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ARTICLE

Iridium Complexes of Perimidine-based *N*-Heterocyclic Carbene Pincer Ligands via Aminal C-H Activation

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The reactions of *N,N'*-bis(phosphinomethyl)dihydroperimidine pro-ligands $H_2C(NCH_2PR_2)_2C_{10}H_6$-1,8 (R = Ph **1a**, R = Cy **1b**) with iridium(I) substrates have been investigated and shown to readily result in chelate-assisted C–H activation processes. The reaction of **1b** with $[Ir_2Cl_2(COE)_4]$ (COE = *cyclo*-octene) affords the 18-electron iridium(III) dihydrido complex $[IrH_2Cl\{\kappa^3\text{-}C,P,P'\text{-}C(NCH_2PCy_2)_2C_{10}H_6\}]$, which forms $[IrHCl_2\{\kappa^3\text{-}C,P,P'\text{-}C(NCH_2PCy_2)_2C_{10}H_6\}]$ under acidic (HCl) conditions. In contrast, reaction of **1a** with $[Ir_2Cl_2(COD)_2]$ (COD = 1,5-cyclo-octadiene) affords the complex $[IrCl(COD)\{\kappa^2\text{-}P,P'\text{-}H_2C(NCH_2PPh_2)_2C_{10}H_6\}]$, thermolysis of which affords *cyclo*-octene and the pincer-NHC complex $[IrCl\{\kappa^3\text{-}C,P,P'\text{-}C(NCH_2PPh_2)_2C_{10}H_6\}]$. The reaction of **1a** with two equivalents of $[Ir_2Cl_2(COD)_2]$ provides the binuclear complex $[Ir_2\{\mu\text{-}H_2C(NCH_2PPh_2)_2C_{10}H_6\}Cl_2(COD)_2]$ which is also observed to accumulate and then dissipate during the preceding thermolysis. Related binuclear complexes $[M_2\{\mu\text{-}H_2C(NCH_2PPh_2)_2C_{10}H_6\}Cl_4(\eta\text{-}C_5Me_5)_2]$ (M = Ir, Rh) which obviate C-H activiation were similarly synthesised.

Introduction

Tridentate chelate ligand systems have been an increasingly important theme in the development of organometallic chemistry. Prior to the popularity of meridionally coordinating 'pincer' ligands, studies focused on facially coordinating scorpionate-type ligands, which enforce *pseudo*-octahedral or tetrahedral geometries on their complexes.[1] For late transition metals, however, the meridional coordination of pincer ligands is well-suited to also sustain square planar and trigonal bipyramidal geometries. The high stability and variability offered by pincer systems has led to applications in an extensive range of fields,[2] most notably in catalysis.

N-heterocyclic carbene (NHC) ligands have also provided fertile avenues for the development of effective catalysts.[3] Such ligands are seen as attractive alternatives to tertiary phosphines due to their increased σ-donating abilities[4] and reduced tendency toward dissociation.[5] However, although metal–NHC bonds are inherently strong, they are certainly not inert, and decomposition *via* a variety of pathways has been observed.[6] Enhanced kinetic stability is hence one among many advantages to be derived from the inclusion of NHC donors within pincer scaffolds. The confluence of these two ligand design features has consequently attracted an increasing level of interest, with a particular emphasis on catalytic potential.[7]

Typically NHCs are based on five-membered heterocyclic rings, such as the popular imidazole-based structure **A** (Chart 1).

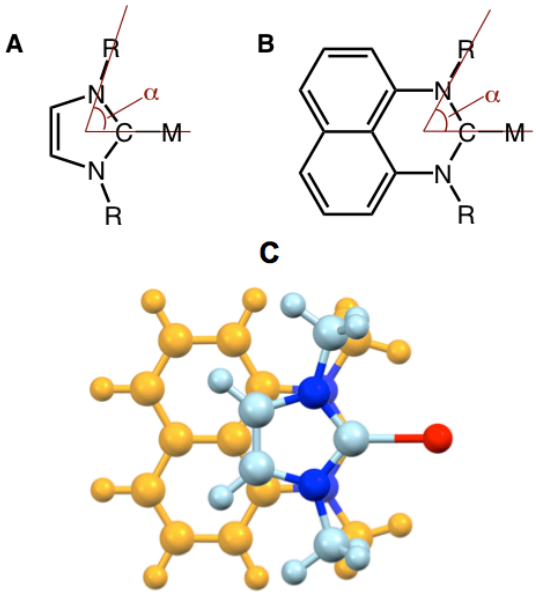

Chart 1. N-heterocyclic carbene ligands with imidazole-based (**A**, α ≈ 72°) and perimidine-based (**B**, α ≈ 60°) structures including (**C**) their superposition.

There is only a small number of examples of NHCs of type **B**, with a perimidine-based scaffold.[8] This framework places the carbene centre in an electron-rich, annulated 14 π-electron aromatic system, as in a perimidine molecule.[9] Furthermore, expanding the NHC ring from five- to six influences the steric impact of the ligand, decreasing the angle α (Chart 1) and directing the amine substituents, R, closer to the coordinated metal.[10] Studies by Richeson and co-workers on a range of free and metallated perimidinylidene-based NHCs (*per*-NHCs)[8b,c] have particularly highlighted these structural features. These reports have included experimental data indicating enhanced σ-basicity for the *per*-NHC ligands relative to their five-membered ring analogues, as did a later report from Hermann

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et al.[8e] Furthermore, studies by the Ozdemir[8d] and Dötz[8f] groups have found palladium *per*-NHC complexes to be effective catalysts, and the latter report noted that a *per*-NHC system which incorporates the *per*-NHCs as the *axial* donors in a pincer framework, was more efficient in Heck coupling reactions than its imidazole and benzimidazole analogues.

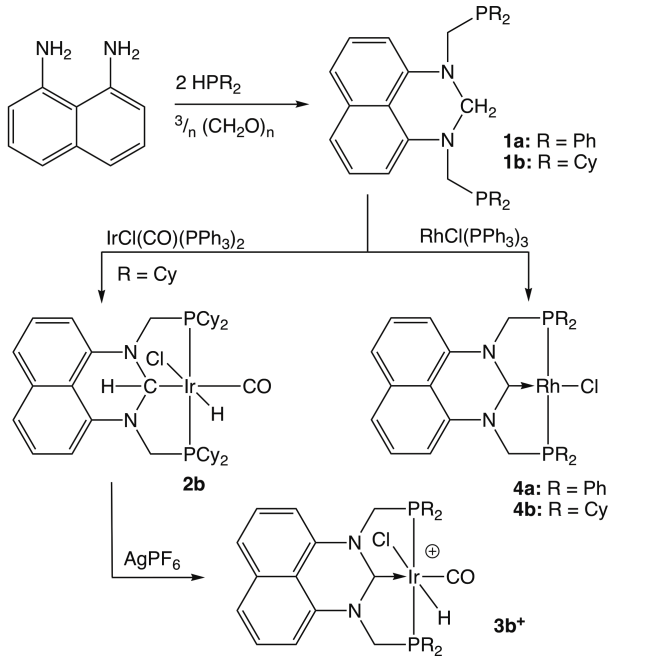
Previously, we described the first examples of *per*-NHC groups incorporated as the central equatorial group of a **PCP-LLL**$^+$ pincer ligand, in the form of rhodium(I), ruthenium(II), osmium(II) and iridium(III) complexes.[8h-j] While the most widely employed methods of preparing NHC complexes involve activation of cationic azolium precursors,[11] which usually requires either an external base, basic co-ligands, or silver transfer reagents, these complexes were prepared *via* a less conventional method involving remarkably facile double *geminal* C-H bond activation of the aminal methylene group of neutral 2,3-dihydroperimidine precursors $H_2C(NCH_2PR_2)_2C_{10}H_6$-1,8 (Scheme 1; R = Ph **1a**, R = Cy **1b**; hereafter '**a**' and '**b**' in compound numbers refer to Ph or Cy derivatives, respectively). The pro-ligands **1a** and **1b** could be prepared by combining 1,8-diaminonaphthalene, paraformaldehyde and a secondary phosphine HPR_2 in a convenient high-yielding one-pot procedure. Their direct reactions with rhodium,[8h] ruthenium[8i] and osmium[8j] complexes have provided rare examples of atom-efficient instances of NHC ligand installation *via* double geminal C–H activation.[12] Gade has also shown that the double C–H activation protocol may be extended to the intriguingly auxochromic 3,4,9,10-tetraaminoperylene scaffold allowing the synthesis of dinuclear rhodium bis(carbene) complexes.[8m] In contrast, Westerhausen,[8n] Li[8o] and ourselves[8j] have identified situations wherein the aminal remains intact following phosphine coordination.

In the reaction of **1b** with Vaska's complex $[IrCl(CO)(PPh_3)_2]$, spontaneous double C–H activation did not occur. Rather, the isolated complex involved a perimidinyl **PCP-LXL**$^+$ pincer complex $[IrHCl(CO)\{\kappa^3\text{-}C,P,P'\text{-}CH(NCH_2PCy_2)_2C_{10}H_6\}]$ (**2b**) that retained one C–H bond, which could be subsequently activated using silver salts (Ir–H abstraction) to afford the **PCP-LLL** NHC complex $[IrHCl(CO)\{C(NCH_2PCy_2)_2C_{10}H_6\}]^+$ (**3b**$^+$).[8h] This d^6-octahedral complex, being coordinatively saturated, is somewhat unreactive in contrast to the d^8-square planar rhodium complexes $[RhCl\{C(NCH_2PR_2)_2C_{10}H_6\}]$ (R = Ph **4a**, Cy **4b**),[8h] the iridium analogues of which have not yet been described.

To better understand the facility and mechanism of chelate-assisted C–H activation processes for the pro-ligands **1**, we now report the extension of such reactions to alternative iridium precursors, leading *inter alia* to the first iridium(I) examples and a further example of perimidinyl **PCP-LXL** coordination.

Results and Discussion

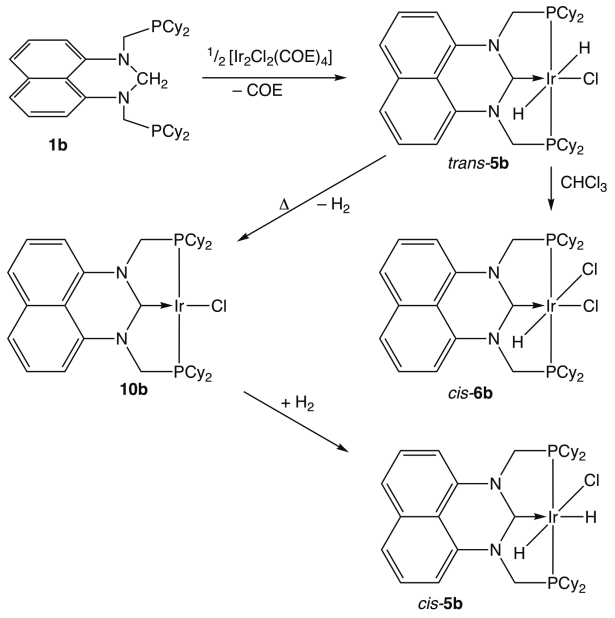
In attempts to synthesise iridium(I) analogues of **4**, the dimeric complex $[Ir_2(\mu\text{-}Cl)_2(COE)_4]$ (COE = *cyclo*-octene) was



Scheme 1. Previous Synthesis of Rhodium(I) and Iridium(III) Perimidinylidene Pincer Complexes.

employed. Both **1a** and **1b** reacted completely with $[Ir_2(\mu\text{-}Cl)_2(COE)_4]$ within three hours at room temperature. Though the reaction with **1a** resulted in a mixture of products that could not be separated, the reaction with **1b** proceeded cleanly to give a product that appears to be the octahedral dihydrido iridium(III) complex $[IrH_2Cl\{C(NCH_2PCy_2)_2C_{10}H_6\}]$ (**5b**, Scheme 2), rather than a square planar iridium(I) complex analogous to **4b**. However, this is perhaps not unexpected given the propensity of the more electron-rich iridium centre to support a higher oxidation state. The rhodium analogues $[RhH_2Cl\{C(NCH_2PR_2)_2C_{10}H_6\}]$ (R = Ph, Cy) are presumed intermediates in the formation of **4a** and **4b** *via* subsequent reductive elimination of dihydrogen, which could be observed spectroscopically and which, under mild conditions, was not found to be reversible.

The hydride ligands are evident in both the infrared and NMR spectra of **5b**. Infrared ν_{IrH} absorptions for complexes with a *trans*-IrH_2 geometry tend to give bands at low frequency (1700-1800 cm^{-1}),[13] while for *trans*-IrHCl geometries these characteristically appear at higher frequencies of 2000-2300 cm^{-1}.[14] The infrared spectrum shows a single ν_{IrH} band at 1724 cm^{-1} (DCM) in an otherwise barren region of the spectrum, reflecting *trans* coordination of two hydride ligands (the ν_{as} mode), as depicted in Scheme 2. The ^1H NMR spectrum supports this stereochemistry, displaying one triplet resonance at $\delta_H = -6.97$ (*cis*-$^2J_{PH}$ = 16 Hz) that integrates for two protons. The $^{31}P\{^1H\}$ resonance appears as a singlet at $\delta_P = 27.3$, and in the proton-coupled ^{31}P NMR spectrum,[15] this resonance becomes a well resolved triplet with $^2J_{PH}$ = 15 Hz. NHC formation is confirmed by the presence of a ^{13}C resonance at $\delta_C = 193.3$, close to that of the related iridium(III) pincer complex $[IrHCl(CO)\{C(NCH_2PCy_2)_2C_{10}H_6\}]^+$ (**3b**$^+$)[8h] and within the range observed for other reported non-chelated iridium(III) *per*-NHC complexes.[8g,k]



Scheme 2. Reaction of $H_2C(NCH_2PCy_2)_2C_{10}H_6$ (**1b**) with $[Ir_2(\mu\text{-}Cl)_2(COE)_2]_2$ to give a dihydrido *per*-NHC pincer complex **5b**.

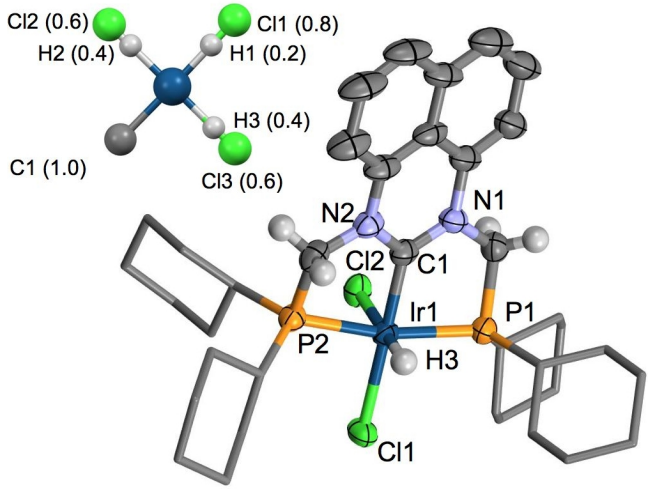


Figure 1. Molecular structure of **6b** in a crystal of **6b**.$(C_6H_6)_2$ (cyclohexyl and naphthyl hydrogen atoms omitted, 50% displacement ellipsoids, one of 3 positionally disordered arrangements). Selected bond lengths (Å) and angles (deg.): Ir1–C1 = 1.962(6), Ir1–P1 = 2.3087(15), Ir1–P2 = 2.3048(15), Ir1–Cl1 = 2.4113(18), Ir1–Cl2 = 2.318(2), Ir1–Cl3 = 2.313(2), C1–N1 = 1.366(7), C1–N2 = 1.373(7), C1–Ir1–P1 = 84.25(17), C1–Ir1–P2 = 83.85(17), P1–Ir1–P2 = 168.08(5). The inset displays the refined occupancies for hydride and chloride ligands.

Under mild conditions, no reductive elimination of dihydrogen from **5b** was observed, consistent with the *trans*-IrH_2 geometry that follows from spectroscopic data. However, a solution of *trans*-**5b** at elevated temperature (50 °C) with prolonged heating (42h) produced the desired iridium(I) complex $[IrCl\{C(NCH_2PCy_2)_2C_{10}H_6\}]$ (**10b**), which was observed spectroscopically (δ_P = 35.0), with the carbene resonance being located at δ_C = 188 *via* $^1H^{13}C$ HMBC experiments. Although the complex could not be isolated cleanly in sufficient quantities for complete characterisation, the ^1H NMR spectrum of the product of it subsequent reaction with H_2 (1 atmosphere, room temperature, $t_{0.5}$ ≈ 8 minutes) indicated the formation of the alternative *cis* isomer of **5b**.

Although numerous attempts at crystallisation of *trans*-**5b** were made using a range of solvent mixtures, none of these resulted in crystals of suitable quality for X-ray analysis. Crystallographic grade crystals could be obtained by slow evaporation of a C_6D_6 solution of **5b** but proved to be the related complex $[IrHCl_2\{C(NCH_2PCy_2)_2C_{10}H_6\}]$ (**6b**, Figure 1), in which one hydride has been replaced by a chloride ligand. This less soluble dichloro complex was deemed to be a very minor side product as supported by the NMR spectra of **5b**.

The molecular structure of **6b** (Figure 1) in a crystal exhibited positional disorder between the hydride and two chloride ligands, consistent with these not protruding far enough from the sterically cumbersome double cone provided by the phosphine arms to impact upon crystal packing. This disorder was modelled as distinct hydrogen and chlorine atoms in each of the three coordination sites, with partial occupancies 0.8 (Cl1), 0.2 (H1), 0.6 (Cl2-3) and 0.4 (H2-3). The Ir1–Cl1 distance is considerably greater than for the two mutually *trans* Ir–Cl distances, reflecting the stronger *trans* influence of the carbene. The Ir1–C1 bond length of 1.962(6) Å is significantly shorter than in **3b**$^+$ (2.078(4) Å), but is comparable to those observed in several other previously reported Ir(III) *per*-NHC complexes.[8g,i] The 20.5° tilt of the aromatic ring system relative to the equatorial (zonal) coordination plane is more pronounced than in $[IrHCl(CO)\{C(NCH_2PCy_2)_2C_{10}H_6\}]^+$, while the P–Ir–P angle is slightly expanded, both of which may be a consequence of the contracted Ir1–C1 distance and the sterically unimposing hydride ligand.

Complex **6b** could be cleanly synthesised in high yield (82 %) from the reaction of **5b** with chloroform. The hydride resonance of **6b** was located as a triplet at δ_H –18.98 in the ^1H NMR spectrum, and the appearance of the NCH_2P methylene group as two diastereotopically distinct resonances indicating a *cis*-$IrCl_2$ geometry. The NHC remained intact in the formation of **6b** and was manifest as a resonance at 187.2 ppm which was identified via $^1H^{13}C$ HMBC experiments. The initial formation of **5b** occurred quickly and without the detection of any identifiable intermediates. Accordingly, the less reactive iridium substrate $[Ir_2(\mu\text{-}Cl)_2(COD)_2]$ (COD = *cyclo*-octa-1,5-diene) was explored in combination with **1b**. An equimolar mixture of $[Ir_2(\mu\text{-}Cl)_2(COD)_2]$ and **1b** in d^6-benzene solution results in the gradual consumption of **1b** attended by the slow formation and disappearance of four species apparent in the $^{31}P\{^1H\}$ and ^{31}P-^1H HMBC NMR spectra (see SI). One of these corresponds to **5b**, however as heating is required to progress the reaction significantly, this disappears under these conditions and resonances corresponding to **6b** and $[IrCl\{C(NCH_2PCy_2)_2C_{10}H_6\}]$ (**10b**) appear, neither of which could be cleanly isolated from the reaction mixture. However, crystals obtained from the crude mixture yielded the trichloro analogue $[IrCl_3\{C(NCH_2PCy_2)_2C_{10}H_6\}]$ (**7b**, Figure 2). The Ir1–C1 bond length of 1.986(5) is structurally consistent with that observed for **6b**, and the Ir–Cl bond disposed *trans* to the carbene is notably elongated relative to the *cis* analogues (Ir1–Cl1 2.417(1) *cf.* Ir1–Cl2 2.328(2) and Ir1–Cl3 2.335(2)). Attempts to intentionally prepare **7b** from the displacement of the hydride

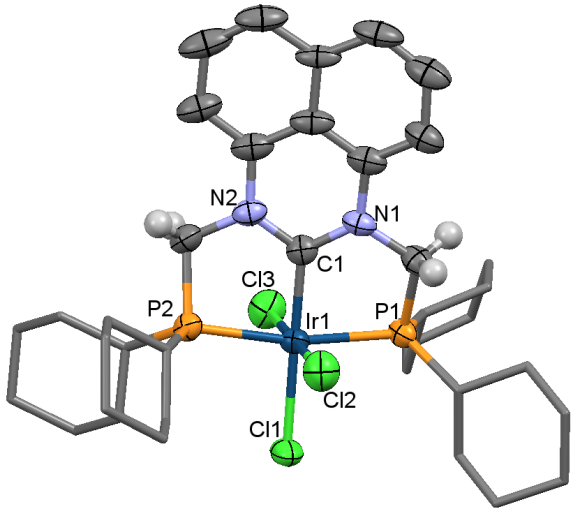


Figure 2. Molecular structure of **7b** in a crystal of **7b**.$(C_6H_6)_2$ (cyclohexyl and naphthyl hydrogen atoms omitted, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (deg.): Ir1–C1 = 1.986(5), Ir1–P1 = 2.307(12), Ir1–P2 = 2.307(12), Ir1–Cl1 = 2.417(12), Ir1–Cl2 = 2.328(17), Ir1–Cl3 = 2.335(16), C1–N1 = 1.356(6), C1–N2 = 1.358(6), C1–Ir1–P1 = 84.27(15), C1–Ir1–P2 = 84.04(15), P1–Ir1–P2 = 168.29(4).

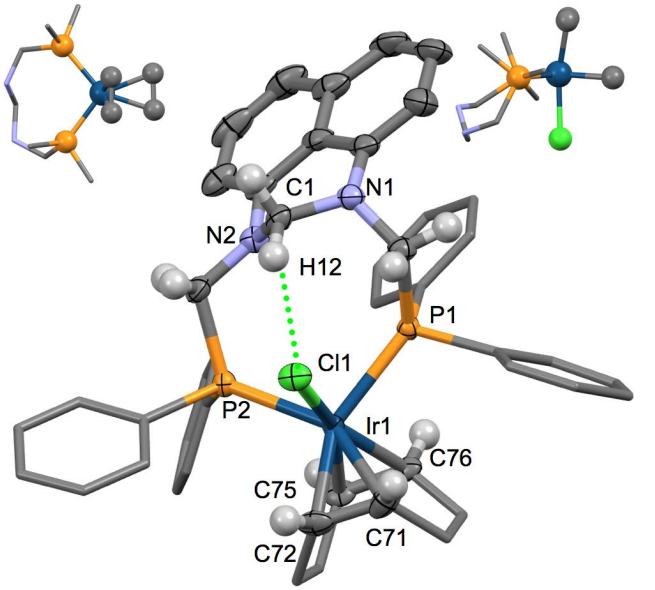
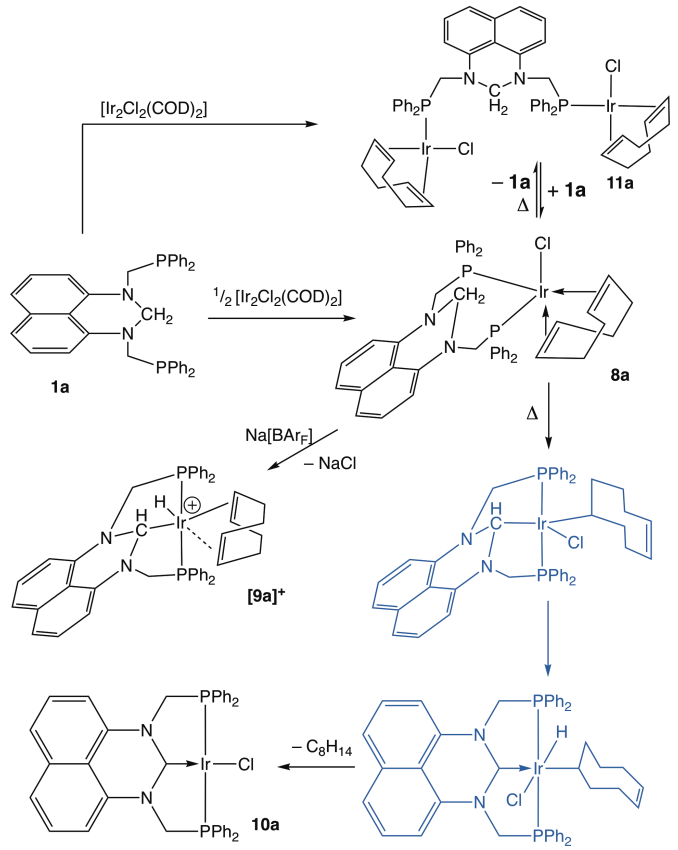


Figure 3. Molecular structure of **8a** in a crystal (aryl and COD methylene hydrogen atoms omitted, phenyl and COD rings simplified, 70% displacement ellipsoids). Selected bond lengths (Å) and angles (deg.): Cl1–Ir1 2.4105(7), Ir1–P1 2.3817(7), Ir1–P2 2.4228(7), Ir1–C71 2.137(3), Ir1–C72 2.132(3), Ir1–C75 2.165(3), Ir1–C76 2.187(3), H12···Cl1 2.53, P1–Ir1–P2 103.19(2), Cl1–Ir1–P1 89.18(3), Cl1–Ir1–P2 86.37(3). Inset: Axial and equatorial views of the inner coordination sphere demonstrating trigonal bipyramidal geometry.

in **5b** via various chlorinating agents resulted in an inseparable mixture (*N*-chlorosuccinimide) or no reaction ($CHCl_3$, CCl_4, HCl).

Circumstantial evidence is beginning to accumulate suggesting that the less electron releasing PPh_2 pincer arms render metal centres less prone to C–H activation of **1a** *cf.* **1b**. Thus, *e.g.*, the reaction of $[RuCl_2(PPh_3)_3]$ with **1b** affords the NHC complexes $[RuCl_2(L)\{\kappa^2\text{-}C,P,P'\text{-}C(NCH_2PCy_2)_2C_{10}H_6\}]$ (L = THF, PPh_3) while with **1a**, the non C–H activated complex $[RuCl_2(PPh_3)\{\kappa^3\text{-}N,P,P'\text{-}H_2C(NCH_2PPh_2)_2C_{10}H_6\}]$ is obtained.[8i] This phenomenon, *i.e.*, interception of the non-activated aminal is also encountered with $[Ir_2(\mu\text{-}Cl)_2(COD)_2]$ except that the isolated mononuclear complex does *not* involve coordination of the nitrogen of a pincer arm. Rather, the 5-coordinate complex $[IrCl(\eta^4\text{-}COD)\{\kappa^2\text{-}P,P'\text{-}H_2C(NCH_2PPh_2)_2C_{10}H_6\}]$ (**8a**, Scheme 3) could be obtained in high yield. In general, d^8 5-coordinate complexes typically adopt trigonal bipyramidal or square-based pyramidal geometries or intermediate geometries that reflect a soft energy profile for interconversion (Berry *pseudo*-rotation). The appearance of single resonances for the methylene and vinylic protons of the *cyclo*-octadiene ligand indicate that a fluxional process must operate, since neither ground-state geometry would allow these to be chemically equivalent. The ground-state adopted in the solid state (Figure 3) involves a trigonal bipyramidal geometry with the tethered alkenes occupying (chemically inequivalent) axial and equatorial sites, thereby arguing for fluxionality in solution, despite the constraints of two chelated ligands. Further spectroscopic analysis of the complex using 2-dimensional $^1H^{13}C$ HSQC and HMBC NMR spectroscopies (see ESI) shows a notable phenomenon. Direct one bond correlation of the COD methylene protons to the methylene carbon nuclei was apparent in the HSQC spectrum, and *one* resonance still remains correlated to the same carbon resonance in the HMBC spectrum. The geometry of **8a** is depicted in Figure 3, which confirms the 5-coordinate geometry and the large 8-membered chelate ring of the bidentate diphosphine, the donors of which occupy equatorial sites (P1–Ir1–P2 = 103.19(2)°). The *tetrahapto*- η^2-η^2 COD ligand occupies one equatorial (Ir1–C71 = 2.137(3), Ir1–C72 = 2.132(3) Å) and one axial (Ir1–C75 = 2.165(3), Ir1–C76 = 2.187(3) Å) site, the former displaying significantly shorter Ir–C bond lengths than the latter, consistent with the general phenomenon that retrodonation from the metal is more effective for equatorial sites.[16] The conformation of the ligand allows one phenyl group bound to P1 to align parallel to the naphthalene ring in a π-stacking interaction. Given that there are numerous examples of complexes of the form $[M(COD)(PP)]^+$ (M = Rh, Ir, PP = a bidentate diphosphine), the reluctance of the chloride to ionise might perhaps be traced to a short hydrogen bonding interaction between the chloride and one hydrogen atom of the unique aminal methylene group of the phosphine chelate (Cl1···H12 = 2.53 Å). Complexes of the form $[IrCl(COD)(PR_3)_2]$ are rare,[17] the first example (R = Et) having been described by Jones[17a] in which the (non-chelated) phosphines are also *pseudo*-equatorial.

The abstraction of the chloride ligand in **8a** was explored by treatment with $AgSbF_6$, however a grey precipitate formed (in the dark) rather than white AgCl, indicating redox processes, whilst the $^{31}P\{^1H\}$ NMR spectrum indicated the formation of a plethora of products. Clean ionisation could be induced by treatment with $Na[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]$ ($Na[BAr_F]$), however this reaction is accompanied by spontaneous C–H activation to



Scheme 3. Reaction of $H_2C(NCH_2PPh_2)_2C_{10}H_6$ (**1a**) with $[Ir_2(\mu\text{-}Cl)_2(COD)_2]$ and Subsequent C–H Activation Processes (Complexes in blue are proposed intermediates).

afford the σ-perimidinyl salt [IrH(η⁴-COD){κ³-*C,P,P'*-$CH(NCH_2PPh_2)_2C_{10}H_6$}] [**9a**][$BAr^F_4$] (Scheme 3).

While we have been unsuccessful in obtaining crystals of [**9a**][BAr_F] suitable for crystallographic analysis, the formulation follows unambiguously from spectroscopic data. Most conspicuous amongst these was the appearance of a high-field triplet resonance in the ^{1}H NMR spectrum (δ_H = – 12.62, $^2J_{PH}$ = 18 Hz) due to the newly installed hydride ligand. Furthermore, the two resonances due to the diastereotopic PCH_2 protons displayed the typical virtual triplet multiplicity characteristic of a *trans*-$M(PCH_2)_2$ connectivity in contrast to the simple broad singlet observed for the methylene protons of the precursor. The resonance for the iridium-bound perimindinyl carbon appeared as a triplet at δ_C = 79.7 with a very small coupling to the two equivalent phosphorus nuclei ($^{2/3}J_{PC}$ = 3 Hz) and the assignment was further confirmed by HSQC correlation with the methine resonance appearing at δ_H = 5.34.

Slow activation of the CH_2 group of **8a** could also be thermally induced to afford the iridium(I) NHC complex [IrCl{κ³-*C,P,P'*-$C(NCH_2PPh_2)_2C_{10}H_6$}] (**10a**). Thus heating **8a** for 16 hours at 90°C resulted in clean formation of **10a** ^{1}H NMR Thus, in contrast to previous double C–H activation processes involving **1a** and olefin-free metal substrates such as $[RhCl(PPh_3)_3]$, $[IrCl(CO)(PPh_3)_2]$, $[Ru(Ph)Cl(CO)(PPh_3)_2]$, $[OsHCl(CO)(PPh_3)_3]$ and $[MCl_2(PPh_3)_3]$ (M = Ru, Os), the co-ligand (COD) could be shown to play a direct role in the mechanism, serving as a hydrogen acceptor. We therefore contend that the conversion proceeds *via* (i) dissociation of one alkene of the COD ligand to afford the requisite vacant site for C–H activation to afford [IrHCl(η²-C_8H_{12}){κ³-*C,P,P'*-$CH(NCH_2PPh_2)_2C_{10}H_6$}], (ii) insertion of the *cyclo*-octadiene into the newly formed Ir–H bond to provide [IrCl(σ-C_8H_{13}){κ³-*C,P,P'*-$CH(NCH_2PPh_2)_2C_{10}H_6$}], followed by (iii) further C–H activation (α-IrH elimination) to install the NHC–Ir–H linkage followed by (iv) reductive elimination of *cyclo*-octene. The presence of the NHC-Ir linkage was evident from the appearance of a resonance at δ_C = 189.9 and whilst this was not immediately obvious in the 1-D $^{13}C\{^1H\}$ NMR spectrum, it could be revealed by ^1H-^{13}C HMBC NMR spectroscopy through correlation with the $^1H(CH_2)$ resonance. As with **9a**⁺, the *trans* disposition of the phosphine donors was confirmed by the appearance of virtual triplet resonances for the PCH_2 groups in both the $^{13}C\{^1H\}$ and ^1H NMR spectra, however in this case only a single resonance was observed in the ^1H NMR spectrum due to the local C_{2v} symmetry of the 4-coordinate iridium.

The molecular geometry of **10a** was confirmed by a crystallographic study of a toluene solvate, the results of which are summarised in Figure 4. These are essentially similar to those observed for the corresponding rhodium analogue **4a**.[8h]

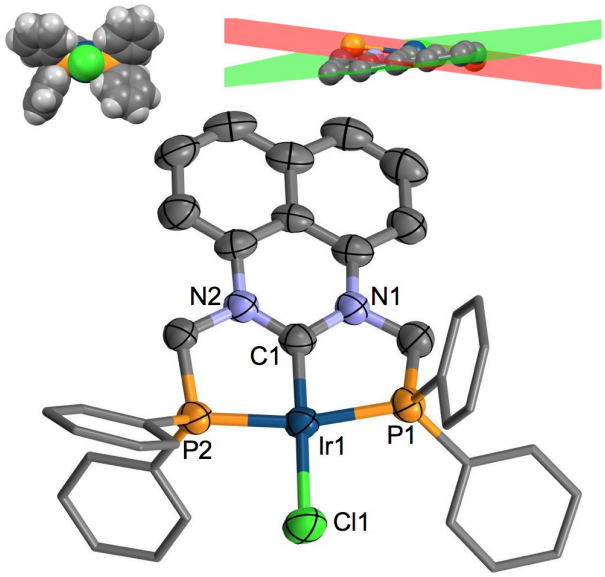
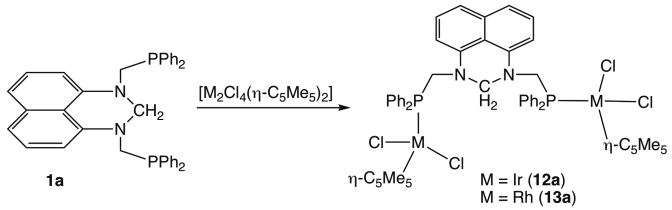


Figure 4. Molecular structure of **10a** in a crystal of **10a**.$C_6H_5CH_3$ (aryl and methylene hydrogen atoms omitted, phenyl rings simplified, 70% displacement ellipsoids). Selected bond lengths (Å) and angles (deg.): Cl1–Ir1 2.3977(16), Ir1–P1 2.2377(16), Ir1–P2–2.2376(16), Ir1–C1 1.943(6), Cl1–Ir1–P1 96.87(6), Cl1–Ir1–P2 94.94(6), P1–Ir1–P2 167.76(6), Cl1–Ir1–C1 178.50(18), P1–Ir1–C1 84.27(18), P2–Ir1–C1 83.98(18). The insets depict a space-filling representation and the canting of the coordination (red) and perimidinyl (green) planes by 14.5°.

Interestingly, monitoring the conversion of **8a** to **10a** using $^{31}P\{^1H\}$ NMR spectroscopy revealed the development and then disappearance of a second compound, which was however not an intermediate, but rather represents a reversible tangential reaction. The complex was identified as the binuclear species $[Ir_2\{\mu\text{-}H_2C(NCH_2PPh_2)_2C_{10}H_6\}Cl_2(COD)_2]$ (**11a**, Scheme 3) which could be prepared independently through treatment of **1a** with one equivalent of $[Ir_2(\mu\text{-}Cl)_2(COD)_2]$. The ligand **1a** is poorly soluble in toluene and accordingly not directly observed in the NMR assay of the reaction, however by the end of the **8a**→**10a** conversion, spectroscopically quantitative formation of **10a** was observed, indicating that whilst **11a** forms under these conditions, it does so reversibly, being thereby able to re-enter

the C–H activation sequence. While **11a** was not structurally characterised, the related binuclear complexes with substitution inert coordination spheres [Ir_2{μ-$H_2C(NCH_2PPh_2)_2C_{10}H_6$}$Cl_4$(η-$C_5Me_5)_2$] **(12a)** and [$Rh_2${μ-$H_2C(NCH_2PPh_2)_2C_{10}H_6$}$Cl_4$(η-$C_5Me_5)_2$] **(13a**) were prepared using similar methodology as described previously for [Ru_2{μ-$H_2C(NCH_2PPh_2)_2C_{10}H_6$}$Cl_4$(η-$C_6H_3Me_3)_2$] and [$Au_2${μ-$H_2C(NCH_2PPh_2)_2C_{10}H_6$}$Cl_2$],[8j] employing one equivalent of [M_2(μ-Cl)$_2Cl_2$(η-$C_5Me_5)_2$] (M = Rh, Ir). The intact NCH_2N group of **12a** and **13a** was observed as a singlet resonance at δ_H 3.55 and 3.56 respectively, and further confirmed by crystallographic determination of the molecular structures (Scheme 4, Figure 5).



Scheme 4. Synthesis of Bimetallic Derivatives of **1a** (M = Rh, Ir).

Given the propensity of per-NHC iridium complexes to support an octahedral geometry and +III(d^6) oxidation number (**3b**$^+$, **5b**, **6b**, **7b**), the reactivity of **10a** towards oxidative addition of H_2 was investigated. Bubbling H_2 into a solution of **10a** in toluene for 10 minutes returned complex **10a** unchanged, likely owing to the less electron rich iridium(I) centre compared to the PCy_2 analogue. However, the trihyrido complex **14a** was synthesised through reaction with an excess amount of $NaBH_4$ in reasonable yield (77 %) and provides the first example of a trihydrido **PCP** pincer complex. The two resonances in the hydride region (δ_H = –9.95 dt and –10.65 tt) are indicative of the formation of the trihydride in **14a**, which is further supported by a broad Ir–H band at 1963 cm^{-1} in the IR spectrum, which is much higher than that observed for **5b** (1772 cm^{-1}). Iridium pincer trihydride complexes are scarce in the literature; one of the few examples being [IrH_3{κ^3-*N,P,P'*-($CH_2P^iPr_2)_2C_4H_3N$}] reported by Nozaki and co-workers.[19] Successive replacement of the hydride ligands with chloride was observed from a sample of **14a** in $CDCl_3$ over 3 days. Within two hours both the single and double chloride substituted products, [IrH_2Cl{$C(NCH_2PPh_2)_2C_{10}H_6$}] and [$IrHCl_2${$C(NCH_2PPh_2)_2C_{10}H_6$}], were present in the ^1H and $^{31}P\{^1H\}$ NMR spectra, with full conversion to the latter being achieved after 3 days.

Experimental

General Considerations. All manipulations of air sensitive compounds were carried out under a dry and oxygen-free nitrogen atmosphere using standard Schlenk and vacuum line techniques, with dry and degassed solvents. NMR spectra were recorded at 25°C on Varian Mercury 300 (^1H at 300.1 MHz ^{31}P at 121.5 MHz), Inova 300 (^1H at 299.9 MHz, ^{13}C at 75.42 MHz, ^{31}P at 121.4 MHz), MR 400 (^1H at 399.9 MHz, ^{31}P at 161.9 MHz) or Bruker Avance 600 (^{13}C at 150.9 MHz) spectrometers. The chemical shifts (δ) for ^1H and ^{13}C spectra are given in ppm relative to solvent signals and ^{31}P relative to an external H_3PO_4 reference. Virtual triplet resonances are indicated by t^v with apparent couplings provided. Low and high resolution mass spectra were obtained on a ZAB-SEQ4F spectrometer by +ve ion

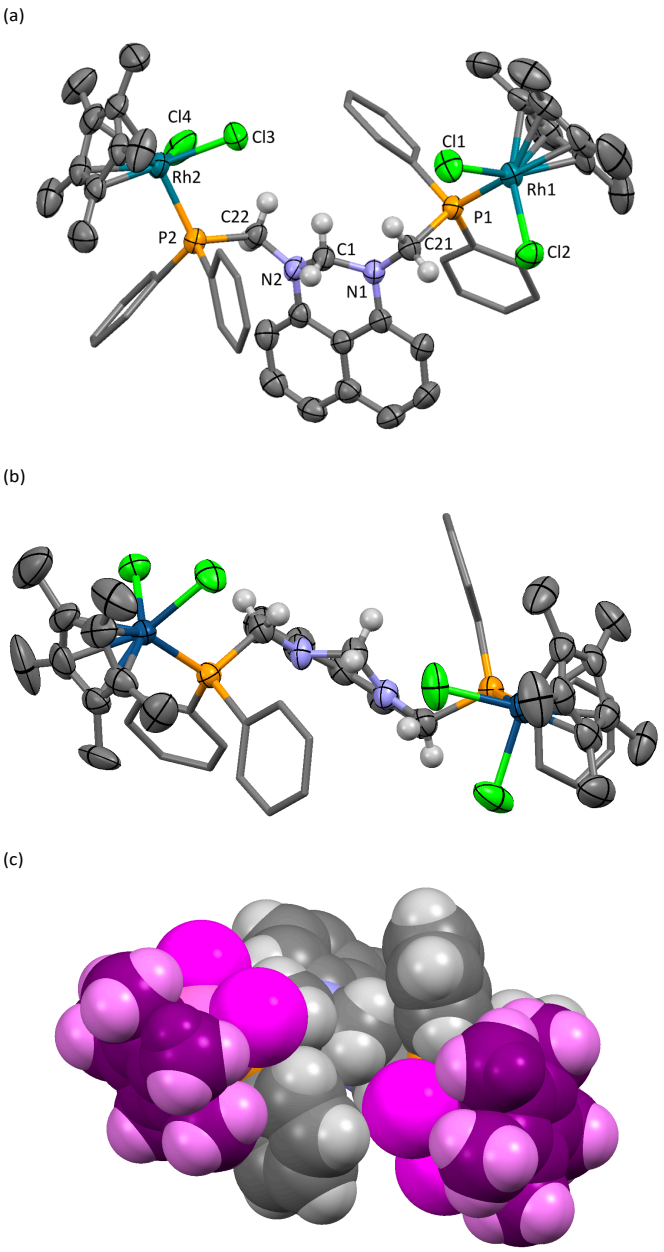


Figure 5. (a) Molecular structure of **12a** in a crystal of **12a**.$CHCl_3$ (solvent and aryl hydrogen atoms omitted, phenyl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (deg.): Ir1−P1 = 2.295(2), Ir1−P2 = 2.310(2), Ir1–Cl1 = 2.399(2), Ir1–Cl2 = 2.407(2), C1–N1 = 1.459(11), C1–N2 = 1.407(11), Cl1–Ir1–P1 = 87.95(8), Cl2–Ir1–P1 = 90.53(9), Cl1–Ir1–Cl2 = 87.16(10). (b) Alternate view of **13a** in a crystal of **13a**.$CHCl_3$. (c) Space filling representation of **13a** in a crystal of **13a**.$CHCl_3$ (solvent omitted) with $IrCl_2$(η-C_5Me_5) caps shown in purple.

ESI techniques using an acetonitrile matrix by the mass spectrometry service of the Australian National University. Assignments were made relative to M, where M is the molecular cation. Assignments were verified by simulation of isotopic composition both for low and high-resolution levels. Elemental microanalysis was performed by the microanalytical services of the Australian National University or the London

Metropolitan University. Data for X-ray crystallography were collected with a Nonius Kappa CCD or Oxford Diffraction SuperNova diffractometer. The compounds $H_2C(NCH_2PR_2)_2C_{10}H_6$ (R = Ph **1a**, R = Cy **1b**),[8h] $[Ir_2(\mu\text{-}Cl)_2(COD)_2]$[19] and $[Ir_2(\mu\text{-}Cl)_2(COE)_4]$[20] were prepared according to published procedures. Other reagents were used as received from commercial suppliers.

Synthesis of *trans*-[$IrH_2Cl\{C(NCH_2PCy_2)_2C_{10}H_6\}$] (*trans*-5b) – The complex $[Ir_2(\mu\text{-}Cl)_2(COE)_4]$[20] (0.100 g, 0.112 mmol) and **1b** (0.133 g, 0.225 mmol) were dissolved in THF (15 mL) with stirring. After 3 hrs, the volatiles were removed under reduced pressure, and the residue washed with diethyl ether (2 x 5 mL), recrystallized from a mixture of THF and hexane and dried *in vacuo*. Yield: 0.139 g (76%). IR (KBr, cm^{-1}): 3056 ν_{aromCH}; 2922, 2848 ν_{CH}; 1708 ν_{IrH}; 1582 ν_{aromCC}. IR (DCM, cm^{-1}): 1724 ν_{IrH}. IR (ATR, cm^{-1}): 2917, 2848 ν_{CH}; 1772 ν_{IrH}; 1582 ν_{aromCC}. NMR (C_6D_6, 298 K) ^{1}H: δ_H = –6.97 (t, 2 H, IrH, $^2J_{PH}$ = 16 Hz), 1.17-2.48 (set of multiplets, 44 H, C_6H_{11}), 3.69 (br s, 4 H, PCH_2N), 6.30 (d, 2 H, $C_{10}H_6$, $^3J_{HH}$ = 8 Hz), 7.10-7.24 (m, 4 H, $C_{10}H_6$). $^{13}C\{^1H\}$: δ_C = 26.5 (C_6H_{11}), 27.1 (t^v, C_6H_{11}, J_{PC} = 6), 27.7, 28.8 (C_6H_{11}) 34.6 (t^v, C_6H_{11}, J_{PC} = 15), 53.5 (t^v, PCH_2, $^{1,3}J_{PC}$ = 14), 106.2 ($C_{10}H_6$), 117.7 ($^4C(C_{10}H_6)$), 120.4, 127.2 ($C_{10}H_6$), 134.7 (t^v, $C^{1,8}(C_{10}H_6)$, $^{3,5}J_{PC}$ = 5 Hz, (not all naphthalene resonances identified due to C_6D_6 overlap, possible overlap of latter peak with other ^{4}C peak), 193.3 (Ir=C, coupling not resolved). $^{31}P\{^1H\}$: δ_P = 27.3. ESI-MS (+ve Ion, MeCN): *m/z* =858.3 $[M – H + MeCN]^+$, 817.3 $[M – H]^+$, 783.4 $[M – Cl]^+$. Accurate Mass: Found 817.3148 $[M – H]^+$, Calcd. for $C_{37}H_{55}{}^{35}Cl^{14}N_2{}^{31}P_2{}^{193}Ir$ 817.3153. Anal. Found: C, 54.26; H, 6.89; N, 3.51%. Calcd. for: $C_{37}H_{56}ClIrN_2P_2$, 54.30; H, 6.90; N, 3.42%.

Slow evaporation of a C_6D_6 solution of the crude product in the presence of chloroform vapour yielded X-ray quality crystals of the compound $[IrHCl_2\{C(NCH_2PCy_2)_2C_{10}H_6\}]$ (**6b**), as a bis(benzene) solvate, which was detected as a minor impurity in the bulk sample by NMR spectroscopy. *Crystal data for* $C_{37}H_{55}Cl_2IrN_2P_2.2(C_6H_6)$: M_r = 1009.16, triclinic, *P*–1 (No. 2), *a* = 12.3421(4), *b* = 13.5109(4), *c* = 14.2016(3) Å, α = 98.4660(19), β = 94.790(2), γ = 100.2717(13)°, *V* = 2290.11(11) Å^3, *Z* = 2, D_x = 1.3463 Mg m^{-3}, μ(Mo Kα) = 3.14 mm^{-1}, *T* = 200(2) K, pale yellow prism, 0.25 x 0.10 x 0.06 mm, 10547 independent reflections. F^2 refinement, *R* = 0.054, *wR* = 0.103 for 8115 reflections ($I > 2\sigma(I)$, $2\theta_{max}$ = 55°), 523 parameters, CCDC 990089.

Synthesis of *cis*-[$IrHCl_2\{C(NCH_2PCy_2)_2C_{10}H_6\}$] (*cis*-6b) - A solution of $[Ir_2(\mu\text{-}Cl)_2(COE)_4]$[20] (0.101 g, 0.113 mmol) and **1b** (0.132 g, 0.223 mmol) in toluene (10 mL) was stirred at room temperature for 4 h. The volatiles were removed under reduced pressure, and chloroform (1 mL) was added, instantly producing a dark brown solution that was stirred overnight. The solvent was removed and the brown precipitate was washed with n-pentane and dried *in vacuo*. Yield: 0.156 g (82 %). IR (ATR, cm^{-1}): 2920, 2849 ν_{CH}; 1636 ν_{IrH}; 1585 ν_{aromCC}. NMR ($CDCl_3$, 298 K) ^{1}H: δ_H = –18.98 (t, 1 H, IrH, $^2J_{PH}$ = 12 Hz), 1.33-2.98 (set of multiplets, 44 H, C_6H_{11}), 4.04 (2 H, PCH_2N, $^2J_{HH}$ = 13 Hz), 4.38 (2 H, PCH_2N, $^2J_{HH}$ = 13 Hz), 6.82 (d, 2 H, $C_{10}H_6$, $^3J_{HH}$ = 8), 7.35 – 7.44 (m, 4 H, $C_{10}H_6$). $^{13}C\{^1H\}$: δ_C = 26.2 (C_6H_{11}), 26.8 (dt^v, C_6H_{11}, J_{PC} = 6, *J* = 17), 27.2 (dt^v, C_6H_{11}, J_{PC} = 6, *J* = 16), 27.7, 27.9, 28.0, 29.6 (C_6H_{11}), 32.6 (t^v, C_6H_{11}, J_{PC} = 14), 35.1 (t^v, C_6H_{11}, J_{PC} = 15), 53.0 (t^v, PCH_2, $^{1,3}J_{PC}$ = 16), 106.7 ($C_{10}H_6$), 118.7 ($^4C(C_{10}H_6)$), 121.5, 128.3 ($C_{10}H_6$), 134.1 (t^v, $C^{1,8}(C_{10}H_6)$, $^{3,5}J_{PC}$ = 4 Hz), 134.4 ($C^4(C_{10}H_6)$), 187.2 (Ir=C, coupling not resolved). $^{31}P\{^1H\}$: δ_P = 16.1. ESI-MS (+ve Ion, MeCN): *m/z* = 817.3 $[M – Cl]^+$, 858.3 $[M – Cl + MeCN]^+$. Accurate Mass: Found 860.3394 $[M – Cl + MeCN]^+$, Calcd. for $C_{39}H_{58}N_3P_2{}^{37}Cl^{193}Ir$ 860.3394. Anal. Found: C, 52.11; H, 6.40; N, 3.36%. Calcd. for: $C_{37}H_{55}Cl_2IrN_2P_2$, 52.10; H, 6.50; N, 3.28%.

Crystal data for [$IrCl_3\{C(NCH_2PCy_2)_2C_{10}H_6\}$] (7b). $C_{37}H_{54}Cl_3IrN_2P_2.2(C_6H_6)$: M_w = 1043.60, triclinic, *P*-1, a = 12.3051 (3) Å, b = 13.4628 (4) Å, c = 14.1870 (3) Å, α = 98.375 (2) °, β = 94.854 (2) °, γ = 100.425 (2) °, *V* = 2271.87 (5) Å^3, Z = 2, ρ_{calcd} = 1.525 Mg m^{-3}, μ(Cu *K*α) = 8.25 mm^{-1}, *T* = 150 K, clear intense yellow block, 0.17 x 0.16 x 0.10 mm, 8912 independent reflections. F^2 refinement, *R* = 0.041, *wR* = 0.116 for 8116 reflections ($I > 2.0\sigma(I)$, $2\theta_{max}$ = 148º), 514 parameters, 48 restraints, CCDC 1579232.

Synthesis of [$IrCl\{CH_2(NCH_2PPh_2)_2C_{10}H_6\}(COD)$] (8a) – A solution of $[Ir_2(\mu\text{-}Cl)_2(COD)_2]$[19] (0.050 g, 0.074 mmol) and **1a** (0.084 g, 0.149 mmol) in toluene (10 mL) was stirred at room temperature for 0.5 h. The light brown precipitate was separated from the supernatant *via* cannula filtration. The solvent was removed *in vacuo* to afford the product **8a** as a yellow solid which was recrystallized from a mixture of benzene and hexane. Yield 0.106 g (79 %). Crystals suitable for crystallographic analysis were obtained from vapour diffusion of *n*-pentane into a solution of **8a** in benzene at room temperature over 2 d. IR (ATR, cm^{-1}): 3045 ν_{aromCH}, 1586 $\nu_{C=C}$. NMR (CD_2Cl_2, 25 °C) ^{1}H (400 MHz): δ_H = 7.52 [m, 8 H, C_6H_5 and NCH_2N (not definitively assigned in the aromatic region)], 7.21 (m, 14 H, C_6H_5 and $C_{10}H_6$), 7.07 (m, 4 H, C_6H_5 and $C_{10}H_6$), 6.66 [d, 2 H, $^3J_{HH}$ = 7.6 Hz, $H^{2,7}(C_{10}H_6)$], 4.56 (m, 4 H, CH_2P), 3.12 (m, 4 H, CH of C_8H_{12}), 1.50 (m, 4 H, CH_2 of C_8H_{12}), 1.28 (m, 4 H, CH_2 of C_8H_{12}). $^{13}C\{^1H\}$ (100 MHz): δ_C = 32.5 (CH_2 of C_8H_{12}), 50.2 (m, CH_2P), 65.2 (t, $^2J_{PC}$ = 7, CH of C_8H_{12}), 108.4 ($C_{10}H_6$), 118.9 ($C_{10}H_6$), 119.2 [$^4C(C_{10}H_6)$], 126.1 ($C_{10}H_6$), 127.8, 129.4, 133.7, 135.7 [$^4C(C_{10}H_6)$], 144.3 [$^4C(C_{10}H_6)$]. Not all carbon resonances could be unambiguously identified. $^{31}P\{^1H\}$ (162 MHz): δ_P = –6.3. ESI-MS(+): *m/z* = 867.3 $[M – Cl]^+$. Accurate mass found: 867.2608 $[M – Cl]^+$. Calcd. for $C_{45}H_{44}N_2P_2{}^{193}Ir$: 867.2609. Anal. Found: C, 59.70; H, 5.04; N, 3.10 %. Calcd. for $C_{45}H_{44}ClN_2P_2Ir$: C, 59.89; H, 4.91; N, 3.10 %. *Crystal data for* $C_{45}H_{44}IrClN_2P_2$: M_w = 902.48, monoclinic, $P2_1/n$, *a* = 13.4385(2), *b* = 14.7888(2), *c* = 18.0161(2) Å, β = 90.1360(11)°, *V* = 3580.5(8) Å^3, *Z* = 4, D_x = 1.674 Mg m^{-3}, μ(Mo *K*α) = 3.93 mm^{-1}, *T* = 150(2) K, orange prism, 0.25 x 0.11 x 0.06 mm, 8,929 independent reflections. F^2 refinement, *R* = 0.023, *wR* = 0.045 for 7,571 reflections ($I > 2.0\sigma(I)$, $2\theta_{max}$ = 60°), 460 parameters, CCDC 1039762.

Synthesis of [$IrH\{CH(NCH_2PPh_2)_2C_{10}H_6\}(\eta^4\text{-}C_8H_{12})$][$BAr_F$] ([9a][$BAr_F$]) – The complex **8a** (0.200 g, 0.222 mmol) and Na[BAr_F] (0.198 g, 0.223 mmol) were stirred in dichloromethane (8 mL) for 5 h. The red solution was passed through a pad of diatomaceous earth and the solvent removed under reduced pressure. The product [**9a**][BAr_F] was washed with *n*-hexane and dried *in vacuo*. Yield 0.211 g (56 %). Attempts to obtain crystals suitable for diffractometry invariably resulted in the formation of oils. IR (ATR, cm^{-1}): 2963 $\nu_{aliphaticCH}$, 1353, 1273 ν_{CF}. NMR (CD_2Cl_2, 25 °C) ^{1}H (400 MHz): δ_H = 7.83 – 7.54 [set of multiplets, 32 H, C_6H_5 and $C_6H_3(CF_3)_2$], 7.39 (m, 4 H, $C_{10}H_6$), 6.89 (d, 2 H, $^3J_{HH}$ = 8, $C_{10}H_6$), 5.34 (s, 1 H, NCHN), 4.98 (m, 2 H, =CH of

C_8H_{12}), 4.79 (d t^v, 2 H, $^2J_{HH}$ = 13, $^{2,4}J_{HH}$ = 6, PCH_2N), 4.02 (d, 2 H, $^2J_{HH}$ = 13, PCH_2N), 3.96 (m, 2 H, =CH of C_8H_{12}), 2.20 (m, 4 H, CH_2 of C_8H_{12}), 1.59 (m, 2 H, CH_2 of C_8H_{12}), 1.18 (m, 2 H, CH_2 of C_8H_{12}), –12.62 (t, 1 H, $^2J_{PH}$ = 18 Hz, IrH). $^{13}C\{^1H\}$ **(**100 MHz): δ_C = 28.0 (CH_2 of C_8H_{12}), 32.2 (CH_2 of C_8H_{12}), 63.4 (t, $^1J_{PC}$ = 26 Hz, CH_2P), 79.7 (t, J_{PC} = 3 Hz, NCHN, correlates with δ_H = 5.34), 86.9 (CH of C_8H_{12}), 93.4 (CH of C_8H_{12}), 111.5 ($C_{10}H_6$), 117.9 [d.t^v, d not resolved, J_{PC} = 4, $C^4(C_{10}H_6)$], 121.2 ($C_{10}H_6$), 125.1 [q, $^1J_{CF}$ = 271, CF_3], 127.3 ($C_{10}H_6$), 129.3 [qq overlayed with septet, $^2J_{CF}$ = 31, $^4J_{CF}$ = 3, $C^{1,3}(BC_6H_3)$], 130.2 [septet, $C^2(BC_6H_3)$], 131.9 [t, $^{2,3}J_{PC}$ = 5, $C^{2,3,5,6}(C_6H_5)$], 132.8 [t, $^1J_{PC}$ = 70, $C^1(C_6H_5)$], 133.5 [$C^4(C_6H_5)$], 134.2 [t, $^{2,3}J_{PC}$ = 5, $C^{2,3,5,6}(C_6H_5)$], 135.3 [br s, $C^4(BC_6H_3)$], 135.8 [$C^4(C_{10}H_6)$], 142.2 [t^v, $^3J_{PC}$ = 8, $C^4(C_{10}H_6)$], 162.2 [q 1:1:1:1, $^1J_{CB}$ = 50 Hz, CB]. $^{31}P\{^1H\}$ (162 MHz) δ_P = 8.2. ESI-MS(+ve Ion, MeCN): *m/z* = 867.3 $[M]^+$. Accurate mass: Found 867.2612 $[M]^+$, Calcd. for $C_{45}H_{44}N_2P_2{}^{193}Ir$ 867.2609. ESI-MS(−ve Ion, MeCN): *m/z* = 863.0 $[M]^-$. Anal. Found: C, 53.33; H, 3.00; N, 1.75 %. Calcd. for $C_{77}H_{56}BF_{24}IrN_2P_2$: C, 53.45; H, 3.26; N, 1.62 %.

Synthesis of [IrCl{C(NCH$_2$PPh$_2$)$_2$C$_{10}$H$_6$}] (10a) – The complex **8a** (0.105 g, 0.116 mmol) was suspended in toluene (8 mL) and heated to 90 ºC for 16 h. The orange supernatant was separated from the brown precipitate via cannula filtration, and the solvent removed under reduced pressure. Product **10a** was washed with *n*-hexane and dried *in vacuo* overnight. Yield 0.054 g (59 %). Crystals suitable for crystallographic analysis were obtained from slow evaporation of compound **10a** in toluene at 25 ºC over 5 d. IR (ATR, cm^{-1}): 3049 ν_{aromCH}, 1579, 1432 ν_{aromCC}. NMR (C_6D_6, 25 ºC) ^1H (400 MHz): δ_H = 8.11 (m, 8 H, C_6H_5), 7.31 (d, 2 H, $^3J_{HH}$ = 8.4, $C_{10}H_6$), 7.12 – 7.00 (m, 14 H, C_6H_5 and $C_{10}H_6$), 6.19 (d, 2 H, $^3J_{HH}$ = 8.0, $C_{10}H_6$), 4.14 (d.t^v, d not resolved, 4 H, CH_2P). $^{13}C\{^1H\}$ (100 MHz) δ/ppm: 57.9 [t^v, $^1J_{PC}$ = 18, CH_2P], 105.8 ($C_{10}H_6$), 116.9 [$C^4(C_{10}H_6)$], 119.1 ($C_{10}H_6$), 128.6 ($C_{10}H_6$), 128.8 [t^v, $^{2,3}J_{PC}$ = 5, $C^{2,3,5,6}(C_6H_5)$], 130.3 [$C^4(C_6H_5)$], 133.9 [t^v, $^{2,3}J_{PC}$ = 7 Hz, $C^{2,3,5,6}(C_6H_5)$], 134.3 [$C^4(C_6H_4)$], 189.9 (C=Ir from HMBC). $^{31}P\{^1H\}$ (162 MHz) δ_P = 23.7. MS-ESI(+ve Ion, MeCN): *m/z*: 793.1 $[M+H]^+$. Accurate mass: found 793.1280 $[M+H]^+$, Calcd. for $C_{37}H_{31}N_2P_2{}^{35}Cl{}^{193}Ir$: 793.1280. Anal. found: C, 56.32; H, 4.01; N, 3.42 %. Calcd. for $C_{37}H_{30}ClIrN_2P_2$: C, 56.09; H, 3.82; N, 3.54 %. *Crystal data for* $C_{37}H_{30}ClIrN_2P_2.C_7H_8$: M_w = 884.42, monoclinic, $P2_1/c$, a = 13.1881 (3), b = 13.2047 (2), c = 21.6283 (3) Å, β = 97.0755 (17) º, V = 3737.78 (12) Å^3, Z = 4, D_x = 1.572 Mg m^{-3}, μ(Cu $K\alpha$) = 8.64 mm^{-1}, T = 150 (2) K, orange block, 0.10 x 0.06 x 0.04 mm, 7,277 independent reflections. F^2 refinement, R = 0.047, wR = 0.134 for 6,158 reflections ($I > 2.0\sigma(I)$, $2\theta_{max}$ = 144º), 451 parameters, CCDC 1039765.

Synthesis of [Ir$_2${μ-H$_2$C(NCH$_2$PPh$_2$)$_2$C$_{10}$H$_6$}Cl$_2$(η-C$_8$H$_{12}$)$_2$] (11a) – A solution of $[Ir_2(\mu\text{-}Cl)_2(COD)_2]$ (0.077 g, 0.115 mmol) and **1a** (0.065 g, 0.115 mmol) in dichloromethane (5 mL) was stirred at room temperature for 5 h. The solution was concentrated to approximately 1 mL, and diluted with diethyl ether (4 mL). The resulting orange supernatant was separated from the yellow precipitate via cannula filtration. The solvent from the supernatant fraction was removed under reduced pressure to afford product **11a** as a yellow-orange solid. Yield 0.110 g (77 %). Attempts to obtain crystals suitable for diffractometry resulted in precipitation as a microcrystalline powder. IR (ATR, cm^{-1}): 3049 ν_{aromCH}, 2875 $\nu_{aliphaticCH}$, 1586, 1416 ν_{aromCC}. NMR (C_6D_6, 25 ºC) ^1H (400 MHz): δ_H = 7.81 (m, 8 H, C_6H_5), 7.08 – 6.98 (m, 16 H, C_6H_5, $C_{10}H_6$), 6.76 [d, 2 H, $^3J_{HH}$ = 7.2 Hz, $H^{2,7}(C_{10}H_6)$], 5.53 (m, 4 H, =CH of C_8H_{12}), 5.18 (s, 4 H, CH_2P), 4.71 (s, 2 H, NCH_2N), 2.75 (d, m, 4 H, =CH of C_8H_{12}), 2.18 (m, 4 H, C_8H_{12}), 2.07 (m, 4 H, C_8H_{12}), 1.64 (m, 4 H, C_8H_{12}), 1.34 (m, 4 H, C_8H_{12}). $^{13}C\{^1H\}$ (100 MHz): δ_C = 29.9 (CH_2 of C_8H_{12}), 33.6 (CH_2 of C_8H_{12}), 50.0 (d, $^1J_{PC}$ = 28, CH_2P), 54.2 (=CH of C_8H_{12}), 67.8 (NCH_2N), 93.9 (d, $^2J_{PC}$ = 14, =CH of C_8H_{12} *trans* to PPh_2), 105.8 ($C_{10}H_6$), 115.8 [$C^4(C_{10}H_6)$], 117.9 ($C_{10}H_6$), 126.8 ($C_{10}H_6$), 128.4 [d, $^{2,3}J_{PC}$ = 9 Hz, $C^{2,3,5,6}(C_6H_5)$], 129.8 [d, $^1J_{PC}$ = 45, $C^1(C_6H_5)$], 130.8 [d, $^4J_{PC}$ = 2, $C^4(C_6H_5)$], 135.5 [d, $^{2,3}J_{PC}$ = 11 Hz, $C^{2,3,5,6}(C_6H_5)$], 135.8 [$C^4(C_{10}H_6)$], 142.5 [$C^4(C_{10}H_6)$]. $^{31}P\{^1H\}$ (162 MHz): δ_P = 9.6. MS-ESI(+ve Ion, MeCN): *m/z*: 1239.3 $[M + H]^+$. Accurate mass: Found 1239.2637 $[M+H]^+$, Calcd. for $C_{53}H_{57}N_2P_2{}^{35}Cl_2{}^{193}Ir_2$: 1239.2637. Anal. Found: C, 51.17; H, 4.69; N, 2.22 %. Calcd. for $C_{53}H_{56}Cl_2Ir_2N_2P_2$: C, 51.41; H, 4.56; N, 2.26 %.

Synthesis of [Ir$_2${μ-H$_2$C(NCH$_2$PPh$_2$)$_2$C$_{10}$H$_6$}Cl$_4$(η-C$_5$Me$_5$)$_2$] (12a) – A solution of $[Ir_2(\mu\text{-}Cl)_2Cl_2(\eta\text{-}C_5Me_5)_2]$ (0.100 g, 0.131 mmol) and **1a** (0.074 g, 0.126 mmol) in dichloromethane (10 mL) was stirred at room temperature for 3 h. The solvent was removed under reduced pressure and the yellow residue was redissolved in chloroform. An equal amount of ethanol was added and the solution concentrated to half volume under reduced pressure. The resulting yellow solid was collected on a sintered frit and washed with ethanol (x2), *n*-pentane (x2) and dried *in vacuo* overnight. Yield 0.127 g (74%). Crystals suitable for crystallographic analysis were obtained from vapour diffusion of n-pentane into a solution of **12a** in $CHCl_3$ over several days. IR (ATR) ν/cm^{-1}: 3052 ν_{aromCH}, 2974, 2907 $\nu_{alphaticCH}$, 1586 ν_{aromCC}. NMR ($CDCl_3$, 25 ºC) ^1H (400 MHz) δ_H = 7.80 (m, 8 H, C_6H_5), 7.35 (m, 12 H, C_6H_5), 6.62 (m, 4 H, $C_{10}H_6$), 5.81 [d, 2 H, $^3J_{HH}$ = 6.8, $H^{2,7}(C_{10}H_6)$], 4.56 (br s, 4 H, CH_2P), 3.55 (s, 2 H, NCH_2N), 1.36 (d, 30 H, $^4J_{PH}$ = 2.0 Hz, CH_3). $^{13}C\{^1H\}$ (100 MHz) δ_C = 8.3 (CH_3), 49.7 (d, $^1J_{PC}$ = 31, CH_2P), 67.0 (NCH_2N), 92.1 (d, $^2J_{PC}$ = 2, ^{4}ClrP), 102.6 ($C_{10}H_6$), 113.0 [$^4C(C_{10}H_6)$], 115.7 ($C_{10}H_6$), 126.0 ($C_{10}H_6$), 127.5 [d, $^1J_{PC}$ = 51, $C^1(C_6H_5)$], 128.2 [d, $^{2,3}J_{PC}$ = 10, $C^{2,3,5,6}(C_6H_5)$], 131.7 [d, $^4J_{PC}$ = 2, $C^4(C_6H_5)$], 134.4 [$C^4(C_{10}H_6)$], 134.7 [d, $^{2,3}J_{PC}$ = 11, $C^{2,3,5,6}(C_6H_5)$], 140.6 [d, $^3J_{PC}$ = 2 Hz, $C^4(C_{10}H_6)$]. $^{31}P\{^1H\}$ (162 MHz) δ_P = −5.7. MS-ESI(+ve Ion, MeCN): *m/z*: 1363.2 $[M – Cl]^+$. Accurate mass: found 1363.2477 $[M+H]^+$, Calcd. for $C_{57}H_{63}N_2P_2{}^{35}Cl_4{}^{193}Ir_2$ 1363.2479. Anal. found: C, 46.85; H, 4.32; N, 1.82%. Calcd. for $C_{57}H_{62}Ir_2Cl_4N_2P_2.(CHCl_3)$: C, 47.02; H, 4.22; N, 1.89%. *Crystal data for* $C_{57}H_{62}Ir_2Cl_4N_2P_2.CHCl_3$: M_w = 1482.71, monoclinic, $P2_1/a$, a = 15.2252(2), b = 23.9867(4), c = 15.3547(2) Å, ⍰ = 91.9066(9)º, V = 5604.47(14) Å^3, Z = 4, D_x = 1.757 Mg m^{-3}, μ(Mo $K\alpha$) = 5.18 mm^{-1}, T = 200(2) K, orange lath, 0.19 x 0.11 x 0.07 mm, 9,877 independent reflections. F^2 refinement, R = 0.045, wR = 0.127 for 7,367 reflections ($I > 2.0\sigma(I)$, $2\theta_{max}$ = 60º), 640 parameters, CCDC 1039772.

Synthesis of [Rh$_2${μ-H$_2$C(NCH$_2$PPh$_2$)$_2$C$_{10}$H$_6$}Cl$_4$(η-C$_5$Me$_5$)$_2$] (13a) – A solution of $[Rh_2(\mu\text{-}Cl)_2Cl_2(\eta\text{-}C_5Me_5)_2]$ (0.204 g, 0.330 mmol) and **1a** (0.186 g, 0.328 mmol) in dichloromethane (15 mL) was stirred for 4 h. The solvent was removed *in vacuo* to afford an orange solid that was washed with *n*-pentane and dried under high vacuum overnight. Yield 0.356g (92%). Crystals of a chloroform solvate suitable for crystallographic analysis were obtained from vapour diffusion of *n*-pentane into a solution of **13a** in $CHCl_3$ over 2 days. IR (ATR) ν/cm^{-1}: 3055 ν_{aromCH}, 2963, 2907 $\nu_{aliphaticCH}$, 1587 ν_{aromCC}. NMR ($CDCl_3$, 25 ºC)

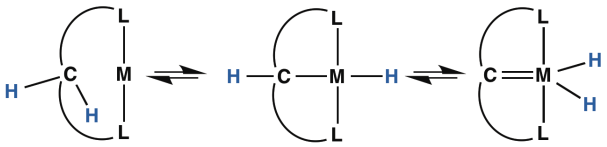
^{1}H (400 MHz) δ_H = 7.86 (m, 8 H, C_6H_5), 7.36 (m, 12 H, C_6H_5), 6.61 (m, 4 H, $C_{10}H_6$), 5.86 [d, 2 H, $^3J_{HH}$ = 6.8, $H^{2,7}(C_{10}H_6)$], 4.58 (br. s, 4 H, CH_2P), 3.56 (s, 2 H, NCH_2N), 1.37 (d, 30 H, $^4J_{PH}$ = 3.2 Hz, CH_3). ^{13}C{^{1}H} (100 MHz) δ_C = 8.7 (d, $^3J_{PC}$ = 1, CH_3), 51.0 (d, $^1J_{PC}$ = 23, CH_2P), 67.0 (NCH_2N), 98.7 (dd, $^1J_{RhC,}$ $^2J_{PC}$ = 3, 7, Rh–C), 102.7 ($C_{10}H_6$), 112.7 [$C^4(C_{10}H_6)$], 115.7 ($C_{10}H_6$), 126.0 ($C_{10}H_6$), 127.5 [d, $^1J_{PC}$ = 40, $C^1(C_6H_5)$], 128.3 [d, $^{2,3}J_{PC}$ = 9, $C^{2,3,5,6}(C_6H_5)$], 131.7 [d, $^4J_{PC}$ = 2, $C^4(C_6H_5)$], 134.3 [$C^4(C_{10}H_6)$], 134.8 [d, $^{2,3}J_{PC}$ = 13, $C^{2,3,5,6}(C_6H_5)$], 140.4 [d, $^3J_{PC}$ = 2 Hz, $C^4(C_{10}H_6)$]. ^{31}P{^{1}H} (162 MHz) δ_P = 27.6 (d, $^1J_{RhP}$ = 141 Hz). MS-ESI(+ve Ion, MeCN): *m/z*: 1149.2 [M – Cl]$^+$. Accurate mass: found 1187.1271 [M+H]$^+$, Calcd. for $C_{57}H_{63}N_2P_2{}^{35}Cl_2{}^{37}Cl_2{}^{103}Rh_2$ 1187.1272; found 1153.1475 [M – Cl]$^+$, Calcd. for $C_{57}H_{62}N_2P_2{}^{37}Cl_3{}^{103}Rh_2$ 1153.1475. Anal. found: C, 54.33; H, 5.32; N, 2.55%. Calcd. for $C_{57}H_{62}Cl_4N_2P_2Rh_2$: C, 57.79; H, 5.27; N, 2.36%. Calcd. for $C_{57}H_{62}Cl_4N_2P_2Rh_2.CHCl_3$: C, 53.42; H, 4.87; N, 2.15%. Crystal data for $C_{57}H_{62}Cl_4N_2P_2Rh_2.CHCl_3$: M_w = 1304.08, monoclinic, $P2_1/a$, a = 15.2362(2), b = 23.9600(3), c = 15.3332(1) Å, β = 91.8919(6)°, V = 5594.48(11) Å^3, Z = 4, D_x = 1.548 Mg m^{-3}, μ(Mo $K\alpha$) = 1.02 mm^{-1}, T = 200(2) K, red block, 0.25 x 0.22 x 0.12 mm, 12,798 independent reflections. F^2 refinement, R = 0.050, wR = 0.144 for 9,781 reflections (I > 2.0σ(I), $2\theta_{max}$ = 55°), 640 parameters, CCDC 1039832.

Synthesis of [IrH$_3${C(NCH$_2$PPh$_2$)$_2$C$_{10}$H$_6$}] (14a) – The complex **10a** (0.078 g, 0.098 mmol) and $NaBH_4$ (0.039 g, 1.03 mmol) were stirred in methanol/toluene (2:7 mL) for 3 d. The solvent was removed under reduced pressure and methanol (10 mL) was added to give a beige precipitate. The precipitate was isolated via cannula filtration, washed with n-pentane and dried *in vacuo*. Yield 0.058 g (77 %). IR (ATR, cm^{-1}): 3046 ν_{CH}, 1963 ν_{IrH}. NMR (C_6D_6, 25 °C) ^{1}H (400 MHz): δ_H = 8.10 (m, 6 H, C_6H_5 and $C_{10}H_6$), 7.22 (m, 3 H, $C_{10}H_6$ and C_6H_5), 7.07 – 6.98 (m, 15 H, $C_{10}H_6$ and C_6H_5), 6.20 (d, 2 H, $^3J_{HH}$ = 7, $C_{10}H_6$), 4.64 (4 H, PCH_2N), –9.95 (dt, 2 H, $^2J_{HH}$ = 7 Hz, $^2J_{PH}$ = 14 Hz, IrH), –10.65 (tt, 1 H, $^2J_{HH}$ = 7 Hz, $^2J_{PH}$ = 14 Hz, IrH). ^{13}C{^{1}H} (100 MHz): δ_C = Due to poor solubility of **14a**, a satisfactory 1-D spectrum could not be obtained. ^{31}P{^{1}H} (162 MHz) δ_P = 20.4. ESI-MS(+ve Ion, MeCN): *m/z* = 759.2 [M – H]$^+$. Accurate mass: Found 759.1672 [M – H]$^+$, Calcd. for $C_{37}H_{32}N_2P_2{}^{193}Ir$ 759.1670; Found 800.1935 [M + MeCN – H]$^+$, Calcd. for $C_{39}H_{35}N_3P_2{}^{193}Ir$ 800.1936. Satisfactory elemental microanalytical data not obtained for multiple samples, attributed to high air-sensitivity and possible, residual but spectroscopically clandestine chloride salts. Anal. Found: C, 53.28; H, 4.37; N, 3.41 %. Calcd. for $C_{37}H_{33}IrN_2P_2$: C, 58.49; H, 4.38; N, 3.69 %.

Conclusions

Further examples of per-NHC pincer ligand installation *via* chelate-assisted double C–H activation have been demonstrated, though these were found to each be mechanistically distinct. In the formation of **5b**, the geometry involving *trans* hydride ligands precludes facile reductive elimination to afford **10b**. In contrast, the thermally induced C–H activation of **8a** generates a putative iridium hydride into which the *cyclo*-octadiene ligand inserts to provide a pathway for dehydrogenation of the complex. Alternatively, halide ionisation of **8a** results in spontaneous C–H activation at room temperature.

Notably, despite Shaw setting the stage for **PCP-LLL** pincer ligands in which the central donor is a carbene with the archetypal complex **PCP-LLL** [IrCl{=C($C_2H_4P^tBu_2$)$_2$}],[21] **PCP-LLL** pincer complexes remain comparatively rare within group 9,[22,23] though there exists a multitude of aryl **PCP-LXL** pincer complexes. The possibility of installing such pincer carbenes *via* double C–H activation is attractive, not only in terms of atom economy, but from the perspective of microreversibility, *i.e.*, that the reverse reaction, hydrogenation of the M=C double bond provides an intriguing possibility for small-molecule activation. This has been elegantly described by Piers[23] who has exploited the *reversible* coordinative activation of bis(2-phosphinoaryl)methanes (Scheme 5). The promise that M=C linkages need be neither unreactive (*cf.* NHC ligands), nor irreversibly reactive, raises the possibility that they serve as truly functional groups, rather than as spectators or alternatively stoichiometrically consumed units, emphasising the importance of further exploring the factors that control chelate-assisted C–H activation.



Scheme 5. Reversible double geminal C–H activation.

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Notes and references

† To unambiguously describe the nature of the pincer donor set, we employ Green's covalent bond classification, *i.e.*, a bis(phosphino)carbene **PCP**-**LLL** pincer provides 6 valence electrons, whilst **PCP**-**LXL** refers to a 5 valence electron bis(phosphino) alkyl or aryl pincer: M. L. H. Green, *J. Organomet. Chem.* 1995, **500**, 127 – 148.

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