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Addition of N–H bonds to iridium: Synthesis and characterization of N–Ir–H complexes and the observation that an iridium N-bonded indole ring becomes activated for Michael addition to alkynes

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ABSTRACT

The thermal reaction between the electron-rich iridium complex, [IrCOD(PMe_3)$_3$]Cl, **1a**, and pyrrolic or anilinic N–H bonds results in the oxidative addition of the N–H bond and the formation of an amido iridium hydride complex, HIr(amido)(Cl)(PMe_3)$_3$ with loss of COD. The only isomer formed in this reaction has a meridional arrangement of PMe_3 ligands, with H trans to Cl and the amido group trans to PMe_3. The reaction products of **1a** with pyrrole, indole and 3-methyl indole were fully characterized included by single crystal X-ray diffraction. Attachment of the pyrrolic ring nitrogen to the iridium results in an electron rich ring system that is activated and adds to alkynes in a Michael addition reaction under mild conditions without a catalyst.

1. Introduction

While much has been published in the area of C–H activation over the past several years [1–4], there has been less published on N–H activation [5–11]. At the time this study was begun, very few examples of the oxidative addition of a N–H bond to a metal had been documented in the literature. The feasibility of an insertion–reductive elimination sequence for the reaction of a hydrido amido complex has been demonstrated by Trogler and Cowan for PtH(NHPh)(PEt_3)$_2$ and the activated olefin acrylonitrile [12]. Examples of catalytic amination based on oxidative addition of a N–H bond followed by an insertion–reductive elimination sequence have been reported. More recent attention to N–H activation has increased [13–21].

Results obtained in our laboratories on the oxidative addition of aromatic C–H bonds to iridium(I), starting with the electron rich complex [Ir(COD)(PMe_3)$_3$]Cl (COD = 1,5-cyclooctadiene) (**1a**) [22], prompted an investigation of the general oxidative addition reactions of a series of N–H compounds. The ultimate goal was the development of catalysts for N–H addition to unsaturates based on a subsequent insertion–reductive elimination sequence. While the ultimate goal was not realized, an intriguing series of Ir–N compounds was synthesized via N–H activation and this report details their syntheses, structures and properties.

2. Results and discussion

2.1. Oxidative addition of N–H compounds

The oxidative addition of N–H compounds to the series of electron rich complexes, [Ir(COD)(PMe_3)$_3$]X [22,23] (where X = Cl, **1a**; X = I, **1b**; X = $BF4^-$, **1c**; X = $BPh4^-$, **1d**) was investigated. Refluxing [Ir(COD)(PMe_3)$_3$]Cl (**1a**) with the heterocyclic amines, pyrrole, indole, 3-methylindole, 7-azaindole, or carbazole (the latter four in mesitylene) leads to the formation of mer-hydrido amido iridium(III) complexes (**2a**–**2e**) through loss of COD, oxidative addition of the N–H bond, and chloride coordination to the iridium (Eq. (1)). The yields for these complexes are fair to excellent. These complexes are stable as solids, but solutions slowly decompose, especially on exposure to air. The acyclic amine, aniline, reacts with [Ir(COD)(PMe_3)$_3$]Cl (**1a**) in mesitylene at 75 °C to give the hydrido anilido iridium(III) complex, Ir(NHPh)H(PMe_3)$_3$Cl **2f** (Eq. (2)). This complex has previously been prepared by Milstein and co-workers from the cyclooctene complex, Ir(PMe_3)$_3$(C_8H_{14})Cl and aniline [24]. [Ir(COD)(PMe_3)$_3$]I (**1b**) reacts with indole in mesitylene at reflux for 18 h to give the iodido hydrido amido iridium(III) complex, **2g** (Eq. (3)). Neither salt, [Ir(COD)(PMe_3)$_3$]BF_4 (**1c**) nor [Ir(COD)(PMe_3)$_3$]BPh_4 (**1d**), reacted with indole to form

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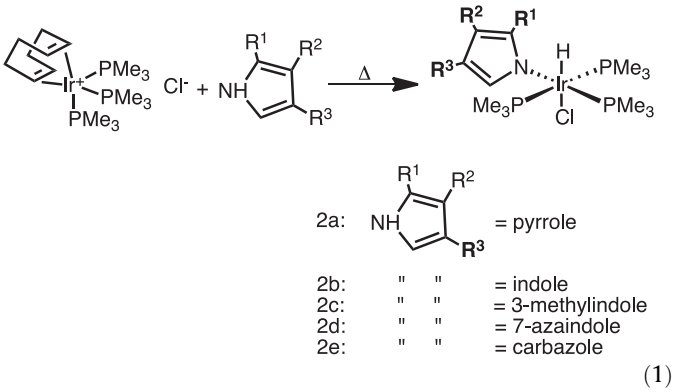
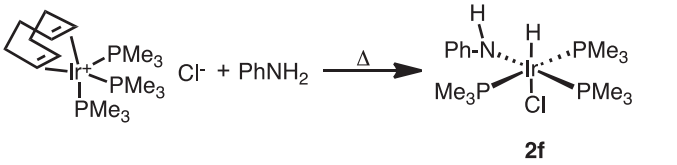
the corresponding hydrido amido complex under a number of conditions in mesitylene.



(1)



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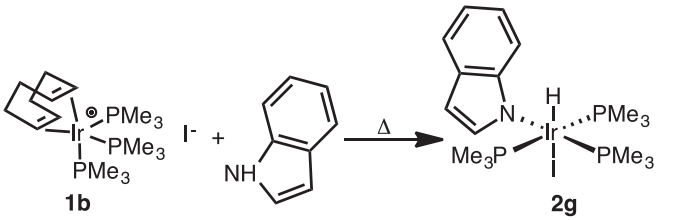


(3)

Only the complex salts $[Ir(COD)(PMe_3)_3]X$ (X = Cl or I) undergo a clean reaction to generate the corresponding six coordinate hydrido amido iridium(III) products. While the oxidative addition of amine N–H bonds to $[Ir(COD)(PMe_3)_3]X$ (X = BF_4 or BPh_4) may occur, the reaction does not lead to an isolable iridium hydride. It is likely that the N–H oxidative addition to Ir(I) proceeds through an unsaturated 14e− intermediate (resulting from loss of the chelating COD ligand) to give an unsaturated five-coordinate, 16e− Ir(III) complex, $(R_2N)(H)IrP_3^+$, that is then trapped by the counter-ion, X−. The inability of BF_4− and BPh_4− to coordinate strongly to the iridium may be the reason why the hydrido amido products are not formed or, more likely, why the resulting products are unstable and decompose under the reaction conditions. That a sixth ligand is required to trap the 16e− Ir(III) complex is supported by the results obtained from the reactions of the five coordinate, bis(phosphine)-iridium(I) complex, $Ir(COD)(PMe_3)_2Cl$ [25], with indole and aniline. Refluxing a mesitylene solution of $Ir(COD)(PMe_3)_2Cl$ and indole for 8.5 h results in the isolation of the tris(phosphine)-iridium(III) complex, **2b**, as the only clean product after work-up. Reaction of $Ir(COD)(PMe_3)_2Cl$ with excess aniline in mesitylene at 70 °C for 6 h results in the analogous formation of the tris(phosphine)anilido iridium(III) complex, **2f**. These results support the postulate that a sixth ligand is required to trap the five-coordinate, 16e− Ir(III) complex formed as described above. In this case, that five-coordinate intermediate scavenges a PMe_3 ligand (most likely from some decomposed starting complex) to form the tris(phosphine) complex.

$[IrCOD(PMe_3)_3]Cl$ appears to give isolable products only for N–H substrates in which the N–Ir bonded group fits into a narrow pocket defined by the trans-PMe_3 ligands. This was observed to be the case for C–H and O–H addition and results in very high barriers to rotation about the Ir–E bonds, a feature we will see in these Ir–N compounds as well. Although pyrrolidine, 3-pyrroline, pyrazole or tert-butylamine did not cleanly react with $[Ir(COD)(PMe_3)_3]Cl$ via oxidative addition of the N–H bond, this electron rich iridium(I) complex is nonetheless a versatile system.

In a previous paper, we showed that sulfur and nitrogen containing rings such as thiazole resulted in a ring-opening C–S bond cleavage reactions. So, the iridium(I) complex is capable of attacking quite a number of sites in different molecules with the ultimate product most likely being determined by the stability of the end product. A study was done recently calculating N–H versus C–H addition in pyrrole imines [7]. It was shown previously that $[Ir(COD)(PMe_3)_3]Cl$ reacts with aromatic C–H bonds [26–28], but this current work shows that all of the compounds with both C–H and N–H bonds react selectively with the N–H bond.

The pyrrole complex (**2a**) typifies these complexes and ^1H, ^{13}C and ^{31}P NMR spectroscopy all indicate the structure as shown in Eq. (1). That the iridium is bonded to nitrogen in the ring is clearest from the ^{13}C NMR spectrum – there is no resonance attributable to a carbon atom directly bound to iridium (a doublet of triplets due to P–C coupling would be expected) therefore pyrrole must be bound to iridium via the nitrogen atom. These complexes were also characterized by IR spectroscopy. There is no N–H stretch in the IR spectra of any of these complexes. Typically, the amine N–H stretch appears in the 3200–3600 cm^{-1} region of the IR spectrum. For pyrrole, the N–H stretch appears at 3530 cm^{-1} (CH_2Cl_2) but is completely absent in the pyrrole–iridium complex, **2a**. An Ir–H stretch is observed at 2221 cm^{-1} (CH_2Cl_2). This is in line with Ir–H stretching frequencies observed for similar hydrido amido compounds [24].

Although spectroscopy made it clear that the N–H bond was being added to iridium in all cases, it was decided to establish this beyond any doubt by examining the product from the reaction with 3-methylindole, complex **2c**. The point of attachment of the ring to iridium with respect to the methyl group would unequivocally establish the position of the nitrogen atom and the presence or absence of an Ir–N bond. As the information presented below concerning the X-ray crystal structure shows, the point of attachment of iridium to the indole ring can only be the N.

2.2. Solid state structures

Single crystal X-ray structures were obtained for **2a**, **2b** and **2c**. The thermal ellipsoid plot of complex **2a** is depicted in Fig. 1, that of **2b** is shown in Fig. 2 and that of **2c** is shown in Fig. 3. The solid-state structure of all compounds confirmed the structure assigned by spectroscopy: an octahedral arrangement of ligands about the iridium with the three PMe_3 groups in a meridional arrangement and the nitrogen ring group trans to PMe_3. The Ir–N distances of the three complexes are the same within error and average 2.1 Å. This value is in line with those found in other crystallographically characterized Ir–N(sp^2) compounds [20] and shorter than Ir–N(sp^3) compounds [6,24]. The relatively short Ir–P distance for the PMe_3 trans to the heterocyclic nitrogen (2.26–2.28 Å) compared to those for the mutually trans PMe_3 ligands (2.32–2.34 Å) shows that pyrrole and indole (unlike phenyl where the same values are 2.339(2) Å versus 2.307(2) Å and 2.306(2) Å [26]) does not exert as strong a trans influence as phenyl and is weaker than PMe_3. The Ir–Cl bond distances range from 2.48–2.50 Å.

2.3. Solution structures

The NMR spectra of compounds **2a**–**2c** show evidence for hindered rotation about the Ir–N bond in solution. This is most clearly

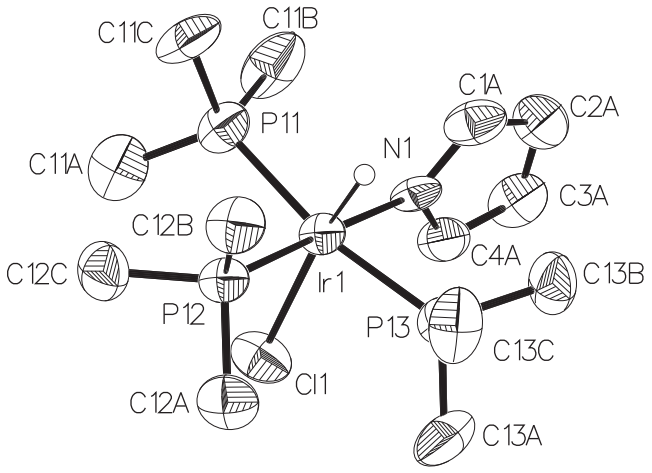
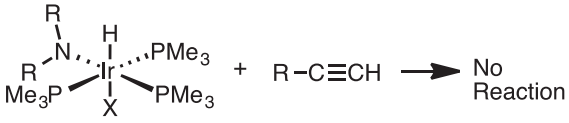


Fig. 1. X-ray Crystal Structure of one of the independent molecules of Ir($N_1C_4H_4$)(H)(PMe_3)$_3$(Cl) (**2a**). Ellipsoids are drawn at the 50% probability level and hydrogen atoms (with the exception of the iridium hydride) are omitted for clarity. Important bond distances: Ir1–N1, 2.109(10); Ir1–P11, 2.333(4); Ir1–P12, 2.280(3); Ir1–P13, 2.332(4); Ir1–Cl1, 2.502(3); Ir2–N2, 2.093(11); Ir2–P21, 2.323(4); Ir2–P22, 2.260(4); Ir2–P23, 2.335(4); Ir2–Cl2, 2.483(4); Ir3–N3, 2.106(10); Ir3–P31, 2.323(4); Ir3–P32, 2.276(4); Ir3–P33, 2.319(4); Ir3–Cl3, 2.497(4); Ir4–N4, 2.088(12); Ir4–P41, 2.321(5); Ir4–P42, 2.272(4); Ir4–P43, 2.334(4); Ir4–Cl4, 2.498(4) Å.

seen in the case of the pyrrole compound, **2a**, where the four pyrrole protons in the ^{1}H NMR spectrum and the four pyrrole carbons in the ^{13}C NMR spectrum are all inequivalent. Neither ^{1}H nor ^{13}C spectra of toluene-d8 solutions heated over 373 K showed evidence for rotation. DFT [29] calculation of the Ir–N rotational barrier predicts a large barrier – over 90 kJ/mol – for rotation about the Ir–N bond. From examination of some of the high energy conformations needed for rotation, it is clear that there is significant distortion of bonds to allow the pyrrole ring to rotate past the flanking PMe_3 groups. This distortion may account for the asymmetry in the energy plot in the Supplementary material since it is unlikely that these distorted structures are ever able to fully minimize and so different calculations starting from different angles give slightly different energies. Moreover, for the indole compounds the barrier is much higher and could not even be calculated. Because of the asymmetry of the indole system, there are two different conformations possible: the first with the C_6 ring on the same side of the Ir as the hydride ligand and the second with the C_6 ring on the same side of the iridium as the chloride ligand. The solid-state structures for **2b** and **2c** are those with the C_6 ring on the same side as hydride. The solution ^{1}H and ^{13}C NMR spectra would indicate that there is only one conformation in solution and so we conclude that the solid state structure persists in solution due to hindered rotation about the Ir–N bond and it is this conformation with the C_6 ring on the same side as of the iridium as hydride which minimizes unfavorable interactions between Cl and the hydrogens on the C_6 ring.

2.4. Reactions at the metal

Having fully characterized these complexes and established oxidative addition of the N–H bond, an exploration of the reactivity of these complexes was undertaken. An NMR study of the reaction of these hydrido amido complexes with a series of alkynes was conducted. Alkynes were used because previous studies in our group showed that vinyl complexes formed from insertion into either Ir–H or Ir–C bonds were stable enough to be isolated and structurally characterized [26,28,30]. For compounds **2a**–**2f** described in this study, unfortunately, no reaction occurred at the metal center with any of the alkynes (Eq. (4)) at room temperature over several days as monitored by ^{1}H NMR spectroscopy.



(4)

2b, $NR_2 = NC_8H_6$; X=Cl
2d, $NR_2 = N_2C_7H_6$; X=Cl
2g, $NR_2 = NC_8H_6$; X=I

Our previous experience showed that the analogous system generated by oxidative addition of catecholborane underwent chloride loss in even low polarity solvents allowing for alkyne insertion into the iridium–hydride bond [31]. On the other hand, the phenyl iridium hydride complexes formed by C–H addition of benzene did *not* undergo spontaneous Cl^- dissociation but did undergo reactions with alkynes upon removal of the chloride with Tl^+ [26,28].

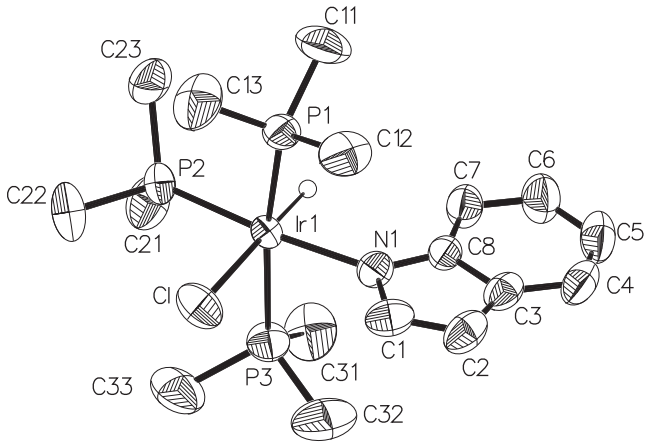


Fig. 2. X-ray Crystal structure of Ir(NC_8H_6)(H)(PMe_3)$_3$(Cl) (**2b**). Ellipsoids are drawn at the 50% probability level and hydrogen atoms (with the exception of the iridium hydride) are omitted for clarity. Important bond distances: Ir1–N1, 2.128(4); Ir1–P1, 2.3264(14); Ir1–P2, 2.2699(13); Ir1–P3, 2.337(14); and Ir1–Cl, 2.4914(13) Å.

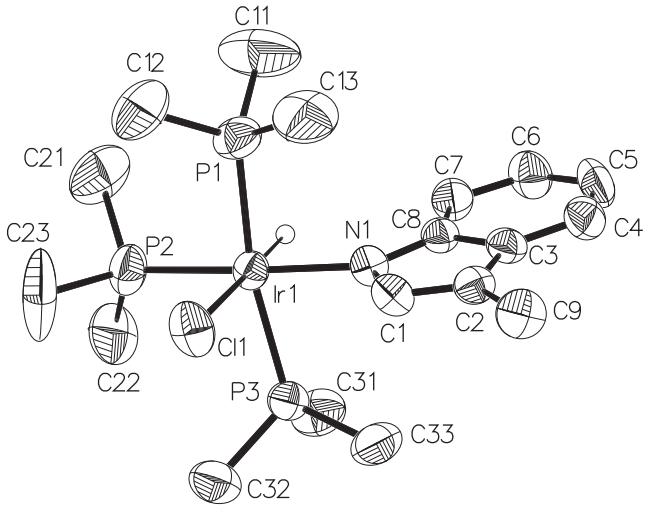
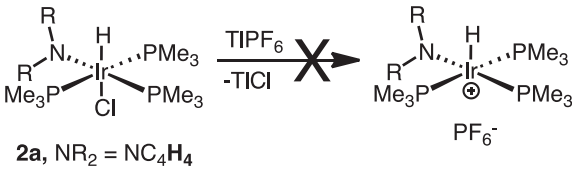


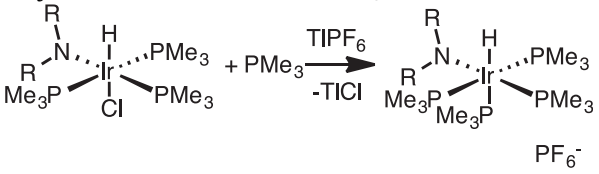
Fig. 3. Structure of Ir(NC_9H_8)(H)(PMe_3)$_3$(Cl) product, **2c**. Ellipsoids are drawn at the 50% probability level and hydrogen atoms (with the exception of the iridium hydride) are omitted for clarity. Important bond distances: Ir1–N1, 2.112(5); Ir1–P1, 2.340(2); Ir1–P2, 2.272(2); Ir1–P3, 2.3260(18); Ir1–Cl1, 2.5070(17) Å.



(5)

2a, $NR_2 = NC_4\mathbf{H_4}$
2b, $NR_2 = NC_8\mathbf{H_6}$
2c, $NR_2 = NC_6\mathbf{H_6}$

Therefore, reactions between these amido complexes and Tl^+ in the presence of alkynes were investigated in hopes that the alkyne could trap the 16e– species generated upon loss of Cl^- if it is formed. The reactions were very sluggish (days to weeks at moderate temperatures) and did not proceed cleanly. It was not possible to identify a specific product as decomposition reactions set in before the reactions could proceed very far. The carbazole complex (**2e**), for example, did not react with dimethylacetylenedicarboxylate (DMAD) but underwent reductive elimination of carbazole. Only in the presence of the strong sigma donor PMe_3 did abstraction of the chloride by Tl^+ occur leading to isolable products (Eq. (6)). While these compounds were not isolated, the ^1H NMR resonance for the hydride (as well as other features of the spectra) was unambiguously diagnostic for the formation of the tetrakis PMe_3 complex displaying a very large trans P–H coupling constant and 3 smaller cis P–H coupling constants. The reactions were still very slow for the reaction with PMe_3.



(6)

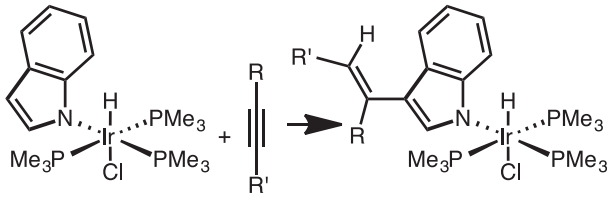
2a, $NR_2 = NC_4H_4$
2b, $NR_2 = NC_8H_6$
2f, $NR_2 = NC_6H_6$

3a, $NR_2 = NC_4H_4$
3b, $NR_2 = NC_8H_6$
3f, $NR_2 = NC_6H_6$

The pyrrole complex, **2a**, reacted to completion only after five days at room temperature. The analogous reaction of the indole complex, **2b**, was still incomplete after one week at room temperature. However, the anilido complex, **2f**, reacted much faster than the heterocyclic amido complexes. The reaction proceeded with significant formation of the tetrakis(phosphine) complex (**3f**) in minutes and to completion in two days. So the reaction of **2f** with PMe_3 shows that it is may be possible to abstract the chloride and open up a coordination site and trap it. However, reactions with alkynes may be too slow to lead to product formation compared with decomposition pathways.

2.5. Reaction at the indole ring

The lack of reactivity of alkynes at the metal center was a disappointment. However, when the substrate was the electron deficient acetylene DMAD and the indole complex, **2b**, was used, an unusual reaction did occur at the indole ring. The indole complex, **2b**, reacted with DMAD (as well as but-3-yn-2-one) at the indole ring at room temperature to give **4a**, **b** (Eq. (7)). Free indole does not react with these alkynes under the same conditions. Usually, a Lewis acid is required for addition



(7)

4a R = R' = CO_2CH_3
4b R = H; R' = $C(O)CH_3$

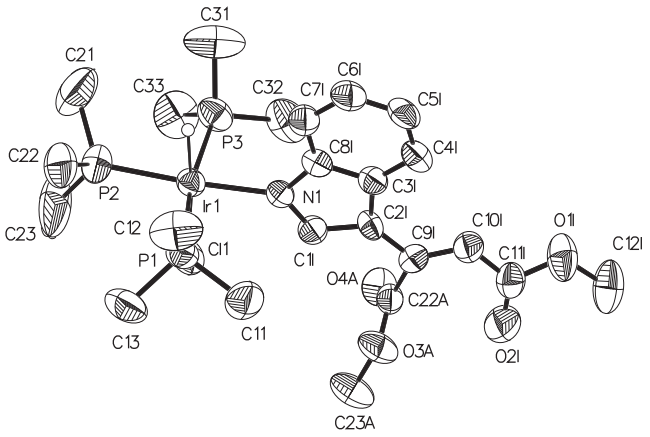


Fig. 4. X-ray structure of the product of Michael addition of **2b** to dimethylacetylenedicarboxylate, DMAD, **4a**. Ellipsoids are drawn at the 50% probability level and hydrogen atoms with the exception of the Ir–H, are omitted for clarity. Important bond distances: Ir1–N1, 2.135(8); Ir1–P1, 2.340(3); Ir1–P2, 2.263(3); Ir1–P3, 2.343(3); and Ir1–Cl1, 2.479(3) Å.

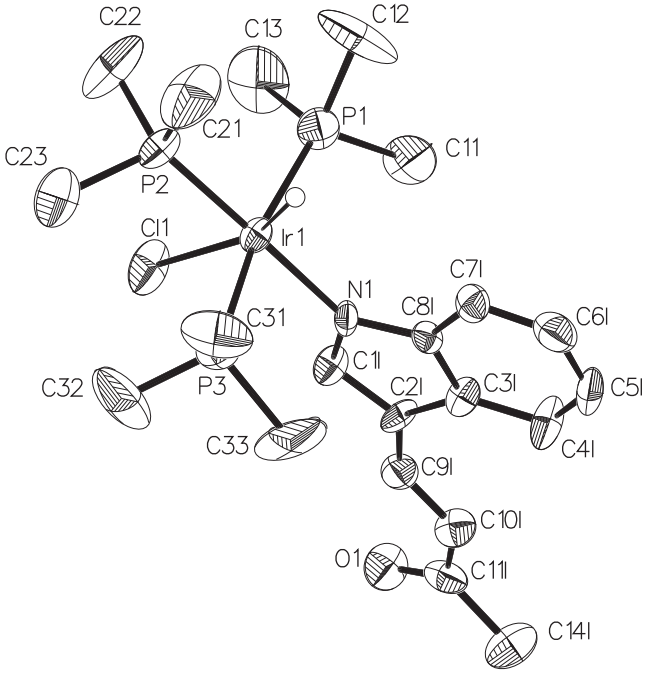


Fig. 5. X-ray structure of the product of Michael addition of **2b** to but-3-yn-2-one, **4b**. Ellipsoids are drawn at the 50% probability level and hydrogen atoms (with the exception of the iridium hydride) are omitted for clarity. Important bond distances: Ir1–N1, 2.135(7), Ir1–P1, 2.335(4); Ir1–P2, 2.270(3); Ir1–P3, 2.333(3) and Ir1–Cl1, 2.508(2) Å.

to the three position of indole [32]. Therefore, the coordinated indole ring in **2b** must be more electron rich than in uncoordinated indole providing a more activated ring for the Michael-type addition. This is consistent with a report by Trogler and Cowan that the anilide ligand in $PtH(NHPh)(PEt_3)_3$ displayed chemistry consistent with a high electron density at nitrogen [33]. **4a** was fully characterized and, although **4b** was only characterized by single-crystal X-ray diffraction, its formation clearly underscores the electron-rich enhancement of the indole ring. The solid state structures of **4a** and **4b** (Figs. 4 and 5) show an octahedral arrangement of ligands about the iridium with the three PMe_3 groups in a meridional arrangement and a vinyl group attached to the indole ring at the 3-position.

Structural parameters are little changed in the iridium core upon Michael addition to the alkyne. In the case of **4a**, the X-ray structure showed significant disorder of the carbomethoxy group closest to the indole ring. The disorder was treated with a two-site model that approximates rotation about the C9I–C22A bond and the occupancies refined to a 57/43 split between the two positions. Only one of the apparent rotamers is shown in Fig. 4.

3. Conclusions

The electron-rich system [Ir(COD)(PMe_3)$_3$]Cl continues to be a valuable one for the study of oxidative addition reactions of various element-H bonds. In this report, the oxidative addition reactions of N–H bonds was demonstrated but, unfortunately, further reaction chemistry that could be exploited to develop catalytic systems for the addition of N–H bonds across alkynes or alkenes was not realized. The activation of the indole ring toward the Michael reaction with activated alkynes was an unusual finding but, again, not one that could be utilized in a catalytic scheme. Nevertheless, this body of information contributes to the understanding of N–H additions and the chemistry of iridium trimethylphosphine complexes.

4. Experimental

4.1. General

All reactions were carried out under an atmosphere of prepurified nitrogen. All solvents were dried by the appropriate procedure and distilled under a nitrogen atmosphere prior to use. Conventional glass vessels were used and standard Schlenk line techniques were employed. $IrCl_3{\cdot}3H_2O$ was purchased from Johnson Matthey.

The ^{1}H NMR spectra were obtained on either a Bruker WP270SY or a WP200SY instrument and referenced either to solvent resonance or TMS. The ^{31}P NMR spectra were obtained on Bruker WP81SY instrument and referenced either to an internal or external standard of 85% H3PO4. ^{13}C NMR spectra were obtained on a Bruker WP200SY (at 50 MHz), Bruker WP270SY (at 67 MHz) or a Varian Unity 400 instrument (at 100 MHz) and referenced to solvent resonance. FT-IR spectra were obtained on a Nicolet 5DX W/C instrument. Elemental analyses were performed by Atlantic Microlab Inc.

Carbazole, indole, 3-methylindole, and 7-azaindole, aniline and pyrrole were obtained from Aldrich Chemical Company. Aniline and pyrrole were further purified via distillation from barium oxide (BaO). All other chemicals were of reagent grade and used without further purification. [Ir(COD)(PMe_3)$_3$]Cl [22], Ir(COD)(PMe_3)$_2$Cl [34] and [Ir(COD)(PMe_3)$_3$]BF_4 [22] were synthesized by the literature methods. [Ir(COD)(PMe_3)$_3$]X, where X = I (**1b**) or BPh_4 (**1d**), were prepared via metathetical reactions between Ir(COD)(PMe_3)$_3$]Cl and potassium iodide or sodium tetraphenylborate, respectively.

4.1.1. Synthesis of Ir(COD)(PMe_3)$_3$]BPh_4. (**1d**)

0.300 g (0.532 mmol) of [Ir(COD)(PMe_3)$_3$]Cl (**1a**) was charged into a 25 mL Erlenmeyer flask and dissolved in 5.0 mL of distilled water. In a second 25 mL Erlenmeyer, 0.364 g (2 eq) of sodium tetraphenylborate was dissolved in 5.0 mL of distilled water. The [Ir(COD)(PMe_3)$_3$]Cl (**1a**) solution was then introduced into the sodium tetraphenylborate solution. White solids immediately precipitate out of solution. The solids were filtered in air and dried in vacuo to yield 0.360 g (0.425 mmol) of Ir(COD)(PMe_3)$_3$]BPh_4 (**1d**) (80% based on amount of [Ir(COD)(PMe_3)$_3$]Cl) identified on the basis of the following data:

^{1}H NMR ($CDCl_3$): δ 1.33–1.37 (m, 27H, PMe_3 ligands), 2.22–2.31 (m, 8H, COD), 3.10 (br s, 4H, COD), 6.84–6.91 (m, 4H, para protons, phenyl rings), 6.99–7.06 (m, 8H, meta protons, phenyl rings), 7.39 (bm, 8H, ortho protons, phenyl rings).

The corresponding iodide salt **1b** was prepared in an analogous manner and identified on the basis of the following data:

^{1}H NMR ($CDCl_3$): δ 1.63–1.63 (m, 27H, PMe_3 ligands), 2.49–2.19 (m, 8H, COD), 3.22 (br s, 4H, COD).

4.1.2. General procedure for addition of N–H compounds to [Ir(COD)(PMe_3)$_3$]Cl

A 10.0 mL one-necked side-armed flask, equipped with a magnetic stirrer and a septum, was charged with the appropriate amount of [Ir(COD)(PMe_3)$_3$]Cl (**1a**) under N_2 in a dry box. The flask was then connected to a double manifold (vacuum/nitrogen) Schlenk line and a slight excess of the N–H compound was added by syringe. If the N–H compound were a solid, it was added in the dry box along with **1a** and 4.0 mL of mesitylene was added by syringe. The flask was then fitted with a reflux column equipped with a nitrogen inlet and connected to the Schlenk line. The light-yellow slurry was stirred magnetically and heated to reflux. After 16 h at reflux, the solutions were homogeneous and an appropriate workup was performed, usually involving isolation and recrystallization of solids. The solids were then dried under reduced pressure and analyzed by NMR spectroscopies, C,H analyses and, in several cases, by X-ray crystallography.

4.1.3. Synthesis of Ir(NC_4H_4)(H)(PMe_3)$_3$(Cl) (**2a**)

The general procedure was followed using 0.420 g (0.745 mmol) of [Ir(COD)(PMe_3)$_3$]Cl (**1a**) and 2.00 mL of dry pyrrole. The pyrrole was removed under reduced pressure and the resulting oil was treated with ~5.0 mL of dry THF and stirred for 5 min. The solids observed were filtered off and the solution was concentrated to ~0.5 mL. 2.0 mL of dry pentane was used to crystallize light green solids. The solids were dried under reduced pressure to yield 0.360 g (0.691 mmol) of Ir(NC_4H_4)(H)(PMe_3)$_3$(Cl), **2a**, (93% based on amount of [Ir(COD)(PMe_3)$_3$]Cl) identified on the basis of the following data:

Anal. Calc. (Found) for $C_{13}H_{32}ClP_3IrN$: C, 29.86 (29.92); H, 6.17 (6.19).

^{1}H NMR ($CDCl_3$): δ −22.12 (dt, J_{P-H} = 17 Hz, 15 Hz, 1H, Ir–H), 1.28 (t, J_{P-H} = 3.6 Hz, 18H, trans PMe_3),1.65 (d, J_{P-H} = 9.4 Hz, 9H, cis PMe_3), 5.98–5.99 (m, 2H, H(3) and H(4), NC_4H_4), 6.39 (m, 1H, H(5), NC_4H_4), 7.18 (m, 1H, H(2), NC_4H_4).

^{31}P NMR ($CDCl_3$): δ −50.85 (br t, 1P, cis PMe_3), −34.02 (d, J_{P-P} = 42 Hz, 2P, trans PMe_3). ^{13}C NMR ($CDCl_3$): δ 15.88 (t, J_{C-P} = 18.3 Hz, 6C, trans PMe_3), 20.48 (d, J_{C-P} = 37 Hz, 3C, cis PMe_3), 104.2 (s, 1C, NC_4H_4), 106.9 (s, 1C, NC_4H_4), 128.6 (s, 1C, NC_4H_4), 135.1 (s, 1C, NC_4H_4).

4.1.4. Synthesis of Ir(NC_8H_6)(H)(PMe_3)$_3$(Cl) (**2b**)

The general procedure was followed with 1.00 g (1.78 mmol) of [Ir(COD)(PMe_3)$_3$]Cl (**1a**) and 0.208 g (1.78 mmol) of indole under in 4.0 mL of mesitylene. After reflux, slightly pink solids were filtered, washed with pentane and dried under reduced pressure to yield 0.695 g (1.21 mmol) of Ir(NC_8H_6)(H)(PMe_3)$_3$(Cl), (**2b**). (68% based on amount of **1a**) identified on the basis of the following data:

Anal. Calc. (Found) for $C_{17}H_{34}ClP_3IrN$: C, 35.63 (35.36); H, 5.98 (5.85).

^{1}H NMR (Acetone-d_6): δ −20.86 (dt, J_{P-H} = 16 Hz, 14 Hz, 1H, Ir–H), 1.15 (t, J_{P-H} = 3.6 Hz, 18H, trans PMe_3), 1.79 (d, J_{P-H} = 9.8 Hz, 9H, cis PMe_3), 6.24 (d, J_{H-H} = 1.2 Hz, 1H, H(3), NC_8H_6), 6.67 (dt, J = 7.7 Hz, 0.9 Hz, 1H, H(5), NC_8H_6), 6.78–6.84 (m, 1H, H(6), NC_8H_6), 7.34 (dd, J = 7.7 Hz, 0.6 Hz, 1H, H(7), NC_8H_6), 7.43 (dd, J = 8.3 Hz, 0.6 Hz, 1H, H(4), NC_8H_6), 8.04–8.03 (m, 1H, H(2), NC_8H_6). ^{31}P NMR ($CDCl_3$): δ −49.44 (br t, J_{P-P} = 22 Hz, 1P, cis PMe_3), −33.70 (d, J_{P-P} = 21 Hz, 2P, trans PMe_3).

^{13}C NMR (Acetone-d_6): δ 16.18 (t, J_{C-P} = 18.5 Hz, 6C, trans PMe_3), 20.20 (d, J_{C-P} = 38 Hz, 3C, cis PMe_3), 99.14 (s, 1C, C(3), NC_8H_6), 116.6 (s, 1C, NC_8H_6), 117.1 (s, 1C, NC_8H_6), 118.0 (s, 1C, NC_8H_6), 120.0 (s, 1C, NC_8H_6), 137.4 (s, 1C, C(2), NC_8H_6).

*4.1.5. Synthesis of Ir(NC_9H_8)(H)(PMe_3)$_3$(Cl) (**2c**)*

The general procedure was followed with 0.250 g (0.444 mmol) of [Ir(COD)(PMe_3)$_3$]Cl (**1a**) and 0.064 g (0.488 mmol, 1.1 eq) of 3-methylindole in 3.00 mL of mesitylene. White solids were filtered, washed with pentane and dried under reduced pressure to yield 0.161 g (0.274 mmol) of Ir(NC_9H_8)(H)(PMe_3)$_3$(Cl), (**2c**), (62% based on amount of [Ir(COD)(PMe_3)$_3$]Cl) identified on the basis of the following data:

Anal. Calc. (Found) for $C_{18}H_{36}ClP_3IrN$: C, 36.82 (36.86); H, 6.18 (6.22).

^{1}H NMR (Acetone-d_6): δ −20.92 (q, J_{P-H} = 16 Hz, 1H, Ir–H), 1.14 (t, J_{P-H} = 3.6 Hz, 18H, trans PMe_3), 1.78 (d, J_{P-H} = 9.8 Hz, 9H, cis PMe_3), 2.31 (s, 3H, 3-methyl), 6.63–6.84 (m, 2H, H(5) and H(6), NC_9H_8), 7.25–7.35 (m, 2H, H(4) and H(7), NC_9H_8), 7.81 (s, 1H, H(2), NC_9H_8). ^{31}P NMR ($CDCl_3$): δ −49.00 (br t, J_{P-P} = 22 Hz, 1P, cis PMe_3), −33.42 (d, J_{P-P} = 21 Hz, 2P, trans PMe_3). ^{13}C NMR (CD_2Cl_2): δ 10.32 (s, 1C, 3-methyl), 16.44 (t, J_{C-P} = 18.3 Hz, 6C, trans PMe_3), 20.47 (d, J_{C-P} = 38 Hz, 3C, cis PMe_3), 115.4 (s, 1C, NC_9H_8), 116.6 (s, 1C, NC_9H_8), 117.6 (s, 1C, NC_9H_8), 117.6 (s, 1C, NC_9H_8), 135.3 (s, 1C, C(2), NC_9H_8).

*4.1.6. Synthesis of Ir($N_2C_7H_5$)(H)(PMe_3)$_3$(Cl) (**2d**)*

The general procedure was followed with 0.250 g (0.444 mmol) of [Ir(COD)(PMe_3)$_3$]Cl (**1a**) and 0.058 g (0.491 mmol, 1.1 eq) of 7-azaindole in 3.00 mL of mesitylene. After 15 h at reflux, white solids were filtered, washed with pentane and dried under reduced pressure to yield 0.132 g (0.230 mmol) of Ir($N_2C_7H_5$)(H)(PMe_3)$_3$(Cl) (52% based on amount of [Ir(COD)(PMe_3)$_3$]Cl) identified on the basis of the following data:

Anal. Calc. (Found) for $C_{16}H_{33}ClP_3IrN_2$: C, 33.48 (33.25); H, 5.79 (5.84).

^{1}H NMR ($CDCl_3$): δ −20.66 (q, J_{P-H} = 16 Hz, 14 Hz, 1H, Ir–H), 1.14 (t, J_{P-H} = 3.5 Hz, 18H, trans PMe_3), 1.72 (d, J_{P-H} = 9.6 Hz, 9H, cis PMe_3), 6.36 (d, J_{H-H} = 2.9 Hz, 1H, H(3), $N_2C_7H_5$), 6.74 (dd, J_{H-H} = 7.4 Hz, 4.6 Hz, 1H, H(5), $N_2C_7H_5$), 7.75 (dd, J_{H-H} = 7.1 Hz, 1.1 Hz, 1H, H(2), $N_2C_7H_5$), 8.19–8.23 (m, 2H, H(4) and H(6), $N_2C_7H_5$).

^{31}P NMR ($CDCl_3$): δ −49.09 (br t, J_{P-P} = 22 Hz, 1P, cis PMe_3), −33.82 (d, J_{P-P} = 22 Hz, 2P, trans PMe_3). ^{13}C NMR ($CDCl_3$): δ 16.44 (t, J_{C-P} = 18.0 Hz, 6C, trans PMe_3), 20.16 (d, J_{C-P} = 38 Hz, 3C, cis PMe_3), 97.87 (s, 1C, C(3), $N_2C_7H_5$), 112.3 (s, 1C, C(4), $N_2C_7H_5$), 126.6 (s, 1C, C(5), $N_2C_7H_5$), 138.0 (s, 1C, C(6), $N_2C_7H_5$), 139.9 (s, 1C, C(2), $N_2C_7H_5$).

*4.1.7. Synthesis of Ir($NC_{12}H_8$)(H)(PMe_3)$_3$(Cl) (**2e**)*

The general procedure was followed with 0.500 g (0.887 mmol) of [Ir(COD)(PMe_3)$_3$]Cl (**1a**) and 0.164 g (0.976 mmol, 1.1 eq) of carbazole in 5.00 mL of mesitylene. After 24 h at reflux, white solids were filtered and then dissolved in CH_2Cl_2 (0.5 mL). Diethyl ether (3.0 mL) was then introduced to recrystallize solids. The off-white solids were filtered and dried under reduced pressure to yield 0.285 g (0.458 mmol) of Ir($NC_{12}H_8$)(H)(PMe_3)$_3$(Cl) (52% based on amount of [Ir(COD)(PMe_3)$_3$]Cl) identified on the basis of the following data:

Anal. Calc. (Found) for $C_{21}H_{36}ClP_3IrN$: C, 40.44 (40.34); H, 5.82 (5.85).

^{1}H NMR (d_6-acetone): δ −21.06 (q, J_{P-H} = 15 Hz, 1H, Ir–H), 1.16 (t, J_{P-H} = 3.7 Hz, 18H, trans PMe_3), 1.82 (d, J_{P-H} = 9.9 Hz, 9H, cis PMe_3), 6.82–6.87 (m, 2H, $NC_{12}H_8$), 7.09–7.23 (m, 2H, $NC_{12}H_8$), 7.86 (d, JH–H = 8.4 Hz, 1H, $NC_{12}H_8$), 7.91–7.95 (m, 2H, $NC_{12}H_8$), 9.34 (d, JH–H = 8.5 Hz, 1H, $NC_{12}H_8$). ^{31}P NMR (d_6-acetone): δ −48.22 (br t, J_{P-P} = 23 Hz, 1P, cis PMe_3), −33.77 (d, J_{P-P} = 23 Hz, 2P, trans PMe_3).

*4.1.8. Synthesis of Ir(NHC_6H_5)(H)(PMe_3)$_3$(Cl) (**2f**)*

The general procedure was followed with 0.478 g (0.848 mmol) of [Ir(COD)(PMe_3)$_3$]Cl (**1a**) and 160 μL (1.70 mmol, 2 eq) of aniline in 6.00 mL of mesitylene. After 6 h at 75° (not reflux) off-white solids were filtered and washed with copious amounts of pentane and then ether (3 × 5.00 mL). The off-white solids were dried under reduced pressure to yield 0.237 g (0.432 mmol) of Ir(NHC_6H_5)(H)(PMe_3)$_3$(Cl), (**2f**), (51% based on amount of [Ir(COD)(PMe_3)$_3$]Cl) identified on the basis of the following data:

Analysis. Calc.(found) for $C_{15}H_{34}ClP_3IrN$: C, 32.78 (32.23); H, 6.24 (6.21).

^{1}H NMR (d5-pyridine): δ −21.62 (dt, J_{P-H} = 20 Hz, 14 Hz, 1H, Ir–H), 1.45 (t, J_{P-H} = 3.7 Hz, 18H, trans PMe_3), 1.57 (d, J_{P-H} = 9.3 Hz, 9H, cis PMe_3), 2.8 (br s, 1H, NH), 6.31 (t, J_{H-H} = 7 Hz, 1H, phenyl), 6.51 (br d, JH–H = 7.8 Hz, 1H, phenyl), 6.72 (br d, J_{H-H} = 7.8 Hz, 1H, phenyl), 7.03 (br t, JH–H = 7.5 Hz, 1H, phenyl), 7.22 (m, 1H, phenyl). ^{13}C NMR (d5-pyridine): δ 16.2 (t, J_{C-P} = 18.3 Hz, 6C, trans PMe_3), 20.62 (d, J_{C-P} = 36.6 Hz, 3C, cis PMe_3), 113.2 (s, 1C, phenyl), 116.1 (s, 1C, phenyl), 116.2 (s, 1C, phenyl), 129.4 (s, 1C, phenyl), 129.8 (s, 1C, phenyl), 158.9 (s, 1C, phenyl).

*4.1.9. Synthesis of Ir(NC_8H_6)(H)(PMe_3)$_3$(I) (**2g**)*

The general procedure was followed with 0.200 g (0.305 mmol) [Ir(COD)(PMe_3)$_3$]I (**1b**)and 0.040 g (0.336 mmol, 1.1 eq) indole in 4.0 mL mesitylene and identified on the basis of the following data:

^{1}H NMR (d_6-acetone): δ −18.16 (dt, J_{P-H} = 19 Hz, 14 Hz, 1H, Ir–H), 1.29 (t, J_{P-H} = 3.7 Hz, 18H, trans PMe_3), 1.92 (d, J_{P-H} = 9.7 Hz, 9H, cis PMe_3), 6.19 (d, 1H, H(3), NC_8H_6), 6.66 (dt, J = 7.5 Hz, 1H, H(5), NC_8H_6), 6.80–6.87 (m, 1H, H(6), NC_8H_6), 7.36 (d, J = 7.7 Hz, 1H, H(7), NC_8H_6), 7.54 (dd, J = 8.2 Hz, 1H, H(4), NC_8H_6), 8.32–8.29 (m, 1H, H(2), NC_8H_6). ^{31}P NMR (d_6-acetone): δ −56.40 (br t, J_{P-P} = 19 Hz, 1P, cis PMe_3), −42.64 (d, J_{P-P} = 21 Hz, 2P, trans PMe_3).

*4.1.10. Reaction of Ir(NC_8H_6)(H)(PMe_3)$_3$(Cl) (**2b**) and dimethyl acetylenedicarboxylate*

A 10 mL one-necked side-armed flask, equipped with a magnetic stirrer and a septum, was charged with 0.215 g (0.376 mmol) of Ir(NC_8H_6)(H)(PMe_3)$_3$(Cl) (**2b**) under N_2, in a dry box. The flask was then connected to a double manifold (vacuum/nitrogen) Schlenk line. 4.0 mL of dry acetone was added by syringe. 71.0 μl (0.564 mmol, 1.5 eq) of dimethyl acetylenedicarboxylate was then introduced into the yellow homogenous solution. The solution went orange and then gradually dark red. After 6 h, acetone was stripped off and deep orange solids were obtained. The solids were washed three times with copious amounts of pentane and dried in vacuo to yield 0.250 g (0.350 mmol) of **4a** (93% based on amount of Ir(NC_8H_6)(H)(PMe_3)$_3$(Cl)) identified on the basis of the following data:

Anal. Calc. (Found) for $C_{23}H_{40}ClP_3IrNO4$: C, 38.63 (38.44); H, 5.64 (5.51)

^{1}H NMR (CDCl3): δ −20.89(dt, J_{P-H} = 19 Hz, 14 Hz, 1H, Ir–H), 1.16 (t, J_{P-H} = 3.5 Hz, 18H, trans PMe_3), 1.73 (d, J_{P-H} = 9.6 Hz, 9H, cis PMe_3), 3.71 (s, 3H, OCH3), 4.00 (s, 3H, OCH3), 6.19 (s, 1H, vinyl proton), 7.02–7.06 (m, 2H, phenyl ring), 7.53–7.49 (m, 1H, phenyl ring), 7.73–7.70 (m, 1H, phenyl ring), 8.35 ppm(d, J_{H-H} = 1.4 Hz, 1H, H(2), indole ring). ^{31}P NMR (d_6-acetone): δ −48.35 (br t, J_{P-P} = 22 Hz, 1P, cis PMe_3), −34.71 (d, J_{P-P} = 22 Hz, 2P, trans PMe_3). ^{13}C NMR (d_6-acetone): δ 16.22 (t, J_{C-P} = 18.5 Hz, 6C, trans PMe_3), 20.29 (d, J_{C-P} = 37.3 Hz, 3C, cis PMe_3), 51.04 (s, 1C, OCH3), 52.32 (s, 1C, OCH3), 101.7 (s, 1C, phenyl), 117.5 (s, 1C, phenyl), 119.8 (s, 1C, phenyl), 120.0 (s, 1C, phenyl), 128.3 (s, 1C, C(2), indole ring), 144.6 (s, 1C, vinylcarbon).

Table 1
Experimental details for compounds characterized by X-ray crystallography.

Compound	**2a**	**2b**	**2c**	**4a**	**4b**
Deposition code	CCDC: 1034926	CCDC: 1034944	CCDC: 1034928	CCDC: 1034925	CCDC: 1034927
Empirical formula	$C_{13}H_{32}NP_3ClIr$	$C_{17}H_{34}NP_3ClIr$	$C_{18}H_{36}NP_3ClIr$	$C_{23}H_{40}NO_4P_3ClIr$	$C_{21}H_{38}NP_3ClOIr$
Formula weight	522.96	573.01	587.04	715.12	641.08
Temperature (K)	293	293	293	293.0	292.0
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a (Å)	9.602(3)	9.3166(3)	9.008(2)	13.136(3)	9.876(2)
b (Å)	21.093(7)	13.647(3)	26.098(4)	11.790(2)	15.470(3)
c (Å)	21.310(6)	18.288(4)	10.206(2)	19.937(4)	17.223(5)
α (°)	107.33(2)	90	90.00	90.00	90
β (°)	98.02(2)	95.74(2)	96.00(2)	102.35(3)	94.54(2)
γ (°)	90.57(3)	90	90.00	90.00	90
Volume (Å^3)	4074(2)	2313.4(10)	2386.2(8)	3016.3(10)	2623.1(11)
Z	8	4	4	4	4
ρ_{calc} (mg/mm^3)	1.705	1.645	1.634	1.575	1.623
μ (mm^{-1})	6.912	6.094	5.910	4.701	5.387
$F(000)$	2048.0	1128.0	1160.0	1424.0	12720
Crystal size (mm^3)	0.4 × 0.3 × 0.3	0.3 × 0.3 × 0.2	0.5 × 0.2 × 0.15	0.4 × 0.4 × 0.2	0.4 × 0.3 × 0.2
2Θ range	4.04° to 45.1°	3.74° to 50.1°	4.3° to 50.1°	4.04° to 50.1°	3.45° to 50.00°
Index ranges	$0 \leqslant h \leqslant 10$, $-22 \leqslant k \leqslant 22$ $-22 \leqslant l \leqslant 22$	$0 \leqslant h \leqslant 11$ $0 \leqslant k \leqslant 16$, $-21 \leqslant l \leqslant 21$	$-0 \leqslant h \leqslant 10$ $0 \leqslant k \leqslant 31$ $-12 \leqslant l \leqslant 12$	$0 \leqslant h \leqslant 15$ $0 \leqslant k \leqslant 10$ $-23 \leqslant l \leqslant 23$	$-11 \leqslant h \leqslant 11$, $0 \leqslant k \leqslant 18$ $0 \leqslant l \leqslant 20$
Reflections collected	11371	4367	4508	4579	4622
Independent reflections	10605 [R_{int} = 0.0446]	4097 [R_{int} = 0.0175]	4229 [R_{int} = 0.0450]	4395 [R_{int} = 0.0398]	4622 [R_{int} = 0.0000]
Data/restraints/parameters	10605/3/734	4097/1/209	4229/1/231	4395/1/312	4622/1/266
Goodness-of-fit (GOF) on F^2	1.064	1.053	1.0524	1.017	0.628
Final R indexes [$I \geqslant 2\sigma(I)$]	R_1 = 0.0538, wR_2 = 0.1342	R_1 = 0.0239, wR_2 = 0.0512	R_1 = 0.0348, wR_2 = 0.0776	R_1 = 0.0479, wR_2 = 0.1128	R_1 = 0.0384, wR_2 = 0.0638
Final R indexes [all data]	R_1 = 0.0737, wR_2 = 0.1488	R_1 = 0.0328, wR_2 = 0.0539	R_1 = 0.0488, wR_2 = 0.0843	R_1 = 0.0726, wR_2 = 0.1270	R_1 = 0.0974, wR_2 = 0.0715
Largest difference in peak/hole/ e Å^{-3}	1.84/−2.31	0.49/−0.44	0.92/−0.80	1.27/−2.77	0.76/−0.88

*General survey of reactions of **2a–f** with alkynes in the presence of Tl[PF$_6$].* In general, a screw-capped NMR tube equipped with a septum was charged with solid reagents in a glove box and sealed. via syringe, the solvent (CD_2Cl_2 or acetone-d_6) and the alkyne were introduced by syringe and the tubes were shaken vigorously to ensure complete mixing. The reactions were monitored by NMR spectroscopy over a period of several days.

*General survey of reactions of **2a–f** with PMe$_3$ in the presence of Tl[PF$_6$].* In general, a screw-capped NMR tube equipped with a septum was charged with solid reagents in a glove box and sealed via syringe, the solvent (CD_2Cl_2 or acetone-d_6) and PMe_3 were introduced by syringe and the tubes were shaken vigorously to ensure complete mixing. The reactions were monitored by NMR spectroscopy over a period of several days. No attempts were made to isolate the products.

*4.1.11. Reaction of Ir(NC$_4$H$_4$)(H)(PMe$_3$)$_3$(Cl) (**2a**) and trimethylphosphine in the presence of thallium hexafluorophosphate*

A screw-capped NMR tube, equipped with a septum, was charged with 0.010 g (0.0191 mmol) of $Ir(NC_4H_4)(H)(PMe_3)_3(Cl)$ (**2a**) and ~0.007 g (~0.0191 mmol) TlPF6 under N2 in a dry box and brought out. 0.50 mL CD2Cl2 was introduced by syringe followed by 2.00 μl (~0.0191 mmol) of PMe3. The tube was shaken vigorously and the reaction was monitored at room temperature for ~5 days. The reaction yielded the tetrakisphosphine complex, $[Ir(NC_4H_4)(H)(PMe_3)_4]PF6$ (**3a**), which was identified on the basis of the following data:

^{1}H NMR (CD2Cl2): δ −11.87 (dq, $J_{P-Htrans}$ = 145 Hz, J_{P-Hcis} = 18 Hz, 1H, Ir–H), 1.42 (t, J_{P-H} = 3.7 Hz, 18H, trans PMe_3), 1.76 (d, J_{P-H} = 7.4 Hz, 9H, cis PMe_3), 1.81 (d, J_{P-H} = 9.0 Hz, 9H, cis PMe_3) 5.92 (br s, 2H, NC_4H_4), 6.29 (br s, 1H, NC_4H_4), 6.47 (br s, 1H, NC_4H_4).

*4.1.12. Reaction of Ir(NC$_8$H$_6$)(H)(PMe$_3$)$_3$(Cl) (**2b**) and trimethylphosphine in the presence of thallium hexafluorophosphate*

The general procedure was followed with $Ir(NC_8H_6)(H)(PMe_3)_3$(Cl) (**2b**) 0.010 g (0.175 mmol), trimethylphosphine 1.80 μl (0.175 mmol) and TlPF6 0.006 g (0.175 mmol)

The reaction yielded the tetrakis(phosphine) complex, $[Ir(NC_8H_6)(H)(PMe_3)_4]PF6$ (**3b**) which was identified on the basis of the following data:

^{1}H NMR (CD2Cl2): δ −11.29 (dq, $J_{P-Htrans}$ = 142 Hz, J_{P-Hcis} = 18.6 Hz, 1H, Ir–H), 1.29 (t, J_{P-H} = 3.5 Hz, 18H, trans PMe_3), 1.84 (d, J_{P-H} = 7.2 Hz, 9H, cis PMe_3), 1.92 (d, J_{P-H} = 9.1 Hz, 9H, cis PMe_3) 6.47 (br s, 1H, NC_8H_6), 6.84–6.89 (br s, 2H, NC_8H_6), 7.06 (t, 1H, J_{H-H} = 7.7 Hz, NC_8H_6), 7.46–7.52 (m, 2H, NC8H6).

*4.1.13. Reaction of Ir(NHC$_6$H$_5$)(H)(PMe$_3$)$_3$(Cl) (**2f**) and trimethylphosphine in the presence of thallium hexafluorophosphate*

The general procedure was followed with 0.010 g (0.0182 mmol) of $Ir(NHC_6H_5)(H)(PMe_3)_3$(Cl) (**2f**) and 0.006 g (0.0182 mmol) TlPF6 2.00 μl (~0.0200 mmol, 1.1 eq) of PMe_3 and 0.50 mL d_6-acetone. The reaction yielded the tetrakis(phosphine) complex, $[Ir(NHC_6H_5)(H)(PMe_3)_4]PF6$ (**3c**), which was identified on the basis of the following data:

^{1}H NMR (d_6-acetone): δ −11.25 (dq, $J_{P-Htrans}$ = 140 Hz, J_{P-Hcis} = 18.5 Hz, 1H, Ir–H), 1.68 (t, J_{P-H} = 3.7 Hz, 18H, trans PMe_3), 1.73 (d, J_{P-H} = 7.9 Hz, 9H, cis PMe_3), 1.90 (d, J_{P-H} = 9.4 Hz, 9H, cis PMe_3) 6.04 (t, 1H, NHC_6H_5), 6.41–6.58 (m, 2H, NHC_6H_5), 6.70–6.93 (m, 2H, NHC_6H_5).

4.1.14. X-ray crystallography

X-ray crystal structures were obtained using a Nicolet R3 m/V diffractometer and a Mo Kα (λ = 0.71073 Å) radiation at 298 K. Data collected was more recently re-reduced using updated versions of SHELX [35] and graphics were created using the program

OLEX2 [36]. Hydrogen atoms attached to iridium were located on difference Fourier maps and positional parameters were refined with DFIX = −1.6 and Uiso = 1.5 IrUiso. Table 1 summarizes the important parameters for the crystal structures reported in this paper. Experimental parameters and .cif files for all structures discussed in this paper as well complete listings of bond lengths and angles may be found in the Supplementary information.

4.1.15. Computations

Full details of the DFT [29] calculations of the barrier to rotation about the Ir–N bond in compound **2a** may be found in the Supplementary information.

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Appendix A. Supplementary data

CCDC 1034925–1034928 and 1034944 contain the supplementary crystallographic data for all structures in this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2015.02.002. These data include MOL files and InChiKeys of the most important compounds described in this article.

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