

Anomalous reactivity of triphenylarsine and triarylphosphines of low basicity with $[\text{Ir}(\text{cod})(\text{py})_2][\text{PF}_6]$ and use of the complexes as precatalysts for imine hydrogenation

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Abstract

Reaction of $[\text{Ir}(\text{cod})(\text{py})_2][\text{PF}_6]$ with PPh_3 or $\text{P}(\text{C}_6\text{H}_4\text{-4-F})_3$ gives the bis(phosphine) derivative $[\text{Ir}(\text{cod})\text{L}_2][\text{PF}_6]$, but with the poorly basic phosphine $\text{P}(\text{C}_6\text{H}_4\text{-4-CF}_3)_3$ or AsPh_3 the mixed ligand complexes $[\text{Ir}(\text{cod})\text{L}(\text{py})][\text{PF}_6]$ are obtained. The synthesis of $[\text{Ir}(\text{AsPh}_3)(\text{cod})(\text{PPh}_3)][\text{CF}_3\text{SO}_3]$ is described, and the structures of this and of $[\text{Ir}(\text{AsPh}_3)(\text{cod})(\text{py})][\text{PF}_6]$ determined by X-ray crystallography. The use of some of the complexes as catalysts for imine hydrogenation is described.

Keywords: Iridium; Hydrogenation; X-ray diffraction; Imine; Arsine

1. Introduction

Cationic iridium complexes of the type $[\text{Ir}(\text{cod})(\text{L})(\text{PR}_3)]^+$ (cod = 1,5-cyclooctadiene, L = py, PR_3) have proved to be versatile homogeneous hydrogenation catalysts [1]. For example, Crabtree's catalyst $[\text{Ir}(\text{cod})(\text{py})(\text{PCy}_3)]^+$ catalyses the hydrogenation of sterically demanding alkenes such as 2,3-dimethyl-2-butene [2], α -pinene [3] and Δ^4 -3-ketosteroids [4]. Our interest in these complexes stems from our investigations into the homogeneous hydrogenation of imines [5]. We found that, whilst Crabtree's catalyst shows reasonable activity in the hydrogenation of *N*-benzylidene aniline (30 bar, 40°C), higher rates are achieved when the tricyclohexylphosphine is replaced with triphenylphosphine or tris(4-methoxyphenyl)phosphine. Even higher activities were noted with the bis(phosphine) systems $[\text{Ir}(\text{cod})(\text{PAryl})_2][\text{PF}_6]$ (Aryl = Ph, $\text{C}_6\text{H}_4\text{-4-OMe}$).

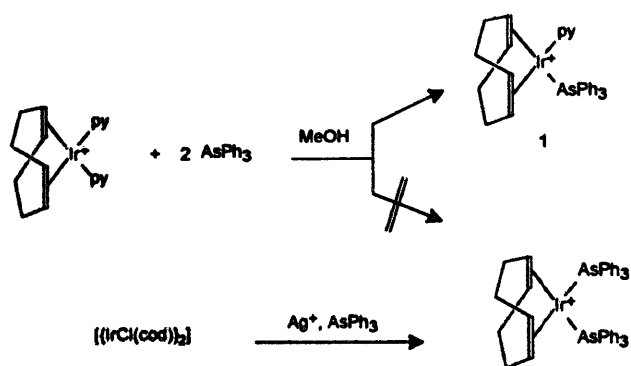
We were interested to see what effect the use of complexes with triphenylarsine and triarylphosphines of relatively low basicity would have on the rate of imine hydrogenation. We now report the synthesis of

$[\text{Ir}(\text{AsPh}_3)(\text{cod})(\text{py})][\text{PF}_6]$ (1) and highlight the difference in reactivity between AsPh_3 and PPh_3 . A similar difference in reactivity is also noted between $\text{P}(\text{C}_6\text{H}_4\text{-4-CF}_3)_3$ and PPh_3 in the synthesis of $[\text{Ir}(\text{cod})(\text{py})(\text{P}(\text{C}_6\text{H}_4\text{-4-CF}_3)_3)][\text{PF}_6]$ (2). The synthesis of $[\text{Ir}(\text{AsPh}_3)(\text{cod})(\text{PPh}_3)][\text{CF}_3\text{SO}_3]$ (5) is described and the single crystal X-ray structures of 1 and 5 are presented.

2. Results and discussion

Reaction of $[\text{Ir}(\text{cod})(\text{py})_2][\text{PF}_6]$ with two equivalents of triphenylphosphine gives $[\text{Ir}(\text{cod})(\text{PPh}_3)_2][\text{PF}_6]$ [6]. However, the analogous reaction of $[\text{Ir}(\text{cod})(\text{py})_2][\text{PF}_6]$ with triphenylarsine does not produce the previously reported $[\text{Ir}(\text{cod})(\text{AsPh}_3)_2]^+$ [7], but rather $[\text{Ir}(\text{AsPh}_3)(\text{cod})(\text{py})][\text{PF}_6]$ (1) (Scheme 1). $[\text{Ir}(\text{cod})(\text{AsPh}_3)_2]^+$ is readily prepared by the bridge fission reaction of $[\text{IrCl}(\text{cod})]_2$ with AsPh_3 and a silver(I) salt such as $\text{Ag}[\text{CF}_3\text{SO}_3]$. We have previously found [8] that the reaction of $[\text{Ir}(\text{cod})(\text{py})_2][\text{PF}_6]$ with two equivalents of (*S*)-PAMP (*S*-(2-methoxyphenyl)methylphenylphosphine) in methanol to form $[\text{Ir}(\text{cod})(\text{S-PAMP})_2][\text{PF}_6]$ proceeds via the formation of $[\text{Ir}(\text{cod})(\text{py})(\text{S-PAMP})][\text{PF}_6]$, although this could

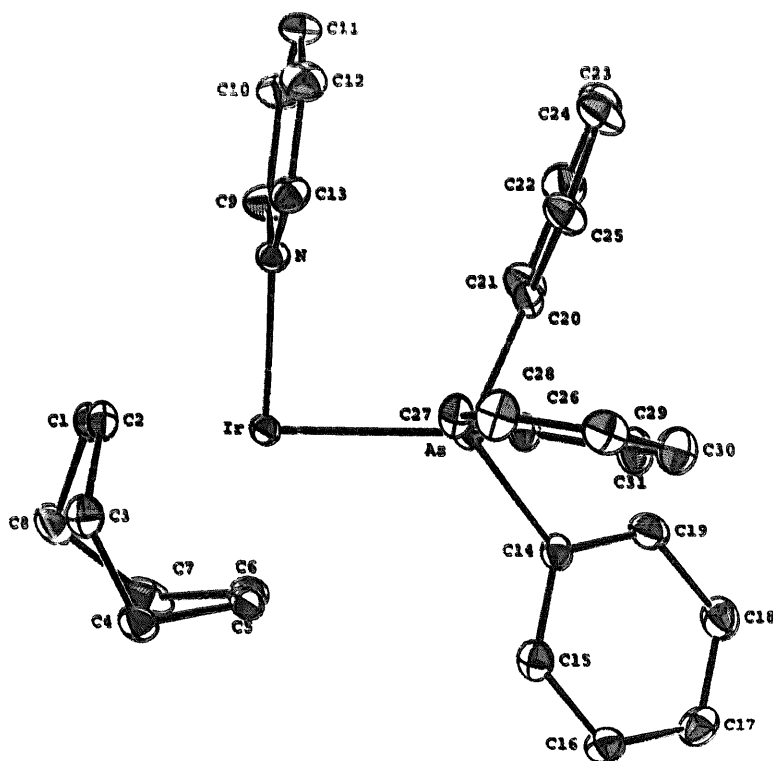
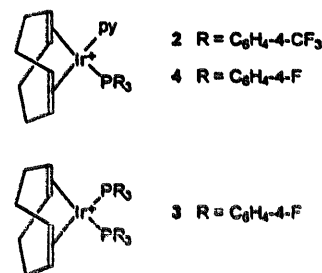
* Corresponding author.

Scheme 1. Synthesis of **1** and $[\text{Ir}(\text{cod})(\text{AsPh}_3)_2]^+$.

not be isolated pure. It is expected that similar intermediates would be formed in the cases of reactions with triphenylphosphine and triphenylarsine. Whilst in the case of the phosphine the N/P mixed ligand complex is labile and the bis(phosphine) compound is rapidly formed, the arsine As/N mixed ligand compound **1** appears to be kinetically inert. We conjectured that this difference might be due to solubility, as $[\text{Ir}(\text{AsPh}_3)(\text{cod})(\text{py})]^+$ precipitates rapidly from methanol. However, the triphenylphosphine analogue also has low solubility in methanol, but still reacts with an excess of phosphine to form the bis(phosphine) complex. Presumably, therefore, the reduced lability of **1** is due to the lower σ -basicity of the arsine compared with the phosphine.

Similarly, in the reaction of $[\text{Ir}(\text{cod})(\text{py})_2][\text{PF}_6]$ with two molar equivalents of tris(4-trifluorometh-

ylphenyl)phosphine in methanol, the mixed ligand complex **2** is formed. A trace of the bis(phosphine) product was observed in the FAB mass spectrum. The monosubstitution may be attributed to the low σ -basicity of the phosphine (calculated $\text{p}K_a = -1.52$ [9]). Tris(4-fluorophenyl)phosphine ($\text{p}K_a = 1.97$ [9]), whilst being less basic than triphenylphosphine ($\text{p}K_a = 2.73$ [9]), shows the same reactivity with $[\text{Ir}(\text{cod})(\text{py})_2][\text{PF}_6]$, $[\text{Ir}(\text{cod})\{\text{P}(\text{C}_6\text{H}_4\text{-4-F})_3\}_2][\text{PF}_6]$ (**3**) being produced in high yield [5]. The even more poorly basic phosphine $\text{P}(\text{C}_6\text{F}_5)_3$ does not react with $[\text{Ir}(\text{cod})(\text{py})_2]^+$. We have previously shown that very bulky phosphines react with $[\text{Ir}(\text{cod})(\text{py})_2]^+$ to give $[\text{Ir}(\text{cod})\text{L}(\text{py})]^+$ even when the phosphine is very basic [10]. The mixed complex $[\text{Ir}(\text{cod})(\text{py})\{\text{P}(\text{C}_6\text{H}_4\text{-4-F})_3\}][\text{PF}_6]$ (**4**) may be synthesised by reaction of the phosphine with $[\text{IrCl}(\text{cod})_2]$ to give $[\text{IrCl}(\text{cod})\text{L}]$. This intermediate was not isolated, but was treated with pyridine and $[\text{NH}_4][\text{PF}_6]$ to give **4** in 88% yield.

Fig. 1. ORTEP representation (non-H atoms as 20% thermal vibration ellipsoids) of the cation of $[\text{Ir}(\text{AsPh}_3)(\text{cod})(\text{py})][\text{PF}_6]$.

[Ir(AsPh₃)(cod)(PPh₃)]⁺[CF₃SO₃]⁻ (**5**) was prepared by the reaction of AsPh₃ and Ag[CF₃SO₃] with [IrCl(cod)(PPh₃)]. The bulk product could not be obtained pure, but contained [Ir(cod)(PPh₃)₂]⁺ (about 19% by integration of cod alkene region of ¹H NMR spectrum) and [Ir(AsPh₃)₂(cod)]⁺ (about 11%), which indicates a ligand exchange reaction. We undertook a preliminary experiment to see if the pyridine ligand in [Ir(cod)(py)(PPh₃)]⁺[PF₆]⁻ could be cleanly replaced by triphenylarsine to give **5**. On addition of AsPh₃ to a dichloromethane solution of the monophosphine com-

Table 1
Fractional atomic coordinates and equivalent isotropic thermal parameters for compound **1**

Atom	x	y	z	U _{eq}
Ir	0.51330(2)	0.22775(2)	0.07446(1)	0.032(1)
As	0.35366(6)	0.35566(4)	0.08159(3)	0.034(1)
N	0.3690(5)	0.1676(3)	0.0039(2)	0.036(2)
C1	0.6642(6)	0.1323(5)	0.0495(3)	0.045(3)
C2	0.6003(6)	0.0918(4)	0.0972(3)	0.042(3)
C3	0.6553(7)	0.0842(5)	0.1669(3)	0.053(3)
C4	0.7164(7)	0.1754(5)	0.1951(3)	0.049(3)
C5	0.6450(6)	0.2613(5)	0.1632(3)	0.043(3)
C6	0.6859(6)	0.3078(5)	0.1117(3)	0.043(3)
C7	0.8032(6)	0.2790(6)	0.0794(3)	0.058(4)
C8	0.8039(6)	0.1761(6)	0.0630(3)	0.054(4)
C9	0.3743(7)	0.1848(6)	-0.0580(3)	0.057(4)
C10	0.2795(8)	0.1552(6)	-0.1078(3)	0.064(4)
C11	0.1730(7)	0.1053(5)	-0.0944(4)	0.059(4)
C12	0.1669(7)	0.0848(5)	-0.0318(4)	0.062(4)
C13	0.2652(6)	0.1165(5)	0.0167(3)	0.048(3)
C14	0.4042(5)	0.4830(4)	0.1068(3)	0.038(3)
C15	0.4926(6)	0.4964(5)	0.1637(3)	0.046(3)
C16	0.5191(7)	0.5854(5)	0.1865(3)	0.050(3)
C17	0.4588(7)	0.6620(5)	0.1551(3)	0.051(3)
C18	0.3717(7)	0.6486(5)	0.0988(4)	0.056(4)
C19	0.3434(6)	0.5593(5)	0.0745(3)	0.050(3)
C20	0.2283(6)	0.3718(4)	0.0024(3)	0.037(3)
C21	0.2703(6)	0.4119(5)	-0.0514(3)	0.052(3)
C22	0.1823(8)	0.4198(6)	-0.1091(3)	0.062(4)
C23	0.0571(7)	0.3827(6)	-0.1145(3)	0.063(4)
C24	0.0151(7)	0.3401(6)	-0.0626(4)	0.066(4)
C25	0.1006(6)	0.3354(6)	-0.0038(3)	0.055(4)
C26	0.2391(6)	0.3285(4)	0.1451(3)	0.039(3)
C27	0.2419(7)	0.2418(5)	0.1728(3)	0.050(3)
C28	0.1590(8)	0.2224(5)	0.2183(3)	0.063(4)
C29	0.0768(7)	0.2893(6)	0.2362(3)	0.058(4)
C30	0.0753(7)	0.3764(5)	0.2096(3)	0.061(4)
C31	0.1570(6)	0.3964(5)	0.1639(3)	0.052(3)
P	0.7575(2)	0.0745(1)	0.8386(1)	0.052(1)
F1	0.6749(5)	-0.0188(3)	0.8367(2)	0.085(3)
F2	0.8766(5)	0.0223(5)	0.8783(4)	0.179(5)
F3	0.7060(8)	0.1046(5)	0.9001(2)	0.156(5)
F4	0.8422(6)	0.1662(4)	0.8385(3)	0.131(4)
F5	0.6342(6)	0.1250(4)	0.7985(3)	0.117(4)
F6	0.7979(7)	0.0462(5)	0.7731(3)	0.164(4)
M1	0.6322(6)	0.1121(5)	0.0733(3)	
M2	0.6655(6)	0.2846(5)	0.1374(3)	

U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

M1 and M2 are the midpoints of the C1–C2 and C5–C6 bonds.

Table 2
Selected intramolecular bond lengths (Å) and angles (°) for **1** with estimated standard deviations in parentheses

Ir–As	2.460(1)	Ir–N	2.088(4)
Ir–M1	2.048(7)	Ir–M2	2.028(6)
C1–C2	1.400(9)	C5–C6	1.387(9)
As–Ir–N	87.7(1)	M1–Ir–M2	87.0(3)
M1–Ir–As	173.6(2)	M1–Ir–N	90.1(2)
M2–Ir–As	95.6(2)	M2–Ir–N	174.8(2)

M1 and M2 are the midpoints of the C1–C2 and C5–C6 bonds.

plex, a colour change from orange to red was observed. After 1 h the solvent was removed from the reaction mixture in vacuo. ¹H and ³¹P{¹H} NMR spectroscopy of the solid residue showed it to consist predominantly of [Ir(cod)(py)(PPh₃)]⁺[PF₆]⁻ and [Ir(cod)(PPh₃)₂]⁺[PF₆]⁻ (about 5:1). Only trace amounts of the cation of **5** were observed by ¹H NMR spectroscopy and FAB mass spectrometry. Some triphenylphosphine oxide had also been produced, since some phosphine was liberated by displacement, and air was not rigorously excluded. Thus, whilst the formation of the cation of **5** is not favoured under these conditions, addition of triphenylarsine can induce some ligand scrambling. Further work is necessary to deduce the mechanism of this process.

The structure of **1** is shown in Fig. 1, atomic coordinates are given in Table 1 and selected bond lengths and angles in Table 2. Iridium adopts approximately square-planar coordination geometry, with angles about the metal virtually identical to those in [Ir(cod)(py)(P(C₆H₄-4-OMe)₃)]⁺[PF₆]⁻ [11] (P–Ir–N = 88.0(1)°, M1–Ir–M2 = 86.5(2)°, M1–Ir–P = 95.8(2)° and M2–Ir–N = 89.8(2)°). The Ir–As bond length (2.460(1) Å) is shorter not only than those reported for neutral iridium(I) triphenylarsine complexes [IrCl(AsPh₃)₂(CO)(tetraacyanoethylene)] (2.478(2) and 2.481(2) Å) [12] and [Ir(C₈H₁₃)(AsPh₃)(CO)₂] (2.472(1) Å) [13], but also than that in the [Ir(AsPh₃)₂(2,3-dimethylbutadiene)₂]⁺ cation (2.471(3) Å) [14]. This bond is also considerably longer than the Ir–P bond lengths in [Ir(cod)(py)(P(C₆H₄-4-OMe)₃)]⁺[PF₆]⁻ (2.327(1) Å) [11] or [Ir(cod)(PPh₃)₂]⁺[PF₆]⁻ (2.367(2) and 2.426(3) Å) [6], reflecting the larger covalent radius and lower σ-basicity of arsenic compared with phosphorus.

Fig. 2 shows the molecular structure of **5**, whilst atomic coordinates are given in Table 3 and selected bond lengths and angles in Table 4. Refinement of an ordered model resulted in a slightly high thermal parameter for the As atom and a low thermal parameter for the P atom. Occupancies were refined for these two atoms giving 0.9 for As and 1.2 for P. This corresponds to disorder between the AsPh₃ and PPh₃ ligands, such that the molecule is 85% as depicted in Fig. 2 and 15% with the two Group 15 ligands interchanged. Similar

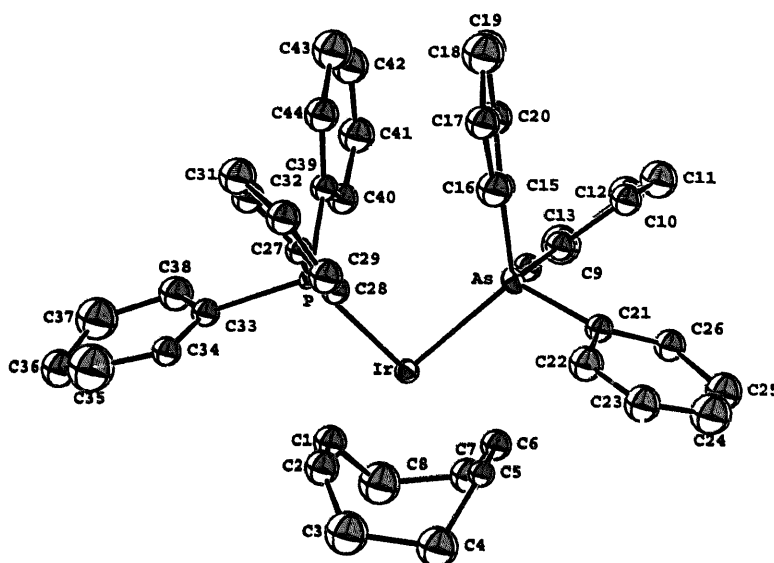


Fig. 2. ORTEP representation (non-H atoms as 20% thermal vibration ellipsoids) of the cation of [Ir(AsPh₃)(cod)(PPh₃)]⁺[CF₃SO₃]⁻.

results might be due to isomorphous replacement in the crystal of **5**, since the bulk material was known to contain both the bis(arsine) and the bis(phosphine). Attempts to refine anisotropic thermal parameters for the carbon atoms and the atoms of the anion resulted in some non-positive-definite values, and these were therefore reset isotropic. The anion is poorly defined with very high thermal parameters. The only other published example of a crystal structure of a mixed arsine/phosphine system with comparable Group 15 donor ligands is for [RhH(AsPh₃)(PPh₃)₃]·0.5C₆H₆, where it was found that the three P and one As atoms were disordered, with each of the four heavy atom ligand positions occupied at random [15].

The geometry about the iridium atom in **5** is approximately square-planar. The Ir–As bond length (2.437(1) Å) is significantly longer than the Ir–P bond (2.357(2) Å). The disorder in the system acts to foreshorten the calculated length of Ir–As and lengthen Ir–P, as implied by comparison with the Ir–As bond length in **1** (2.460(1) Å). Therefore the true disparity is probably larger than it appears. We have previously reported the crystal structure of [Ir(cod)(PPh₃)₂][PF₆] [6]; unusually this molecule is not symmetric, with significantly different Ir–P bond lengths (2.367(2) and 2.426(3) Å). Interestingly, this is also quite clear in the solid state ³¹P NMR spectrum of the complex, which shows two peaks for the phosphine ligands (δ_{iso} 17.8, 19.9 ppm) and the usual signal for the [PF₆]⁻ anion (δ_{iso} –143.4, J_{PF} = 713 Hz). The calculated Ir–P bond length in **5** (2.357(2) Å) is somewhat shorter than either of these two, which may be due to slight alleviation of steric hindrance due to the long Ir–As bond. The Ir–M1 distance (*trans* to As) (2.08(1) Å) is shorter than the Ir–M2 distance (2.12(1) Å), implying the expected dis-

tinction in the *trans*-influence. A similar *trans*-influence is seen in [PtCl(Me)(AsPh₃)(PEt₃)] [16], which has a relatively short Pt–P bond length (2.271(6) Å) *trans* to the Pt–As bond and a high ¹J_{PP} of 3738 Hz compared with 2400–2800 Hz for *trans*-[PtCl₂(PR₃)₂] complexes [17]. Evidence of steric crowding is provided by the As–Ir–P angle (93.76(7)°), which is greater than that for ideal square-planar geometry and significantly higher than the As–Ir–N angle in **1** (87.7(1)°). Also, the cod M1–Ir–M2 bite angle (83.5(5)°) is smaller than that in **1** (87.0(3)°), but similar to that in [Ir(cod)(PPh₃)₂][PF₆] (83.3°) [6]. The lower steric profile of the arsine ligand is apparent in the more acute angle M2–Ir–As (89.8(4)°) compared with M1–Ir–P (93.0(4)°).

3. Hydrogenation experiments

The atmospheric pressure hydrogenation of *N*-benzylidene aniline catalysed by **1**, **2** and **4** was studied. The product was identified by ¹H NMR spectroscopy and GLC, in comparison with an authentic commercial sample of PhNHCH₂Ph. A comparison of the rates with these precatalysts with those using [Ir(cod)(py)(PPh₃)][PF₆], or [Ir(cod)(py)(P(C₆H₄-4-OMe)₃)] [PF₆], is given in Table 5. There has been a preliminary report of some of these data [5]. **5** was not tested as a catalyst as the presence of bis(phosphine) and bis(arsine) impurities would render comparison pointless.

In the case of the triarylphosphine bearing precatalysts, higher rates are seen with more basic phosphines, the order being [Ir(cod)(py)(P(C₆H₄-4-OMe)₃)] [PF₆] > [Ir(cod)(py)(PPh₃)] [PF₆] > **4** > **2**. This implies that activity is enhanced by higher electron density at the

Table 3

Fractional atomic coordinates and equivalent isotropic thermal parameters for compound 5

Atom	x	y	z	U_{eq}
Ir	0.70551(4)	0.55311(3)	0.77598(2)	0.037(1)
As	0.62364(12)	0.67300(8)	0.73370(8)	0.038(1)
P	0.83393(18)	0.61939(13)	0.84308(12)	0.031(1)
C1	0.7987(11)	0.4482(8)	0.7637(7)	0.066(3) ^a
C2	0.7462(12)	0.4413(9)	0.8246(9)	0.072(4) ^a
C3	0.6547(16)	0.3946(11)	0.8434(11)	0.109(7) ^a
C4	0.5628(15)	0.4065(11)	0.7933(10)	0.098(6) ^a
C5	0.5692(10)	0.4820(7)	0.7490(7)	0.048(3) ^a
C6	0.6187(11)	0.4921(8)	0.6871(7)	0.056(4) ^a
C7	0.6889(13)	0.4373(10)	0.6495(9)	0.083(5) ^a
C8	0.7738(15)	0.4044(11)	0.6943(11)	0.101(6) ^a
C9	0.6600(10)	0.6949(7)	0.6361(7)	0.051(3) ^a
C10	0.6205(12)	0.7562(8)	0.5953(8)	0.067(4) ^a
C11	0.6428(14)	0.7656(10)	0.5227(9)	0.081(5) ^a
C12	0.7195(15)	0.7252(10)	0.4898(11)	0.096(6) ^a
C13	0.7601(13)	0.6583(11)	0.5269(9)	0.087(5) ^a
C14	0.7325(10)	0.6459(8)	0.6006(7)	0.054(3) ^a
C15	0.6372(10)	0.7713(7)	0.7797(7)	0.051(3) ^a
C16	0.5829(12)	0.7881(8)	0.8447(8)	0.066(4) ^a
C17	0.5963(13)	0.8583(9)	0.8798(9)	0.074(5) ^a
C18	0.6570(15)	0.9154(11)	0.8528(10)	0.099(6) ^a
C19	0.7128(14)	0.8988(10)	0.7902(9)	0.091(5) ^a
C20	0.7039(13)	0.8267(9)	0.7531(8)	0.073(4) ^a
C21	0.4755(9)	0.6619(7)	0.7269(7)	0.048(3) ^a
C22	0.4217(12)	0.6460(9)	0.7893(9)	0.077(5) ^a
C23	0.3163(14)	0.6326(10)	0.7897(10)	0.092(5) ^a
C24	0.2682(15)	0.6358(11)	0.7234(11)	0.105(6) ^a
C25	0.3168(13)	0.6470(10)	0.6623(9)	0.084(5) ^a
C26	0.4246(12)	0.6580(9)	0.6603(8)	0.066(4) ^a
C27	0.7849(10)	0.6687(7)	0.9265(6)	0.044(3) ^a
C28	0.6858(10)	0.6543(7)	0.9479(7)	0.054(3) ^a
C29	0.6492(12)	0.6849(9)	1.0113(9)	0.073(4) ^a
C30	0.7027(14)	0.7334(9)	1.0510(8)	0.079(4) ^a
C31	0.8057(14)	0.7480(10)	1.0328(8)	0.081(5) ^a
C32	0.8461(12)	0.7102(8)	0.9694(8)	0.065(4) ^a
C33	0.9399(9)	0.5563(7)	0.8826(6)	0.046(3) ^a
C34	0.9218(11)	0.5209(8)	0.9494(8)	0.056(4) ^a
C35	0.9922(17)	0.4759(12)	0.9822(12)	0.114(7) ^a
C36	1.0863(15)	0.4523(11)	0.9426(10)	0.100(6) ^a
C37	1.1058(15)	0.4985(10)	0.8834(11)	0.097(6) ^a
C38	1.0296(12)	0.5443(9)	0.8469(8)	0.071(4) ^a
C39	0.9038(9)	0.6909(6)	0.7855(7)	0.044(3) ^a
C40	0.9355(11)	0.6674(8)	0.7192(9)	0.070(4) ^a
C41	0.9871(13)	0.7187(10)	0.6691(10)	0.086(5) ^a
C42	1.0071(13)	0.7895(10)	0.6928(9)	0.086(5) ^a
C43	0.9746(14)	0.8178(10)	0.7590(10)	0.094(6) ^a
C44	0.9206(12)	0.7687(9)	0.8066(9)	0.076(5) ^a
S	0.4629(7)	0.4948(5)	1.0699(5)	0.160(4) ^a
O1	0.5388(20)	0.4509(15)	1.0306(14)	0.257(11) ^a
O2	0.4629(25)	0.5568(17)	1.1043(17)	0.309(14) ^a
O3	0.3773(24)	0.4415(15)	1.0992(16)	0.289(13) ^a
C45	0.4160(21)	0.5164(15)	0.9904(17)	0.165(10) ^a
F1	0.4606(13)	0.5579(10)	0.9463(9)	0.195(7) ^a
F2	0.3075(16)	0.5411(11)	1.0019(13)	0.248(9) ^a
F3	0.3704(21)	0.4631(14)	0.9476(13)	0.314(12) ^a
M1	0.7725(12)	0.4448(9)	0.7941(9)	
M2	0.5940(11)	0.4870(8)	0.7181(7)	

U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

^a U_{iso} .

Table 4

Selected intramolecular bond lengths (Å) and angles (°) for 5 with estimated standard deviations in parentheses

Ir–As	2.437(1)	Ir–P	2.357(2)
Ir–M1	2.08(1)	Ir–M2	2.12(1)
C1–C2	1.31(2)	C5–C6	1.31(2)
As–Ir–P	93.76(7)	M1–Ir–M2	83.5(5)
M1–Ir–As	170.5(4)	M1–Ir–P	93.0(4)
M2–Ir–As	89.8(4)	M2–Ir–P	176.5(4)

M1 and M2 are the midpoints of the C1–C2 and C5–C6 bonds.

metal centre. The data correlate roughly with the C_B parameter proposed by Drago as paralleling the covalent/frontier orbital controlled interactions for the phosphine, but less well with E_B which is related to the tendency for the phosphine to undergo electrostatic or charge-based interactions [18]. However, the triphenylarsine bearing precatalyst is superior to the triarylphosphine containing systems, even though the metal centre is expected to be less electron rich than in the triphenylphosphine analogue. It may be possible that catalysis with 1 proceeds via a different mechanism. The success of $AsPh_3$ as a ligand at palladium in Stille couplings of organotin compounds with vinyl triflates was attributed to its being a weaker and softer donor, this allowing acceleration of the transmetallation step [19].

4. Experimental

4.1. Starting materials

The complexes $\{[IrCl(cod)]_2\}$ [20], $[Ir(cod)(py)_2][PF_6]$ [21], $[Ir(cod)(py)(PPh_3)][PF_6]$ [22], $[Ir(cod)(py)\{P(C_6H_4-4-OMe)_3\}][PF_6]$ [11] and $[IrCl(cod)(PPh_3)]$ [23] were prepared according to literature methods, as was the substrate *N*-benzylidene aniline [24]. Triphenylarsine was purchased from Aldrich Chemical Co. Ltd. and used as received. Solvents were freshly distilled under dry nitrogen prior to use, methanol from magnesium methoxide, diethyl ether from sodium–potassium alloy and dichloromethane from calcium hydride.

4.2. Reaction procedures

All reactions were performed under an atmosphere of dry nitrogen using standard Schlenk techniques.

4.3. Preparation of $[Ir(AsPh_3)(cod)(py)][PF_6]$ (1)

A mixture of $[Ir(cod)(py)_2][PF_6]$ (0.101 g, 0.167 mmol) and triphenylarsine (0.108 g, 0.353 mmol)

Table 5

Rates of atmospheric pressure hydrogenation of *N*-benzylidene aniline catalysed by 1, 2, 4, [Ir(cod)(PPh₃)(py)](PF₆) and [Ir(cod)(P(C₆H₄-4-OMe)₃)(py)](PF₆). Substrate:precatalyst ratio 50:1, CH₂Cl₂:MeOH 1:1

Time (h)	Conversion (%) by [Ir(cod)(py)(L)] ⁺				
	L = PPh ₃	L = P(C ₆ H ₄ -4-OMe) ₃	L = AsPh ₃	L = P(C ₆ H ₄ -4-F) ₃	L = P(C ₆ H ₄ -4-CF ₃) ₃
0.25	7.7	5.6	—	5.6	—
0.5	10.7	11.7	—	6.1	—
0.75	13.5	14.4	18.0	6.7	—
1	18.9	17.6	25.5	9.5	3.4
1.25	21.2	21.7	31.1	12.1	—
1.5	24.7	27.9	37.8	—	—
1.75	—	—	—	15.8	—
2	30.3	34.9	48.7	17.4	4.9
2.5	39.2	42.6	59.4	20.5	—
3	43.7	52.8	69.8	24.4	10.7
3.5	47.8	59.0	78.1	35.4	—

in methanol (5 ml) was stirred at 25 °C for 3 h. The supernatant liquid was removed from the resultant orange precipitate via a cannula. The precipitate was washed with methanol (5 ml) and recrystallised (dichloromethane/ether) to give 1 as orange blocks (0.13 g, 94%). Anal. Found: C, 44.53; H, 3.90; N, 1.63. C₃₁H₃₂AsF₆IrNP Calc.: C, 44.82; H, 3.88; N, 1.67%. ν_{\max} (KBr): 3084w, 3063w, 3050w, 3033w, 1609m, 1580w, 1484m, 1450m, 1437s, 1399w, 1331w, 1305w, 1217w, 1185w, 1158m, 1078m, 1068m, 1024w, 999m, 975w, 874sh, 840vs, 756s, 748s, 738s, 692s, 558s, 476s, 462m cm⁻¹. δ_{H} (CDCl₃): 8.50 (s, br, 2H, α -py); 7.55–7.25 (m, 18H, aryl, β -py, γ -py); 4.31 (s, br, 2H, cod alkene); 4.05 (s, br, 2H, cod alkene); 2.44 (s, br, 4H, cod alkane); 1.86 (d, br, 4H, cod alkane) ppm. m/z (+ve FAB) 686 (98%) M⁺; 605 (100%) M⁺ – (py + 2H).

4.4. Reaction of P(C₆H₄-4-CF₃)₃ with [Ir(cod)(py)₂](PF₆)

A mixture of [Ir(cod)(py)₂](PF₆) (0.153 g, 0.253 mmol) and tris(4-trifluoromethylphenyl)phosphine (0.262 g, 0.561 mmol) in methanol/dichloromethane (1:1, 20 ml) was stirred overnight. The solution was then concentrated in vacuo and the supernatant liquid removed by syringe from the orange precipitate which was then washed (methanol, 5 ml). Recrystallisation (dichloromethane/ether) gave 2 as orange rods (0.20 g, 80%). The mass spectrum indicates the presence of a trace amount of [Ir(cod)(P(C₆H₄-4-CF₃)₃)₂]⁺ (m/z 1233) as well as [Ir(cod)(py)(P(C₆H₄-4-CF₃)₃)]⁺ (m/z 846). For this reason, satisfactory microanalysis was not obtained. ν_{\max} (KBr): 2965w, 2924w, 2886w, 2838w, 1608m, 1450m, 1399m, 1327vs, 1176sh, 1162s, 1134vs, 1062vs, 1016m, 836vs, 760w, 705m, 698sh, 608m, 559s, 537m, 482w, 451w, 419w cm⁻¹. δ_{H} (CDCl₃): 8.67 (d, 2H, α -py. ³J_{HH} = 5.1 Hz); 7.99 (m, 6H, aromatic); 7.88 (m, 6H, aromatic); 7.76 (t, 1H, γ -py,

³J_{HH} = 7.8 Hz); 7.34 (m, 2H, β -py); 4.79 (s, br, 2H, cod alkene); 3.73 (s, br, 2H cod alkene); 2.50 (s, br, 4H, cod alkane); 2.07 (m, 4H, cod alkane) ppm. δ_{P} (CDCl₃): 19.33 (s, Ir–P); –142.78 (sept. PF₆, ¹J_{PF} = 708 Hz) ppm.

4.5. Preparation of [Ir(cod)(P(C₆H₄-4-F)₃)₂](PF₆) (3)

A mixture of [Ir(cod)(py)₂](PF₆) (0.148 g, 0.245 mmol) and P(C₆H₄-4-F)₃ (0.143 g, 0.542 mmol) in methanol was stirred for 12 h at 25 °C. The supernatant liquid was removed by syringe, and the pink–red precipitate washed (methanol, 2 × 5 ml) and recrystallised (dichloromethane/ether) to give 3 as red rods (0.17 g, 64%). ν_{\max} (KBr): 3105w, 3059w, 3035w, 2951w, 2928w, 2893w, 2844w, 1623m, 1590vs, 1495vs, 1453m, 1432m, 1395s, 1343m, 1312m, 1244vs, 1228vs, 1164vs, 1089s, 1082s, 1015m, 1005m, 975w, 943w, 834vs, 714m, 639m, 610m, 558s, 531s, 486w, 468m, 450s, 442s, 428m, 411m cm⁻¹. δ_{H} (CDCl₃): 7.48 (m, 12H, aromatic); 7.08 (m, 12H, aromatic); 4.25 (s, br, 4H, alkene); 2.39 (m, 4H, CH₂); 2.05 (m, 8H, CH₂) ppm. δ_{P} (CDCl₃): 16.41 (s, Ir–P); –142.6 (sept, ¹J_{PF} = 713 Hz, PF₆) ppm. m/z (+ve FAB) 933 (50%, M⁺), 823 (20%), 613 (100%).

4.6. Preparation of [Ir(cod)(py)(P(C₆H₄-4-F)₃)](PF₆) (4)

A solution of [IrCl(cod)]₂ (0.307 g, 0.457 mmol) and P(C₆H₄-4-F)₃ (0.283 g, 0.895 mmol) in dichloromethane/light petroleum (b.p. 60–80 °C, ratio 1:3, 30 ml) was stirred for 12 h at 25 °C. The solvent was removed in vacuo, yielding an orange solid which was then suspended in methanol (30 ml). Pyridine (0.5 ml, 6.2 mmol) was added and the resultant mixture left to stir for 1.5 h. A solution of ammonium hexafluorophosphate (0.5 g, 3.1 mmol) in methanol (10 ml) was added. The solution was filtered and then concentrated

in vacuo. Cooling to -20°C completed the precipitation. The supernatant liquid was removed by syringe, the orange precipitate washed with water (2×5 ml) then diethyl ether (2×5 ml), and then recrystallised from dichloromethane/diethyl ether to give $[\text{Ir}(\text{cod})(\text{py})\{\text{P}(\text{C}_6\text{H}_4\text{-4-F})_3\}][\text{PF}_6]$ as a brilliant orange powder (0.68 g, 88%). ν_{max} (KBr): 2946w, 2925w, 2889w, 1607sh, 1590vs, 1498s, 1448m, 1434w, 1400w, 1395w, 1226s, 1209sh, 1171m, 1164s, 1094m, 1012w, 879sh, 852vs, 801sh, 760m, 742w, 715w, 694m, 635w, 612w, 558s, 537s, 513sh, 478w, 452m, 443m cm^{-1} . δ_{H} (CDCl_3): 2.03 (m, 4H, CH_2); 2.49 (m, 4H, CH_2); 3.51 (s, br, $\text{CH}=\text{CH}$); 4.57 (s, br, 2H, $\text{CH}=\text{CH}$); 7.21 (m, 8H, aromatic and β -py); 7.54 (m, 7H, aromatic and γ -py); 8.44 (d, $J = 5.1$ Hz, 2H, α -py) ppm. δ_{P} (CDCl_3): 17.1 (s); -142.7 (septet, $^1J_{\text{PF}} = 713$ Hz) ppm. m/z (+ve FAB) 696 (63%, $M+1$), 613 (100%). Anal. Found: C, 44.05; H, 3.48; N, 1.62. $\text{C}_{31}\text{H}_{29}\text{F}_9\text{IrNP}_2$ Calc.: C, 44.28; H, 3.48; N, 1.67%.

4.7. Preparation of $[\text{Ir}(\text{AsPh}_3)(\text{cod})(\text{PPh}_3)][\text{CF}_3\text{SO}_3]$ (5)

A mixture of $[\text{IrCl}(\text{cod})(\text{PPh}_3)]$ (0.161 g, 0.269 mmol), triphenylarsine (0.083 g, 0.271 mmol) and silver trifluoromethanesulfonate (0.078 g, 0.304 mmol) in methanol (20 ml) was stirred at 25°C for 5 h. The resultant mixture was filtered through a Celite pad and the residues extracted with dichloromethane. The solvent was removed from the combined filtrate and dichloromethane extracts in vacuo. Recrystallisation (dichloromethane/hexane) gave **5** as deep red blocks (0.23 g, 71%). $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra showed that the product was not pure, but rather contained $[\text{Ir}(\text{cod})(\text{PPh}_3)_2]^+$ (approximately 19%) and $[\text{Ir}(\text{cod})(\text{AsPh}_3)_2]^+$ (approximately 11%). Thus, neither microanalysis nor a useful infrared spectrum could be obtained. δ_{H} (CDCl_3): 7.5–7.1 (m, 30H, aryl); 4.56 (s, br, 2H, cod alkene); 3.96 (s, br, 2H, cod alkene); 2.34 (m, 4H, cod alkane); 1.94 (m, 4H, cod alkane) ppm. δ_{P} (CDCl_3): 19.31 (s) ppm. m/z (+ve FAB) 913 (M^+ , $[\text{Ir}(\text{AsPh}_3)_2(\text{cod})]^+$), 869 (M^+ , $[\text{Ir}(\text{AsPh}_3)(\text{cod})(\text{PPh}_3)]^+$), 825 (M^+ , $[\text{Ir}(\text{cod})(\text{PPh}_3)_2]^+$).

4.8. Reaction of AsPh_3 with $[\text{Ir}(\text{cod})(\text{py})(\text{PPh}_3)][\text{PF}_6]$

Triphenylarsine (0.114 g, 0.372 mmol) was added in one portion to a solution of $[\text{Ir}(\text{cod})(\text{py})(\text{PPh}_3)][\text{PF}_6]$ (0.293 g, 0.372 mmol) in dichloromethane (20 ml), and the colour of the solution turned immediately from orange to red. The reaction mixture was stirred for 1 h, after which time the solvent was removed in vacuo to yield an orange–red solid residue. The composition of the residue was deduced by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and (+ve) FAB mass spectrometry.

4.9. Hydrogenation of imines

The vessel used for the atmospheric pressure hydrogenations was a 100 ml round-bottomed flask with a 15 cm long neck and an attached Teflon stopcock. A solution of the appropriate precatalyst (0.08 mmol) and *N*-benzylidene aniline (0.724 g, 4.0 mmol) in dichloromethane/methanol 1:1 (8 ml) was thoroughly degassed in the reaction vessel. After a final evacuation hydrogen gas was admitted to the thoroughly stirred solution after warming to 20°C . The Teflon stopcock was replaced by a subseal through which aliquots were removed at appropriate intervals. A blanket of hydrogen at about 10 mm Hg above atmospheric pressure was maintained in the vessel throughout the reaction.

4.10. X-ray structural analyses of **1** and **5**

Orange blocks of **1** were grown by slow diffusion at a dichloromethane/ether interface. Suitable crystals of **5** were grown from the same solvent system as purple–red rods. Crystallographic data for **1** and **5** are summarised in Table 6. Data were collected using crystals of dimensions $0.2 \times 0.2 \times 0.2$ mm³ for **1** and $0.35 \times 0.3 \times 0.2$ mm³ for **5** on an Enraf–Nonius CAD4 diffractometer, graphite monochromated Mo K α radiation in the θ – 2θ mode. In the case of **1**, 9032 unique reflections were measured for $2^{\circ} < \theta < 30^{\circ}$ and h $0 \rightarrow 14$, k $0 \rightarrow 20$, l $-29 \rightarrow 29$. For **5**, 6502 unique reflections were measured for $2^{\circ} < \theta < 30^{\circ}$ and h $0 \rightarrow 18$, k $0 \rightarrow 24$, l $0 \rightarrow 25$. In the case of **1**, 6052 reflections for which $|F^2| > 2\sigma(F^2)$, where $\sigma(F^2) = \{\sigma^2(I) +$

Table 6
Crystallographic data for $[\text{Ir}(\text{AsPh}_3)(\text{cod})(\text{py})][\text{PF}_6]$ (**1**) and $[\text{Ir}(\text{AsPh}_3)(\text{cod})(\text{PPh}_3)][\text{CF}_3\text{SO}_3]$ (**5**)

	1	5
Chemical formula	$\text{C}_{31}\text{H}_{32}\text{AsF}_6\text{IrNP}$	$\text{C}_{45}\text{H}_{42}\text{AsF}_3\text{IrO}_3\text{PS}$
Formula weight	830.7	1018
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)
a (Å)	10.097(2)	12.964(1)
b (Å)	14.319(2)	17.134(2)
c (Å)	20.959(3)	18.228(6)
α (°)	90	90
β (°)	99.24(1)	90
γ (°)	90	90
V (Å ³)	2991	4049
Z	4	4
T (K)	293	293
λ (Mo K α) (Å)	0.71073	0.71073
ρ_{calc} (g cm^{-3})	1.85	1.67
μ (Mo K α) (cm^{-1})	56.5	41.8
Transmission coefficient	1.00, 0.80	1.00, 0.79
$T_{\text{max}} \cdot T_{\text{min}}$		
R	0.045	0.060
R_w	0.045	0.059

$(0.04I)^2)^{1/2}/Lp$ were used in the refinement. For **5**, the number of reflections that fitted the criterion was 4557. In both cases unit cell parameters were obtained by least-squares fit of 25 reflections with $7^\circ < \theta < 9^\circ$ for **1** and $9^\circ < \theta < 11^\circ$ for **5**, and the space groups $P2_1/c$ (No. 14) and $P2_12_12_1$ (No. 19) were established for **1** and **5** respectively from systematic absences. Two reference reflections measured every hour showed a maximum variation of -0.7% for **1** and 2.2% for **5**; no decay correction was applied in either case. Absorption corrections were applied based on psi scan measurements. The structures were solved using routine heavy atom methods (SHELXS-86); for **1** all non-H atoms were refined anisotropically by full-matrix least-squares. In **5** the Ir, As and P atoms were refined anisotropically, C atoms and atoms of the anion were refined isotropically. In both cases H atoms were held at calculated positions with $U_{iso} = 1.3U_{eq}$ for the atom to which they are bonded. With a weighting scheme of $\omega = 1/\sigma^2(F)$, $\Sigma\omega(|F_o| - |F_c|)^2$ minimised, the final residuals were $R = 0.045$, $wR = 0.045$, $S = 1.2$, $\Delta/\sigma_{max} = 0.01$, $\Delta\rho_{max} = +1.34 e \text{ \AA}^{-3}$, $\Delta\rho_{min} = -0.35 e \text{ \AA}^{-3}$ (near Ir atom) for **1** and $R = 0.060$, $wR = 0.059$, $S = 1.6$, $\Delta/\sigma_{max} = 0.5$, $\Delta\rho_{max} = +1.29 e \text{ \AA}^{-3}$, $\Delta\rho_{min} = -0.84 e \text{ \AA}^{-3}$ (near As and P atoms) for **5**. Refinement of **5** as the opposite absolute configuration gave $R = 0.073$, $wR = 0.076$ and $S = 2.1$.

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