Dalton Transactions

PAPER

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Cite this: Dalton Trans., 2017, 46, 15407

Received 1st October 2017, Accepted 23rd October 2017 DOI: 10.1039/c7dt03690f

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Introduction

Pincer ligands are tridentate *meridional* ligands that offer unique rigidity, selective activity and complex stability for transition metal centers.¹ Such ligands have played an instrumental role in the development of transition metal catalysts capable of performing difficult bond transformations. Among various pincer ligand scaffolds, PCP type pincers, containing a metal–carbon bond, enable the exploits of organometallic chemistry to be invoked for a range of bond transformations and/or catalysis. PCP pincers can be classified based on the hybridization of the metal bound carbon donor, namely as either sp³ or sp² (sp PCP pincers are yet to be reported).

The sp² PCP pincer ligand class is dominated by aromatic based designs, where the central carbon donor belongs to an aromatic system. However, $PC_{carbene}P$ pincers, where the central carbon is an alkylidene donor, have displayed unique reactivity due to their extremely strong *trans* effect and their ability to partake in ligand–metal cooperativity.^{2,3}

 $PC_{carbene}P$ pincers have been readily accessible for Ir, Ru and Os centres since early reports by Shaw, and then Gusev demonstrated double C–H activation.⁴ However, the alkyl backbones of such systems were unstable and conducive to

Facile generation of iridium PC_{carbene}P pincer complexes *via* water elimination from an alcohol proligand[†]

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We report the facile generation of Ir $PC_{carbene}P$ pincer systems. These systems are accessed from the reaction between $[IrCl(COD)]_2$ and a bis(diphenyl)phenylene P(OH)P proligand (**1**) with concomitant dehydration, followed by salt metathesis/ligand exchange in the case of cationic examples. In contrast to previously reported double C-H activation synthetic strategies to access similar complexes, accessing Ir $PC_{carbene}P$ complexes through dehydration proceeds rapidly at room temperature and provides the first example of the incorporation of phosphino aryl substituents. The generated complexes are shown to possess the ability to activate inert C-H bonds and partake in ligand cooperativity. Mechanistic evidence suggests that divergent C-H and O-H activation pathways of ligand **1** ultimately lead to the same Ir $PC_{carbene}P$ product (**2**). It is hoped that the stability and synthetic accessibility of these complexes will encourage their increased use in catalyst surveys.

β-hydride elimination. More recently, Ozerov (and later Piers) introduced β-hydride elimination resistant $PC_{carbene}P$ ligands.⁵ Since then, the metals accommodated in $PC_{carbene}P$ scaffolds have expanded to include Ni, Pd and Rh.^{2a,g,6} However, accessing $PC_{carbene}P$ pincers through double C–H activation is limited to noble metals well-known for their C–H activation abilities (Ni $PC_{carbene}P$ complexes were accessed through HX elimination). Perhaps because of this, much attention has been focused on various designs of iridium $PC_{carbene}P$ pincer complexes (Fig. 1).

Reports have demonstrated the ability of iridium PC_{carbene}P pincer complexes to reversibly activate E-H bonds (E = H, O, N, C), perform challenging catalysis, and to partake in difficult redox and catalytic processes.7 The exploration of iridium PCcarbeneP pincer complexes has led to a variety of pincer designs incorporating various carbocycles and heterocycles into the spinal positions, and featuring a range of phosphino alkyl substituents. However, phosphino donors with aryl substituents are yet to be reported, despite their higher stability, affordability and easier synthetic/commercial access as compared to alkyl phosphines. This is likely due to the need for electron rich metal centres to induce double C-H activation. As such, the powerful reactivity presented by iridium PCcarbeneP pincer complexes has only been utilized by synthetic organometallic groups capable of synthesizing and handling alkyl phosphino PC_{carbene}P pincer proligands.

We have recently reported the protonolysis of rhodium α -hydroxyalkyl complexes to access $PC_{carbene}P$ pincer complexes, avoiding double C–H activation.⁸ Herein, the formal de-

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[†]Electronic supplementary information (ESI) available. CCDC 1568119-1568125. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt03690f



Fig. 1 (Above) Ir sp² PCP architectures based on alkylidenyl and aryl carbon attachments. (Below) Examples of selected $PC_{carbene}P$ architectures.

hydration of an air-stable bis(diphenylphosphino) alcohol POP pro-ligand to an iridium $PC_{carbene}P$ pincer complex is detailed. Competing C–H and O–H activation is suggested with the isolation of a rare α -hydroxylalkyl complex and an iridium alkoxide intermediate. Although other $PC_{carbene}P$ iridium complexes featuring diaryl phosphino substituents have yet to be reported in the literature, the activity of the iridium $PC_{carbene}P^{Ph}$ platform is demonstrated with ligand exchange and C–H activation chemistry under mild conditions.

Results and discussion

Addition of compound **1** to $[IrCl(COD)]_2$ results in rapid generation of the PC_{carbene}P complex **2** and liberation of H₂O and 1,5-cyclooctadiene (COD) (Scheme 1). At room temperature, ³¹P NMR suggested that conversion to **2** was >50% after 15 minutes. In comparison, double C-H activation approaches to generate Ir PC_{carbene}P^{alkyl} complexes require prolonged heating (hours) above 100 °C.^{5b} Compound **2** was isolated in high yield (76%) *via* precipitation with *n*-hexane.

Compound 2 possesses a single ³¹P NMR resonance at $\delta_{\rm P}$ 29.0, and a ¹H NMR spectrum of 2 displays only aryl proton resonances, which provide little definitive evidence for the



Scheme 1 Synthesis of $PC_{carbene}P$ iridium complex 2 via dehydration of ligand 1. Metathesis of 2 with $Na[BAr^{F}_{4}]$ in the presence of PPh₃ or PCy₃ generates 3 and 4 respectively.

identity of 2. However, ¹³C NMR spectroscopic data for 2 revealed a highly deshielded triplet signal at 207.4 ppm (${}^{2}J_{CP} =$ 2.8 Hz), supporting the assigned alkylidene attachment. X-ray quality crystals of 2, grown by vapour diffusion between *n*-hexane and a concentrated solution of 2 in DCM at room temperature, allowed a diffraction study to be performed. From this, the determined molecular structure of 2 (Fig. 2) confirmed the formation of the PC_{carbene}P backbone, with an Ir1–C1 bond length of 1.940(2) Å suggestive of Ir–C double bond character (*cf.* 1.899(7) Å for the PC_{carbene}P^{iPr} analogue).^{5b} This Ir=C bond length lies within the range of previously reported iridium PC_{carbene}P complexes, with a minimum observed value of 1.86(1) Å and a maximum value of 2.038(9) Å.^{6b,7c}

The molecular structure of **2** reveals that **2** possesses C_2 symmetry, as opposed to C_{2v} symmetry, as often observed in aryl PCP pincer complexes. Consequently, **2** exists as a racemic mixture of *R* and *S* conformers.

Cationic iridium $PC_{carbene}P$ complexes could be generated *via* salt metathesis between Na[BAr^F₄] and compound 2 in the presence of a suitable ligand. Such methodology has been previously described by Piers.^{6b,9} Thus, compounds 3 and 4 were generated by the addition of Na[BAr^F₄] to an equimolar amount of 2 and either PPh₃ or PCy₃ respectively (Scheme 1). The molecular structures of 3 (Fig. 3) and 4 (Fig. 4) reveal slightly elongated Ir1–C1 distances in the cationic complexes {1.994(8) Å in 3 and 1.953(8) Å in 4}, reflecting the sensitivity of the π -acidic alkylidene linkage to electron density change at the iridium centre due to the π -basic nature of the chloride ligand in 2 and the cationic nature of complexes 3 and 4.

The ¹³C NMR resonances arising from the carbonic carbon positions in compounds **2**, **3** and **4** follow the trend that **2** $(\delta_c 207.4) < 4 (\delta_c 231.9) < 3 (\delta_c 241.6)$. This trend roughly correlates with Ir=C bond lengths, and reflects an increase in 'free' carbone character from **2** to **4** to **3**.¹⁰

Metathesis of 2 in the presence of two equivalents of PPh_3 led to the formation of metallacycle 5 (Fig. 5). Compound 5



Fig. 2 Molecular structure of 2. Hydrogen atoms omitted, thermal ellipsoids shown at 50%. Selected bond distances (Å) and angles (°): Ir1-P1, 2.291(1); Ir1-C1, 1.940(2); Ir1-C1, 2.350(3); C1-Ir1-C1, 180.0(1); P1-Ir1-P2, 166.0(1).



Fig. 3 Molecular structure of 3. Hydrogen atoms and anion omitted, thermal ellipsoids shown at 50%. Selected bond distances (Å) and angles (°): Ir1–P1, 2.298(2); Ir1–C1, 1.994(8); Ir1–P2, 2.282(2); Ir1–P3, 2.394(2); C1–Ir1–P3, 178.3(3); P1–Ir1–P2, 164.1(1).



Fig. 4 Molecular structure of 4. Hydrogen atoms and anion omitted, thermal ellipsoids shown at 50%. Selected bond distances (Å) and angles (°): Ir1-P1, 2.269(2); Ir1-C1, 1.953(8); Ir1-P2, 2.317(2); Ir1-P3, 2.423(2); C1-Ir1-P3, 169.2(2); P1-Ir1-P2, 158.0(1).

could also be generated by adding an equivalent of PPh₃ to isolated 3 (Scheme 2). Thus, 5 is likely generated *via* coordination of PPh₃ to the electrophilic carbene position in 3 and subsequent cyclometallation at the iridium centre. Cyclometallation of PPh₃ is well-documented on iridium,¹¹ but iridium-alkylidene cooperative cyclometallation is less reported.¹² Such a ligand directed substrate activation mirrors cooperative PPh₃ C-H activation and CO₂ activation on related ruthenium vinylidene and carbodiphosphorane complexes.¹³

We recently reported the rhodium analogue of 3, $[PC_{carbene}P^{Ph}Rh(PPh_3)][BAr^{F_4}]$.^{8a} Although the rhodium carbene position was found to be electrophilic in this complex, it was stable in the presence of excess PPh₃, even upon heating. By comparison, the carbene position in 3 proves to be much more electrophilic than its rhodium analogue. This is somewhat expected, given that iridium stablises the singlet state of the carbene ligand to a greater extend than rhodium.



Fig. 5 Molecular structure of **5**. Hydrogen atoms (except H1) and anion omitted, thermal ellipsoids shown at 50%. H1 was located in a Fourier Difference map. Selected bond distances (Å) and angles (°): Ir1–P1, 2.343 (1); Ir1–C1, 2.232(3); Ir1–P2, 2.397(1); Ir1–P4, 2.343(1); Ir1–C43, 2.095(3); C1–P3, 1.840(4); C1–Ir1–P4, 172.5(1); P1–Ir1–C43, 162.53(9).



Scheme 2 (Above) Reaction of 3 with PPh₃ results in ligand cooperative C-H activation of PPh₃. (Below) A cationic PC_{carbene}P intermediate, generated *via* metathesis of Na[BAr^F₄] with 2, C-H activates 1,5-cyclooctodiene generating iridium(III) allyl 6.

Metathesis of 2 in the presence of 1,5-cyclooctadiene as the supporting ligand led to product 6 (Scheme 2). A molecular structure of compound 6 (Fig. 6) reveals that the COD ligand had undergone C–H activation, resulting in an allylic coordination. The concomitantly generated hydrido group then transfers from the iridium centre to the carbene ligand transforming the pincer into a *facially* coordinated $PC_{sp^3}P$ ligand, which is also evident by ¹H NMR analysis that reveals a resonance at 4.59 ppm correlating to this hydrogen. The resulting Ir–C bond distance in the $PC_{sp^3}P$ ligand of 6 is observed at a increased length of 2.158(4) Å (*cf.* 1.890(4) Å in 2).

The activation of C–H bonds, and also C–C bonds, in iridium dienes is well known in accessing resonance stabilised ligands.¹⁴

Compound **6** could also be generated directly by heating compound **1** and $[Ir(COD)_2][BAr^F_4]$ at 95 °C for 18 hours. The stability of **6** supports the premise that electron poor iridium centres perform poorly at α -hydrogen elimination. In sharp contrast, cationic iridaepoxide complexes, or intermediates



Fig. 6 Molecular structure of 6. Hydrogen atoms (except H11, H441, H451 and H461) and anion omitted, thermal ellipsoids shown at 50%. Selected bond distances (Å) and angles (°): Ir1-P1, 2.298(1); Ir1-C1, 2.158(4); Ir1-P2, 2.328(1); C44-C45, 1.422(7); C45-C46, 1.420(7); C1-Ir1-P1, 80.7(1); P1-Ir1-P2, 102.2(1).

en route to **2** (see below) readily undergo α -hydroxyl elimination, suggesting that this may be a more facile process.⁹

It was found that the presence of PPh₃ arrested the reaction between **1** and [IrCl(COD)]₂, and prevented formation of **2**. As such, treatment of compound **1** with [IrCl(COD)PPh₃] at room temperature followed by heating at 55 °C for 2 days led to a mixture of two products, alkoxide **7a** and α -hydroxylalkyl **7b** in a **1**:4 ratio according to the relative integrations by ³¹P NMR spectroscopy (Scheme 3). Fractional crystallization allowed the isolation and characterization of each compound.

The structure of **7a** was established *via* ¹H, ¹³C and ³¹P NMR spectroscopies. Correlation spectroscopy confirmed the formulation of **7a** as an alkoxide, with a ¹³C NMR resonance at δ_c 78.7 correlating strongly to a methine proton at δ_H 5.05 in a HSQC experiment (see ESI†). Strong ³¹P coupling observed for the signal at δ_H 5.05 suggested a *trans* PPh₃ position. The *mer* configuration of the pincer was established by ³¹P NMR, where two signals were observed in a 2:1 ratio at δ_P –6.1 (2 P, d, ²*J*_{PP} = 11.4 Hz) and –1.2 (1 P, t, ²*J*_{PP} = 11.4 Hz).



Compound **7b** represents a direct route to access an iridium α -hydroxylalkyl, with previous reported examples either relying on formation of the α -hydroxyalkyl moiety within the metal coordination sphere, or being resonance supported forms better described as protonated β -diketones.¹⁵ X-ray diffraction quality crystals of **7b** allowed the determination of its molecular structure (Fig. 7). The structure of **7b** reveals that it is coordinatively saturated (O_h geometry), preventing potential α -hydroxyl elimination.

In order to investigate which of 7a or 7b represents a more likely model intermediate for the formation of 2, samples of each were heated to promote PPh₃ dissociation. However in both cases, our inability to eliminate coordinated PPh₃ prevented transformation of 7a or 7b into 2.

Addition of Na[BAr^F₄] to either complexes **7a** or **7b** readily led to metathesis, but failed to generate a cationic iridium PC_{carbene}P complex (*i.e.* **3**) even when heated to 80 °C. This is in contrast to previously described rhodium analogues, and may suggest against a proton transfer mechanism for dehydration. In the case of **7a**, the known cation fragment [Ir(CO) (PPh₃)₃][BAr^F₄]¹⁶ was generated as the sole product, whereas **7b** decomposed into multiple unknown products. Piers has reported the decomposition of [κ^3 -P'(η^2 -CO)P"IrCl] iridaepoxides into related [IrCl(CO)(PR₃)₂] products, suggesting a plausible decomposition route that proceeds *via* the β-hydride elimination in **7a**.¹⁷

Monitoring of the reaction between 1 and $[IrCl(COD)]_2$ at various temperatures between 253 K and 298 K revealed that intermediate complex I forms prior to any bond activation (Scheme 4). The ¹H NMR spectrum of complex I at 263 K displays a downfield signal at 11.07 ppm that has been associated with a C-H/metal anagostic interaction in related rhodium intermediates.^{6a,8a} However, ¹H-¹³C NMR correlation experiments, and isotopic labelling experiments suggested the signal was due to the OH motif (see ESI[†]). Thus, the interaction



Fig. 7 Molecular structure of **7b**. Hydrogen atoms (except H1 and H11) omitted, thermal ellipsoids shown at 50%. H1 and H11 were located in a Fourier Difference map. Selected bond distances (Å) and angles (°): Ir1–P1, 2.296(2); Ir1–C1, 2.195(9); Ir1–P2, 2.310(2); Ir1–P3, 2.369(3); Ir1–C11, 2.499(2); C1–Ir1–P3, 175.6(3); P1–Ir1–P2, 154.0(1).



Scheme 4 Possible reaction mechanism for the formation of 2. * denotes κ^1 -COD coordination. N. D. denotes not detected by NMR spectroscopy.

between the linkage of ligand ${\bf 1}$ and the metal centre in complex I can not be defined with any certainty.

Given that compound **1** has been shown to be susceptible to O–H and C–H activation (*i.e.* in generation of **7a–b**), it is possible that both intermediates **II** and **VI** shown in Scheme 4 could be produced upon C–H or O–H activation (respectively) of the chelate ligand in **I**, representing divergent reaction pathways.

At 253 K, as complex I diminishes in concentration, two independent iridium hydride species are observed, complexes II and VI. Intermediate II was characterized by ¹H and ³¹P NMR spectroscopy, and by reaction with isotopologues 1a and 1b that contained deuterated methine and hydroxyl positions respectively (see ESI†). Intermediate II supports a C-H activation pathway (pathway A, Scheme 4) that proceeds *via* an α -hydroxylalkyl complex. In contrast to 7b, complex II is characterized by a *fac* coordination of the α -hydroxyalkyl ligand. The flexibility of PC_{sp3}P ligands, related to 1, to adopt both *fac* and *mer* configurations is well-documented.¹⁸ As the signal intensities from II diminish, signals for product 2 grow in intensity.

Isomerisation of the tridentate PCP ligand from *fac* to *mer* generates **III**. Concomitant dissociation of COD would allow this process to proceed *via* a 5-coordinate intermediate, as has been reported for related Rh(\mathfrak{m}) POP pincer systems.¹⁹

As stated above, addition of Na[BAr^F₄] to either complexes 7a or 7b failed to generate a cationic iridium PC_{carbene}P complex (*i.e.* 3). This may imply that formation of 2 proceeds *via* α -hydroxyl elimination in **III** to give **IV**, as suggested by Piers,^{2b,c,9} rather than proton transfer from iridium to the α -hydroxylalkyl position to give **V**, which was observed for more Brønsted acidic rhodium examples.^{8a} α -Alkyl elimination in closely related iridium PCP complexes has been directly observed by Wendt.²⁰ The product of C–O activation, intermediate **IV** (Scheme 4), can then undergo H/OH reductive elimination to give **2** and eliminate water.

The hydrido complex VI was observed simultaneously with II, and represents the β -hydrogen elimination product of an initial O–H activation intermediate (V) for pathway B (Scheme 4). Intermediate VI was characterized by ¹H, ³¹P NMR spectroscopy, and reaction with isotopologues 1a and 1b. Although the hydride positions in VI are inequivalent, dynamic exchange between the positions gives rise to a single triplet signal at $\delta_{\rm H}$ –12.57. The possibility of VI existing as a dihydrogen complex was precluded by the absence of any observable D–H coupling while employing isotopologues 1a–b. Furthermore, VI displays an η^2 -carbonyl ¹³C NMR signal at $\delta_{\rm C}$ 132.1, more indicative of an iridium(III) oxidation state.^{2c}

Intermediate **VI** can in-principle also be generated from β -hydride elimination from an α -hydroxylalkyl ligand (*i.e.* from **III** of pathway A, Scheme 4). Indeed, this likely marks the convergence of pathways A and B. However, using the isotopologue **1a** (methine position deuterated), very little of complex **II** is generated, and much higher concentrations of **VI** are observed, indicative of a notable kinetic isotope effect for C–H activation. From this reaction solution, X-ray quality crystals of complex **VII** precipitated. Structural characterization of **VII** demonstrates it to be an O–H activation product arising from HCl elimination from **V** (Scheme 4 inset). Indeed, addition of ethereal HCl to crystals of **VII** generated product **2** and intermediates **I**, **II** and **VI**, which indicates the presence of equilibria between species of pathways A and B.

Further evidence for the identity of VI is garnered from the addition of the dehydrogenated, keto form of 1 (1-H₂), with $[IrCl(COD)]_2$ under a H₂ atmosphere. At room temperature, intermediates VI and VII are readily identified as the major species after 5–10 minutes, after which time 2 is generated. However, this does not represent a practical synthesis of 2, as

it was found that 2 further reacts with H_2 to give hydrogenation products.

Conclusions

In conclusion, we have reported a facile method of accessing iridium PCcarbeneP complexes via dehydration of an alcoholic bisphosphino proligand. Mechanistic studies suggest two competing, divergent C-H and O-H activation pathways, ultimately leading to the same iridium PC_{carbene}P product (2). The above described reactivity demonstrates the activity of the PC_{carbene}P^{Ph} platform. This system is able to partake in ligandmetal cooperativity to perform difficult bond activations such as C-H activation, as demonstrated in the generation of compounds 5 and 6. Given recent reports of the use of PC_{carbene}P iridium complexes in catalysis, the ability to access this ligand platform from stable, commercially available (or simple to synthesise and store) components allows synthetic chemists a potentially new catalytic tool for difficult transformations that have already been demonstrated in-practice using previously reported PCcarbeneP complexes.

Experimental

See ESI† for general experimental conditions.

Preparation of complex 2

A solution of $[IrCl(COD)]_2$ (134.3 mg, 0.20 mmol) in DCM (3 mL) was treated with a solution of compound 1 (221.0 mg, 0.40 mmol) in DCM (3 mL) at room temperature to give a green coloured solution and then stirred at room temperature for 30 h in a closed vessel. The solution was filtered and then the filtrate was evaporated. The residue was washed with *n*-hexane (3 × 10 mL) and then dissolved in DCM (3 mL), layered with *n*-hexane (5 mL) and left to stand at room temperature. The resultant green solid of complex 2 were isolated by filtration and then dried under vacuum (231 mg, 76%).

¹H NMR (500 MHz, CD₂Cl₂, 298 K) $\delta_{\rm H}$ 6.85 (2 H, t, J = 7.4 Hz, Ar–H), 7.34–7.41 (2 H, m, Ar–H), 7.41–7.57 (12 H, m, PPh₂ H's), 7.77–8.02 (8 H, m, PPh₂ H's), 8.20 (2 H, d, J = 7.6 Hz, Ar–H), 8.26–8.31 (2 H, m, Ar–H). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂, 298 K) $\delta_{\rm C}$ 124.6 (t, J = 7.3 Hz), 129.1 (t, J = 5.2 Hz), 129.2 (s), 131.0 (s), 132.1 (t, J = 25.0 Hz), 133.8 (s), 134.6 (t, J = 6.9 Hz), 137.0 (s), 138.5 (t, J = 24.1 Hz), 174.8 (t, J = 19.2 Hz), 207.4 (t, ² $J_{\rm CP} =$ 2.8 Hz, Ir=C). ³¹P{¹H} NMR (202 MHz, CD₂Cl₂, 298 K) $\delta_{\rm P}$ 29.0 (2 P, s, PCP pincer P's). HRMS (ESI-TOF) *m*/*z*: [M + H]⁺ calcd for C₃₇H₂₉ClIrP₂ 763.1050; found 763.1021. Elemental analysis: calc. for C₃₇H₂₈ClIrP₂: C, 58.3; H, 3.7; found: C, 58.1; H, 3.7%.

Preparation of complex 3

A solution of complex 2 (22.9 mg, 0.030 mmol) in DCM (5 mL) at -78 °C was treated dropwise with a solution of Na[BAr^F₄]·2THF (34.0 mg, 0.033 mmol) in DCM (5 mL) and

then a solution of PPh₃ (7.9 mg, 0.030 mmol) in DCM (5 mL). The solution was allowed to slowly come to room temperature and was stirred for an additional 2 hours. The reaction mixture was filtered and then the filtrate was evaporated to approx. 1 mL. The solution was layered with *n*-hexane (10 mL) and then left to stand at room temperature. Dark green crystals of **3** were isolated by filtration and then dried under vacuum (38 mg, 68%).

¹H NMR (500 MHz, CD₂Cl₂, 298 K) $\delta_{\rm H}$ 6.77 (6 H, ddd, J = 11.2 Hz, J = 8.2 Hz, J = 1.4 Hz, Ar-H), 6.97 (6 H, td, J = 7.9 Hz, J = 2.1 Hz, Ar-H), 7.05 (2 H, t, J = 7.6 Hz, Ar-H), 7.20-7.29 (10 H, m, Ar-H), 7.29–7.49 (15 H, m, Ar-H), 7.56 (4 H, s, [BAr^F₄] Ar-H), 7.73 (8 H, s, [BAr^F₄] Ar-H), 7.96 (2 H, d, J = 7.8 Hz, Ar-H), 8.35 (2 H, td, J = 7.5 Hz, J = 1.3 Hz, Ar-H). ¹³C{¹H} NMR (126 MHz, CD_2Cl_2 , 298 K) δ_C 117.7–118.1 (m, [BAr^F₄] Ar–C), 121.5–128.3 (m), 128.6–129.0 (m), 129.2 (t, J = 5.2 Hz), 129.3–130.2 (m), 131.0 (d, J = 1.8 Hz), 131.7 (s), 133.3 (s), 133.6-133.8 (m), 134.3 (s), 134.6 (s), 134.6-134.9 (m), 135.2 (s, $[BAr_{4}^{F}]$ Ar–C), 135.5 (s), 145.3 (d, J = 7.1 Hz), 162.2 (q, ${}^{1}J_{CB}$ = 49.7 Hz, [BAr^F₄] Ar–C), 169.3 (td, *J* = 18.7 Hz, *J* = 2.9 Hz), 241.6 (d, ${}^{2}J_{CP} = 72.7$ Hz, Ir=C). ${}^{31}P{}^{1}H{}$ NMR (202 MHz, $CD_{2}Cl_{2}$, 298 K) $\delta_{\rm P}$ 14.0 (1 P, t, ${}^{2}J_{\rm PP}$ = 16.4 Hz, PPh₃), 30.8 (2 P, d, ${}^{2}J_{\rm PP}$ = 16.4 Hz, PCP pincer P's). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for C55H43IrP3 989.2206; found 989.2227. Elemental analysis: calc. for C₈₇H₅₅BF₂₄IrP₃: C, 56.4; H, 3.0; found: C, 56.0; H, 3.2%.

Preparation of complex 4

A solution of complex 2 (22.9 mg, 0.030 mmol) in DCM (5 mL) at -78 °C was treated dropwise with a solution of Na[BAr^F₄]·2THF (34.0 mg, 0.033 mmol) in DCM (5 mL) and then a solution of PCy₃ (8.4 mg, 0.030 mmol) in DCM (5 mL). The solution was allowed to slowly come to room temperature and was stirred for an additional 2 hours. The reaction mixture was filtered and then the filtrate was evaporated to approx. 1 mL. The solution was layered with *n*-hexane (10 mL) and then left to stand at room temperature. Dark green crystals of 4 were isolated by filtration and then dried under vacuum (43 mg, 77%).

¹H NMR (500 MHz, CD_2Cl_2 , 298 K) δ_H 0.63–0.74 (5 H, m, Cy-H), 0.87-0.95 (4 H, m, Cy-H), 1.03-1.15 (5 H, m, Cy-H), 1.27-1.52 (16 H, m, Cy-H), 1.74-1.94 (3 H, m, Cy-H), 6.93 (2 H, t, J = 7.4 Hz, 2 H, Ar-H), 7.36 (2 H, dt, J = 7.7, 4.0 Hz, Ar-H), 7.50-7.68 (16 H, m, Ar-H), 7.70-7.82 (10 H, m, Ar-H), 7.99 (8 H, q, J = 5.7 Hz, Ar–H), 8.31–8.43 (2 H, m, Ar–H). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂, 298 K) $\delta_{\rm C}$ 26.1 (s, Cy–C), 27.2 (d, ²J_{CP} = 10.2 Hz, Cy–C), 30.7 (s, Cy–C), 38.4 (d, ${}^{1}J_{CP}$ = 20.1 Hz), 117.8–118.0 (m, [BAr^F₄] Ar-C), 121.7–128.4 (m), 128.8–129.8 (m), 131.2 (t, J = 25.5 Hz), 132.3 (s), 132.9 (t, J = 3.2 Hz), 134.4 (s), 134.9 (s), 135.3 (s, $[BAr_4^F]$ Ar-C), 135.6 (t, J = 6.0 Hz), 145.7 (td, J = 24.9, 6.3 Hz), 162.2 (q, ${}^{1}J_{CB}$ = 49.8 Hz, [BAr^F₄] Ar–C), 170.3 (td, J = 18.5, 2.8 Hz), 231.9 (d, ${}^{2}J_{CP}$ = 69.5 Hz, Ir=C). ${}^{31}P{}^{1}H$ NMR (202 MHz, CD_2Cl_2 , 298 K) δ_P 21.2 (1 P, t, ${}^2J_{PP}$ = 16.9 Hz, PCy_3), 26.7 (2 P, d, ${}^{2}J_{PP}$ = 16.9 Hz, PCP pincer P's). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for C₅₅H₆₁IrP₃ 1007.3620; found 1007.3620. Elemental analysis: calc. for C₈₇H₇₃BF₂₄IrP₃: C, 55.9; H, 3.9; found: C, 55.9; H, 3.4%.

Preparation of complex 5

Method A: A solution of complex 2 (22.9 mg, 0.030 mmol) in DCM (5 mL) at -78 °C was treated dropwise with a solution of Na[BAr^F₄]·2THF (34.0 mg, 0.033 mmol) in DCM (5 mL) and then a solution of PPh₃ (19.7 mg, 0.075 mmol) in DCM (10 mL). The solution was allowed to slowly come to room temperature and was stirred for an additional 2 hours. The reaction mixture was filtered and then the filtrate was evaporated fully. *n*-Hexane was added to the residue, triturated and then decanted. This process was repeated two additional times. The remaining residue was dissolved in DCM (1 mL), layered with *n*-hexane (10 mL) and then left to stand at room temperature. Light yellow crystals of 5 formed from the solution were isolated by filtration and then dried under vacuum (45 mg, 71%).

Method B: PPh₃ (1.4 mg, 5.5 μ mol) was added to a solution of complex 3 (9.3 mg, 5 μ mol) in CD₂Cl₂ (0.6 mL) at room temperature. The reaction solution was mixed well and then left to stand at room temperature overnight. ¹H and ³¹P NMR analyses confirmed the formation of complex 5 in quantitative yield.

¹H NMR (500 MHz, CD₂Cl₂, 298 K) $\delta_{\rm H}$ -9.63 (1 H, dddd, J_{HP} = 133.1, 20.6, 17.0, 7.6 Hz, Ir–H), 5.985–6.09 (4 H, m, Ar–H), 6.23-6.33 (1 H, m, Ar-H), 6.46 (1 H, t, J = 8.2 Hz, Ar-H), 6.59-6.72 (3 H, m, Ar-H), 6.79-7.22 (37 H, m, Ar-H), 7.24-7.42 (4 H, m, Ar-H), 7.44-7.65 (8 H, m, Ar-H), 7.66-7.84 (10 H, m, Ar-H), 8.17 (1 H, dd, I = 8.3, 3.6 Hz, Ar-H). ¹³C{¹H} NMR (126 MHz, CD_2Cl_2 , 298 K) δ_C 55.1 (dd, J_{CP} = 74.8, 27.3 Hz, Ir-C-P), 117.7-118.1 (m, [BAr^F₄] Ar-C), 121.7-128.3 (m), 128.3-130.6 (m), 131.6-131.7 (m), 132.5-134.4 (m), 134.7 (s), 135.1 (s), 135.2 (s), 135.3 (s, [BAr^F₄] Ar-C), 136.2 (s), 137.2 (s), 142.5 (dd, J = 49.6, 8.6 Hz), 144.6-145.3 (m), 146.5-147.7 (m), 151.2 (d, J = 28.3 Hz), 153.6 (dt, J = 22.8, 2.7 Hz), 162.2 (q, ${}^{1}J_{CB}$ = 49.8 Hz, [BAr^F₄] Ar–C). ${}^{31}P{}^{1}H$ NMR (202 MHz, CD₂Cl₂, 298 K) $\delta_{\rm P}$ 3.0 (1 P, apparent dd, $J_{\rm PP}$ = 10.8, $J_{\rm PP}$ = 10.1 Hz, Ir–P), 10.4–11.0 (2 P, m), 36.9 (1 P, apparent dt, ${}^{3}J_{PP} = 25.9$, ${}^{3}J_{PP} =$ 8.7 Hz, Ir–C–P). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{73}H_{58}IrP_4$ 1251.3120; found 1251.3144. Elemental analysis: calc. for C₁₀₅H₇₀BF₂₄IrP₄: C, 59.6; H, 3.3; found: C, 59.3; H, 3.4%.

Preparation of complex 6

Method A: A solution of complex 2 (39.5 mg, 0.052 mmol) in DCM (5 mL) at -90 °C was treated dropwise with a solution of Na[BAr^F₄]·2THF (53.4 mg, 0.052 mmol) in DCM (10 mL) and then 1,5-cyclooctadiene (7 µL, 0.057 mmol). The solution was allowed to come to room temperature and was stirred overnight. The reaction mixture was filtered and then the filtrate was evaporated fully. *n*-Hexane (5 mL) was added to the residue, triturated and then decanted. This process was repeated two additional times. The remaining residue was dissolved in DCM (1 mL), layered with *n*-hexane (10 mL) and then left to stand at room temperature. Colourless crystals of **6** formed from the solution were isolated by filtration and then dried under vacuum (70 mg, 79%).

Method B: A solution of compound 1 (5.5 mg, 0.01 mmol) in 1,2-dichloroethane (0.4 mL) was added dropwise to a solu-

tion of $[Ir(COD)_2][BAr^F_4]$ (12.7 mg, 0.01 mmol) in 1,2-dichloroethane (0.4 mL) at room temperature. The reaction solution was then heated to 95 °C for 18 h. ${}^{31}P{}^{1}H$ NMR spectroscopic analysis confirmed the formation of complex **6** in almost quantitative yield.

¹H NMR (500 MHz, CD_2Cl_2 , 298 K) δ_H 1.15–1.26 (1 H, m, cyclooctadienylium), 1.55-1.68 (1 H, m, cyclooctadienylium), 1.68-1.80 (1 H, m, cyclooctadienylium), 1.80-1.91 (1 H, m, cyclooctadienylium), 2.53 (1 H, dt, J = 14.1, 8.8 Hz, cyclooctadienylium), 2.98-3.11 (1 H, m, cyclooctadienylium), 3.20-3.34 (1 H, m, cyclooctadienylium), 3.69-3.85 (2 H, m, cyclooctadienylium), 3.95 (1 H, t, J = 7.7 Hz, cyclooctadienylium), 4.59 (1 H, s, Ir–C–H), 4.92 (1 H, t, J = 7.9 Hz, cyclooctadienylium), 7.05-7.13 (6 H, m, Ar-H), 7.17-7.59 (26 H, m, Ar-H), 7.73 (8 H, s, [BAr^F₄] Ar-H). ¹³C{¹H} (126 MHz, CD₂Cl₂, 298 K) $\delta_{\rm C}$ 20.5 (d, J = 3.8 Hz), 28.4 (d, J = 4.9 Hz), 31.8 (s), 40.5 (s), 49.9 (d, J =15.5 Hz), 55.4 (d, J = 2.5 Hz), 69.1 (d, J = 32.6 Hz), 100.9 (s), 105.3 (s), 117.7-118.3 (m, [BAr^F₄] Ar-C), 121.7-128.4 (m), 128.5 (s), 128.6-128.9 (m), 128.9-129.1 (m), 129.2-129.3 (m), 129.5 (s), 129.6–129.8 (m), 131.2 (d, J = 9.3 Hz), 131.7 (s), 131.8 (d, J = 11.0 Hz), 131.9 (s), 132.4 (d, J = 9.9 Hz), 134.5 (dd, J = 41.0, 10.6 Hz), 135.1 (s), 135.3 (s, $[BAr_4^F]$ Ar–C), 135.7 (d, J =39.9 Hz), 137.1 (d, J = 6.7 Hz), 137.6 (d, J = 16.6 Hz), 157.6 (d, J = 29.7 Hz), 159.1 (d, J = 27.0 Hz), 162.3 (q, ${}^{1}J_{CB} = 49.8$ Hz, $[BAr_{4}^{F}]$ Ar-C). ³¹P{¹H} (202 MHz, CD₂Cl₂, 298 K) δ_{P} 9.1 (1 P, d, ${}^{2}J_{PP}$ 7.7 Hz, PCP pincer P), 17.5 (1 P, d, ${}^{2}J_{PP}$ = 7.7 Hz, PCP pincer P). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{45}H_{40}IrP_2$ 835.2232; found 835.2232. calc. for C77H52BF24IrP2: C, 54.5; H, 3.1; found: C, 54.3; H, 3.4%.

Preparation of complexes 7a and 7b

Toluene (20 mL) was added to [IrCl(COD)(PPh₃)] (119.6 mg, 0.20 mmol) and compound 1 (110.5 mg, 0.2 mmol) at room temperature and stirred overnight. The solution was then heated at 55 °C for two days. Afterwards, the solution was concentrated to approx. 5 mL and n-hexane (15 mL) was added to precipitate complexes 7a and 7b. The solids were filtered, washed with *n*-hexane $(3 \times 10 \text{ mL})$ and then dissolved in toluene (10 mL). The toluene solution was layered with n-hexane (20 mL) and left to stand at room temperature. Initially, colourless crystals of 7b were isolated by fractional crystallization, filtration and then dried under vacuum. The filtrate was evaporated under vacuum, re-dissolved in toluene (5 mL) and then layered with n-hexane (15 mL) and left to stand at room temperature. Crystals of 7a were isolated by filtration and then dried under vacuum (7a: 31 mg, 15%; 7b: 105 mg, 50%).

7a: ¹H NMR (500 MHz, CD₂Cl₂, 298 K) $\delta_{\rm H}$ −18.34 (1 H, td, ${}^{2}J_{\rm HP}$ = 19.7, 13.8 Hz, Ir–H), 5.05 (1 H, d, ${}^{4}J_{\rm HP}$ = 15.2 Hz, methine C–H), 6.72–6.87 (9 H, m, Ar–H), 6.90 (4 H, td, *J* = 8.2, 2.3 Hz, Ar–H), 7.00–7.46 (28 H, m, Ar–H), 7.70 (2 H, d, *J* = 7.7 Hz, Ar–H). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂, 298 K) $\delta_{\rm C}$ 78.6–78.8 (m, methine C), 126.0 (t, *J* = 4.3 Hz), 127.3 (d, *J* = 10.0 Hz), 127.5 (t, *J* = 5.2 Hz), 127.8–128.1 (m), 129.4–129.6 (m), 129.7 (d, *J* = 6.7 Hz), 130.8 (d, *J* = 2.0 Hz), 134.4 (t, *J* = 5.4 Hz), 134.7 (s), 134.7–134.9 (m), 135.4 (t, *J* = 3.0 Hz), 136.1

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(d, J = 10.8 Hz), 153.1 (t, J = 3.2 Hz). ³¹P{¹H} NMR (202 MHz, CD₂Cl₂, 298 K) $\delta_{\rm P} - 6.1$ (2 P, d, ² $J_{\rm PP} = 11.4$ Hz, POP pincer P's), -1.2 (1 P, t, ² $J_{\rm PP} = 11.4$ Hz, PPh₃).

7b: ¹H NMR (500 MHz, C₆D₆, 298 K) $\delta_{\rm H}$ –20.23 (1 H, td, ²J_{HP} = 16.9, 9.3 Hz, Ir–H), 6.62–7.90 (44 H, m, Ar–H and O–H). ¹³C{¹H} NMR (126 MHz, C₆D₆, 298 K) $\delta_{\rm C}$ 84.7 (d, ²J_{CP} = 82.5 Hz, C–OH), 126.5–126.8 (m), 126.8–127.1 (m), 127.4 (d, J = 9.1 Hz), 127.7 (t, J = 4.0 Hz), 128.6 (s), 129.4 (dd, J = 13.3, 8.8 Hz), 132.3 (t, J = 26.1 Hz), 133.5 (s), 133.9 (t, J = 5.3 Hz), 134.6 (t, J = 5.4 Hz), 134.9–135.7 (m), 136.1 (t, J = 27.1 Hz), 143.2 (d, J = 6.8 Hz), 165.5 (t, J = 14.1 Hz). ³¹P{¹H} NMR (202 MHz, C₆D₆, 298 K) $\delta_{\rm P}$ –2.1 (1 P, t, ²J_{PP} = 12.7 Hz, PPh₃), 13.2 (2 P, d, ²J_{PP} = 12.7 Hz, PCP pincer P's). HRMS (ESI-TOF) *m*/z: [M – Cl]⁺ calcd for C₅₅H₄₅IrOP₃ 1007.2311; found 1007.2294.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

We thank the National University of Singapore and the Singapore Ministry of Education for financial support (WBS R-143-000-586-112, R-143-000-697-114 and R-143-000-666-114).

Notes and references

- 1 (a) G. van Koten and D. Milstein, Organometallic Pincer Chemistry, Topics in Organometallic Chemistry, Springer, Berlin, 2013, vol. 40; (b) G. van Koten and R. A. Gossage, The Privileged Pincer-Metal Platform: Coordination Chemistry & Applications, Springer, 2015.
- 2 (a) D. V. Gutsulyak, W. E. Piers, J. Borau-Garcia and M. Parvez, J. Am. Chem. Soc., 2013, 135, 11776;
 (b) L. E. Doyle, W. E. Piers and J. Borau-Garcia, J. Am. Chem. Soc., 2015, 137, 2187; (c) L. E. Doyle, W. E. Piers, J. Borau-Garcia, M. J. Sgro and D. M. Spasyuk, Chem. Sci., 2016, 7, 921; (d) R. J. Burford, W. E. Piers and M. Parvez, Organometallics, 2012, 31, 2949; (e) C. C. Comanescu and V. M. Iluc, Chem. Commun., 2016, 52, 9048;
 (f) C. C. Comanescu and V. M. Iluc, Organometallics, 2015, 34, 4684; (g) C. C. Comanescu and V. M. Iluc, Organometallics, 2014, 33, 6059.
- 3 Ir NHC PCP pincers are known, but their electronic structure differs greatly from PC_{carbene}P pincers, as defined herein. See: A. F. Hill and C. M. A. McQueen, *Organometallics*, 2012, 31, 8051.
- 4 (a) C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1976, 1020; (b) H. D. Empsall, E. M. Hyde, R. Markham, W. S. McDonald, M. C. Norton, B. L. Shaw and B. Weeks, *J. Chem. Soc., Chem. Commun.*, 1977, 589; (c) D. G. Gusev and A. J. Lough, *Organometallics*, 2002, 21, 2601.

- 5 (a) W. Weng, S. Parkin and O. V. Ozerov, Organometallics, 2006, 25, 5345; (b) R. J. Burford, W. E. Piers and M. Parvez, Organometallics, 2012, 31, 2949.
- 6 (a) J. R. Logan, W. E. Piers, J. Borau-Garcia and D. Spasyuk, Organometallics, 2016, 35, 1279; (b) J. D. Smith, J. R. Logan, L. E. Doyle, R. J. Burford, S. Sugawara, C. Ohnita, Y. Yamamoto, W. E. Piers, D. M. Spasyuk and J. Borau-Garcia, *Dalton Trans.*, 2016, 45, 12669.
- 7 (a) R. J. Burford, W. E. Piers, D. H. Ess and M. Parvez, J. Am. Chem. Soc., 2014, 136, 3256; (b) A. V. Polukeev, R. Marcos, M. S. G. Ahlquist and O. F. Wendt, Chem. Sci., 2015, 6, 2060; (c) A. V. Polukeev and O. F. Wendt, Organometallics, 2017, 36, 639; (d) A. V. Polukeev, R. Marcos, M. S. G. Ahlquist and O. F. Wendt, Organometallics, 2016, 35, 2600; (e) M. S. Balakrishna, Polyhedron, 2017, DOI: 10.1016/j.poly.2017.07.026.
- 8 (a) S. Sung, T. Joachim, T. Krämer and R. D. Young, Organometallics, 2017, 36, 3117; (b) S. Sung, J. K. Boon, J. J. C. Lee, N. A. Rajabi, S. A. Macgregor, T. Krämer and R. D. Young, Organometallics, 2017, 36, 1609.
- 9 L. E. Doyle, W. E. Piers and D. W. Bi, *Dalton Trans.*, 2017, **46**, 4346.
- 10 Q. Teng and H. V. Huynh, Dalton Trans., 2017, 46, 614.
- 11 M. A. Bennett and D. L. Milner, J. Chem. Soc., Chem. Commun., 1967, 581.
- 12 G. R. Clark, W. R. Roper and A. H. Wright, *J. Organomet. Chem.*, 1984, 273, C17.
- (a) K. Onitsuka, M. Nishii, Y. Matsushima and S. Takahashi, Organometallics, 2004, 23, 5630;
 (b) L. M. Milner, L. M. Hall, N. E. Pridmore, M. K. Skeats, A. C. Whitwood, J. M. Lynam and J. M. Slattery, Dalton Trans., 2016, 45, 1717; (c) V. Cadierno, J. Díez, J. García-Álvarez and J. Gimeno, Organometallics, 2005, 24, 2801;
 (d) R. P. Kamalesh Babu, R. McDonald and R. G. Cavell, Organometallics, 2000, 19, 3462.
- 14 (a) R. H. Crabtree and C. P. Parnell, *Organometallics*, 1985,
 4, 519; (b) R. H. Crabtree, C. P. Parnell and R. J. Uriarte, *Organometallics*, 1987, 6, 696; (c) R. H. Crabtree, R. P. Dion,
 D. J. Gibboni, D. V. McCrath and E. M. Holt, *J. Am. Chem. Soc.*, 1986, 108, 7222.
- (a) I. Zumeta, C. Mendicute-Fierro, A. Rodríguez-Diéguez, J. M. Seco and M. A. Garralda, Organometallics, 2015, 34, 348; (b) D. L. Thorn, Organometallics, 1982, 1, 197; (c) D. L. Thorn and J. C. Calabrese, J. Organomet. Chem., 1984, 272, 283.
- 16 J. Peone Jr. and L. Vaska, Angew. Chem., Int. Ed. Engl., 1971, 10, 511.
- 17 J. D. Smith, J. Borau-Garcia, W. E. Piers and D. Spasyuk, *Can. J. Chem.*, 2016, **94**, 293.
- 18 J. Arras, H. Speth, H. A. Mayer and L. Wesemann, *Organometallics*, 2015, 34, 3629.
- 19 R. Dallanegra, A. B. Chaplin and A. S. Weller, *Organometallics*, 2012, **31**, 2720.
- 20 K. J. Jonasson, A. V. Polukeev, R. Marcos, M. S. G. Ahlquist and O. F. Wendt, *Angew. Chem.*, *Int. Ed.*, 2015, 54, 9372.