Synthesis and reactivity of iridium complexes of a macrocyclic PNP pincer ligand†

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Having recently reported on the synthesis and rhodium complexes of the novel macrocyclic pincer ligand PNP-14, which is derived fromlutidine and features terminal phosphine donors trans-substituted with a tetradecamethylene linker (*Dalton Trans.*, 2020, 49, 2077–2086 and *Dalton Trans.*, 2020, 49, 16649–16652), we herein describe our findings critically examining the chemistry of iridium homologues. The five-coordinate iridium(i) and iridium(III) complexes [Ir(PNP-14)η2:η2-cyclooctadiene][BARF4] and [Ir(PNP-14)(2,2′-biphenyl)][BARF4] are readily prepared and shown to be effective precursors for the generation of iridium(i) dihydride dihydrogen, iridium(i) bis(ethylened), and iridium(i) carbonyl derivatives that highlight important periodic trends by comparison to rhodium counterparts. Reaction of [Ir(PNP-14)H2(H2)][BARF4] with 3,3-dimethylbutene induced triple C–H bond activation of the methylene chain, yielding an iridium(III) allyl hydride derivative [Ir(PNP-14)H][BARF4], whilst catalytic homocoupling of 3,3-dimethylbutylene into Z-iBuC≡CCHiBu could be promoted at RT by [Ir(PNP-14)(η2:η2-cyclooctadiene)][BARF4] (TOFinitial = 28 h−1). The mechanism of the latter is proposed to involve formation and direct reaction of a vinylidene derivative with HC≡CtBu outside of the macrocyclic ring and this suggestion is supported experimentally by isolation and crystallographic characterisation of a catalyst deactivation product.

1. Introduction

Phosphine-based pincers are robust ancillary ligands that continue to find notable applications in organometallic chemistry and homogenous catalysis.1,2 In particular, rhodium and iridium complexes of these ligands are associated with fundamental and applied breakthroughs in the chemistry of C–H bond activation reactions; exemplified by the characterisation of σ-alkane complexes and development of high-performance alkane dehydrogenation catalysts, respectively.3,4 These mer-tridentate ligands are evidently well-suited to supporting the formation of highly reactive M(i) derivatives necessary to bring about cleavage of strong C–H bonds,5 able to accommodate the changes in geometry associated with M(i)/M(III) redox shuffling, and suitably modular in composition to enable augmentation of metal-based reactivity through considered change of the central donor atom, wingtip substituents, or backbone constituents.2 As marked out by lower carbonyl stretching frequencies,6 the heavier iridium congeners are particularly notable for a more pronounced tendency for oxidative addition of H2,7,8 C(sp3)−H bonds,3,9 and C(sp2)−H bonds10 compared to their rhodium counterparts.

Motivated by the potential to exploit additional reaction control though their unique steric profile, use in the construction of interlocked assemblies, and as an extension of our related work with NHC-based variants,11–13 we have recently become interested in the chemistry of macrocyclic phosphine-based pincers.14–16 Last year we reported on the synthesis and rhodium complexes of the lutidine-derived macrocyclic pincer PNP-14, where the chiral P-donors are trans-substituted with a tetradecamethylene linker (Chart 1).14,15 As a novel platform for exploring the organometallic chemistry of Group 9 pincer complexes, we now present our findings critically examining...
the chemistry of iridium PNP-14 homologues aided by reference to acyclic complexes of 2,6-\{R,PCH\}_2C\_2H\_2N (PNP-R; e.g. R = \textit{t}Bu, \textit{i}Pr).

2. Results and discussion

Mirroring synthetic strategies that we have successfully employed for rhodium homologues,\(^{14,15}\) the preparation of iridium(I) and iridium(III) complexes of PNP-14 was attempted through substitution reactions of [Ir(COD)\_2][\textit{BArF}_4] in 1,2-difluorobenzene (DFB) and [Ir(COD)(biph)Cl]\_2,\(^{16}\) in fluorobenzene, respectively, with the latter exploiting Na[\textit{BArF}_4] as a halide abstracting agent (COD = 1,5-cyclooctadiene, \textit{Ar} = 3,5-(CF\_3)\_2C\_6H\_4, biph = 2,2'-biphenyl; Scheme 1). These reactions produced five-coordinate cationic derivatives [Ir(PNP-14)(\textit{η}^2-\textit{η}^1-COD)][\textit{BArF}_4] and [Ir(PNP-14)(biph)][\textit{BArF}_4] under mild conditions, which were subsequently isolated as analytically pure crystalline materials in good yield (ca. 80%) and fully characterised (Scheme 1).

Iridium(I) complex 1 adopts a distorted trigonal bipyramidal metal geometry (18 VE), with the terminal phosphine donors positioned in the equatorial coordination sites conforming to a distinctly puckered pincer ligand geometry. Distortion of the PNP ligand towards a \textit{fac} coordination mode in this manner is associated with a compressed P–Ir–P bite angle of 115.24(2)° in the solid state and a pair of \textit{31}P resonances at \(\delta\) 17.0 and 13.4 with no appreciable \(J_{pp}\) coupling in DFB solution. While unusual, the formulation of 1 simply appears to be a consequence of COD chelation, although this is contingent upon the flexible lutidine-based backbone and asymmetric steric profile of the phosphine donors.\(^{19}\) Moreover, given the rhodium(i) homologue is instead characterised as a \(C_1\)-symmetric square planar complex, viz. [Rh(PNP-14)(\textit{η}^2-COD)]\_2 (1', 16 VE; \(\delta_{\nu_{\text{p}}}: 57.4, 45.9, J_{pp} = 312\) Hz),\(^{15,20}\) the capacity of the heavier metal congener to from stronger metal–ligand bonds is clearly a decisive factor. Bulk purity was established by combustion analysis and the structure of 1 was fully corroborated in solution by NMR spectroscopy and HR ESI-MS.

Coordination of PNP-14 is more conventional in the formally 16 VE square pyramidal iridium(III) complex 2, as evidenced by a P–Ir–P bite angle of 163.24(5)° in the solid state and \(C_1\) symmetry in CD\_2Cl\_2 solution; with a pair of \textit{31}P resonances at \(\delta\) 38.7 and 20.9 exhibiting a characteristically large \textit{trans}-phosphine \(J_{pp}\) coupling constant of 307 Hz.\(^{21}\) The crystal structure of 2 is isomorphous to the direct rhodium homologue 2',\(^{14}\) with the tetradecamethylene linker skewed to one side of the basal plane away from the biph ligand and contorted in such a way as to enable adoption of a weak \(\gamma\)-agostic interaction (2, \(\text{Ir}1\cdots\text{H}–\text{C}_{129} = 3.152(7)\) Å; cf. 3.184(2) Å for 2'). Previously reported five-coordinate complexes of the form [M(pincer)(biph)][\textit{BArF}_4] provide further structural precedent for 2 and the metal-based metrics of the acyclic analogue [Ir(PNP-\textit{Bu})(biph)][\textit{BArF}_4] (II) are similar.\(^{6,11,14}\) Moreover, as II is fluxional in solution as a result

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\begin{align*}
\text{Scheme 1} \quad & \text{Synthesis and solid-state structures of iridium pincer complexes 1 and 2: thermal ellipsoids at 50\% and 30\% probability, respectively; anions omitted. Selected bond lengths (Å) and angles (°): 1, \text{Ir}1–\text{P2}: 2.3743(7); \text{Ir}1–\text{P3}: 2.3846(7); \text{P2}–\text{Ir}1–\text{P3}: 115.24(2); \text{Ir}1–\text{N101}: 2.107(2); \text{Ir}1–\text{C4}: 2.083(2); \text{Ir}1–\text{Cnt}(\text{C4}, \text{C5}): 2.036; \text{Ir}1–\text{Cnt}(\text{C8}, \text{C9}): 2.036(2); \text{N101}–\text{Ir}1–\text{Cnt}(\text{C4}, \text{C5}): 172.52(8); \text{Cnt}(\text{C4}, \text{C5})–\text{Ir}1–\text{Cnt}(\text{C8}, \text{C9}): 84.29(9); 2, \text{Ir}1–\text{P2}: 2.3253(15); \text{Ir}1–\text{P3}: 2.2849(15); \text{P2}–\text{Ir}1–\text{P3}: 163.24(5); \text{Ir}1–\text{N101}: 2.158(5); \text{Ir}1–\text{C4}: 2.048(6); \text{Ir}1–\text{C15}: 2.044(6); \text{N101}–\text{Ir}1–\text{C15}: 172.5(2); \text{C4}–\text{Ir}1–\text{C15}: 81.9(2); \text{Ir}1–\text{C129}: 3.152(7); \text{Ir}1–\text{C129}: 2.54; \text{Cnt} = \text{centroid.}
\end{align*}
\]
of facile biph pseudorotation on the NMR timescale,\textsuperscript{6} retention of C\textsubscript{4} symmetry in solution suggests that butressing with the methylene strap prevents such dynamics in 2.

Reaction of 2 with dihydrogen (1 atm) in DFB at RT resulted in immediate and full conversion into [Ir(PNP-14)][2-biphenyl]H\textsubscript{2}[BAR\textsubscript{F\textsubscript{4}}] \textdegree 3 (\textdelta\textsubscript{\textnu P} 40.6, 36.5, \textgamma\textsubscript{PP} = 302 Hz; \textdelta\textsubscript{\textnu H} = 21.6; Scheme 2). No further reaction was observed after 18 h, but heating at 85 °C for 6 h resulted in complete hydrolysis of the biph ligand and formation of dihydroide dihydrogen complex [Ir(PNP-14)H\textsubscript{2}][BAR\textsubscript{F\textsubscript{4}}] \textdegree 4 in quantitative spectroscopic yield. Hydrolysis also occurs for \textdegree 2 and \textdegree \textdegree II, but longer reaction times are required under otherwise equivalent conditions (both \texttextit{ca.} 2 days).\textsuperscript{14} Coordinately saturated 1 rapidly affords 4 upon reaction with dihydrogen (1 atm) in DFB at RT (<5 min), invoking facile and reversible chelation of COD.

Complex 4 was characterised \textit{in situ} using NMR spectroscopy, with adoption of time-averaged C\textsubscript{4} symmetry, a single \textnu P resonance at \textdelta 42.1, and a broad 4H resonance at \textdelta = 9.26 (\texttau\textsubscript{I} \textsubscript{1} = 88.8 ± 0.7 ms, 600 MHz, argon) the most diagnostic features at 298 K. The hydride signal remained broad upon cooling to 253 K but exhibits faster spin–lattice relaxation (\textdelta = 9.27, \texttau\textsubscript{I} \textsubscript{1} = 50 ± 1 ms, 600 MHz, argon). The acyclic analogue [Ir(PNP-\textnu Bu)H\textsubscript{2}][BAR\textsubscript{F\textsubscript{4}}] (IV) is known and formulation as a dihydroide dihydrogen complex was corroborated in a similar manner \textit{in situ} by NMR spectroscopy.\textsuperscript{7} Whilst the data was recorded under different conditions, the similarly of the hydride signatures is striking (IV, \textdelta\textsubscript{\textnu H} = 9.31, \texttau\textsubscript{I} \textsubscript{1} = 24 ms, 400 MHz, 233 K in CD\textsubscript{3}OD). In line with the reduced propensity for oxidative addition, the rhodium homologue of \textdegree 4 was instead observed as a dihydrogen complex, \textit{viz.} [Rh(PNP-14)(H\textsubscript{2})][BAR\textsubscript{F\textsubscript{4}}] \textdegree 4.\textsuperscript{14}

Further supporting the assignment of 4, reaction with ethylene (1 atm) generated the corresponding C\textsubscript{4}-symmetric dihydroidene \pi-complex 5 (\textdelta\textsubscript{\textnu P} 33.4, 12.4, \textgamma\textsubscript{PP} = 314; \textdelta\textsubscript{\textnu H} = 7.89, −17.80) within 5 min at RT (Scheme 2). Subsequent heating at 85 °C for 16 h yielded the bis(ethylene) complex 6 (\textdelta\textsubscript{\textnu P} 9.0) in quantitative spectroscopic yield, with concomitant formation of ethane. C\textsubscript{4} symmetry and coordination of two molecules of ethylene was established \textit{in situ} by NMR spectroscopy. The latter is associated with four chemically inequivalent 2H signals at \textdelta 3.23, 2.80, 2.49 and 1.97 and two \textnu P resonances at \textdelta 26.0 and 18.0, and reinforces the disposition of iridium(i) centres to adopt five-coordinate geometries: as seen in 2, but contrasting that observed under the same conditions in the rhodium(i) system, \textit{viz.} [Rh(PNP-14)(C\textsubscript{2}H\textsubscript{4})][BAR\textsubscript{F\textsubscript{4}}].\textsuperscript{6,14} Structurally-related bis(ethylene) iridium(i) complexes of CNC- and pybox-based pincer ligands have been crystallographically characterised, exhibiting distorted trigonal bipyramidal metal geometries with the ethylene ligands located in the equatorial sites,\textsuperscript{22} but are unknown for PNP- and PONOP-based ligands.\textsuperscript{23}

When 2 was instead treated with an excess of 3,3-dimethyl-butene (5 equivalents) the allyl hydride derivative [Ir(PNP-14*)H\textsubscript{2}[BAR\textsubscript{F\textsubscript{4}}] 7 was produced in quantitative spectroscopic yield after 5 days heating at 100 °C, presumably through intramolecular transfer dehydrogenation of the methylene chain followed by allylic C–H activation (Scheme 2).\textsuperscript{24} As precedent for this reactivity, examples of cyclometallated rhodium(m) and iridium(m) pincer complexes can be found in the literature.\textsuperscript{25} Complex 7 was subsequentially isolated in 49% yield and fully characterised, including in the solid state by single crystal X-ray diffraction (Fig. 1). In solution 7 is distinctly C\textsubscript{4}-symmetric, with a pair of \textnu P resonances at \textdelta 81.4 and 25.8 with \textgamma\textsubscript{PP} = 313 Hz, allyl \textnu C resonances at \textdelta 81.9, 66.0, and 38.9, and a 1H hydride resonance at \textdelta = −8.49 (\textgamma\textsubscript{PP} \textsubscript{H} = 19.6, 9.7 Hz). The crystal structure demonstrates that 7 adopts a pseudo-octahedral metal geometry in the solid state, with \kappa\textnu\textnu\textnu\textnu\textnu\textnu coordination of PNP-14* creating iridacyclopentyl and iridacyclocloeyl rings, and the hydride ligand was located from the Fourier difference map. Little distortion of the PNP-core is evident in 7 and the associated metal-based metrics are broadly comparable to those in 2 (e.g. P–Ir–P ca. 163°). There is considerable variance in the allyl Ir=C bond lengths, with the longest contact trans to the hydride ligand (Ir1–C119 = 2.311(4) Å, Ir1–C120, 2.155(3) Å, Ir1–C121, 2.199(3) Å), but all the internal carbon bond angles are >120°. The geometry of

![Scheme 2 Synthesis and reactivity of iridium dihydride dihydrogen complex 4.][1]

\[\text{[Ir(COD)] + H}_2 \xrightarrow{< 5 \text{ min}} \text{[Ir(biph)]}\]
\[\text{[Ir(biph)] + H}_2 \xrightarrow{< 5 \text{ min}} \text{[Ir(2-biphenyl)H]}\]
\[\text{[Ir(2-biphenyl)H] + H}_2 \xrightarrow{6 \text{ h} 85 ^\circ \text{C}} \text{[Ir(COD)]}\]
\[\text{[Ir(COD)] + H}_2 \xrightarrow{< 5 \text{ min}} \text{[Ir(2-biphenyl)H]}\]
\[\text{[Ir(2-biphenyl)H] + H}_2 \xrightarrow{16 \text{ h} 85 ^\circ \text{C}} \text{[Ir(COD)]}\]

\[\text{(i) + CO, - C}_2\text{H}_4 \xrightarrow{< 5 \text{ min}} \text{[Ir] - CO}\]

\[\text{Ar, 5 days 100 °C} \rightarrow \text{[Ir] - CO}\]

\[\text{[Ir] = [Ir(PNP-14*)]^+}\]

Reactions performed in DFB at RT using 1 atm of gaseous reagent, unless otherwise stated.

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Dalton Trans.
the iridacyclooctyl ring is reminiscent of the quadrilateral conformations adopted by 12-membered cycloalkanes.26

The onward reactivity of 6 was harnessed to access the C₈-symmetric Ir(I) carbonyl derivative 8 (δₗ₉ 62.5) by reaction with carbon monoxide, which was isolated in 89% yield (overall from 2; Scheme 2). Complexes of this nature are of interest as the carbonyl ligand is a convenient spectroscopic reporter group for the electronic characteristics of the metal-pincer fragment.27,28 In this case, the ν(CO) band of 8 (1984 cm⁻¹) is shifted to considerably lower frequency compared to the rhodium(I) homologue 8' (1997 cm⁻¹) under the same conditions (CH₂Cl₂, solution, Table 1). This is in line with expected periodic trends, which are also apparent from the IR data collected for tBu- and tPr-substituted analogues. These data suggest that PNP-14 is a marginally weaker net donor than PNP-IBu, but equivalent to PNP-tPr.29

Of the organometallic chemistry we have discovered so far using PNP-14, the capacity for rhodium complexes to promote the stoichiometric homocoupling of 3,3-dimethylbutyne through the annulus of the macrocyclic ligand stands out (1' → 9' in Scheme 3).15 Given that a structurally related Ir(PCP) system has also been shown to promote stoichiometric term-

| Pincer | ν(CO)/cm⁻¹ | Ref. |
|--------|------------|------|
| Ir(PNP)(CO) | 8 | 1984 | This work |
| Rh(PNP)(CO) | 8' | 1997 | 14 |
| Ir(PNP-tBu)(CO) | | 1977 | 6 |
| Rh(PNP-tBu)(CO) | | 1990 | 6 |
| Ir(PNP-tPr)(CO) | | 1986 | 29 |
| Rh(PNP-tPr)(CO) | | 1998 | 27 |

* Measured in the solid state (ATR).
mechanistic features of the terminal alkyne coupling reactions promoted by 1 and 1’: \[ [M] = M(PNP-14)^+ \] and \[ [\text{BARF}_2]^– \] counter anions omitted. Solid-state structure of 10 depicted with thermal ellipsoids at 30% probability for selected atoms; minor disordered component (IrP2 core), most H atoms, and anion omitted; structural diagram provided in the experimental section. Selected bond lengths (Å) and angles (°): Ir1–P3, 2.3659(5); P2–Ir1–P3, 163.56(2); Ir1–N101, 2.122(2); Ir1–C4, 2.043(2); Ir1–C4–C5, 129.59(15); C4–C5, 1.330(3); Ir1–C6, 2.053(2); Ir1–C6–C9, 147.4(2); C6–C9, 1.329(3); Ir1–Cnt(C7, C8), 2.505(2); C6–C7–C8, 161.9(2); C7–C8, 1.216(3); N101–Ir1–C6, 159.3(8); C4–Ir1–Cnt(C7, C8), 153.16(7); C4–Ir1–C6, 102.50(9); Cnt = centroid.

determined by X-ray crystallography was fully corroborated in solution using NMR spectroscopy. For instance, the alkenyl 1H resonances are located at \( \delta \) 7.81 (IrCHCHtBu); \( \delta \) 1.21 (tBu) in a 1:1:1 ratio, with the associated \( \delta \) 13C resonances at \( \delta \) 143.5 (IrCHCHtBu), 142.2 (IrCCHtBu), 105.3 (IrCCHtBu), and 95.7 (IrCHCHtBu); the \( \alpha \)-carbons exhibiting coupling to \( \delta \) 31P (\( \delta \) IrPC = 5–10 Hz). The HR-ESI MS of 10 is also notable for a strong \([M]^+ \) ion signal at 916.5623 (calcd 916.5628) \( m/z \) and bulk purity of was confirmed by combustion analysis.

Terminal alkyne homocoupling reactions that produce Z-enzyme products are generally understood to proceed via vinylidene intermediates, with 11 implicated in this case (Scheme 4).\(^{35,36}\) Indeed, the rhodium homologue 11’ is produced initially upon reaction of 1’ with HC==CtBu.\(^{15}\) Reaction with the second alkyne equivalent, by net 1,2-addition of the constituent C(sp)-H bond across the vinylidene M==C linkage (concerted or step-wise) followed by reductive elimination, would thereafter confer the enyne product. E-Enyne isomers such as that observed in the rhodium system can also be produced in this manner, although an indirect route involving equilibrium generation of the rhodium(III) alkynyl hydride 12’ is instead invoked in the formation of 9’ from 11’ (Scheme 4). Whilst 11 was not detected during the formation of Z-tBuC==CCHBrBu, the generation of 10 provides strong circumstantial evidence for its intermediate presence.

between 1 and independently synthesised Z-tBuC==CCHCHBu in DFB was observed, even upon heating at 50 °C for 1 h. The formation of the bis(alkenyl) is, therefore, most reasonably reconciled by irreversible reaction of Z-tBuC==CCHCHBu with 11; involving net 1,2-addition of the \( \{C==C\}(sp^2)-H \) bond across the Ir==C linkage. The addition evidently takes place through the ring in this instance, with the macrocycle preventing subsequent reductive elimination.\(^{12}\)

We therefore attribute the generation of 10 to catalyst deactivation by irreversible product inhibition. The postulated reactivity of the Group 9 vinylidenes derived from 1 and 1’ is clearly nuanced by the nature of the metal and impact of the unique steric constraints imposed by the tetracadmethylene linker. We believe that the more facile Ir([i]Ir[III]) redox couple and propensity of the \([\text{Ir}(\text{PNP-14})]^+ \) fragment to adopt geometries with the pincer ligand in a non-meridional conformation are the decisive factors. Specifically, we propose that the Z-selective homocoupling of HC==CtBu proceeds catalytically outside the ring via C(sp)-H bond oxidative addition of HC==CtBu to 11 affording fac-[Ir(PNP-14)(CCHBrBu)]\( ^+ \), alkynyl migration yielding an enynyl hydride, and finally release of Z-tBuC==CCHCHBu by reductive elimination. In contrast, 1’ mediates the stoichiometric E-selective homocoupling of HC==CtBu through the ring ultimately via a pathway bypassing the vinylidene intermediate 11’. Further computational analysis would be required to corroborate these sug-
gestions, although accurately modelling the effect of the methylene chain is non-trivial.

3. Conclusions

The organometallic chemistry of iridium complexes of the macrocyclic PNP-14 pincer ligand has been explored. The five-coordinate iridium(i) and iridium(iii) complexes [Ir(PNP-14) \((\eta^2-\eta^2\text{-COD})][\text{BARF}_4]\) 1 and [Ir(PNP-14)[biph][BARF\(_4\)] 2 are readily prepared and fully characterised derivatives, with the former notable for a distorted trigonal bipyramidal metal geometry in which the pincer ligand adopts an unusual non-meridional confirmation, and the latter for adoption of a square pyramidal metal geometry. This is notable for a distorted trigonal bipyramidal metal geometry in the homologous rhodium precursor \(\eta^1\text{-tBuC}^\parallel\text{COD})[\text{BARF}_4]\) 7, whilst 1 is an effective pre-catalyst for the homocoupling of 3,3-dimethylbutyne into \(\eta^2\text{-tBuC}^\parallel\text{COD})[\text{BARF}_4]\) 7, whilst 1 is an effective pre-catalyst for the homocoupling of 3,3-dimethylbutyne into \(Z\text{-tBuC}^\parallel\text{CCCHCHBu}\) under mild conditions. The latter is particularly remarkable given that reaction of the homologous rhodium precursor 1 results in the formation of an interpenetrated E-enzyme complex (9). The mechanism of the homocoupling promoted by 1 is proposed to involve formation and direct reaction of the (unobserved) vinylidene derivative [Ir(PNP-14)[CCCHBu][BARF\(_4\)] 11] with \(\text{HC}^\parallel\text{CCBu}\) outside of the macrocyclic ring. This suggestion is supported experimentally by isolation and crystallographic characterisation of [Ir(PNP-14)[\(\eta^2\text{-E-C}(\text{CCBu})\text{CCCHBu})[\eta^2\text{-E-CCHCHBu}]][\text{BARF}_4]\) 10, which results from deactivation of the catalyst by product inhibition.

4. Experimental

4.1 General methods

All manipulations were performed under an atmosphere of argon using Schlenk and glove box techniques unless otherwise stated. Dihydrogen and ethylene were dried by passage through a column of activated 3 Å molecular sieves. Glassware was oven dried at 150 °C overnight and flame-dried under vacuum prior to use. Molecular sieves were activated by heating at 300 °C in vacuo overnight. Fluorobenzene and DFB were pre-dried over \(\text{Al}_2\text{O}_3\), distilled from calcium hydride and dried twice over 3 Å molecular sieves. \(\text{CD}_2\text{Cl}_2\) was freeze–thaw degassed and dried over 3 Å molecular sieves. \(\text{C}_6\text{D}_6\) was distilled from sodium and stored over 3 Å molecular sieves. SiMe\(_4\) was distilled from liquid Na/K alloy and stored over a potassium mirror. Other anhydrous solvents and liquid reagents were purchased from Acros Organics or Sigma-Aldrich, freeze–pump–thaw degassed and stored over 3 Å molecular sieves. PNP-14, \([\text{Ir}(\text{COD})][\text{BARF}_4]\), \([\text{Ir}(\text{biph})(\text{COD})\text{Cl}_2]\), \(\text{Na}[\text{BARF}_4]\) and [Ir(PNP-bu)[biph][BARF\(_4\)] 11 were synthesized according to published procedures. All other solid reagents are commercial products and were used as received. NMR spectra were recorded on Bruker spectrometers under argon at 298 K unless otherwise stated. Chemical shifts are quoted in ppm and coupling constants in Hz. Virtual coupling constants are reported as the separation between the first and third lines. NMR spectra in DFB were recorded using an internal capillary of \(\text{C}_6\text{D}_6\) as an internal standard. High resolution ESI-MS were recorded on Bruker Maxis Plus instrument. Infrared spectra were recorded on a Jasco FT-IR-4700 using a KBr transmission cell in \(\text{CH}_2\text{Cl}_2\). Microanalyses were performed at the London Metropolitan University by Stephen Boyer or Elemental Microanalysis Ltd.

4.2 Preparation of [Ir(PNP-14)[\(\eta^2\text{-E-C}][\text{CCBu})\text{CCCHBu})[\eta^2\text{-E-CCHCHBu}]][\text{BARF}_4]\) (1)

A solution of [Ir(COD)][BARF\(_4\)] (29.3 mg, 23.0 μmol) and PNP-14 (11.0 mg, 23.0 μmol) in DFB (0.5 mL) was mixed for 5 min at RT, the volatiles were removed in vacuo and the resulting orange oil washed with pentane (2 × 2 mL). The analytically pure product was obtained as a yellow crystalline solid by slow diffusion of \(\text{SiMe}_4\) (ca. 10 mL) into a DFB solution (0.5 mL) at −30 °C. Yield: 29.0 mg (17.7 μmol, 77%).

\(^1\text{H NMR}\) (500 MHz, DFB): δ 8.11–8.16 (m, 8H, \(\text{ArF}\)), 7.50 (br, 4H, \(\text{ArF}\)), 7.33 (t, \(\delta = 7.7, 1\text{H, py}\)), 7.08 (d, \(\delta = 7.7, 1\text{H, py}\)), 7.03 (observed, py), 4.25–4.34 (m, 1H, Ir(CH=CH)[axial]), 4.34–4.44 (m, 1H, Ir(CH=CH)[axial]), 3.72 (d, \(\delta = 6.6, 2\text{H, pyCH}_2\)), 3.51 (dd, \(\delta = 18.2, 6\text{H, pyCH}_2\)), 3.34 (dd, \(\delta = 18.2, 6\text{H, pyCH}_2\)), 2.54–2.66 (m, 2H, CH\(_2\)), 2.15–2.45 (m, 6H, CH\(_2\) + 1 × Ir(CH=CH)[equatorial] [6 2.39]), 1.38–2.04 (m, 9H, CH\(_2\) + 1 × Ir(CH=CH)[equatorial] [6 1.83]), 1.38 (d, \(\delta = 12.7, 9\text{H, tBu}\)), 0.94–1.32 (m, 19H, CH\(_2\)), 0.65 (d, \(\delta = 12.5, 9\text{H, tBu}\)).

\(^{13}\text{C}[\text{H}]\) NMR (126 MHz, DFB): δ 163.7 (d, \(\delta = 5, 4\text{H, py}\)), 162.5 (q, \(\delta = 50, 2\text{H, py}\)), 162.4 (observed, py), 138.2 (s, py), 135.1 (s, \(\text{ArF}\)), 129.7 (qd, \(\delta = 32, 2\text{H, py}\)), 124.9 (q, \(\delta = 272, 2\text{H, py}\)), 122.0 (d, \(\delta = 6, 2\text{H, py}\)), 120.7 (d, \(\delta = 8, 2\text{H, py}\)), 117.6 (sept, \(\delta = 4, 2\text{H, py}\)), 64.7 (br, Ir(CH=CH)[axial]), 60.9 (d, \(\delta = 3, 2\text{H, py}\)), 60.2 (d, \(\delta = 27, 2\text{H, py}\)), 50.1 (d, \(\delta = 29, 2\text{H, py}\)), 45.6 (d, \(\delta = 27, 2\text{H, py}\)), 42.3 (d, \(\delta = 22, 2\text{H, py}\)), 35.8 (d, \(\delta = 10, 2\text{H, py}\)), 35.5 (br, \(\text{CH}_2\)), 35.2 (d, \(\delta = 19, 2\text{H, py}\)), 34.1 (d, \(\delta = 7, 2\text{H, py}\)), 33.4 (br, \(\text{BuCH}_2\)), 31.1 (d, \(\delta = 10, 2\text{H, py}\)), 29.8 (d, \(\delta = 9, 2\text{H, py}\)), 29.7 (s, \(\text{CH}_2\)), 29.5 (s, \(\text{CH}_2\)), 29.3 (d, \(\delta = 17, 2\text{H, py}\)), 29.0 (s, \(\text{CH}_2\)), 28.8 (s, \(\text{CH}_2\)), 28.7 (s, \(\text{CH}_2\)), 28.6 (br, \(\text{CH}_2\)), 28.3 (s, \(\text{CH}_2\)), 28.12 (s, \(\text{CH}_2\)), 28.05 (s, \(\text{CH}_2\)), 27.8 (d, \(\delta = 4, 2\text{BuCH}_2\)), 27.1 (d, \(\delta = 7, 2\text{H, py}\)), 27.0 (s, \(\text{CH}_2\)), 26.6 (s, \(\text{CH}_2\)), 26.4 (d, \(\delta = 5, 2\text{BuCH}_2\)).

\(^{31}\text{P}[\text{H}]\) NMR (162 MHz, DFB): δ 17.0 (s, 1P), 13.4 (s, 1P).
HR ESI-MS (positive ion 4 kV): 778.4221 ([M]+, calcld 778.4218) m/z.

Anal. calcd for C_{69}H_{73}BF_{24}IrNP_{2} (1641.32 g mol\(^{-1}\)): C, 50.49; H, 4.73; N, 0.85. Found: C, 50.40; H, 4.64; N, 0.87.

4.3 NMR scale reaction of 1 with dihydrogen

A solution of 1 (12.2 mg, 7.43 \(\mu\)mol) in DFB (0.5 mL) within a J. Young valve NMR tube was freeze–pump–thaw degassed and placed under an atmosphere of dihydrogen (1 atm). Analysis by NMR spectroscopy indicated quantitative formation of 4 with concomitant formation of COD within 5 min at RT.

4.4 Preparation of [Ir(PNP-14)(biph)][BARF\(^4\)] (2)

A suspension of PNP-14 (13.3 mg, 27.8 \(\mu\)mol) and [Ir(biph) (COD)Cl]\(_2\) (13.7 mg, 14.0 \(\mu\)mol) in fluorobenzene (0.50 mL) was stirred for 2 days at 50 °C to give a pale-yellow solution. As a yellow solid was formed, the yellow solution was quenched to room temperature and the volatiles were removed in vacuo. The residue was dissolved in DFB and then the product extracted into CH\(_2\)Cl\(_2\) (2 mL). The analytically pure product was obtained as a purple crystalline solid by recrystallisation from CH\(_2\)Cl\(_2\)–hexane (1:20) at −30 °C.

4.5 NMR scale reactions of 2

The following reactions were carried out starting with a solution of 2 (16.9 mg, 10.0 \(\mu\)mol) in DFB (0.5 mL) within a J. Young valve NMR tube and analysed in situ by NMR spectroscopy.

4.5.1 Synthesis of [Ir(PNP-14)(2-biphenyl)][BARF\(^4\)] (3).

The solution of 2 was freeze–pump–thaw degassed and placed under dihydrogen (1 atm), resulting in quantitative formation of 3 within 5 min at RT. No free biphenyl was observed.

1H NMR (400 MHz, DFB, H\(_2\), selected data): \(\delta\) 7.61 (t, \(J_{\text{HH}} = 7.8\), 1H, py), 3.66–3.82 (m, 2H, 2 × pyCH\(_2\)), 3.06 (dd, \(J_{\text{HH}} = 17.3, J_{\text{PH}} = 6.4, 1H, pyCH\(_2\))

13C\(_1\) NMR (126 MHz, DFB, H\(_2\), selected data): \(\delta\) 162.3 (q, \(J_{PC} = 50\), Ar\(_F\)), 162.4 (t, \(J_{PH} = 8\), 2H, pyCH\(_2\)).

4.5.2 Synthesis of [Ir(PNP-14)H\(_2\)(C\(_2\)H\(_4\))][BARF\(^4\)] (4).

The solution of 3 was heated at 85 °C for 6 h, resulting in quantitative formation of 4 with concomitant formation of biphenyl (\(\delta_{\text{H}}\) 7.42, 7.25, 7.16).

1H NMR (500 MHz, DFB, H\(_2\)); \(\delta\) 8.10–8.16 (m, 8H, Ar\(_F\)), 7.49 (br, 4H, Ar\(_F\)), 7.47 (t, \(J_{\text{HH}} = 7.8\), 1H, py), 7.19 (d, \(J_{\text{HH}} = 7.8, 2H, pyCH\(_2\))

13C\(_1\) NMR (126 MHz, DFB, H\(_2\), selected data): \(\delta\) 162.3 (q, \(J_{PC} = 50\), Ar\(_F\)), 162.4 (t, \(J_{PH} = 6\), py), 138.9 (s, py), 135.1 (s, Ar\(_F\)), 129.7 (qq, \(J_{PC} = 32, J_{CB} = 3\), Ar\(_F\)), 124.9 (q, \(J_{PC} = 272\), Ar\(_F\)), 120.4 (xt, \(J_{PC} = 10\), 117.6 (sept, \(J_{PC} = 4\), Ar\(_F\)), 44.4 (vt, \(J_{PC} = 28\), pyCH\(_2\)), 30.0 (vt, \(J_{PC} = 32, 2\times\text{Bu(C)}\)), 29.0 (s, CH\(_3\)), 28.9 (vt, \(J_{JC} = 8\), CH\(_3\)), 28.3 (s, CH\(_2\)), 28.2 (s, CH\(_2\)), 27.5 (s, CH\(_2\)), 26.3 (s, CH\(_2\)), 25.8 (vt, \(J_{JC} = 32, \text{PCH}3\)), 24.5 (vt, \(J_{JC} = 6\), \text{Bu(CH\(_2\))}).

31P\(_{\text{H}}\) NMR (162 MHz, DFB, H\(_2\)); \(\delta\) 42.1 (s, 2P).

4.5.3 Synthesis of [Ir(PNP-14)H\(_2\)(C\(_2\)H\(_4\))][BARF\(^4\)] (5).

The solution of 4 was freeze–pump–thaw degassed and placed under ethylene (1 atm), resulting in quantitative formation of 5 within 5 min at RT.

4.5.4 Synthesis of [Ir(PNP-14)(CH\(_3\)C\(_2\)H\(_4\))][BARF\(^4\)] (6).

The solution of 5 was heated at 85 °C for 16 h, resulting in quantitative formation of 6, with concomitant formation of ethane (\(\delta_{\text{H}}\) 0.70, \(\delta_{\text{C}}\) 6.1).
placed under dihydrogen (1 atm) and then heated at 80 °C for 16 h. A solution of 7 (7.7 mg, 5.03 µmol) in DFB (0.5 mL) within a J. Young valve NMR tube was treated with 3,3-dimethylbutene (8.8 µL, 71.4 µmol) and the solution heated at 100 °C for 5 days. Analysis by NMR spectroscopy indicated quantitative formation of the product. The volatiles were removed in vacuo and the resulting pink/red oil washed with SiMe3 (2 × 0.5 mL). The analytically pure product was obtained as pale red blocks by the slow diffusion of excess SiMe3 into a DFB solution at −30 °C. Yield: 10.2 mg (6.66 µmol, 94%).

1H NMR (500 MHz, CD2Cl2): δ 7.70–7.75 (m, 8H, ArF), 7.65 (t, 3JPC = 5.0, ArF), 161.9 (br, 4H, ArF), 7.34 (d, 3JHH = 7.8, 1H, py), 7.31 (d, 3JHH = 7.8, 1H, py), 4.86 (app q, 3JHH = 9, 1H, IrCH), 4.47 (app t, 3JHH = 7, 1H, IrCH), 3.71–3.81 (m, 2H, 2 × pyCH2, 3.41 (dd, 3JHH = 17.1, 3JPH = 9.3, 1H, pyCH3, 3.26 (dd, 3JHH = 17.4, 3JPH = 9.2, 1H, pyCH2), 2.35–2.52 (m, 1H, CH2), 1.98–2.11 (m, 1H, CH2), 0.94–1.95 (m, 20H, IrCH [δ 1.89] + CH3), 1.17 (d, 3JPH = 15.4, 9H, tBu), 1.01 (d, 3JPH = 13.5, 9H, tBu), −8.49 (dd, 3JPH = 19.6, 9.7, 1H, IrH).

13C{1H} NMR (126 MHz, CD2Cl2): δ 163.4 (br, py), 162.3 (q, 3JCC = 50, ArF), 161.9 (br, py), 138.5 (s, py), 135.4 (s, ArF), 129.4 (qq, 3JPC = 32, 3JCC = 3, ArF), 125.1 (q, 3JPC = 272, ArF), 121.0 (d, 3JPC = 9, py), 120.8 (d, 3JPC = 9, py), 118.0 (sept, 3JPC = 4, ArF), 81.9 (s, IrCH), 66.0 (d, 3JPC = 5, IrCH), 41.9 (d, 3JPC = 30, pyCH3), 39.2 (d, 3JPC = 29, pyCH2), 38.9 (s, IrCH), 33.9 (s, CH3), 35.0 (dd, 3JPC = 22, 3JPH = 5, tBuCH), 30.4 (dd, 3JPC = 22, 3JPH = 5, tBuCH), 29.6 (s, CH3), 27.8 (d, 3JPC = 14, CH3), 27.4 (s, CH3), 27.0 (d, 3JPC = 3, tBuCH), 25.7 (d, 3JPC = 4, tBuCH), 24.8 (dd, 3JPC = 28, 3JPH = 1, PCH2), 24.4 (s, CH2), 24.3 (d, 3JPH = 5, CH2), 22.9 (s, CH3), 22.3 (s, CH2), 21.6 (s, CH2), 20.8 (dd, 3JPH = 24, 3JPC = 4, PCH2).

13P{1H} NMR (162 MHz, CD2Cl2): δ 181.4 (s, 2P), 25.8 (d, 3JPP = 313, 1P).

13P{1H} NMR (162 MHz, DFB): δ 80.9 (d, 3JPP = 313, 1P), 25.5 (d, 3JPP = 313, 1P).

HR ESI-MS (positive ion 4 kV): 668.3128 ([M]+, calcld 668.3122) m/z.

Analyzed for Ca3H7BF24IrNp2 (1531.12 g mol−1): C, 47.85; H, 4.15; N, 0.91. Found: C, 47.65; H, 4.03; N, 1.01.

4.8 NMR scale reaction of 7 with dihydrogen
A solution of 7 (7.7 mg, 5.03 µmol) in DFB (0.5 mL) within a J. Young valve NMR tube was freeze–pump–thaw degassed and placed under dihydrogen (1 atm) and then heated at 80 °C for 2 days. Analysis by NMR spectroscopy indicated quantitative formation of 4.

4.9 Catalytic homolytic of 3,3-dimethylbutyne promoted by 1
A solution of 1 (8.2 mg, 5.0 µmol) in DFB (400 µL) within a J. Young NMR tube was treated with a solution of 3,3-dimethylbutyne (62 µL, 503 µmol) and the resulting homologuing...
reaction producing only $\text{ZtBuC} = \text{CHCHBu}$ followed at RT in situ using NMR spectroscopy. The solution was mixed constantly when not in the spectrometer. Analysis after 1 hour indicated 28 TONS, with complete conversion observed within 6 h. At this point, 10 was observed as the major organometallic species (88%), with 1 the minor organometallic species (10%). Further 3,3-dimethylbutyne (31 µL, 252 µmol) was added, resulting in further homocoupling, totalling 65 TONS and complete conversion of 1 to 10 after 24 h. Spectroscopic data for $\text{ZtBuC} = \text{CHCHBu}$ is consistent with literature values.32

Data for $\text{ZtBuC} = \text{CHCHBu}$: $\delta$ 5.53 (d, $^1J_{HH} = 11.9$, 1H, CH=CH), 5.25 (d, $^1J_{HH} = 11.9$, 1H, CH=CH), 1.12 (s, 9H, tBu), 1.11 (s, 9H, tBu).

### 4.10 Preparation of [Ir(PNP-14)(η^3-E-C(≡CtBu)CHBu)](η^3-E-CHCHBu)[BAR^2]_4 (10)

A solution of 1 (14.0 mg, 8.53 µmol) in DFB (0.5 mL) within a J Young valve NMR tube was treated with 3,3-dimethylbutyne (210 µL, 1.71 mmol) and stirred for 6 h at RT. Analysis by NMR spectroscopy indicated quantitative formation of the product. The volatiles were removed in vacuo, the resulting yellow oil washed with SiMe₄ (2 × 0.5 mL) and dried in vacuo to afford the analytically product as a yellow solid. Yield: 11.6 mg (6.52 µmol, 76%). Crystals suitable X-ray crystallography were obtained by slow diffusion of excess SiMe₄ into an Et₂O solution. From the SiMe₄ washings $\text{ZtBuC} = \text{CHCHBu}$ was obtained as a colourless oil in low yield. Yield: 4.6 mg (28.0 µmol, 2%).

### 1H NMR (500 MHz, CD₂Cl₂): $\delta$ 7.83 (t, $^1J_{HH} = 6.7$, 1H, py), 7.81 (dd, $^1J_{HH} = 15.0$, 1H, CH=CH), 7.70–7.75 (m, 8H, Ar²), 7.36 (br, 4H, Ar²), 7.30 (d, $^1J_{HH} = 7.9$, 1H, py), 7.49 (d, $^1J_{HH} = 7.9$, 1H, py), 5.68 (t, $^1J_{PC} = 2$, 1H, IrCHCHBu), 4.78 (dt, $^1J_{HH} = 15.2$, 4JPH = 2, 1H, IrCHCHBu), 4.28 (ddd, $^2J_{HH} = 16.5$, $^1J_{HH} = 10.3$, $^1J_{HH} = 3.0$, 1H, pyCH₂), 3.69 (ddd, $^2J_{HH} = 17.4$, $^1J_{HH} = 10.1$, $^1J_{HH} = 1.3$, 1H, pyCH₂), 3.64 (dd, $^1J_{HH} = 17.4$, $^1J_{HH} = 9.9$, 1H, pyCH₂), 3.22 (dd, $^1J_{HH} = 16.5$, $^1J_{HH} = 7.9$, 1H, pyCH₂), 2.28–2.43 (m, 2H, CH₂), 2.08–2.19 (m, 1H, CH₂), 0.88–1.96 (m, 25H, CH₂), 1.24 (s, 9H, IrCHCHBu), 1.17 (s, 9H, C≡CtBu), 1.02 (d, $^3J_{PC} = 14$, 18H, 2 × PBu₃), 1.00 (s, 9H, IrCHCHBu).

### 31P{1H} NMR (126 MHz, CD₂Cl₂): $\delta$ 164.2 (app t, $^3J_{PC} = 3$, py), 163.3 (app t, $^3J_{PC} = 3$, py), 162.3 (q, $^3J_{PC} = 50$, Ar²), 143.5 (app t, $^3J_{PC} = 4$, IrCHCHBu), 142.2 (br, IrCHCHBu), 139.4 (s, py), 135.4 (s, Ar²), 129.4 (q, $^3J_{PC} = 32$, $^2J_{PC} = 3$, Ar²), 125.1 (q, $^3J_{PC} = 272$, Ar²), 121.7 (d, $^3J_{PC} = 8$, py), 121.5 (d, $^3J_{PC} = 8$, py), 118.0 (sept, $^3J_{FC} = 4$, Ar²), 116.9 (s, C≡CtBu), 105.3 (dd, $^2J_{FC} = 8$, $^3J_{FC} = 5$, IrCHCHBu), 95.7 (app t, $^3J_{PC} = 10$, IrCHCHBu), 60.1 (s, C≡CtBu), 46.0 (d, $^1J_{PC} = 25$, pyCH₂), 40.8 (d, $^1J_{PC} = 30$, pyCH₂), 37.3 (s, CHCHCHBu), 37.1 (s, CHCHCHBu), 36.6 (dd, $^1J_{PC} = 21$, $^3J_{PC} = 4$, PBU₃), 34.6 (dd, $^1J_{PC} = 21$, $^3J_{PC} = 6$, PBU₃), 33.3 (d, $^1J_{PC} = 15$, CH₂), 32.2 (s, CH₂), 31.8 (s, C≡CtBu), 31.4 (s, CH₂), 31.28 (s, tBu(CH₃)), 31.26 (s, tBu(CH₃)), 31.1 (s, CH₂), 30.5 (s, CH₂), 30.3 (s, CH₂), 30.2 (s, CH₂), 29.7 (s, CHCHCHBu), 28.8 (br, CH₂), 28.20 (d, $^1J_{PC} = 4$, CH₂), 28.17 (s, CH₂), 27.1 (d, $^1J_{PC} = 3$, 2 × PBU₃), 26.6 (s, CH₂), 24.9 (s, CH₂), 21.9 (dd, $^1J_{PC} = 30$, $^3J_{PC} = 3$, PCH₂), 19.5 (dd, $^1J_{PC} = 19$, $^3J_{PC} = 3$, PCH₂).

The volatiles were removed in vacuo (210 µL, 1.71 mmol) and stirred for 6 h at RT. Analysis by NMR spectroscopy was apparent upon analysis by NMR spectroscopy.

### 4.11 NMR scale reaction of 1 with $\text{ZtBuC} = \text{CHCHBu}$

A solution of 1 (16.1, 9.8 µmol) in DFB (0.5 mL) within a J Young valve NMR tube was treated with $\text{ZtBuC} = \text{CHCHBu}$ (4.6 mg, 28.0 µmol) and then heated at 50 °C for 1 h. No reaction was apparent upon analysis by NMR spectroscopy.

### 4.12 Crystallography

Data were collected on a Rigaku Oxford Diffraction SuperNova AtlasS2 CCD diffractometer using graphite monochromated Mo Kα (λ = 0.71073 Å) or CuKα (λ = 1.54184 Å) radiation and an Oxford Cryosystems N-HeliX low temperature device [150(2) K]. Data were collected and reduced using CrysalisPro and refined using SHELX19 through the Olex2 interface.40 Full details about the collection, solution, and refinement are documented in CIF format, which have been deposited with the Cambridge Crystallographic Data Centre under CCDC 2051203 (1), 2051204 (2), 2051205 (7), 2051206 (10), 2051207 ([Rh(PNP-14)(η^3-norborenone)][BAR²]),

**Conflicts of interest**

There are no conflicts to declare.

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