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P,N-type phosphaalkene-based Ir(I) complexes: synthesis, coordination chemistry, and catalytic applications†

Priyanka Gupta, [a,b] Hans-Joachim Drexler, [a] Richard Wingad, [b] Duncan Wass, [b] Eszter Baráth, [a] Torsten Beweries *[a] and Christian Hering-Junghans *[a]

Phosphaalkenes are an emerging class of ligands with unique electronic properties that can be regarded as tuneable variants of the ubiquitous CO ligand. Our group has recently reported the synthesis of the P, N-type phosphaalkene ligand quin-CHvPMes* (1, quin = 2-quinolinyl) and its coordination chemistry with Rh(I) was investigated. In this study, we present the synthesis and characterisation of iridium(I) complex [(quin-CHvPMes*)$_2$IrCl] (5), which showed a versatile reactivity upon chloride abstraction with AgOTf in different coordinating solvents affording pyridine-coordinated cationic Ir(I) complex [(quin-CHvPMes*)$_2$Ir(py)][OTf] (6) and C–H bond activated cyclometallated Ir(III)-hydrido complex 8. Treatment of complex 5 with CO, $(CH_3)_2Mg$ or NaN_3, respectively, produced three types of five-coordinate Ir(I) com-plexes 9, 10 and 11 in excellent yields. Complex 6 was found to be less active as a catalyst in the N-alkylation of aniline with benzyl alcohol than complex 5, likely due to the instability of Ir complex 6 in the presence of base at higher temperatures. Complex 5 has also been tested as a catalyst in the Guerbet-type coupling of methanol and ethanol to iso-butanol, which is a promising biofuel candidate, and showed good conversion and selectivity towards the desired iso-butanol.

Introduction

Over the past three decades, there has been a growing interest to incorporate phosphaalkenes (PAs) in transition metal cata-lysts. This interest is based on the energetically low-lying π* orbitals in PAs, thereby serving as effective π-acceptors towards transition metals.[1,2] The lone pair on phosphorus in PAs pos-sesses high s-character and thus, their σ-donating ability can be compared to carbon monoxide rather than to imines. The lone pair on carbon (n_C) in CuO is formally in an sp-hybrid orbital (50% 2s), similar in s-character to the lone pair of the parent PA $\mathrm{HPvCH_2}$ (66% 3s). In addition to the similar σ-donor properties, the analogy between PAs and carbon monox-ide extends to their excellent π-accepting ability (Fig. 1a).[3] This particular ligand property is useful, as it should in principle facilitate the reductive elimination step in a given catalytic cycle, leading to efficient systems for a wide range of catalytic organic transformations in conjunction with group

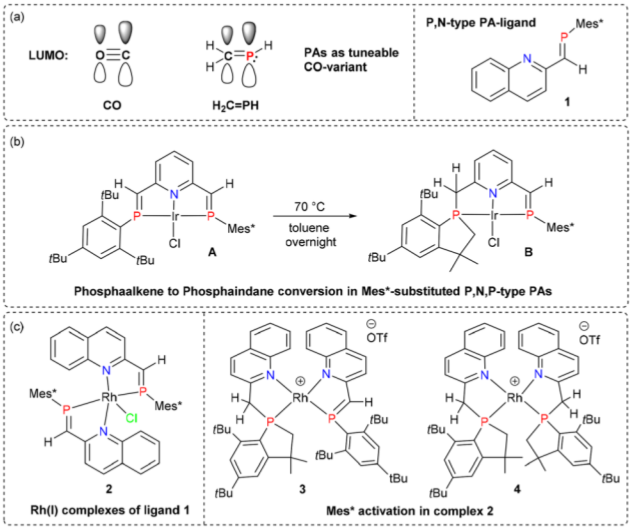

Fig. 1 (a) Illustration of the analogy between CO and phosphaalkenes; ligand activation in (b) previously reported Ir P,N,P phosphalkene pincer complexes[29] and (c) Rh P,N phosphaalkene complexes.[32]

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[a] Leibniz Institut für Katalyse e.V. (LIKAT), A.-Einstein-Str. 29a, 18059 Rostock, Germany. E-mail: torsten.beweries@catalysis.de, christian.hering-junghans@catalysis.de

[b] Cardiff Catalysis Institute, Cardiff University, Translational Research Hub, Maindy Road, Cathays, Cardiff, Wales, CF24 4HQ, UK

8–10 metals.[4–6] Representative examples, in which PA-containing metal complexes were utilised, include the hydroamination of 1,3-dienes (Pd),[7] the dehydrative allylation with allylic alcohols (Pd),[8,9] the Z-selective hydrosilylation of alkynes (Ru),[10,11] the hydroamidation of enones (Rh)[12] and the N-alkylation of amines with alcohols (Ir).[13] N-Alkylation of amines with alcohols is an environmentally benign process of preparing amines, which produces water as the sole byproduct.[14–16] Although both heterogeneous and homogeneous catalysts have been reported to promote the reaction, ruthenium[17–19] and iridium[20–23] complexes have constituted a vast majority of the homogeneous catalysts. While this area of research is still growing, the field of PA-based ligands remains underexplored compared with the ubiquitously used related phosphine- or imine-based P,N ligands, which have been at the forefront of development in various areas of catalysis research.[24,25] The groups of Geoffroy and Yoshifuji reported a series of kinetically protected mono-, di- and tridentate PA-ligands following the "phospha–Peterson" route that involves the reaction of a silylated phosphide-anion of the type $RP^{(-)}Si(tBu)Me_2$ with an aldehyde or ketone.[26,27] Later, Bickelhaupt and co-workers improved the "phospha-Peterson" protocol and the variant $Mes^{*}PvC(SiMe_3)Py$ (Mes^{*} = 2,4,6-$tBu_3C_6H_2$) was synthesised using a Pd catalysed route employing a phosphaalkene Grignard reagent.[28] So far, PA-based P,N,P-pincer complexes of late transition metal complexes have been comparably well-studied while the reports on related bidentate PA-based P,N-ligands are still limited. In particular, Ozawa et al. have demonstrated that one of the PvC bonds installed in a P,N,P-pincer type iridium complex, [IrCl(BPEP-H)] (BPEP = 2,6-bis[2-(2,4,6-tri-tert-butylphenyl)-2-phosphaethenyl]pyridine; A (Fig. 1b), undergoes intramolecular C–H activation at one of the Mes*-substituents on P and cyclisation to afford a modified, unsymmetric P,N,P-pincer featuring phospholane, pyridine, and phosphaalkene donor sites (B, Fig. 1b). P,N,P-pincer iridium complexes with a phosphanylmethyl group (B) on the pyridine core undergo deprotonation at the benzylic position, resulting in dearomatisation of the pyridine ring. The dearomatised complexes have shown potential in the activation of small molecules in a heterolytic manner, particularly towards N–H bond activation of ammonia and amines via metal– ligand cooperativity.[29] Mixed bidentate P,N-ligands, featuring a phosphaalkene moiety and an imine donor, on reaction with [Pd(cod)MeCl] (cod = 1,5-cyclooctadiene) have been reported to give bimetallic macrocyclic derivatives.[30] We have recently reported on the synthesis and characterisation of the P,N-type quinoline-based phosphaalkene ligand quin-CHvPMes* (1, quin = 2-quinolinyl), synthesised by the combination of the phospha-Wittig reagent $Mes^{*}P(PMe_3)$[31] with 2-quinolinecarboxaldehyde and investigated its coordination chemistry with Rh(I), giving complex 2, with Rh in a distorted trigonal bipyramidal coordination mode and two ligands of 1 being mutually trans-oriented.[32] 2 was shown to undergo a selective cyclisation of one or two of the P,N-ligands by using sub- or superstoichiometric amounts of AgOTf ($OTf^{-} = O_3SCF_3^{-}$) resulting in the formation of complexes 3 and 4 (Fig. 1c). Also, we proposed a new type of bond activation pathway that involves an oxidative proton shift from the tBu group to the Rh centre along with formation of a phosphaindane unit instead of initial oxidative addition of the tBu group at Rh(I).

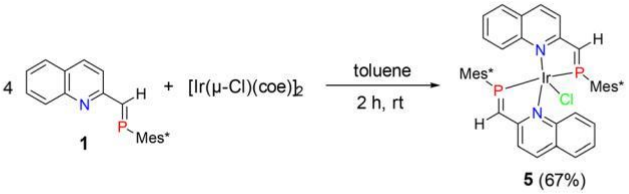
Intrigued by the general question of reactivity differences between 4d and 5d metals, we have now investigated structurally related iridium systems. In this paper, we report the multifaceted coordination chemistry of the P,N-phosphaalkene ligand quin-CHvPMes* (1, quin = 2-quinolinyl) at Ir(I) and highlight the reactivity of these complexes using spectroscopic methods. Moreover, these complexes were tested as catalysts in the N-alkylation of aniline with benzyl alcohol and in the Guerbet-type upgrading of ethanol to iso-butanol. Ruthenium complexes are active for the Guerbet-type synthesis of both n-and iso-butanol,[33–39] Homogeneous iridium systems have been previously reported for the Guerbet reaction of ethanol to n-butanol.[40–43] The only example of an iridium system for the upgrading of ethanol/methanol to iso-butanol was reported by Xu and Mu using iridium complexes immobilised on N-functionalised carbon materials.[44] Therefore, we turned our attention to investigate the efficacy of our iridium complex 5 in the co-condensation of ethanol and methanol to produce iso-butanol.

Results and discussion

Synthesis of Ir(I) complexes

The reaction of quin-CHvPMes* (1) with $[Ir(\mu\text{-}Cl)(coe)_2]_2$ (coe = cyclooctene) in toluene in a 4 : 1 ratio afforded $[(quin\text{-}CHvPMes^{*})_2IrCl]$ (5), which precipitated from the reaction mixture as a dark blue solid and was isolated on a 0.2 g scale (isolated yield: 67%; Scheme 1). Single crystal X-ray diffraction (SC-XRD) analysis of crystals grown from a saturated CH_2Cl_2 solution at −30 °C confirmed the formation of complex 5.

The molecular structure (Fig. 2) of 5 adopts a distorted trigonal bipyramidal geometry with a τ_5 value of 0.75 (the τ_5 parameter is used to categorise five-coordinate metal complexes, with $\tau_5 = 0$ indicating a perfect square-pyramidal C_{4v} geometry, while $\tau_5 = 1$ indicates a perfect trigonal bipyramidal D_{3h} coordination environment).[45,46] The quinoline N atoms occupy the axial positions, whereas both P atoms as well as the Cl^{-} ligand lie in the trigonal plane, with both ligands being trans-oriented with respect to the Mes*-substituent. The P–C bond lengths (P1–C10 1.685(4), P2–C40 1.680(4) Å) are nearly identical to those in its rhodium analogue 2 (1.6821(17), 1.6810(18) Å).[32]



Scheme 1 Synthesis of Ir(I) complex 5 starting from P,N-ligand 1.

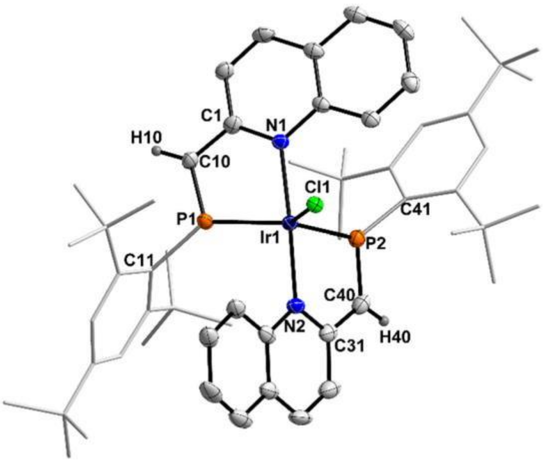


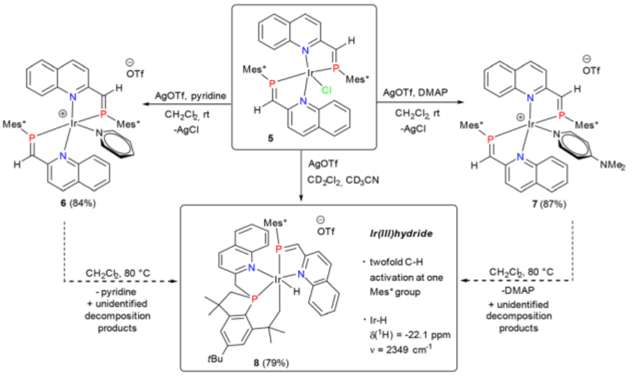
Fig. 2 Molecular structure of complex 5. Thermal ellipsoids drawn at 50% probability. Hydrogen atoms, except on the phosphaalkene unit (C10 and C40), are omitted for clarity. Selected bond lengths (Å) and angles (°) of 5: P1–C10 1.685(4), P2–C40 1.680(4), C10–C1 1.412(5), C40–C31 1.415(6), P1–Ir 2.1959(9), P2–Ir 2.2030(10), N1–Ir 2.116(3), N2–Ir 2.114(3), Ir–Cl 2.4579(10); C1–C10–P1 113.2(3), C31–C40–P2 114.0(3), P1–Ir–P2 129.32(4), N1–Ir–Cl 91.31(8), N2–Ir–Cl 94.10(9), P1– Ir–Cl 116.19(4), P2–Ir–Cl 114.49(3), N1–Ir–N2 174.50(12), P1–Ir–N1 80.48(8), P2–Ir–N2 80.42(9), C10–P1–C11 116.86(17), C40–P2–C41 116.90(19).

The Ir–N distances (2.116(3), 2.114(3) Å) are slightly longer than the typical range for P,N,P-pincer iridium(I) complexes (2.05–2.09 Å).[47–49]

The asymmetric stretching mode of the PvC bonds is clearly identified in the IR spectrum ($ν_{PvC}$) at 939 cm^{-1} (Table 1). In the $^{31}P\{^1H\}$ NMR spectrum the two phosphorus atoms are equivalent giving a singlet for 5 at 250.8 ppm (cf. 2 $δ(^{31}P\{^1H\})$ 262.5 ppm). Interestingly, unlike [IrCl(Mes*$_2$-BPEP)] (A),[29] the phosphaalkene unit in the bis-quinoline-PA complex 5 remained unaffected upon heating at 80 °C and only starts to decompose into some unidentified side products after two days of continuous heating, as ascertained by $^{31}P\{^1H\}$ NMR spectroscopy. Complex 5 is stable in CD_2Cl_2 solution in air, i.e., in the presence of traces of water, and is still present after addition of water and heating, making this species a promising platform for the study of catalytic reactions requiring thermal activation.

Effect of coordinating solvents

Following our recent observation of C–H bond activation at the o-tBu group of the Mes*-substituents in Rh complex 2 during salt metathesis reactions (Fig. 1c),[32] we decided to study the corresponding reaction of Ir P,N-complex 5 with AgOTf. To our surprise, we found that the reaction of complex 5 with AgOTf in non-coordinating solvent such as CD_2Cl_2 at room temperature resulted in the formation of a mixture of products, as observed by $^{31}P\{^1H\}$ NMR spectroscopy. In contrast, upon using a 2 : 1 mixture of CH_2Cl_2 and pyridine as a N-donor coordinating solvent, the $^{31}P\{^1H\}$ NMR spectrum featured a slightly shielded singlet resonance at 244.9 ppm indicating the formation of moisture stable pyridine coordinated Ir(I) complex [(quin-CHvPMes*)$_2$Ir(py)]OTf (6) (Scheme 2). This was corroborated by the molecular structure that was determined from blue-coloured single crystals obtained from a saturated THF solution layered with n-hexane (Fig. 3). Dative coordination of the pyridine to Ir(I) is characterised by the Ir1–N3 distance of 2.157(5) Å, which is minimally longer than the Ir1–N1, Ir1–N2 (2.122(4), 2.115(5) Å) distances to the quinoline N atoms in the axial positions of the distorted trigonal pyramid around the



Scheme 2 Synthesis of cationic Ir(I) complexes 6 and 7 and formation of the Ir(III) complex 8.

Table 1 Summary of characteristic spectroscopic and structural data of compounds 5–11 (C_{PA}: C atom of the phosphaalkene unit; C_R: C atom of the quin-C atom; n.a. = not available)

	$δ(^{31}P)$ [ppm]	d (P–C) [Å]	d (C_{PA}–C_R) [Å]	d (Ir–N) [Å]	d (Ir–P) [Å]	$\tilde{ν}$ (PvC) [cm^{-1}]
5	250.8	1.685(4) 1.680(4)	1.412(5) 1.415(6)	2.116(3) 2.114(3)	2.1959(9) 2.2030(10)	939
6	244.9	1.678(6) 1.699(7)	1.419(8) 1.407(12)	2.122(4) 2.115(5) 2.157(5)	 2.2097(16) 2.2032(15)	941
7	245.5 285.5 (t)	n.a.	n.a.	n.a.	n.a.	939
8	6.8 (t, J = 11.3 Hz)	n.a.	n.a.	n.a.	n.a.	n.a.
9	271.4	n.a.	n.a.	n.a.	n.a.	957
10	250.0	1.696(2) 1.697(2)	1.403(3) 1.401(4)	2.1121(17) 2.1070(18)	2.1987(5) 2.2010(6)	919
11	243.0	n.a.	n.a.	n.a.	n.a.	933

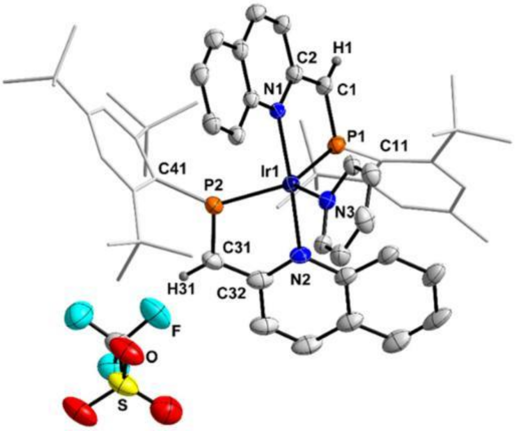


Fig. 3 Molecular structure of complex 6. Thermal ellipsoids drawn at 30% probability. Hydrogen atoms, except on the phosphaalkene unit (C1 and C31), are omitted for clarity. Selected bond lengths (Å) and angles (°) of 6: P1–C1 1.678(6), P2–C31 1.699(7), C1–C2 1.419(8), C31–C32 1.407(12), P1–Ir 2.2097(16), P2–Ir 2.2032(15), N1–Ir 2.122(4), N2–Ir 2.115(5), Ir–N3 2.157(5); C2–C1–P1 113.8(5), C32–C31–P2 112.5(5), P1–Ir–P2 127.21(6), N1–Ir–N3 91.97(19), N2–Ir–N3 93.88(19), P1–Ir–N3 115.27(13), P2–Ir–N3 117.51(14), N1–Ir–N2 174.1(2), P1–Ir–N1 80.65(13), P2–Ir–N2 80.32(16), C1–P1–C11 115.6(3), C31–P2–C41 117.0(3).

central Ir atom (τ_5 = 0.78). In order to show that pyridine coordination is general, complex 5 was treated with 4-(dimethylamino)pyridine (DMAP) in the presence of AgOTf in CH_2Cl_2, producing complex [(quin-CHvPMes*)$_2$Ir(dmap)]OTf (7) in 87% isolated yield (Scheme 2), which was fully character-ised by elemental analysis, NMR spectroscopy ($\delta(^{31}P\{^1H\})$ 245.5 ppm), and infrared spectroscopy. As expected, the spec-troscopic data of the DMAP complex 7 are similar to those of complex 6.

Next, we observed that upon using acetonitrile, the reaction proceeded differently. Upon adding AgOTf to a CH_2Cl_2/aceto-nitrile (2 : 1) solution of complex 5, the colour of the reaction mixture slowly changed from blue to red after stirring over-night at room temperature. The $^{31}P\{^1H\}$ NMR spectrum fea-tured two new doublets at 285.5 and 6.8 ppm, respectively, with a $^2J_{P-P}$ coupling constant of approximately 11 Hz and an additional singlet at 246.7 ppm, which was assigned to the acetonitrile coordinated Ir(I) complex [(quin-CHvPMes*)$_2$Ir (NCMe)]OTf (8a).

Although strongly coordinating to group 9 metals,[50] aceto-nitrile is known to undergo replacement by stronger donors such as pyridine,[51] and complex 8a slowly converted into the complex showing the two doublets at 285.5 and 6.8 ppm. The reaction can be accelerated by heating over a period of 12 h at 60 °C. SC-XRD experiments on weakly diffracting red crystals grown from a saturated dichloromethane solution layered with n-hexane revealed an unexpected C–H bond cleavage of both o-tBu substituents on one of the Mes*-substituents of the P,N-ligand (Fig. S10†). One hydrogen atom formally migrates from the tBu group to the carbon atom of the PvC bond to form a phosphaindane moiety,[29,52] resulting in the loss of the PvC double bond. The second tBu group undergoes cyclometallation to the Ir centre, resulting in the formation of Ir(III) hydride complex 8 (Scheme 2) that is characterised by a triplet signal in the ^1H NMR spectrum at −22.1 ppm for the Ir–H. Moreover, the presence of a terminal Ir–H was further supported by its stretching vibration at 2349 cm^{-1} in the IR spectrum (ν_{calc} = 2347 cm^{-1}). In contrast, pyridine coordinated Ir(I) complex 6 and DMAP coordinated Ir(I) complex 7 remained intact upon heating overnight at 60 °C and start converting into complex 8 only upon prolonged heating at 80 °C along with the formation of some unidentified decomposition products (Fig. S25†).

UV-vis spectroscopic and computational analysis of the electronic structure of the Ir phosphaalkene complexes (Fig. 4) indicates that the deep blue colour of the bis(phosphaalkene) complex 5 stems from two longest wavelength absorptions (λ_{calc} = 692.0, 661.9 nm), which are mainly local excitations at Ir, with partial metal to ligand charge transfer (MLCT) from Ir into the π* of the PvC bonds. Both transitions are HOMO to LUMO or HOMO−1 to LUMO transitions, respectively. For complex 6, the lowest energy absorption is found at 620 nm and can be assigned to similar local excitations found in complex 5. However, the presence of pyridine significantly stabilises the HOMO, resulting in a widening of the HOMO– LUMO gap, which explains the blue-shift of the longest wave-length absorption. In the case of complex 8, we found very good agreement between spectroscopic and computational values. Red coloured complex 8, containing phosphaindane and cyclometallated fragments, formed by twofold C–H acti-vation, shows intense band overlap at 521 nm, which can be attributed to a MLCT from Ir mainly into the π* orbital of the intact phosphaalkene.

Ligand exchange reactions

Complex 5 was reacted with CO (1 atm) at room temperature in the presence of $NaBF_4$ to form a turquoise solution of [(quin-

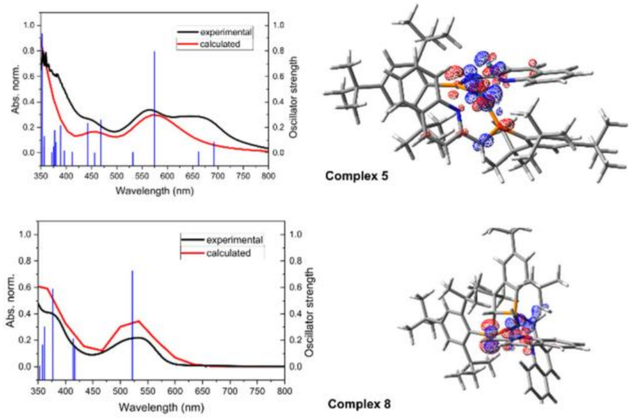


Fig. 4 Left: comparison of experimental (black, 0.2 mM in CH_2Cl_2) and calculated electronic absorption spectra (red) and oscillator strength of the transitions (blue) of complexes 5 (top) and 8 (bottom). Right: charge density difference between the ground state and the first excited state (red regions correspond to the electron, whereas blue regions indicate the electron hole).

CHvPMes*)$_2$Ir(CO)]BF$_4$ (9), which was found to exhibit a ν_{CO} band at 1978 cm^{-1} in the IR spectrum (Scheme 3). This value is higher than that of the neutral complex [Ir(CO)(PPEP*)] (PPEP* = deprotonated 2-(phospholanylmethyl)-6-(2-phosphaethenyl)pyridine)[29] (ν_{CO} = 1958 cm^{-1}) and of the cationic species [Ir(CO)(PNP)]$^+$ (PNP = 2,6-bis((di-tert-butylphosphino) methyl)pyridine)[53] (ν_{CO} = 1962 cm^{-1}). Hence, the iridium centre in 9 is more electron-deficient than in the related complexes. The presence of the carbonyl ligand was further evident from the ^{13}C NMR triplet resonance at δ 168.9 ppm with a $^2J_{P\text{–}C}$ coupling constant of 6.9 Hz. The molecular structure of carbonyl ligated iridium complex 9 was confirmed by SC-XRD analysis of a single crystal grown at room temperature from a saturated 1,2-diflourobenzene solution layered with n-hexane (Fig. S14†). However, the crystals were of poor quality and helped to only verify the connectivity but did not permit a discussion of structural parameters.

Transition-metal methyl complexes can be arguably considered the most important family of compounds with σ-M–C bonds. The chemistry of mononuclear methyl derivatives of iridium is largely dominated by the presence of tridentate P,C, P-,[54,55] P,N,P-,[56–58] N,N,P-[59] and O,N,O-[60] ligands whereas reports on related bidentate ligand coordinated iridium methyl complexes are still rare. We attempted to synthesise methyl complex [(quin-CHvPMes*)$_2$IrCH$_3$] (10) by nucleophilic methylation of the Ir(I) precursor (5). An excess of (CH$_3$)$_2$Mg was added to a CH$_2$Cl$_2$ solution of complex 5, resulting in a turquoise-coloured solution of complex 10 (Scheme 3). The ^{1}H NMR spectrum in CD$_2$Cl$_2$ showed the expected three tBu resonances of the Mes* groups (18H each), and an upfield singlet at δ 0.91 (3H) in the alkyl region. Complex 10 was isolated as a crystalline solid, suitable for X-ray diffraction analysis (Fig. 5), in 68% yield. The Ir–CH$_3$ distance (2.133(2) Å) falls into the range of other reported Ir–CH$_3$ distances (2.03–2.22 Å).[61]

To further evaluate the capability of complex 5 to engage in metathesis reactions, this species was stirred with an excess of sodium azide in THF at room temperature. The addition of lithium chloride as a phase-transfer catalyst[62] to solubilise azide ions through conversion of insoluble NaN$_3$ into soluble LiN$_3$ and NaCl proved to be efficient in reducing the reaction time to 7–10 days, allowing for the isolation of iridium azide complex 11 as a dark green solid in an isolated yield of 79% after workup (Scheme 3). Single crystals grown from a saturated THF solution layered with n-hexane were characterised in a SC-XRD experiment, confirming the structural motif with an azide group in the trigonal plane of an overall distorted bipyramidal structure (Fig. S21†). The found connectivity is in line with a strong IR band for the terminal azide at ν_{NN} = 2020 cm^{-1} and a single signal in the ^{31}P{^{1}H} NMR spectrum at 243 ppm. For a comparison of the most important structural and spectroscopic data of all Ir P,N phosphaalkene complexes discussed in this manuscript see Table 1.

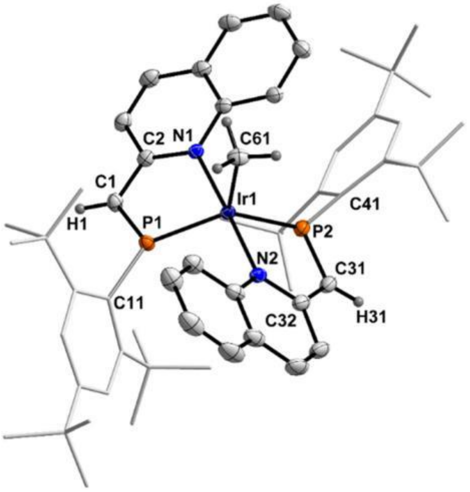
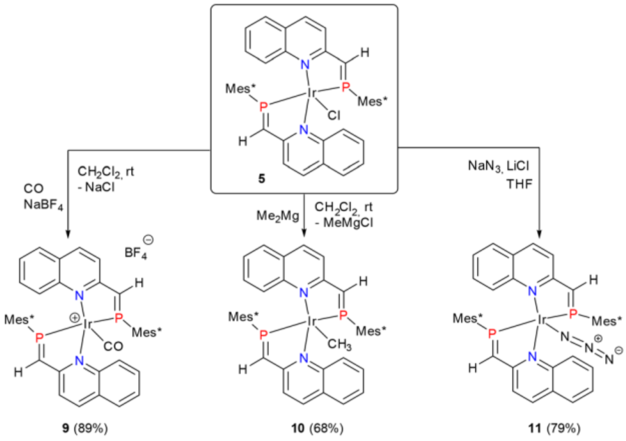


Fig. 5 Molecular structure of complex 10. Thermal ellipsoids drawn at 50% probability. Hydrogen atoms, except on the phosphaalkene unit (C1 and C31), are omitted for clarity. Selected bond lengths (Å) and angles (°) of 10: P1–C1 1.696(2), P2–C31 1.697(2), C1–C2 1.403(3), C31–C32 1.401(4), P1–Ir 2.1987(5), P2–Ir 2.2010(6), N1–Ir 2.1121(17), N2–Ir 2.1070(18), Ir–C61 2.133(2); C2–C1–P1 113.34(16), C32–C31–P2 113.67(17), P1–Ir– P2 131.77(2), N1–Ir–C61 90.30(8), N2–Ir–C61 91.92(8), P1–Ir–C61 115.17 (7), P2–Ir–C61 113.06(7), N1–Ir–N2 177.53(7), P1–Ir–N1 80.63(5), P2–Ir–N2 80.53(5), C1–P1–C11 116.53(10), C31–P2–C41 116.66(11).



Scheme 3 Synthesis of Ir(I) complexes (9, 10 and 11).

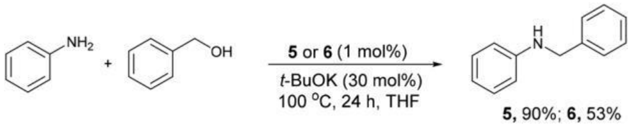
N-Alkylation of aniline with benzyl alcohol catalysed by 5 and 6

Having a set of new P,N-type phosphaalkene-based Ir(I) complexes in hand, we next wanted to evaluate their activity in the catalytic N-alkylation of aniline with benzyl alcohol using KOtBu as an external base. Kempe and co-workers have developed novel iridium(I) complexes coordinated with P,N chelate ligands, which exhibit high catalytic performance in the N-alkylation of aromatic primary amines, in conjunction with a stoichiometric amount of KOtBu.[63–65] The use of iridium(I) bearing a P,N,P pincer-type phosphaalkene ligand (BPEP-H) toward N-alkylation of primary and secondary amines with alcohols is well-precedented.[13] We have tested the catalytic activity of complex 5 and pyridine-coordinated cationic Ir complex 6. The model reaction of aniline and benzyl alcohol was performed at 100 °C for 24 h in THF using 1 mmol of each substrate, 30 mol% of tBuOK and 1 mol% of precatalyst 5 and 6, respectively (Scheme 4).

The catalytic reaction successfully proceeded with complete conversion to obtain N-benzylaniline (90% yield) catalysed by 5, whereas no formation of $PhN(CH_2Ph)_2$ as a dialkylation product was detected. On the other hand, the reaction cata-lysed by 6 afforded N-benzylaniline in only 53% yield in addition to PhNvCHPh (16%). The reduced catalytic activity of complex 6 towards N-alkylation of aniline with benzyl alcohol can be attributed to the instability of the complex at higher temperatures. As discussed above, prolonged heating of complex 6 transforms this species into doubly C–H activated Ir (III) complex 8, which is not catalytically active.

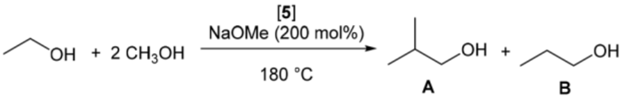
Upgrading of ethanol and methanol to iso-butanol catalysed by 5

The Guerbet-type upgrading of ethanol to n-butanol and ethanol/methanol to iso-butanol is of considerable recent interest because of the use of these C_4 alcohols as advanced biofuels.[66–69] Upon using 0.1 mol% of catalyst 5, a rather low conversion (30%) of ethanol and a low yield of the desired iso-butanol although high selectivity in the liquid fraction (93%) was obtained after two hours (Table 2, entry 1). The discre-pancy between conversion of ethanol and product yield is due to the formation of solid and gaseous side products via com-peting pathways as observed in previous studies.[55] Extending the reaction time to 20 h led to a small increase in iso-butanol yield (36%) with high selectivity (91%) (entry 2). The addition of triphenylphosphine had little effect on the catalysis (entry 3). Interestingly, use of 0.25 mol% of 5 achieved 80% conver-sion of ethanol in 60% yield of iso-butanol with high selecti-vity after 20 h of reaction (entry 4). Reducing the reaction time to 2 h led to a decrease in both iso-butanol yield (35%) and selectivity (88%) (entry 5).



Scheme 4 N-Alkylation of aniline (1 mmol) with benzyl alcohol (1 mmol) catalysed by complexes 5 or 6.

Table 2 Iridium catalysed conversion of ethanol and methanol to iso-butanol (A)



Entry	[5] [mol%]	t [h]	Conversion EtOH[a] [%]	Yield (A) i-BuOH[b,c] [%]	Yield (B) n-PrOH[b,c] [%]
1	0.1	2	30	19 (93)	1.5 (7)
2	0.1	20	74	36 (91)	2.5 (6)
3[d]	0.1	20	65	33 (90)	2.5 (7)
4	0.25	20	80	60 (93)	2.3 (4)
5	0.25	2	47	35 (88)	3.0 (7)

[a] Total conversion of ethanol as determined by GC analysis of the reac-tion mixture revealed the presence of some unidentified side products.

[b] Yield and selectivity in the liquid fraction determined by GC using hexadecane as internal standard. [c] Selectivities for the respective alcohol are given in parentheses. [d] 0.1 mol% of PPh_3 was also added.

As a likely mechanistic scenario, methanol and ethanol are dehydrogenated to formaldehyde and acetaldehyde via a transient iridium alkoxide species, producing a metal hydride complex. Aldol coupling yields, after rehydrogenation, n-propanol. A further dehydrogenation, aldol coupling, re-hydrogenation cycle with a second equivalent of methanol yields iso-butanol.[70,71] The facile β elimination of aldehyde to produce Ir hydrides was probed in a control experiment where NaOEt was added to pre-catalyst 5 at room temperature, yielding a mixture of hydride species that could not be isolated (Fig. S27†). These preliminary results showed the potential of complex 5 as an effective pre-cata-lyst for the upgrading of ethanol/methanol mixtures to iso-butanol. This demonstrates the first use of a P,N-type phos-phaalkene based iridium complex in Guerbet-type catalysis.

Conclusion

In summary, we have presented the synthesis and characterisation of iridium(I) complex 5 bearing two P,N-type phosphaalkene ligands, which produces cationic complexes 6, 7, and 8 in salt metathesis reactions with AgOTf in different coordinating solvents. In the presence of acetonitrile, the unexpected cyclo-metallation of the second o-tBu substituent of the Mes* ligand to afford the Ir(III) monohydride species (8) was observed. We have for the first time rationalised such ligand activation reac-tivity for P,N-type ligands coordinated to Ir(I) by spectroscopic and computational analysis. Complex 5 showcases a diverse coordination chemistry, ranging from carbonyl coordination, to give electron-deficient Ir complex 9, to nucleophilic methyl-ation using organometallic reagent, $(CH_3)_2Mg$, affording Ir– CH_3 complex 10. Additionally, we have demonstrated the cata-lytic activity of complexes 5 and 6 towards N-alkylation of aniline with benzyl alcohol. While the catalytic activity of complex 6 is rather low, complex 5 has proven to be reactive towards aniline. Complex 5 was also an effective pre-catalyst for the upgrading of ethanol/methanol mixtures to iso-butanol in 60% yield and 93% selectivity over 20 hours. Future studies will aim at further evaluating their catalytic potential towards N-alkylation of amines with a variety of primary and secondary alcohols and other alcohol upgrading processes such as ethanol homocoupling to n-butanol. Of particular interest will be the potential of Ir(III)-hydrido complex 8 to act as a catalyst in catalytic dehydrogenation reactions.

Author contributions

P.G. designed and performed the experiments. H.-J.D. and C. H.-J. performed the X-ray experiments and analysed the data.

P.G. carried out the DFT calculations. R.W. and D.W. super-vised the Guerbet catalytic reaction. P.G., H.-J.D., R.W., D.W., E.B., T.B. and C.H.-J. discussed the data. T.B. and C.H.-J. pro-posed and supervised the project. P.G., T.B. and C.H.-J pre-pared and revised the manuscript.

Conflicts of interest

There are no conflicts to declare.

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