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# Synthesis and reactivity of iridium complexes with pyridine and piperidine ligands: models for hydrodenitrogenation<sup>†</sup>

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The complexes  $[Ir(H)_2(\eta^1-N-L)_2(PPh_3)_2]PF_6$ , L = py (1), iQ (2) and pip (3) (py = pyridine, iQ = isoquinoline, pip = piperidine) have been synthesized in high yields by hydrogenation of  $[Ir(cod)(PPh_3)_2]PF_6$  in the presence of the appropriate nitrogen compound. When hydrogen is bubbled through 1,2-dichloroethane solutions of 1 or 2, two new species were formed in each case by C–Cl bond activation of the solvent,  $Ir(H)_2Cl(\eta^1-N-L)(PPh_3)_2$  (L = py, 4; iQ, 5) and  $IrH(Cl)_2(\eta^1-N-L)(PPh_3)_2$  (L = py, 6; iQ, 7). Reaction of 3 with py or iQ yielded complexes 1 and 2, respectively, while under a slow stream of carbon monoxide the complex  $[Ir(H)_2(\eta^1-N-pip)(CO)(PPh_3)_2]PF_6$  (8) was produced. Complex 3 also reacts with halide and 4-bromothiophenolate anions leading to the corresponding neutral species  $Ir(H)_2(X)(\eta^1 N-pip)(PPh_3)_2$ , X = Cl (9), I (10) and 4-BrC<sub>6</sub>H<sub>4</sub>S (11), or with  $[MoS_4]^{2-}$  to yield the hetero-bimetallic complex  $[Ir(H)(PPh_3)_2(\mu-S)_2MoS_2]^-$  (13). All the new complexes were characterized by analytical and spectroscopic methods. The X-ray structures of 1, 2 and 8 consist of distorted octahedra with a mutually *cis* disposition of the two hydrides and mutually *trans* phosphines. Complexes 1, 2 and 3 and their derivatives are of interest as models for the chemisorption step in hydrodenitrogenation reactions on solid catalysts.

# Introduction

The interaction of pyridine and piperidine with transition metal centres is of interest as model chemistry for the industrially important hydrodenitrogenation (HDN) reaction, the catalytic removal of organic nitrogen from petroleum and coal derived liquids. This process is essential to reduce NO<sub>x</sub> emissions produced upon burning of fuels, and also to avoid deactivation or poisoning of e.g. hydrotreating or hydrocracking catalysts by nitrogen compounds. HDN is generally carried out over sulfided CoMo/Al<sub>2</sub>O<sub>3</sub>, NiMo/Al<sub>2</sub>O<sub>3</sub> or NiW/Al<sub>2</sub>O<sub>3</sub> catalysts under rather severe hydrogenation conditions (350-500 °C and 1500-3000 psi H<sub>2</sub>), ultimately removing the organic nitrogen as NH<sub>3</sub>.<sup>1</sup> Kinetic, mechanistic and thermodynamic studies have established that hydrogenation of the N-containing aromatic ring occurs prior to C-N bond cleavage; for instance, in the HDN of pyridine (py), reduction to piperidine (pip) takes place first, followed by hydrogenolysis of the C-N bonds to produce npentylamine and finally pentane + NH<sub>3</sub>.<sup>2</sup>

Homogeneous modelling of heterogeneous catalytic reactions by use of well-defined metal complexes can help in the understanding of specific elementary steps of the reaction mechanisms. This has been extensively used in hydrodesulfurisation (HDS)<sup>3</sup> but HDN model studies using coordination or organometallic complexes are scarce.3-5 Modelling work has primarily focused on the coordination of N-heterocycles on mononuclear metal centres, on the homogeneous catalytic hydrogenation of N-aromatic compounds and on C-N bond activation.<sup>5-8</sup> As part of the organometallic modelling of the chemisorption and subsequent steps involved in HDN, it is important to study the coordination and reactivity of pyridines and of their hydrogenated derivatives with metal centres. In this paper, we report the synthesis and reactivity of stable n<sup>1</sup>-N-bonded complexes of the type  $[Ir(H)_2(\eta^1 - N - L)_2(PPh_3)_2]PF_6$ , L = py (1), iQ (2), and pip (3); the X-ray structures of complexes 1, 2 and of a carbonyl derivative of 3 are also described. Although the coordination chemistry of pyridines is rather extensive, stable metal complexes of piperidine are scarce.

† Electronic supplementary information (ESI) available: Preparation of complexes. See http://www.rsc.org/suppdata/dt/b4/b406949h/

#### **Results and discussion**

# Syntheses of [Ir(H)<sub>2</sub>(η<sup>1</sup>-N-L)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub> complexes

The complex  $[Ir(cod)(PPh_3)_2]PF_6$  reacts readily with hydrogen in the presence of N-aromatic compounds such as pyridine and isoquinoline to form the corresponding derivatives  $[Ir(H)_2(\eta^1-N-L)_2(PPh_3)_2]PF_6$  (L = py (1) and iQ (2)) in good yields (eqn. (1), L = py (1), iQ (2)). Complex 1 has been previously mentioned briefly by Moore *et al.* when studying solvent exchange reactions of complexes of the type  $[Ir(H)_2(solvent)_2(PPh_3)_2]^+$  with py.<sup>9</sup>

$$[Ir(cod)(PPh_{3})_{2}]PF_{6} + 6H_{2} + 2L \rightarrow [Ir(H)_{2}(\eta^{1}-N-L)_{2}(PPh_{3})_{2}]PF_{6} + C_{8}H_{16} \quad (1)$$

In the case of piperidine, this method led to the analogous complex  $[Ir(H)_2(\eta^{1}-N-pip)_2(PPh_3)_2]PF_6$  (3) but usually mixed with a number of other species. A better synthetic route for compound **3** is the addition of an excess of pip to a thf solution of  $[Ir(H)_2(thf)_2(PPh_3)_2]PF_6$  (eqn. (2)), previously generated by hydrogenation of  $[Ir(cod)(PPh_3)_2]PF_6$  in thf.<sup>10</sup> For quinoline (Q), any one of the two methods produced the corresponding complex  $[Ir(H)_2(\eta^1N-Q)_2(PPh_3)_2]PF_6$  in a pure form.

$$[Ir(H)_{2}(thf)_{2}(PPh_{3})_{2}]PF_{6} + 2pip \rightarrow [Ir(H)_{2}(\eta^{1}-N-pip)_{2}(PPh_{3})_{2}]PF_{6} + 2thf \quad (2)$$

Complexes 1–3 are rather air stable materials in the solid state. They are soluble in dichloromethane and chloroform, sparingly soluble in benzene, toluene and alcohols and insoluble in diethyl ether and *n*-pentane. Their <sup>1</sup>H NMR spectra display high field triplets at –21.6 ppm,  $J_{HP}$  17.5 Hz for 1; –21.4 ppm,  $J_{HP}$  17.6 Hz for 2; and –23.35 ppm,  $J_{HP}$  18.9 Hz for 3. The corresponding <sup>31</sup>P {<sup>1</sup>H} spectra consist of singlets at 22.8 ppm for 1 and 2, and 21.5 for 3, which are split into triplets upon selective coupling with the two hydride ligands. The <sup>1</sup>H NMR signals of the piperidine ligands of complex 3 could all be assigned by 2D COSY/HETCORR and NOEDIFF NMR experiments (see ESI†). These results are consistent with the presence of two equivalent hydrides coupled with two equivalent PPh<sub>3</sub> ligands in a stereochemistry involving mutually *trans* phosphines and mutually *cis* pairs of hydrides and N-donor ligands:

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$$L = py (1), iQ (2), pip (3)$$

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E.

**-**+

The solution spectroscopic data are in accord with the solidstate structures determined by X-ray diffraction (*vide infra*). It is interesting to note that all the complexes prefer to adopt the more crowded stereochemistry containing the two nitrogen ligands in mutually *cis* positions rather than an all *trans* disposition of the three pairs of ligands, most likely as a result of the strong *trans* effect of the hydrides. The Ir–H stretching gives rise to bands of medium intensity in the region from 2212 to 2150 cm<sup>-1</sup>.

### Reactivity of complexes 1 and 2 with H<sub>2</sub>

When hydrogen was bubbled through a 1,2-dichloroethane solution of complexes 1 or 2 at 80 °C, the appearance of two new singlets in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum was observed in each case, corresponding to the formation of two new species in equilibrium with each starting complex (integral ratios: 1:5:2 and 1:2:3 after 24 h, where the value of 1 is assigned to the relative integral of 1 or 2, respectively). When such mixtures were precipitated as solids and subsequently re-dissolved in 1,2-dichloroethane, the <sup>31</sup>P NMR features remained essentially unaltered, except for the fact that the signal corresponding to PF<sub>6</sub><sup>-</sup> in those cases integrated approximately 1:1 with respect to the signals of complexes 1 or 2, indicating that the new complexes formed are neutral. They display characteristic <sup>1</sup>H NMR spectra (see ESI<sup>†</sup>) that allowed their identification as  $Ir(H)_2Cl(\eta^1-N-L)(PPh_3)_2$  (L = py, 4; iQ, 5) (two distinct Ir-H signals as high-field doublets of triplets arising from the coupling to two equivalent phosphine ligands and to the other hydride) and IrH(Cl)<sub>2</sub>( $\eta^{1}$ -N-L)(PPh<sub>3</sub>)<sub>2</sub> (L = py, 6; iQ, 7) (a single Ir-H triplet signal). The number of hydrides in each case was also determined by selective coupling in the <sup>31</sup>P NMR spectra. These chlorinated complexes are presumably formed by activation of the C-Cl bonds of the 1,2-dichloroethane solvent, since there is no other source of Cl in the reaction medium, but no attempt was made to study the mechanism of these reactions. A fourth species was detected in some cases in small proportions in the region of 56 to 50 ppm of the  ${}^{31}P{}^{1}H$  spectrum, which corresponds to the square planar Ir(I) complexes  $[Ir(\eta^1-N-L)_2(PPh_3)_2]PF_6$ , formed through reductive elimination of hydrogen from the corresponding dihydride 1 or 2. The analogous reactions of complex 3 with hydrogen at room temperature or at 60 °C in the absence or in the presence of excess free piperidine led to intractable complex mixtures. No transformations of the N-donor ligands themselves were observed for any of the three new complexes.

#### **Reactivity of complex 3**

The piperidine ligands in **3** are more labile than py or iQ in **1** or **2**, and consequently they are readily substituted by different ligands at room temperature, as summarized in Scheme 1.



Scheme 1 Piperidine displacement reactions from complex 3.

At room temperature Py or iQ immediately displace pip from **3** to generate **1** and **2**, respectively. On the other hand, under a slow stream of carbon monoxide at room temperature, only one piperidine ligand of **3** is displaced by CO to produce a stable monopiperidine derivative [Ir(H)<sub>2</sub>( $\eta$ <sup>1</sup>N-pip)(CO)(PPh<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub> (**8**). The <sup>1</sup>H NMR spectrum displays two distinct high-field signals at -8.0 ppm, (triplet of doublets,  $J_{HP} = 17.2$  Hz,  $J_{HH} = 4.8$  Hz) and -18.8 ppm, (triplet of doublets, broadened possibly by the N quadrupolar effect or by interaction with the proton on NH) while the <sup>31</sup>P NMR spectrum consists of a singlet at 15.1 ppm. In the IR spectrum, two Ir–H and a C–O stretching vibrations are observed at 2205m, 2155m and 2040vs cm<sup>-1</sup>. The solution structure thus corresponds to an octahedral arrangement with mutually *cis* hydrides, *cis* CO and pip ligands, and *trans* phosphines, and this structure is maintained in the solid state as confirmed by an X-ray diffraction study (*vide infra*).

Reactions of **3** with anionic ligands X<sup>-</sup> generate the corresponding neutral complexes  $Ir(H)_2(X)(\eta^{1}-N-pip)(PPh_3)_2$  (X = Cl, **9**; I, **10**; 4-BrC<sub>6</sub>H<sub>4</sub>S, **11**) by substitution of one piperidine ligand; the analytical and spectroscopic data (see ESI<sup>†</sup>) are in agreement with the proposed formulation and with the stereochemistry depicted in Scheme 1 for these compounds. Complex **11** slowly loses the remaining pip ligand and the hydrides at room temperature (or very rapidly at 60 °C) to generate a compound whose <sup>31</sup>P NMR spectrum displays only one singlet at -2.1 ppm, and only peaks attributable to phenyl protons in the <sup>1</sup>H NMR spectrum. A possible structure that would be in agreement with these data is the dimer [Ir<sub>2</sub>( $\mu$ -SC<sub>6</sub>H<sub>4</sub>Br)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] (**12**), analogous to the known [Ir<sub>2</sub>( $\mu$ -SR)<sub>2</sub>(CO)<sub>4</sub>] derivatives.<sup>11</sup> Finally complex **3** reacts with the tetrathiomolybdate anion [MoS<sub>4</sub>]<sup>2-</sup> to produce NH<sub>4</sub>[Ir(H)(PPh\_3)<sub>2</sub>( $\mu$ -S)<sub>2</sub>MoS<sub>2</sub>] (**13**).

# Solid-state structures of $[Ir(H)_2(\eta^1-N-L)_2(PPh_3)_2]PF_6$ , L = py (1), iQ (2), and $[Ir(H)_2(\eta^1N-pip)(CO)(PPh_3)_2]PF_6$ (8)

The molecular structures of the complexes 1 and 2 are shown in Figs. 1 and 2, and selected bond distances and angles are listed in Tables 1 and 2, respectively.



Fig. 1 ORTEP drawing of  $[Ir(H)_2(\eta^1-N-C_5H_5N)_2(PPh_3)_2]^+$ .

The coordination geometry around iridium consists in each case of a distorted octahedron with presumed mutually *cis*-hydrides, *cis* N-ligands (py or iQ) and *trans*-phosphines. The two phosphines are bent [P–Ir–P = 164.49(7)° for 1 and 161.79(8)° for 2] toward the smaller hydride ligands in order to minimize steric repulsions. The Ir–N distances in 1 and 2 [2.212(6) and 2.193(7) Å for 1 and 2.199(7) and 2.185 Å for 2] are slightly longer than those found in the closely related bipyridyl complex [Ir(H)<sub>2</sub>(bipy)(PPh<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub> [average 2.150(5) Å],<sup>12</sup> as well as in [AuIr(H)<sub>2</sub>(bipy)(PPh<sub>3</sub>)<sub>3</sub>](BF<sub>4</sub>)<sub>2</sub> [2.102(8) Å]<sup>13</sup> and [Ir(bipy)<sub>3</sub>]<sup>+</sup> [average 2.04(1) Å].<sup>14</sup> The mean planes of the six-membered pyridine rings adopt different mutual orientations, allowing dihedral angles between them of 71.1 and 57.3° for 1 and 2, respectively. All other structural parameters concerning the coordinated py and iQ compare well with those found in other complexes containing these ligands. The Ir–P

Table 1 Selected bond distances (Å) and angles (°) for  $[Ir(H)_2(\eta^1-N-C_5H_3N)_2(PPh_3)_2]PF_6~(1)$ 

$\begin{array}{c} \text{Ir(1)-P(1)} \\ \text{Ir(1)-P(2)} \\ \text{Ir(1)-N(2)} \\ \text{Ir(1)-N(2)} \\ \text{N(1)-C(5)} \\ \text{N(1)-C(5)} \\ \text{N(1)-C(1)} \\ \text{C(1)-C(2)} \\ \text{C(2)-C(3)} \\ \text{C(2)-C(3)} \\ \text{C(3)-C(4)} \\ \text{C(4)-C(5)} \\ \text{P(1)-C(11)} \\ \text{C(12)} \\ \text{C(12)} \\ \text{C(12)} \end{array}$	2.304(2) 2.316(2) 2.212(6) 2.193(7) 1.331(11) 1.334(10) 1.394(12) 1.378(14) 1.365(15) 1.406(13) 1.841(8) 1.327(12)	$\begin{array}{c} N(1)-Ir(1)-N(2) \\ P(2)-Ir(1)-N(2) \\ P(2)-Ir(1)-N(1) \\ P(1)-Ir(1)-N(2) \\ P(1)-Ir(1)-N(2) \\ P(1)-Ir(1)-P(2) \\ Ir(1)-N(1)-C(5) \\ Ir(1)-N(1)-C(5) \\ Ir(1)-N(1)-C(5) \\ N(1)-C(1)-C(2) \\ C(1)-C(2)-C(3) \\ C(2)-C(3) \\ C(2)-C(4) \\ \end{array}$	96.3(3) 90.42(17) 98.12(18) 97.61(18) 94.18(17) 164.49(7) 122.4(6) 119.6(5) 117.5(7) 124.1(9) 117.1(10) 120.2(0)
$\begin{array}{c} C(3) - C(4) \\ C(4) - C(5) \\ P(1) - C(11) \\ C(11) - C(12) \end{array}$	1.305(13) 1.406(13) 1.841(8) 1.387(12)	$\begin{array}{c} C(1) - R(1) - C(3) \\ N(1) - C(1) - C(2) \\ C(1) - C(2) - C(3) \\ C(2) - C(3) - C(4) \\ C(3) - C(4) - C(5) \\ C(4) - C(5) - N(1) \end{array}$	117.5(7) $124.1(9)$ $117.1(10)$ $120.3(9)$ $118.5(10)$ $122.5(9)$

Table 2 Selected bond distances (Å) and angles (°) for  $[Ir(H)_2(\eta^1-N-C_9H_7N)_2(PPh_3)_2]PF_6$  (2)

Ir(1) - P(1)	2.314(2)	N(1)-Ir(1)-N(2)	95.3(3)
Ir(1) - P(2)	2.306(2)	P(2)-Ir(1)-N(2)	90.02(19)
Ir(1) - N(1)	2.199(7)	P(2)-Ir(1)-N(1)	100.02(19)
Ir(1) - N(2)	2.185(7)	P(1)-Ir(1)-N(1)	91.94(19)
N(1)–C(37)	1.332(10)	P(1)-Ir(1)-N(2)	100.56(19)
N(1)–C(45)	1.374(10)	P(1)-Ir(1)-P(2)	161.79(8)
C(45)–C(44)	1.320(12)	Ir(1)-N(1)-C(37)	121.7(6)
C(44)–C(43)	1.416(13)	Ir(1)-N(1)-C(45)	121.0(6)
C(43)C(38)	1.410(10)	C(37)–N(1)–C(45)	115.6(7)
C(43)–C(42)	1.414(13)	N(1)-C(37)-C(38)	125.2(8)
C(42) - C(41)	1.384(15)	C(37)-C(38)-C(39)	122.7(9)
C(41) - C(40)	1.385(15)	C(38)-C(39)-C(40)	120.1(10)
C(40)–C(39)	1.350(14)	C(38)-C(43)-C(44)	115.6(8)
C(39)–C(38)	1.418(13)	C(44)-C(45)-N(1)	123.5(9)
C(38)–C(37)	1.385(12)		



Fig. 2 ORTEP drawing of  $[Ir(H)_2(\eta^1-N-C_9H_7N)_2(PPh_3)_2]^+$ .

distances in complexes 1 [2.304(2) and 2.316(2) Å] and 2 [2.314(2) and 2.306(2) Å] are rather similar to those found in related complexes  $[Ir(H)_2(S)_2(PPh_3)_2]^+$ , S = acetone [average 2.32(2) Å],<sup>15</sup> (THF)(H<sub>2</sub>O) [2.300(3) and 2.297(3) Å],<sup>10</sup> thiophene [2.325(2) Å], tetrahydrothiophene [2.309(3) and 2.303(3) Å],<sup>16</sup> and 2,3-dihydrobenzothiophene [2.319(2) Å].<sup>17</sup>

Fig. 3 shows an ORTEP view of the complex cation of **8**. Selected bond distances and angles are collected in Table 3. The geometry around the iridium atom consists of a distorted octahedron as in complexes **1** and **2**, with presumed mutually *cis* hydrides (not depicted), mutually *trans* phosphines, which bend toward the small hydrides, and the piperidine and carbonyl ligands in *cis* positions with respect to each other.

To the best of our knowledge, this is the first structurally characterized iridium complex containing the piperidine ligand and therefore we cannot offer comparisons with other closely related structures. In the somewhat related Rh–pip complex, RhCl( $C_2H_4$ )(pip)<sub>2</sub>, the Rh–N distance Rh–N [2.114(2) Å]<sup>18</sup> in slightly longer than the Ir–N

Table 3 Selected bond distances (Å) and angles (°) for  $[Ir(H)_2(CO)(\eta^1-N-C_5H_{11}N)(PPh_3)_2]PF_6$  (8)

Ir(1) - P(1)	2.337(8)	C(37)-N(1)-Ir(1)	120(3)
Ir(1) - P(2)	2.346(9)	P(2)-Ir(1)-C(42)	97.4(10)
Ir(1)-N(1)	1.98(3)	P(2)-Ir(1)-N(1)	91.4(6)
Ir(1)-C(42)	2.01(3)	P(1)-Ir(1)-C(42)	89.7(10)
N(1)-C(41)	1.57(3)	P(1)-Ir(1)-N(1)	99.5(7)
N(1)–C(37)	1.37(5)	P(1)-Ir(1)-P(2)	165.70(18)
C(37)–C(38)	1.52(6)	Ir(1)-N(1)-C(41)	120(3)
C(38)–C(39)	1.43(7)	C(42)-Ir(1)-N(1)	101.3(11)
C(39)–C(40)	1.49(9)	C(37)–N(1)–C(41)	113(3)
C(40)–C(41)	1.54(8)	N(1)-C(37)-C(38)	116(4)
C(42)–O(42)	1.06(4)	C(37)–C(38)–C(39)	112(5)
		C(38)-C(39)-C(40)	109(4)
		C(39)-C(40)-C(41)	117(4)
		C(40)-C(41)-N(1)	107(2)
		Ir(1)-C(42)-O(42)	172(3)



Fig. 3 ORTEP drawing of  $[Ir(H)_2(CO)(\eta^1-N-C_5H_{11}N)(PPh_3)_2]^+$ .

distance in **8** [1.98(3) Å], which might suggest that the piperidine is more loosely bound to rhodium in that compound than to iridium in complex **8**. The bond distances and angles in the piperidine ring are rather similar in both structures within experimental errors. Since the Rh derivative is a neutral square-planar compound, comparisons with our cationic octahedral structure must be taken with caution.

#### Final remarks in relation to HDN

Adsorption of pyridines to the active sites of heterogeneous catalysts, followed by hydrogenation to the corresponding saturated cyclic amines constitute the initial steps of the commonly accepted mechanism of HDN. The N-bonded complexes 1 and 2 herein reported can be considered as molecular analogues of the chemisorbed N-heteroaromatics. It is interesting to note that in these complexes two hydrides coexist with two N-heteroaromatic ligands in a cis disposition, which can be considered as a model of the simultaneous adsorption of an organo-nitrogen compound and activation of dihydrogen on a single metal site. This should be favourable for a subsequent attack of the hydride to the heterocyclic ring, but no such reactivity was observed for these very stable complexes. Although the py ligand of complex 1 could not to be directly hydrogenated to piperidine, the corresponding bis(piperidine) analogue 3 could be obtained by an alternative route, thus completing the model for the adsorption of piperidine to a catalytic site. Several reports of pyridine, quinoline and indole metal-complexes are available, but analogues containing their hydrogenated derivatives, e.g. tetrahydroquinoline and indoline are less common;19 and are particularly scarce in the case of piperidine.20 Unfortunately, it was not possible to activate the C-H or C-N bonds of the nitrogen ligands in complexes 1-3, due to the stability of the complexes 1 and 2 and the lability of the piperidine ligands in 3 and related complexes.

	1	2·EtOH	8
Empirical formula M Crystal system Space group a/Å b/Å c/Å $a/^{\circ}$ $\beta/^{\circ}$ $\gamma/^{\circ}$ $\gamma/^{\circ}$ $V/Å^{3}$ Z $\mu/\text{mm}^{-1}$ $D_c/g \text{ cm}^{-3}$ F(000) Reflections collected	$\begin{array}{c} 1\\ \hline C_{46}H_{42}F_{6}IrN_{2}P_{3}\\ 1021.93\\ Monoclinic\\ P2_{1}/n\\ 15.043(3)\\ 16.905(3)\\ 17.553(4)\\ 90.00\\ 107.55(3)\\ 90.00\\ 4255.7(15)\\ 4\\ 3.312\\ 1.595\\ 2032\\ 7772\\ \end{array}$	$\begin{array}{c} \textbf{2-EtOH} \\ \hline C_{56}H_{52}F_{6}IrN_{2}OP_{3} \\ 1178.19 \\ Triclinic \\ P\overline{1} \\ 12.141(2) \\ 14.480(3) \\ 15.414(3) \\ 107.92(3) \\ 99.80(3) \\ 92.72(3) \\ 2526.2(9) \\ 2 \\ 2.802 \\ 1.549 \\ 1192 \\ 9295 \end{array}$	$\begin{array}{c} \textbf{8} \\ \hline C_{42}H_{43}F_6IrNOP_3 \\ 976.88 \\ Triclinic \\ P1 \\ 9.440(2) \\ 10.724(2) \\ 11.638(2) \\ 64.92(3) \\ 74.76(3) \\ 83.89(3) \\ 1029.6(4) \\ 1 \\ 3.419 \\ 1.576 \\ 486 \\ 3837 \\ \end{array}$
Independent reflections GOF $\Delta \rho_{\text{max/min}}$ /e Å <sup>-3</sup> $R_1, wR_2 [I > 2\sigma(I)]$ $R_1, wR_2$ (all data)	7455 1.007 1.64 $^{a}$ /-1.17 0.0481, 0.1096 0.0785, 0.1243	8909 1.012 2.61 <sup>a</sup> /-1.16 0.0562, 0.1108 0.0935, 0.1263	3837 1.156 5.89 <sup>b</sup> /-5.33 0.0880, 0.2321 0.0902, 0.2382

<sup>a</sup>Close to the Ir atom. <sup>b</sup>The first ten peaks (0.9–6 e Å<sup>-3</sup>) are very close (<1.12 Å) to the Ir and P atoms

# Experimental

# General

All the reactions were carried out under argon using standard Schlenk techniques. Solvents were distilled from appropriate drying agents immediately prior to use.  $[Ir(cod)(PPh_3)_2]PF_6$  was prepared by the method described in the literature.<sup>21</sup> Pyridine, piperidine and isoquinoline were purified by distillation under reduced pressure. IrCl<sub>3</sub>·*n*H<sub>2</sub>O and all other chemicals were of commercial sources and were used without further purification. <sup>1</sup>H and <sup>31</sup>P NMR spectra were obtained by use of a Bruker AM 300 instrument (300.234 MHz for <sup>1</sup>H and 121.496 MHz for <sup>31</sup>P). Detailed experimental procedures for the synthesis and reactivity studies described above, together with complete microanalytical and spectroscopic data for all the new compounds can be found as ESI.<sup>†</sup>

# Single-crystal structure determinations for 1, 2 and 8

Crystals of complexes 1, 2 and 8 were obtained by slow concentration of a solution of each complex in a dichloromethane-ethanol mixture at room temperature. The crystal structures of the three compounds were determined using a Rigaku AFC7S diffractometer provided with a graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at room temperature. Selected experimental data for all crystal structure determination are collected in Table 4. All data were corrected for Lorentz and polarization effects and by a semiempirical absorption correction.<sup>22</sup> The structures were solved by direct methods23 and expanded using Fourier techniques.24 For each compound all non-H atoms were refined anisotropically. Hydrogen atoms were included in the last cycle in calculated positions, except those corresponding to the disordered solvent in structure 2. All these hydrogen atoms were refined riding on C or N atoms with a common thermal parameter. The hydrides could not be observed in any residual electron density map. For the crystal structure of 2 an ethanol molecule was found strongly disordered. Two different orientation with a refined occupancy factor of 70:30% were considered. The final cycle of full-matrix least-squares on  $F^2$  was based on all unique reflections. Data reduction were performed using TEXSAN<sup>25</sup> crystallographic software package of the Molecular Structure Corporation, whereas refinement calculations and graphical representations were made using SHELXTL-NT.24

CCDC reference numbers 213808 (1), 213809 (2) and 213810 (8).

# See http://www.rsc.org/suppdata/dt/b4/b406949h/ for crystallographic data in CIF or other electronic format.

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