.14, the anions and the hydrogen atoms have been omitted for clarity.

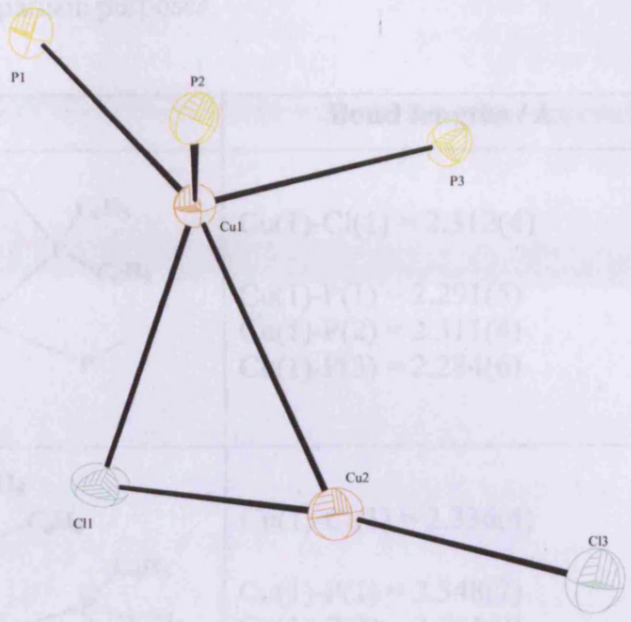


Figure 4.4: A view of the core geometry of 4.14 showing the atom numbering. Displacement ellipsoids are shown at the 30 % probability level.

P(1)-Cu(1)-P(2) = 106.11^0(5)
P(1)-Cu(1)-P(3) = 104.71^0(5)
P(2)-Cu(1)-P(3) = 104.73^0(5)

Cu(1)-Cl(1)-Cu(2) = 72.80^0(4)
Cu(2)-Cu(1)-Cl(1) = 49.08^0(4)

Cu(1)-Cu(2) = 2.7001(8)Å

Cu(1)-μCl(1) = 2.4002(14)Å
Cu(2)-μCl(1) = 2.1359(14)Å

Selected bond lengths of known triphosphorus tripodal ligands are included in the fallowing table for a comparison purposes.

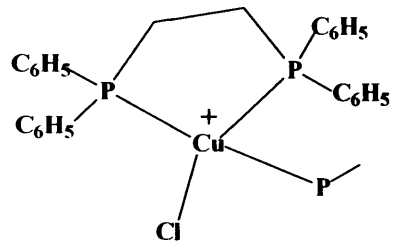
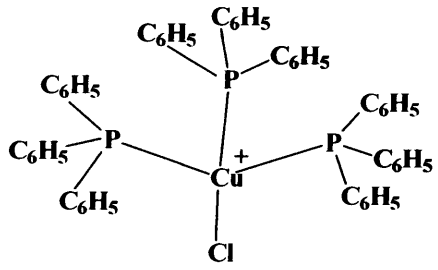
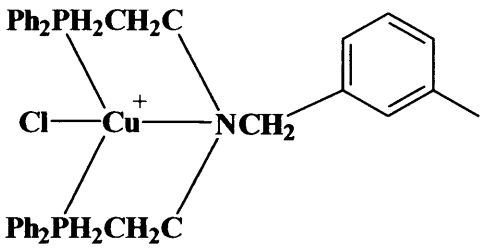
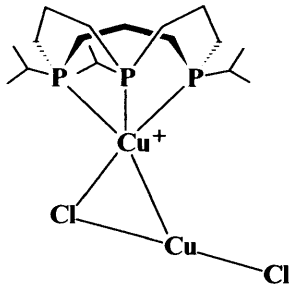
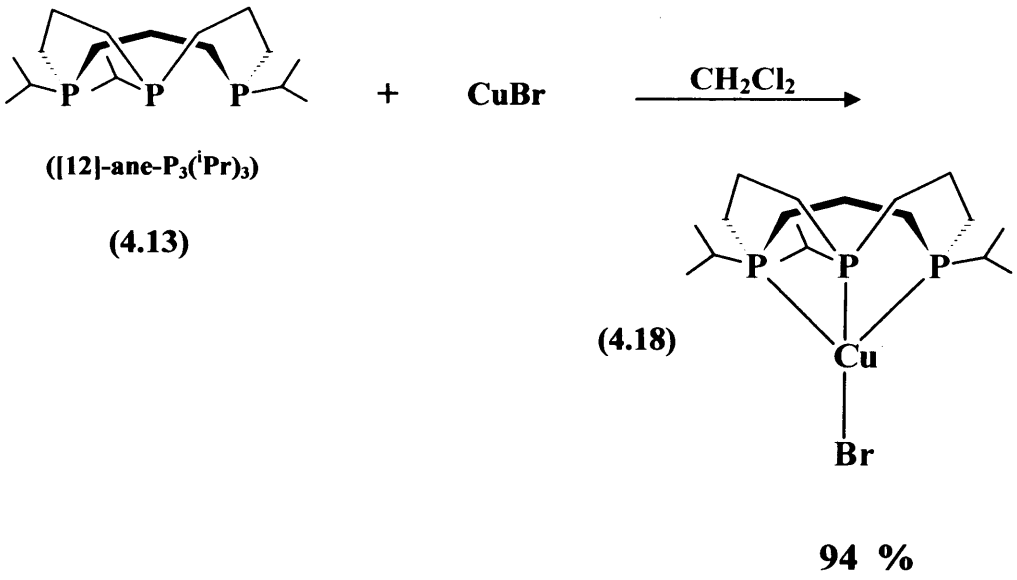
Complex	Bond lengths / Å	Ref.
 4.15	Cu(1)-Cl(1) = 2.312(4) Cu(1)-P(1) = 2.291(5) Cu(1)-P(2) = 2.311(4) Cu(1)-P(3) = 2.284(6)	30
 4.16	Cu(1)-Cl(1) = 2.336(4) Cu(1)-P(1) = 2.348(2) Cu(1)-P(2) = 2.351(2) Cu(1)-P(3) = 2.355(2)	31
 4.17	Cu(1)-Cl(1) = 2.347(2) Cu(1)-P(1) = 2.299(2) Cu(1)-P(2) = 2.319(1) Cu(1)-P(3) = 2.327(1)	32
 4.14	Cu(2)-Cl(3) = 2.1071(14) Cu(1)-P(1) = 2.2383(13) Cu(1)-P(2) = 2.2471(14) Cu(1)-P(3) = 2.2416(14)	This work

Table 4.1: Selected interatomic distances (Å) of M-P and P-P interaction of complex 4.14 and other literature examples

The data in table 4.1 clearly shows that the terminal chlorine-copper bond lengths in copper(I) complexes, (**4.15, 4.16** and **4.17**) are longer than that of the macrocyclic complex, (**4.14**), indicating that the bulky phenyl groups do not allows terminal chlorine to approach to the metal atom quite comfortably. Similar to the copper-chlorine(terminal) bond lengths, the copper-phosphorus bond lengths are shorter for the macrocyclic P_3 donor complex(**4.14**). This may be also due to the steric contribution imposed by the bulky phenyl groups. Unfortunately, there are not any analogous compounds to compare the bridging Cu-Cl-Cu unit.

On the other hand, in both ethyl and isopropyl substituted macrocyclic complexes the metal ion lies at the centre of the significantly distorted tetrahedral geometry with a similar fashion. All mutually *cis* set of donor atoms form significantly less obtuse bond angles than the expected 109^0, P(1)-Cu(1)-Cl(1)(110.53^0(5)), P(2)-Cu(1)-Cl(1)(111.99^0(5)) and P(3)- Cu(1)-Cl(1)(117.89^0(5)) The almost identical nature between the bite angles of the macrocyclic unit may also be another factor for the regular tetrahedron since macrocyclic unit restricts the random arrangement of phosphorus atoms around the central metal centre.

Geometrically, there is no clear significant differences between ethyl and isopropyl substituted macrocyclic complexes but spacially there is a clear difference between them. Ethyl group substituted macrocyclic unit of copper complex has much longer Cu-Cu bond length (2.747(1) Å) than that of isopropyl group substituted analogue.



Scheme 4.5: Synthesis of fac-(η^3 -1,5,9-triisopropyl-1,5,9-triphosphacyclododecane)copper(I) bromide, 4.18

The reaction between [12]-ane-$P_3(^iPr)_3$ and copper(I) bromide in CH_2Cl_2 give a off white **4.18** with 94.0 % yield. The complex **4.18** is diamagnetic and its $^{31}P\{^1H\}$ NMR spectrum is broad at -19.1 ppm indicating the coordination of free macrocycle to the metal centre. Since the room temperature $^{31}P\{^1H\}$ NMR spectrum of **4.18** is broad a variable temperature NMR was performed at 20 ^{0}C, 0 ^{0}C , -20 ^{0}C, -40 ^{0}C, -60 ^{0}C and -70 ^{0}C. The complex **4.18** has been fully characterised by ^1H, $^{13}C\{^1H\}$, mass spectrometry, high resolution mass spectrometry and the microanalysis and data suggest the structure of **4.18** which is compatible with the unpublished data of the ethyl group substituted identical copper complex.

The characteristic resonances of P***CH*$_2$** protons fall in the region of δ 1.75-1.60 ppm and those assigned to the β PCH_2***CH*$_2$** fall in the region δ 2.00-1.80. The protons of the isopropyl P***CH*** appears in the region of δ 1.75-1.60 ppm and PCH***CH*$_3$** are observed at δ 1.05-1.20 ppm.

The $^{13}C\{^1H\}$ NMR spectrum consists of four resonances assignable to the four different carbon environments which are almost identical to the spectra observed for **4.14** complex $\{([12]\text{-ane-}P_3(^iPr)_3\}Cu(\mu\text{-Cl})CuCl$.

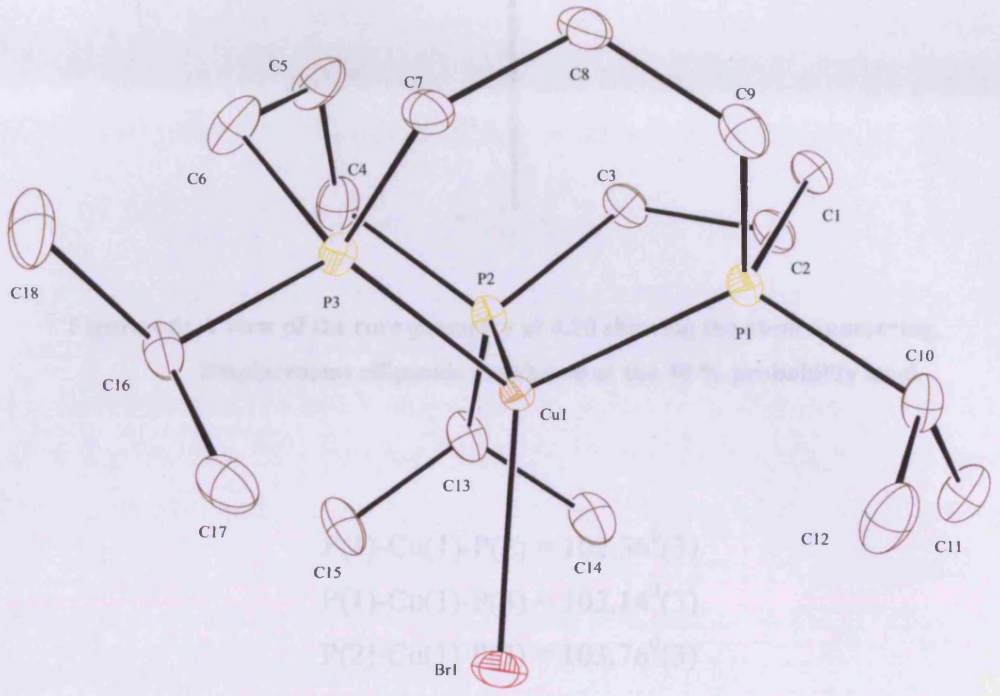


Figure 4.5: Molecular structure of fac-(η^3 -1,5,9-triisopropyl-1,5,9-triphosphacyclododecane)copper(I) bromide, 4.18, the anions and the hydrogen atoms have been omitted for clarity.

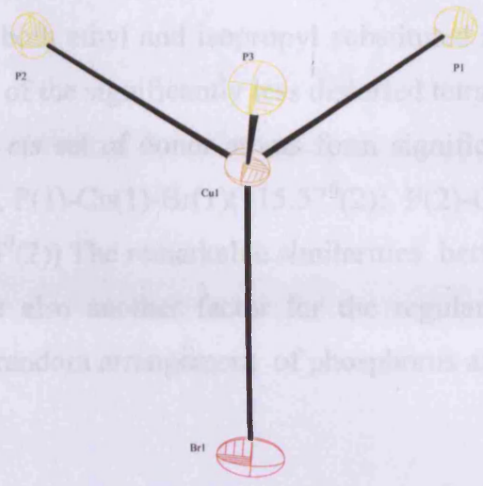


Figure 4.6: A view of the core geometry of 4.18 showing the atom numbering. Displacement ellipsoids are shown at the 30 % probability level.

P(1)-Cu(1)-P(2) = 102.36^0(3)

P(1)-Cu(1)-P(3) = 103.14^0(3)

P(2)-Cu(1)-P(3) = 103.76^0(3)

Br(1)-Cu(1)-P(1) = 115.52^0(2)

Br(1)-Cu(1)-P(2) = 114.66^0(2)

Br(1)-Cu(1)-P(3) = 115.64^0(2)

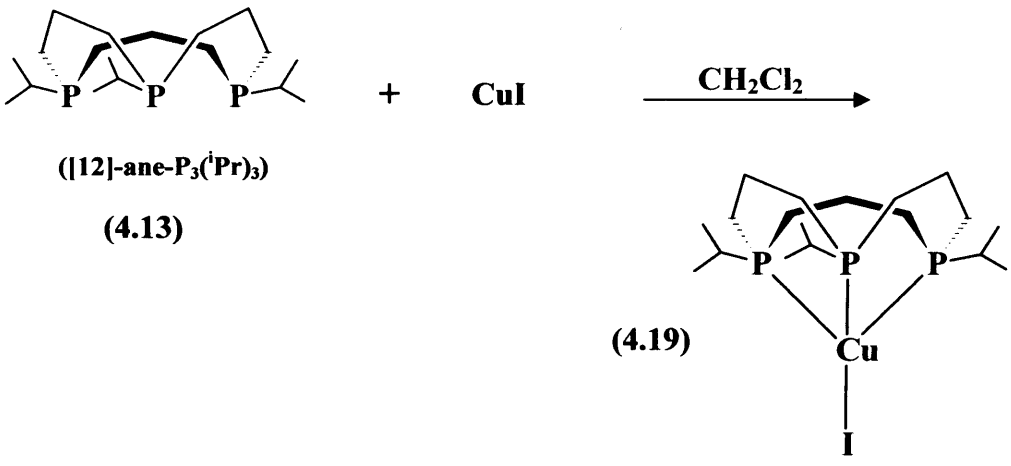
P(1)-Cu(1) = 2.2483(7) Å

P(2)-Cu(1) = 2.2477(7) Å

P(3)-Cu(1) = 2.2592(7) Å

On the other hand, in both ethyl and isopropyl substituted macrocyclic complexes the metal ion lies at the centre of the significantly less distorted tetrahedral geometry with a similar fashion. All mutually *cis* set of donor atoms form significantly less obtuse bond angles than the expected 109^0, P(1)-Cu(1)-Br(1)(115.52^0(2)), P(2)-Cu(1)-Br(1)(114.66^0(2)) and P(3)- Cu(1)-Br(1) (115.64^0(2)) The remarkable similarities between the bite angles of the macrocyclic unit may be also another factor for the regular tetrahedron since the macrocyclic unit restricts the random arrangement of phosphorus atoms around the central metal centre.

Although the macrocycle CuBr unit in both complexes has a closely related pyramidal structure, the overall structures vary very significantly. {[12]-ane-P_3Et_3}CuBr crystallises as both mononuclear and binuclear adduct with CuBr, analogous to its chlorine analogue. For the bulkier ^{i}Pr derivate, **4.18** ({[12]-ane-$P_3(^iPr)_3$}CuBr) however, a mononuclear structure is observed. We presume that this difference is a clear indication of the influence of the bulk of the P-substituents where the larger ^{i}Pr group destabilises bridging arrangement of the larger Br^-(than Cl^-) such that, unlike in the {[12]-ane-P_3Et_3 analogue, a binuclear structure does not form.



Scheme 4.6: Synthesis of fac-(η^3 -1,5,9-triisopropyl-1,5,9-triphosphacyclododecane)copper(I) iodide, 4.19

The reaction between [12]-ane-$P_3(^iPr)_3$ and copper(I) iodide in CH_2Cl_2 results in rapid dissolution of the CuI. From this solution, an off white solid, **4.19** is readily obtained in 91.0 % yield. The complex **4.19** is diamagnetic and its $^{31}P\{^1H\}$ NMR spectrum is broad at -23.2 ppm indicating the coordination of the macrocycle to the metal centre.

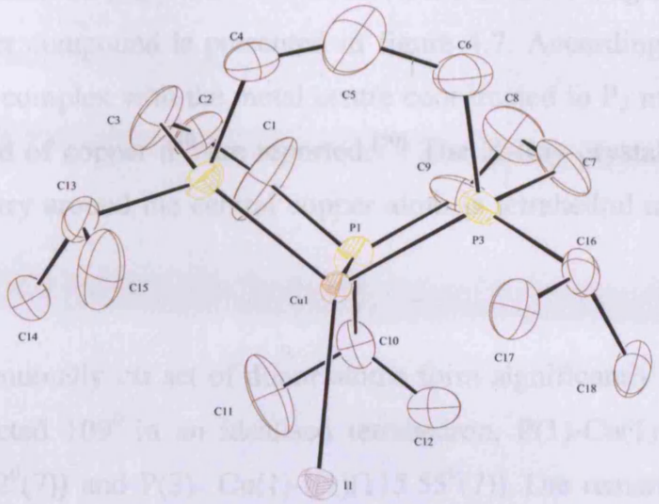
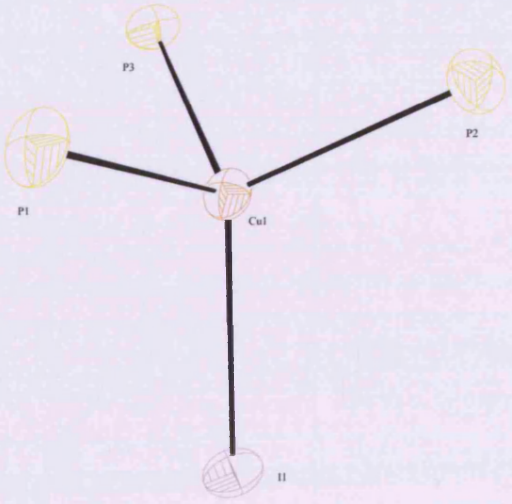


Figure 4.7: Molecular structure of fac-(η^3 -1,5,9-triisopropyl-1,5,9-triphosphacyclododecane)copper(I) iodide, 4.19, the anions and the hydrogen atoms have been omitted for clarity.



P(1)-Cu(1)-P(2) = 103.08^0(9)

P(1)-Cu(1)-P(3) = 102.99^0(9)

P(2)-Cu(1)-P(3) = 101.31^0(9)

I(1)-Cu(1)-P(1) = 114.25^0(8)

I(1)-Cu(1)-P(2) = 117.62^0(7)

I(1)-Cu(1)-P(3) = 115.55^0(7)

P(1)-Cu(1) = 2.248(2)Å

P(2)-Cu(1) = 2.250(2)Å

P(3)-Cu(1) = 2.241(2)Å

Figure 4.8: A view of the core geometry of 4.19 showing the atom numbering. Displacement ellipsoids are shown at the 30 % probability level.

An X –Ray diffraction study has been carried out for the diamagnetic complex **4.19** and this neutral copper compound is presented in figure 4.7. According to the literature, there is no copper d^{10} complex with the metal centre coordinated to P_3 macrocyclic ligand but few tripodal ligand of copper d^{10} are reported.[30] The X-Ray crystal structure clearly shows that the geometry around the central copper atom is tetrahedral and the Cu-I bond length is about 2.6 Å.

Again the all mutually *cis* set of donor atoms form significantly less obtuse bond angles than the expected 109^0 in an idealised tetrahedron, P(1)-Cu(1)-I(1)(114.25^0(8)), P(2)-Cu(1)-I(1)(117.62^0(7)) and P(3)- Cu(1)-I(1)(115.55^0(7)) The remarkable similarities between the bite angles of the macrocyclic unit may also be another factor for the regular tetrahedron since macrocyclic unit restricts the random arrangement of phosphorus atoms around the central metal centre.

Both geometrically and spacially, there is no clear significant differences between ethyl and isopropyl substituted macrocyclic complexes of {[12]-ane-$P_3(^iPr)_3$}CuI.[29]

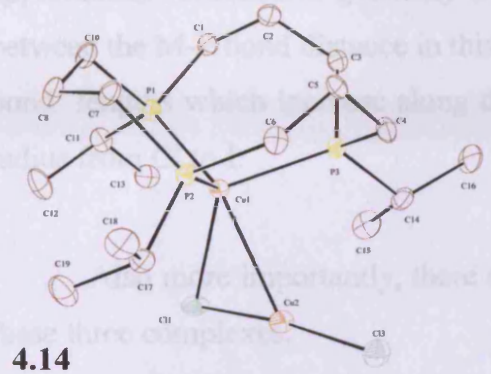
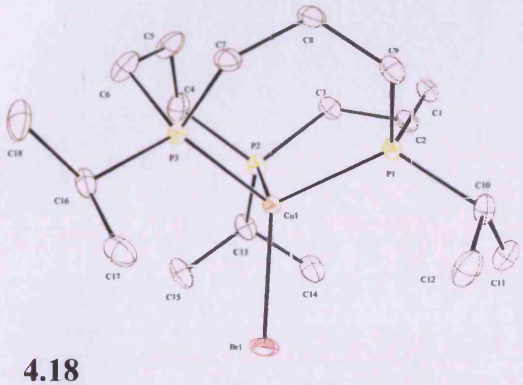
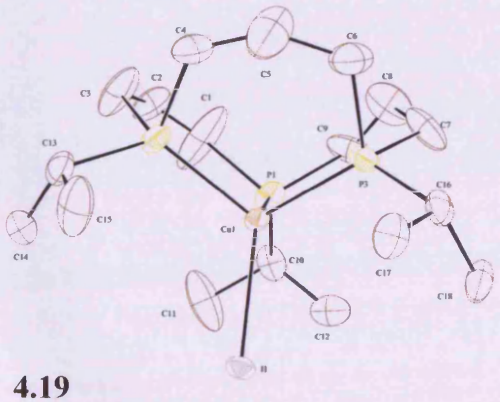
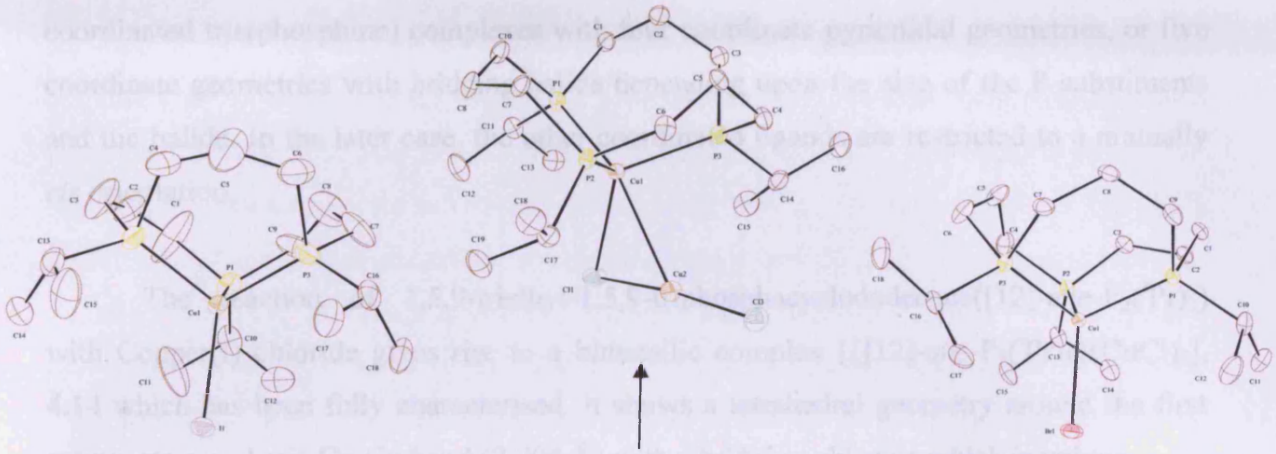
Complex	Cu-P bond length /Å	Cu-X bond length /Å
 **4.14**	P(1) = 2.2383(13) P(2) = 2.2471(14) P(3) = 2.2416(14)	Cu(1)-Cl(1) = 2.4002(14) Cu(2)-Cl(1) = 2.1359(14) Cu(2)-Cl(3) = 2.1071(14)
 **4.18**	P(1) = 2.2483(7) P(2) = 2.2477(7) P(3) = 2.2592(7)	2.4410(4)
 **4.19**	P(1) = 2.248(2) P(2) = 2.250(2) P(3) = 2.241(2)	2.5881(9)

Table 2.2: Selected interatomic distances (Å) of M-P and M- X of complexes of 4.14, 4.18 and 4.19

In the comparison of {[12]-ane-$P_3(^iPr)_3$}Cu(μ-Cl)CuCl, **4.14**, {[12]-ane-$P_3(^iPr)_3$}CuBr, **4.18** and {[12]-ane-$P_3(^iPr)_3$}CuI **4.19** complexes, all these show approximate tetrahedral geometry around the metal centre. There is no clear difference between the M-P bond distance in this series of complexes in contrast to the M-X(Cl, Br, I) bond lengths which increase along the series. This is obvious due to increasing covelent radius from Cl to I.

Also more importantly, there are no clear differences between the bite angles of all these three complexes.



CuCl

CuI **CuBr**

[12]-ane-P_3R_3

CuI **CuBr**

CuCl

{[12]-ane-P_3R_3}CuI

R = $-CH_2CH_3$

Ref 29

{[12]-ane-P_3R_3}Cu(μ-Br)CuBr

R = $-CH_2CH_3$

Ref 29

{[12]-ane-P_3R_3}Cu(μ-Cl)CuCl

R = $-CH_2CH_3$

Ref 29

4.3. Conclusion

The reactions of [12]-ane-$P_3(^iPr)_3$ with group 11 metal with the electronic configuration of d^{10} including Cu(I) precursor complexes rapidly give rise to facially coordinated tris(phosphine) complexes with four coordinate pyramidal geometries, or five coordinate geometries with bridging halide depending upon the size of the P-substituents and the halide. In the later case, the other coordinated ligands are restricted to a mutually *cis* orientation.

The reaction of 1,5,9-triethyl-1,5,9-triphosphacyclododecane([12]-ane-$P_3(^iPr)_3$) with Copper(I) chloride gives rise to a bimetallic complex [{[12]-ane-$P_3(^iPr)_3$}$(CuCl)_2$], **4.14** which has been fully characterised. It shows a tetrahedral geometry around the first copper atom and one Cu-Cu bond (2.700 Å) with a bridging chlorine which is unique.

In contrast to the ethyl substituted bimetallic compound of bromide analogue [{[12]-ane-P_3Et_3}$(CuBr)_2$] the isopropyl substituted gives a monometallic species of [{[12]-ane-$P_3(^iPr)_3$}CuBr], **4.18**. These results clearly prove that the bulkiness of the isopropyl group inhibits the formation of bimetallic species in the bromide analogue.

The same reaction with the copper (I) iodide afforded the monomer [{[12]-ane-$P_3(^iPr)_3$}CuI], **4.19.** The X-Ray structure of **4.19** shows a tetrahedral environment for the copper atom with almost no distortion.

4.4 Experimental

4.4.1. General

Techniques and Instruments: All reactions were carried out in an atmosphere of dry argon. All solvents were dried by refluxing over standard drying agents. The compounds allylphosphine, *syn,syn*-1,5,9-triisopropyl-1,5,9-triphosphacyclododecane, **[12]-ane-$P_3(^iPr)_3$** were prepared by a slight change of literature methods. **Caution:** The organophosphines and some of their complexes described are *highly malodorous* and likely *highly toxic*. Great care should be exercised in their handling. All other reagents were obtained from the Aldrich Chemical Company and, where appropriate, were degassed before use. NMR spectra were recorded on a Bruker DPX-500 instrument at 500 MHz (^1H), and 125.75MHz (^{13}C), Bruker DPX-400 instrument at 400 MHz and 100 MHz (^{13}C), Jeol Lamda Eclipse 300 at 121.65 MHz (^{31}P), 75.57 MHz (^{13}C). ^1H and ^{13}C chemical shifts are quoted in ppm relative to residual solvent peaks, and ^{31}P NMR chemical shifts quoted in ppm relative to 85% external H_3PO_4. The infra-red spectra were recorded on a Nicolet 500 FT-IR spectrometer and the samples were prepared under Ar atmosphere as a KBr disk. Mass spectra of all the samples have been measured by direct injection into a Waters Low Resolution ZQ Mass Spectrometer fitted with ESCI source. Elemental analysis was performed by MedacLTD Analytical Service.

X-Ray Crystallography: data collections were carried out on a Bruker Kappa CCD diffractometer at 150(2) K with Mo $K\alpha$ irradiation (graphite monochromator). Empirical absorption corrections were performed using equivalent reflections. For the solution and refinement of the structures, the program package SHELXL 97 was employed. H atoms were placed into calculated positions and included in the last cycles of refinement. Crystal structure and refinement data are collected in **Appendix A** and supplementary CD.

4.4.2. Preparation of (μ-chloro) fac-(η^3 -1,5,9-triisopropyl-1,5,9-triphosphacyclododecane)copper(I)copper chloride, 4.14:

To a solution of [12]-ane-$P_3(^iPr)_3$ (352 mg, 10.10 x 10^{-4} mol) dissolved in dichloromethane(10 ml) were added CuCl (100 mg, 10.10 x 10^{-4} mol) in dichloromethane(10 ml) at room temperature. The solution was stirred for 3 h, during which time the copper chloride dissolved. The colourless solution was then evaporated to give a white solid and recrystallised by slow diffusion in CH_2Cl_2/petroleum ether to give **4.14** as white air-sensitive needles (507 mg , 9.29 x 10^{-4} mol, 92.0%), Analysis found (calculated): C, 39.19 (39.56); H, 6.82 (7.19). MS(ES), *m/z*: 411.16 [100%, (M^+-$CuCl_2$)], High resolution mass spec actual (calc. mass): 411.1564 (411.1561) NMR ($CDCl_3$): $^{31}P\{^1H\}$, δ -19.70 ppm, ^1H NMR, δ (ppm): 2.10-1.90 (br *s*, PCH_2CH_2); 1.80-1.60 (*br m*, PC*H* and PCH_2); 1.00-1.20 (*br s*, CH). $^{13}C\{^1H\}$ NMR, δ (ppm): 27.14 (*br, s*, PCH_2); 24.85 (*br, s*, PCH_2CH_2); 21.44 (*br, s*, PCH); 17.76 (*s*, CH_3).

4.4.3. Preparation of fac-(η^3 -1,5,9-triisopropyl-1,5,9-triphosphacyclododecane)copper(I) bromide, 4.18:

To a solution of [12]-ane-$P_3(^iPr)_3$ (122 mg, 3.48 x 10^{-4} mol) in dichloromethane(10 ml) were added CuBr (50 mg, 3.48 x 10^{-4} mol) in dichloromethane(10 ml) at room temperature. A part of the CuBr reacted instantly, and then the solution was stirred for 4 hour at ambient temperature. The solution was decantated, concentrated and crystallised in CH_2Cl_2/petroleum ether to afford **4.18** as colourless air-sensitive needles.(161 mg , 3.27 x 10^{-4} mol, 94.0%). Analysis found (calculated): C, 43.81 (43.95); H, 7.88 (7.99). MS(ES), *m/z*: 411.15 [100%, (M^+)], High resolution mass spec actual (calc. mass): 411.1556 (411.1561) NMR ($CDCl_3$): $^{31}P\{^1H\}$, δ -19.11 ppm, ^1H NMR, δ (ppm): 2.00-1.80 (br *m*,

$PCH_2C\boldsymbol{H_2}$); 1.75-1.60 (*br m*, PC***H*** and $PC\boldsymbol{H_2}$); 1.05-1.20 (*br m*, CH). $^{13}C\{^1H\}$ NMR, δ (ppm): 28.08 (*br, s*, $P\boldsymbol{C}H_2$); 26.16 (*br, s*, $PCH_2\boldsymbol{C}H_2$); 21.76 (*br, s*, P***C***H); 17.94 (*s*, $\boldsymbol{C}H_3$).

4.4.4. Preparation of fac-(η^3 -1,5,9-triisopropyl-1,5,9-triphosphacyclododecane)copper(I) iodide, 4.19:

To a solution of [12]-ane-$P_3(^iPr)_3$ (97 mg, 2.78 x 10^{-4} mol) in dichloromethane(10 ml) were added CuI (53 mg, 2.78 x 10^{-4} mol) in dichloromethane(10 ml) at room temperature. The solution was kept stirring for 5 h, during which all the copper iodide has reacted. Then the reaction solution was evaporated to give **4.19** as a white solid and recrystallised by slow diffusion in CH_2Cl_2/petroleum ether to give white needles (136 mg , 2.53 x 10^{-4} mol, 91.0 %) suitable for X-Ray study and which appear to be light stable for a while. Analysis found (calculated): C, 39.95 (40.12); H, 7.35 (7.29). MS(ES), *m/z*: 411.15 [100%, (M^+)], High resolution mass spec actual (calc. mass): 411.1569 (411.1561) NMR ($CDCl_3$): $^{31}P\{^1H\}$, δ -23.22 ppm, ^1H NMR, δ (ppm): 2.00-1.70 (br *m*, $PCH_2C\boldsymbol{H_2}$); 1.65-1.55 (*br m*, PC***H*** and $PC\boldsymbol{H_2}$); 1.05-1.20 (*br m*, CH). $^{13}C\{^1H\}$ NMR, δ (ppm): 28.43 (*br, s*, $P\boldsymbol{C}H_2$); 26.52 (*br, s*, $PCH_2\boldsymbol{C}H_2$); 22.10 (*br, s*, P***C***H); 18.42 (*s*, $\boldsymbol{C}H_3$).

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Appendix:

APPENDIX A

Uncompleted reactions

1) $[Ni(CH_3CN)_6][(BF_4)_2]$ + [12]-ane-$P_3(^iPr)_3$ ⟶ Mixture of products

2) $PtCl_2(COD)$ + [12]-ane-$P_3(^iPr)_3$ ⟶ Mixture of products

3) $PdCl_2(COD)$ + [12]-ane-$P_3(^iPr)_3$ ⟶ Mixture of products

4) $[[[12]\text{-ane-}P_3(^iPr)_3]Ru(CH_3CN)_2][(PF_6)_2]$ + $C_6H_5CHN_2$ ⟶
Complicated NMR

5) $[[12]\text{-ane-}P_3(^iPr)_3]Ru[(\mu\text{-}Cl)_3]Cl$ + $C_6H_5CHN_2$ ⟶
Complicated NMR

Crystallographic data of the complexes of

1.	{{[12]-ane-$P_3(^iPr)_3$}$Fe(CH_3CN)_3$}$(BF_4)_2$,	**2.27**
2.	{{[12]-ane-$P_3(^iPr)_3$}$_2Ru(\mu\text{-}Cl)_3Cl$,	**2.35**
3.	{{[12]-ane-$P_3(^iPr)_3$}$Ru(CH_3CN)_3$}$(PF_6)_2$,	**2.38**
4.	{{[12]-ane-$P_3(^iPr)_3$}NiBr}Br,	**3.3**
5.	{{[12]-ane-$P_3(^iPr)_3$}NiCO}NO_3,	**3.5**
6.	{[12]-ane-$P_3(^iPr)_3$}$Cu(\mu\text{-}Cl)CuCl$,	**4.14**
7.	{[12]-ane-$P_3(^iPr)_3$}CuBr,	**4.18**
8.	{[12]-ane-$P_3(^iPr)_3$}CuI,	**4.19**

Crystallographic data of the complexes of

1.	{{[12]-ane-$P_3(^iPr)_3$}$Fe(CH_3CN)_3$}$(BF_4)_2$,	**2.27**
2.	{{[12]-ane-$P_3(^iPr)_3$}$_2Ru(\mu\text{-}Cl)_3Cl$,	**2.35**
3.	{{[12]-ane-$P_3(^iPr)_3$}$Ru(CH_3CN)_3$}$(PF_6)_2$,	**2.38**
4.	{{[12]-ane-$P_3(^iPr)_3$}NiBr}Br,	**3.3**
5.	{{[12]-ane-$P_3(^iPr)_3$}NiCO}NO_3,	**3.5**
6.	{[12]-ane-$P_3(^iPr)_3$}$Cu(\mu\text{-}Cl)CuCl$,	**4.14**
7.	{[12]-ane-$P_3(^iPr)_3$}CuBr,	**4.18**
8.	{[12]-ane-$P_3(^iPr)_3$}CuI,	**4.19**

ABBREVIATIONS

AIBN		2,2'-Azabiisobutyronitrile
Ar		Aryl group
LAH		Lithium Aluminium Hydride
n-Bu		*n*-Butyl
t-Bu		*t*-Butyl
DCM		Dichloromethane
DMSO		Dimethylsulfoxide
Et_2O		Diethyl ether
IR		Infra-red
	(s)	strong
	(m)	medium
	(w)	weak
L		generic ligand
Me		Methyl
MS		Mass spectrum
NMR		Nuclear Magnetic Resonance
	(s)	singlet
	(b)	broad
	(d)	doublet
	(t)	triplet
	(q)	quartet
	(m)	multiplet
Ph		Phenyl
Pr		Propyl
ppm		Parts per million
R		generic alkyl