Iridium(III)-(hydrido)cyclometallated-imine complexes and metal-promoted hydrolytic cleavage of imines*

*P. Marcazzan, B. O. Patrick, and B. R. James**

Department of Chemistry, The University of British Columbia,
2036 Main Mall, Vancouver, B. C. V6T 1Z1, Canada.
Fax: +1 (604) 822 2847. E-mail: brj@chem.ubc.ca

The room temperature reaction of the complex *cis*,*trans*,*cis*-$[Ir(H)_2(PPh_3)_2(Solv)_2]PF_6$ (Solv is a solvent) with the imine $PhCH_2N{=}CHPh$ in acetone generates (with loss of H_2) the orthometallated complex $[Ir(H)\{PhCH_2N{=}CH(o\text{-}C_6H_4)\}(PPh_3)_2(Me_2CO)]PF_6$ (**3**) containing a five-membered cyclometallated imine moiety. In MeOH, the reaction at an imine : Ir ratio = 1 leads to the corresponding MeOH analog of **3**, while with excess imine, the mixed orthometallated imine/bezylamine complex $[Ir(H)\{PhCH_2N{=}CH(o\text{-}C_6H_4)\}(PPh_3)_2(PhCH_2NH_2)]PF_6$ (**4**) is formed; the source of the coordinated amine is an Ir-promoted hydrolysis of the imine, the water likely coming from imine. Complexes **3** and **4** are fully characterized by elemental analysis, ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, and X-ray crystal structure analysis.

Key words: crystal structure, hydride ligands, imine ligands, triphenylphosphine ligands, imine hydrolysis, iridium complexes, orthometallation.

Complexes of the type $[M(cod)(PPh_3)_2]PF_6$,[1,2] (cod is cycloocta-1,5-diene) are well known catalyst precursors for the homogeneous H_2-hydrogenation of a variety of unsaturated compounds containing the C=C (M = Rh, Ir),[3,4] C=O [5] and C=N moieties (M = Rh).[6] The reactivity of these complexes under H_2 in coordinating solvents (*e.g.*, MeOH, acetone, MeCN) is well documented. For both metals, H_2 oxidative addition and diene reduction to cyclooctane affords the *cis*,*trans*,*cis*-$[M(H)_2(PPh_3)_2(Solv)_2]PF_6$ (Solv is a solvent) complexes.[3,7—9] Our interest in mechanistic aspects of the homogeneous hydrogenation of imines[10,11] prompted investigations of these species as catalytic precursors because they are effective at room temperature and 1 atm H_2,[6] where spectroscopic studies (especially NMR) are rendered facile.

The more forcing reaction conditions generally required for H_2-hydrogenation of imines results, at least in part, from the smaller enthalpic gain associated with H_2-saturation of the C=X moieties when X = N or O (~—60 kJ mol^{-1}) relative to the C=C group (~—130 kJ mol^{-1}).[10] We thus initiated studies of the coordination of imines to the dihydrido complexes at stoichiometric and catalytic substrate/catalyst ratios both under H_2 and Ar when, at least for the Rh systems, the complexes *cis*-$[M(PPh_3)_2(Solv)_2]^+$ are typically present.[9] Imine binding to Rh centers in systems involving catalyzed hydrogenation of imines has been reported earlier.[11—13] Our new results on the Rh systems are presented in Ref. 14. This study focuses on the interaction of imines with the corresponding Ir-based species.

Results and Discussion

The stoichiometric reaction between $PhCH_2N{=}CHPh$ and *cis,trans,cis*-$[Ir(H)_2(PPh_3)_2(Me_2CO)_2]PF_6$ (**1**),[8] which is formed *in situ* from $[Ir(cod)(PPh_3)_2]PF_6$ (**2**) and H_2 in acetone, occurs under Ar in acetone at ~20 °C (when complex **1** persists in solution) to produce the orthometallated complex $[Ir(H)\{PhCH_2N{=}CH(o\text{-}C_6H_4)\}(PPh_3)_2(Me_2CO)]PF_6$ (**3**) (Scheme 1).

In this complex, the benzylidenearyl group of the imine, σ-bound through the N-atom, has undergone oxidative addition of an *ortho*-CH group. The reaction of complex **1** with excess imine similarly produces compound **3**. The structure of complex **3** is shown in Fig. 1, and the selected structural parameters are given in Table 1.

The PPh_3 ligands are mutually *trans*, and the acetone ligand is *trans* to the metallated *ortho*-C atom within the distorted octahedral structure. The somewhat longer Ir—O and C(15)—O distances, noted previously for other

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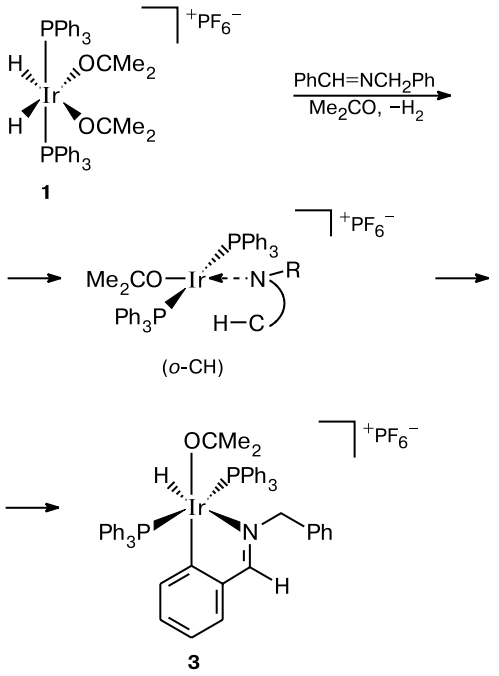
Scheme 1



Ir^{III}-acetone complexes,[15,16] reflect the strong trans-influence of the *ortho*-C ligand. The large Ir—C(1)—C(15) angle of 134.6° suggests that the acetone Me groups may be subjected to steric repulsions by the $Ir(PPh_3)_2$ moiety, and the P(1)—Ir—P(2) angle of 169.2° also indicates that the phosphine ligands are bent away slightly from the acetone ligand toward each other; such a behaviour has also been discussed previously.[15] A comparison of the N(1)—C(7) and N(1)—C(8) bond lengths for the imine ligand shows that the former corresponds to the C=N bond; this observed endocyclic orthometallation (*vs.* a possible exocyclic orthometallation when the C=N group is outside of the ring) is expected for this imine in its thermodynamically favoured *E*-isomeric form.[17] (Further comments on the X-ray structure will be discussed below).

Table 1. Selected bond lengths (*d*) and angles (ω) for complex **3**

Bond	*d*/Å	Angle	ω/deg
Ir(1)—P(1)	2.3161(8)	Ir(1)—O(1)—C(15)	134.6(3)
Ir(1)—P(2)	2.3390(9)	Ir(1)—N(1)—C(7)	112.7(2)
Ir(1)—O(1)	2.203(2)	Ir(1)—C(1)—C(2)	129.1(3)
Ir(1)—N(1)	2.153(3)	Ir(1)—C(1)—C(6)	113.7(3)
Ir(1)—C(1)	2.013(4)	P(1)—Ir(1)—P(2)	169.21(3)
Ir(1)—H(1)	1.48(3)	P(1)—Ir(1)—O(1)	93.49(7)
N(1)—C(7)	1.293(5)	P(1)—Ir(1)—N(1)	93.00(8)
N(1)—C(8)	1.471(5)	P(1)—Ir(1)—C(1)	88.13(9)
C(1)—C(2)	1.398(5)	P(1)—Ir(1)—H(1)	85(1)
C(1)—C(6)	1.417(5)	P(2)—Ir(1)—O(1)	92.68(7)
C(6)—C(7)	1.439(5)	P(2)—Ir(1)—N(1)	95.61(8)
C(8)—C(9)	1.511(5)	P(2)—Ir(1)—C(1)	87.04(9)
C(15)—O(1)	1.227(5)	P(2)—Ir(1)—H(1)	86(1)
C(15)—C(16)	1.502(6)	O(1)—Ir(1)—H(1)	92(1)
		N(1)—Ir(1)—C(1)	79.7(1)
		N(1)—Ir(1)—H(1)	176(1)
		C(1)—Ir(1)—O(1)	171.7(1)
		C(1)—Ir(1)—H(1)	96(1)
		C(1)—C(6)—C(7)	115.9(3)
		C(7)—N(1)—C(8)	121.0(3)

The IR data for complex **3** are consistent with the literature data for the related $IrCl(H)\{MeN{=}CH(o\text{-}C_6H_4)\}(PPh_3)_2$ complex formed by displacement of N_2 from *trans*-$IrCl(N_2)(PPh_3)_2$ by the reaction with MeN=CHPh.[18] The ν(IrH) band is seen at 2211 cm^{-1}, while the cyclometallated C=N moiety gives rise to a band at 1607 cm^{-1} compared to that of the free imine (1644 cm^{-1}), and is consistent with η^1-binding through the N atom lone pair.[18,19] The ν(CO) band for the coordinated acetone is seen at 1651 cm^{-1} (*vs.* 1715 cm^{-1} for free acetone), being consistent with the literature data.[7]

The $^{31}P\{^1H\}$ NMR spectrum of complex **3** in acetone-d_6 shows a singlet at δ 17.05. The ^1H NMR spectrum contains the expected triplet at δ −16.35 ($^2J_{H,P}$ = 17 Hz) for the hydride, a shift that is downfield of the hydride signals of **1** (δ −27.70, $^2J_{H,P}$ = 16 Hz),[8,14] which is consistent with the small trans-influence of the N-atom in complex **3**.[20] The upfield-shifted resonances for the aromatic protons of the orthometallated ring were assigned by the ^1H-^1H COSY NMR data and on the basis of the respective multiplicities and integration data.[14] The CH=N signal is also shifted upfield (δ 7.67 *vs.* 8.50 for the free imine), which is again consistent with η^1-N-binding.[18,21]

More generally, orthometallated compounds have extensively been reviewed, and those containing N-donor ligands form complexes that almost exclusively have a five-membered ring structure.[21] The mechanistic pathway invokes the usual insertion reaction, typical of a nucleophilic metal center with coordinated, relatively basic phosphines.[18] In the formation of complex **3** from **1** (see Scheme 1), the imine presumably displaces initially a solvent ligand, bringing an *ortho* CH group close to the metal,[18] this being accompanied by reductive elimination of the hydrido ligands as H_2, which was detected in solution at δ_H 4.35. The CH oxidative addition, likely promoted by the electron density of the N-donor,[18] then yields complex **3**. Similarly to the earlier Ir work,[18] our study in acetone-d_6 ruled out solvent as the hydride source. Of interest, the reaction of MeN=CHPh with $[RhCl(CO)_2]_2$, containing the more electron-withdrawing CO ligands, produces the η^1-N-imine complex *cis*-$RhCl(CO)_2(MeN{=}CHPh)$ rather than an orthometallated derivative.[18] It should be noted that our group has reported recently on related ortho-metallation of semicarbazones (substituted imines) at the Rh centers.[22]

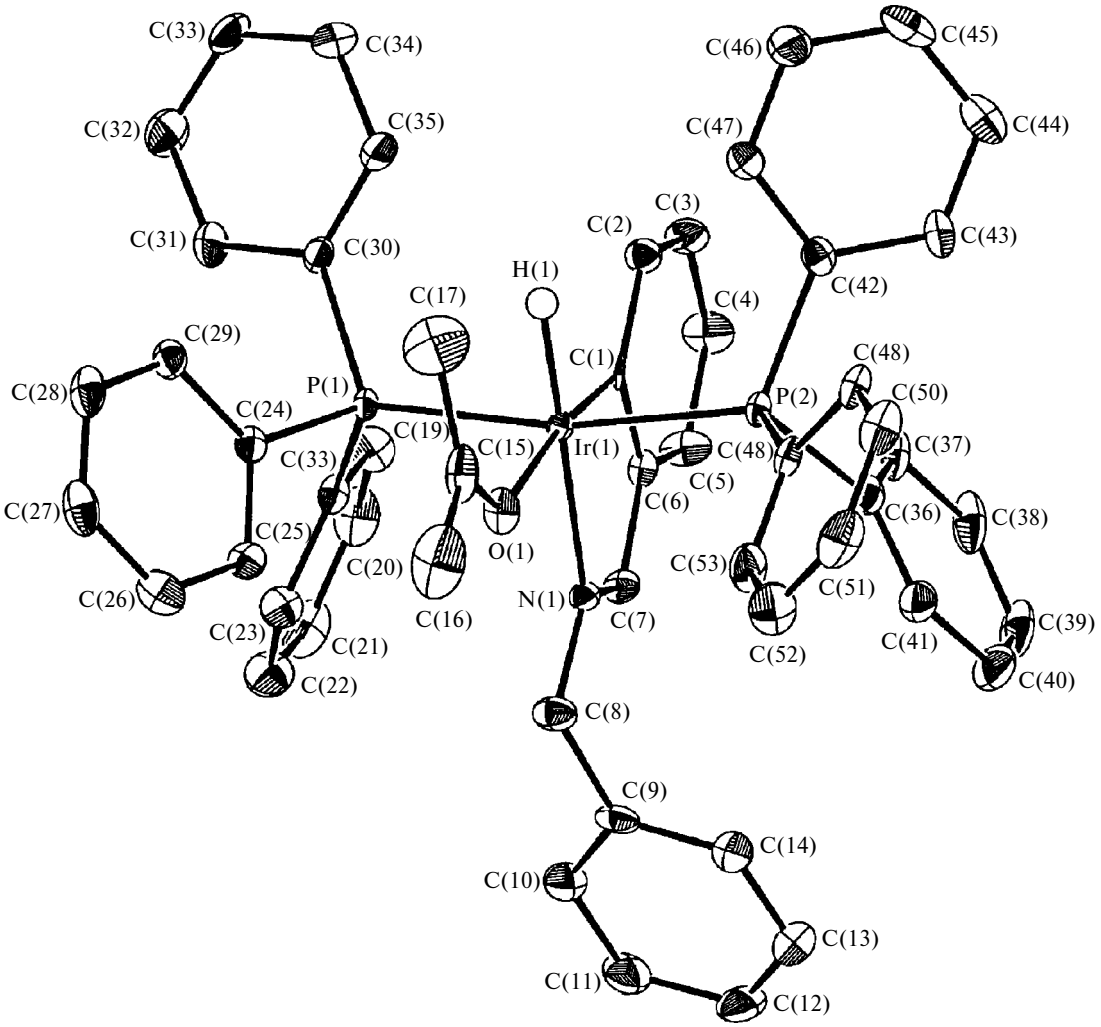
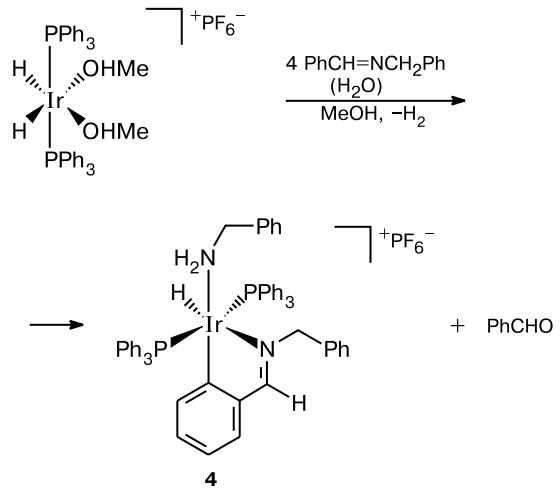


Fig. 1. ORTEP diagram for $[IrH\{PhCH_2N{=}CH(o\text{-}C_6H_4)\}(PPh_3)_2(Me_2CO)]PF_6$ (**3**), with 50% probability ellipsoids.

The corresponding MeOH analog of complex **3** was formed similarly from a 1 : 1 reaction of complex **1** with $PhCH_2N{=}CHPh$ in MeOH, but was not isolable. The *in situ* species, however, was readily identified by solution $^{31}P\{^1H\}$ NMR (CD_3OD, δ_P, 18.01 (s)) and ^1H NMR: δ_H −16.07 (t, 1 H, Ir(H), $^2J_{H,P}$ = 16 Hz); 5.02 (s, 2 H, CH_2); 6.30 (t, 1 H, *p*-C_6H_4, $^3J_{H,H}$ = 6.5 Hz); 6.63 (d, 1 H, *o*-C_6H_4, $^3J_{H,H}$ = 6.5 Hz); 6.74 (m, 2 H, *m*-C_6H_4, $^3J_{H,H}$ = 6.5 Hz); 7.10—7.65 (m, 35 H, H arom.); 7.77 (s, 1 H, N=CH). However, when a four-fold excess of imine was added to a MeOH solution of *cis,trans,cis*-$[Ir(H)_2(PPh_3)_2(MeOH)_2]PF_6$ [8] under Ar, spontaneous precipitation of the ortho-metallated complex $[Ir(H)\{PhCH_2N{=}CH(o\text{-}C_6H_4)\}(PPh_3)_2(PhCH_2NH_2)]PF_6$ (**4**) slowly occurred (Scheme 2).

In place of the acetone ligand in complex **3**, complex **4** contains benzylamine that is derived from hydrolysis of the imine (Scheme 2); benzaldehyde, the hydrolysis co-product, was detected in the filtrate by GLC and

Scheme 2



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^1H NMR analyses. The source of the H_2O has not been established; it could come from the MeOH, although

this was dried over Mg turnings in the presence of I_2 and distilled from the Mg methoxide formed.[23] The imine is a more likely source, especially as excess imine is needed in MeOH to generate the mixed orthometallated imine/amine complex **4**. That hydrolysis in acetone is not seen, even in the presence of excess imine, could be due to acetone competing successfully with the H_2O molecules for the coordination site that is presumably required for the metal-promoted hydrolysis. The lower coordinating ability of MeOH (*vs.* acetone)[24] could account for the accessibility of a coordination site for the H_2O molecules. The distorted octahedral structure of complex **4** is shown in Fig. 2, and it is remarkably similar to the structure of complex **3** after replacement of the coordinated acetone with benzylamine. The bond lengths and angles (Table 2) are very close to those in complex **3**, and even the Ir—$N(2)_{amine}$ distance is the same as the Ir—O distance in molecule **3**.

The Ir—P, Ir—C, and Ir—$N(1)_{imine}$ bond lengths in both complexes are close to those reported for the related Ir^{III} complexes,[16,25–27] while the Ir—H distances are intermediate between some experimentally determined values (*e.g.*, 1.43 Å)[26] and "experimentally fixed" distances (*e.g.*, 1.60 Å).[16]

The IR data for complex **4**, like those for complex **3**, reveal the ν(IrH) and ν(C=N) bands, as well as ν(NH) for the amine at 3301 cm^{-1} (*vs.* 3373 cm^{-1} for free $PhCH_2NH_2$) and, of course, no ν(CO) band. Because of substitution of the amine ligand in more strongly coordinating solvents (see below), NMR characterization (including ^1H-^{13}C HETCOR and ^{13}C APT experiments[14]) of isolated complex **4** was accomplished in CD_2Cl_2. Observed are: a $^{31}P\{^1H\}$ singlet at δ_P 15.04, the hydride signal at δ_H −17.63 (t, $^2J_{H,P}$ = 17 Hz), the non-aromatic, benzylidene-amine protons at δ_H 5.05 (s, $PhCH_2N{=}C$) and 7.30 (s, N=CH), and overlapping signals due to coordi-

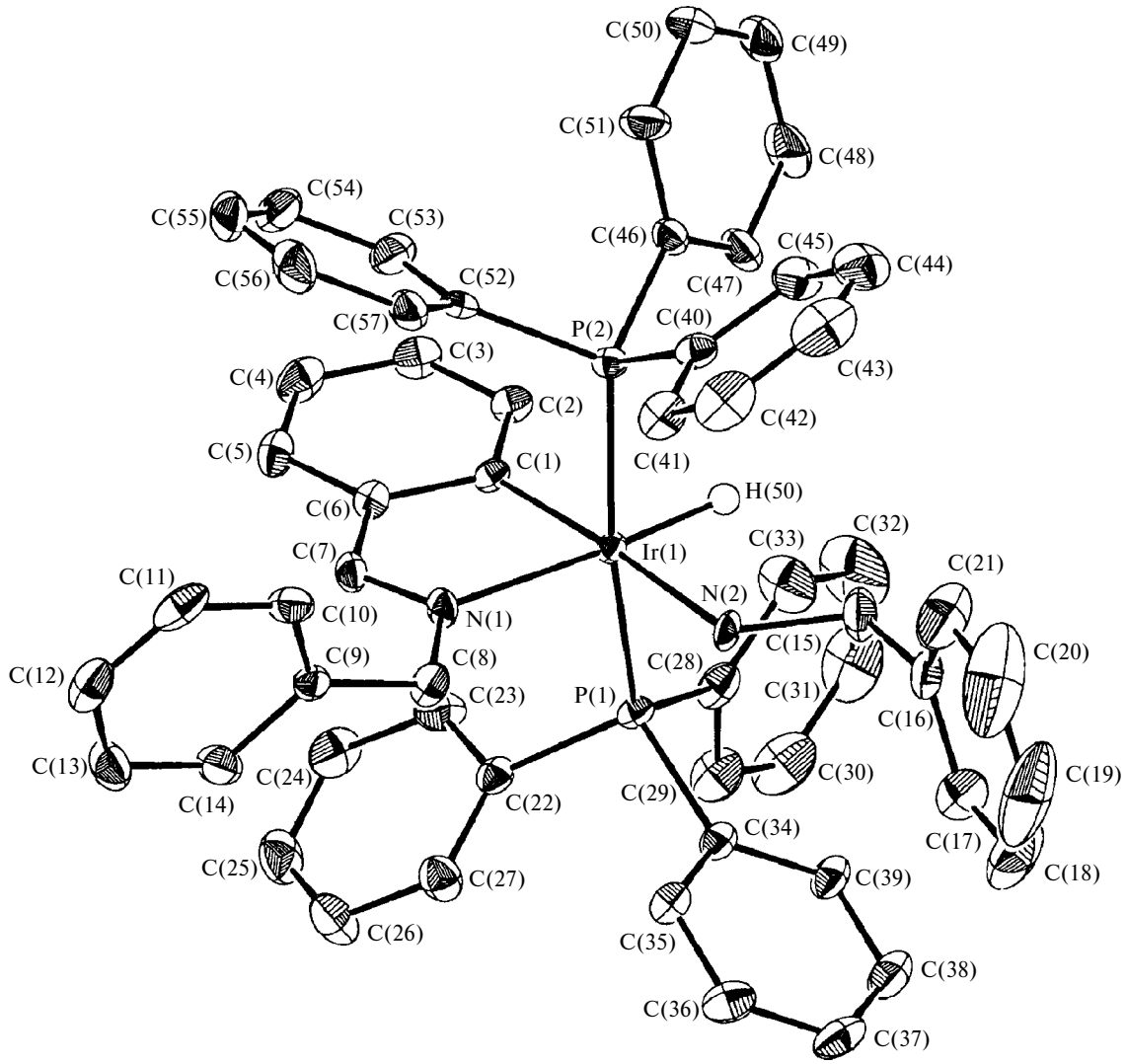

Fig. 2. ORTEP diagram for $[IrH\{PhCH_2N{=}CH(o\text{-}C_6H_4)\}(PPh_3)_2(PhCH_2NH_2)]PF_6$ (**4**), with 50% probability ellipsoids.

Table 2. Selected bond lengths (d) and angles (ω) for complex **4**·2 CH_2Cl_2

Bond	d/Å	Angle	ω/deg
Ir(1)—P(1)	2.331(1)	Ir(1)—N(1)—C(7)	113.6(3)
Ir(1)—P(2)	2.323(1)	Ir(1)—N(1)—C(8)	124.9(2)
Ir(1)—N(1)	2.167(3)	Ir(1)—C(1)—C(2)	129.9(3)
Ir(1)—N(2)	2.202(3)	Ir(1)—C(1)—C(6)	114.1(3)
Ir(1)—C(1)	2.041(4)	P(1)—Ir(1)—P(2)	167.41(3)
Ir(1)—H(50)	1.52(4)	P(1)—Ir(1)—N(1)	95.8(1)
N(1)—C(7)	1.282(5)	P(1)—Ir(1)—N(2)	92.2(1)
N(1)—C(8)	1.480(5)	P(1)—Ir(1)—C(1)	88.9(1)
N(2)—C(15)	1.495(5)	P(1)—Ir(1)—H(50)	85(2)
C(1)—C(2)	1.413(5)	P(2)—Ir(1)—N(1)	94.9(1)
C(1)—C(6)	1.409(5)	P(2)—Ir(1)—N(2)	93.2(1)
C(5)—C(6)	1.400(5)	P(2)—Ir(1)—C(1)	86.7(1)
C(6)—C(7)	1.450(5)	P(2)—Ir(1)—H(50)	84(2)
C(8)—C(9)	1.505(5)	N(1)—Ir(1)—N(2)	96.5(1)
C(15)—C(16)	1.504(6)	N(1)—Ir(1)—C(1)	78.6(1)
		N(1)—Ir(1)—H(50)	175(2)
		N(1)—C(7)—C(6)	117.9(4)
		N(1)—C(8)—C(9)	117.3(3)
		N(2)—Ir(1)—C(1)	175.0(1)
		N(2)—Ir(1)—H(50)	88(2)
		N(2)—C(15)—C(16)	110.9(4)
		C(1)—Ir(1)—H(50)	97(2)
		C(1)—C(6)—C(7)	115.8(3)

nated amine at δ_H 2.80 (m, $C\underline{H}_2NH_2$ and $CH_2N\underline{H}_2$). The upfield-shifted resonances for the orthometallated ring and a doublet at δ 5.70 (2 H, $^3J_{H,H}$ = 7 Hz) are also present. Based on the ^1H-^{13}C HETCOR data, the latter resonance is attributed to the *ortho*-protons of the coordinated $PhCH_2NH_2$ group that each couple to the neighbouring *meta*-protons; these *ortho*-protons are thus strongly affected by the coordination of the amine, and π-arene interactions with Ph groups of the PPh_3 ligands may be present.

Dissolution of complex **4** in acetone-d_6 generates immediately an 8 : 1 mixture of complexes **4** and **3**, as evidenced by the NMR data for **4**, δ_P 15.57 (d, $^2J_{H,P}$ = 15 Hz); δ_H −17.42 (t, $^2J_{H,P}$ = 16 Hz), showing that the benzylamine ligand is partially displaced by acetone. The upfield-shifted resonances for the orthometallated ring of each complex and signals due to free (δ_H 1.28 (s, $CH_2N\underline{H}_2$) and 4.47 (s, $C\underline{H}_2NH_2$)) and coordinated (δ_H 2.80—2.92 (m, $C\underline{H}_2NH_2$ and $CH_2N\underline{H}_2$)) benzylamine were also identified. The upfield-shifted signals of the *ortho*-protons of the coordinated $PhCH_2NH_2$ were seen at δ_H 5.72 (d, 2 H, $^3J_{H,H}$ = 7 Hz). Free imine was not detected, showing that orthometallation is retained. The NMR spectra in acetone-d_6 are time-dependent, and the ratio of the two species increasingly favoured complex **3** that became the only species observed after several days.

The very different behaviour of the systems in acetone and in alcohol is important in the catalytic H_2-hydrogenation of imines using the corresponding Rh precursor complexes,[14] studies that will be presented elsewhere. The occurrence of hydrolysis and the formation of a mixed imine—amine, square planar Rh^I species, under conditions when an initially observed orthometallation of the imine is not retained, can play a key role in catalysis. The metal-promoted hydrolytic cleavage of imines is not new; for example, we have reported[28] on the Ru systems that generate species with coordinated benzylamine formed from the same initially coordinated $PhCH_2N{=}CHPh$ imine.

Complex **3** in the presence of excess imine at 1 atm H_2 is an inactive hydrogenation catalyst for imines because of precipitation of neutral dihydrido species such as $Ir(H)_2\{PhCH_2N{=}CH(o\text{-}C_6H_4)\}(PPh_3)_2$.[14]

Experimental

All manipulations were performed under Ar using standard Schlenk and/or dry-box techniques. Solvents were dried according to standard procedures;[23] and deuterated solvents were also dried and degassed prior to use. The complex $[Ir(cod)(PPh_3)_2]PF_6$ **(2)** was prepared according to a published method,[29] using $IrCl_3 \cdot 3H_2O$ purchased from Colonial Metals Inc. *N*-benzylidenebenzylamine ($PhCH_2N{=}CHPh$ from Aldrich) was purified by distillation and stored under Ar. H_2 (Praxair, Extra Dry) was used as received.

NMR spectra were recorded at ~20 °C on a Bruker AV-300 spectrometer (300 MHz for ^1H, 121 MHz for $^{31}P\{^1H\}$), with residual solvent protons (^1H) and external standard 85% H_3PO_4 ($^{31}P\{^1H\}$) being used as references; the *o*-, *m*-, and *p*-C_6H_4 notation used for the orthometallated ring is defined as for the free imine. GLC analyses were performed on a temperature-programmable Hewlett—Packard 5890A instrument fitted with an HP 17 capillary column and a flame ionization detector, and using He as carrier gas. IR spectra (KBr pellets) were recorded on an ATI Mattson Genesis Series FTIR instrument; IR bands are reported in wavenumbers (cm^{-1}). Microanalyses were performed by P. Borda in the analytical laboratory of this department.

[*N*,*o*-*C*-(*N*-Benzilidenebenzylaminato)]hydrido(acetone)bis(triphenylphosphine)iridium(III) hexafluorophosphate, $[Ir(H)\{PhCH_2N{=}CH(o\text{-}C_6H_4)\}(PPh_3)_2(Me_2CO)]PF_6$ (3). A red solution of complex **2** (0.100 g, 0.103 mmol) in acetone (3 mL) was stirred under H_2 (1 atm) for 1 h at ~20 °C. To the resulting pale yellow solution, $PhCH_2N{=}CHPh$ (19.5 μL, 0.103 mmol) was added under Ar, and the mixture was stirred for 24 h; the volume was then reduced to ~1 mL to afford spontaneous precipitation of a cream solid that was collected, washed with Et_2O (3×4 mL), and dried in vacuo. Yield of complex **3** was 0.090 g (78%). Found (%): C, 57.11; H, 4.46; N, 1.39. $C_{53}H_{49}F_6IrNOP_3$. Calculated (%): C, 57.09; H, 4.43; N, 1.26. IR, ν/cm^{-1}: 2211 (Ir—H); 1651 (C=O); 1607 (C=N); 1580. ^1H NMR (acetone-d_6), δ: −16.35 (t, 1 H, IrH, $^2J_{H,P}$ = 17 Hz); 2.10 (s, 6 H, MeCOMe); 5.22 (s, 2 H, CH_2); 6.40 (t, 1 H, *p*-C_6H_4, $^3J_{H,H}$ = 6.5 Hz); 6.71 (d, 1 H, *o*-C_6H_4, $^3J_{H,H}$ = 6.5 Hz); 6.86 (m, 2 H, *m*-C_6H_4, $^3J_{H,H}$ = 6.5 Hz); 7.00—7.60 (m, 35 H, H arom.); 7.67 (s, 1 H, N=CH). $^{31}P\{^1H\}$ NMR (acetone-d_6), δ: 17.05 (s).

[*N*,*o*-*C*-(*N*-Benzilidenebenzylaminato)]hydrido(benzylamine)bis(triphenylphosphine)iridium(III) hexafluorophosphate, [Ir(H){$PhCH_2N{=}CH(o\text{-}C_6H_4)$}$(PPh_3)_2(PhCH_2NH_2)]PF_6$ (4). A red suspension of **2** (0.080 g, 0.082 mmol) in MeOH (3 mL) was stirred under H_2 (1 atm) for 1 h at ~20 °C. The resulting pale yellow solution was treated with excess $PhCH_2N{=}CHPh$ (60.0 μL, 0.330 mmol) under Ar, and the mixture was stirred for 48 h, during which time spontaneous precipitation of a cream solid occurred. The product was collected, washed with Et_2O (3×4 mL), and dried in vacuo. Yield of complex **4** was 0.050 g (52%). Found (%): C, 58.89; H, 4.94; N, 2.32. $C_{57}H_{52}F_6IrN_2P_3$. Calculated (%): C, 58.80; H, 4.47; N, 2.40. IR, ν/cm^{-1}: 3301 (N—H); 2208 (Ir—H); 1605 (C=N); 1576. ^{1}H NMR (CD_2Cl_2), δ: −17.63 (t, 1 H, IrH, $^2J_{H,P}$ = 17 Hz); 2.80 (m, 4 H, NH_2, $C\underline{H}_2NH_2$); 5.05 (s, 2 H, $CH_2N{=}$); 5.70 (d, 2 H, *o*-C_6H_5, $^3J_{H,H}$ = 7 Hz); 6.55 (t, 1 H, *p*-C_6H_4, $^3J_{H,H}$ = 6.5 Hz); 6.75—7.50 (m, 41 H, H arom.); 7.30 (s, 1 H, N=CH). ^{31}P{^{1}H} NMR (CD_2Cl_2), δ: 15.04 (s).

X-ray diffraction analyses. Yellow crystals of complexes **3** and **4** were grown by slow evaporation of a 1 : 1 CH_2Cl_2—hexanes solution of the respective complexes. The needle-like crystals of **3**, $C_{53}H_{49}F_6IrNOP_3$ (M = 1115.11), are monoclinic, space group $P2_1/n$, a = 11.6903(9), b = 15.498(2), c = 25.7533(7) Å, β = 96.6599(9)°, V = 4634.6(5) Å^3, d_{calc} = 1.598 g cm^{-3}, Z = 4. Yellow platelet-like crystals of **4**·2 CH_2Cl_2, $C_{59}H_{56}Cl_4F_6IrN_2P_3$ (M = 1334.03), are also monoclinic, space group $P2_1/n$, a = 12.7932(4), b = 20.5806(4), c = 21.3390(7) Å, β = 92.469(2)°, V = 5613.2(2) Å^3, d_{calc} = 1.576 g cm^{-3}, Z = 4. The crystallographic data for **3** and **4**·2 CH_2Cl_2 can be obtained from the Cambridge Crystallographic Data Centre.*

The X-ray diffraction data were collected at 173 K on a Rigaku/ADSC CCD area detector with graphite monochromated Mo-Kα radiation. For complex **3**, of the 37530 reflections collected, 10205 were unique (R_{int} = 0.047), the corresponding numbers for **4** being 46909 and 12040 (R_{int} = 0.052); equivalent reflections were merged. Data were collected and processed using the d*TREK program,[30] and corrected for the Lorentz and polarization effects. The structures were solved by direct methods[31] and expanded using Fourier techniques.[32] The non-H atoms were refined anisotropically; the H atoms bound to Ir were refined isotropically, and the rest were included in fixed positions. For **4**, two CH_2Cl_2 molecules were found in the asymmetric unit. The final cycle of full-matrix least-squares refinement for **3** was based on 9884 observed reflections ($I > 0.00\sigma(I)$) and 590 variable parameters, the corresponding numbers for **4** being 11720 and 688. Neutral atom scattering factors were taken from Cromer and Waber.[33] Anomalous dispersion effects were included in F_{calc};[34] the values of $\Delta f'$ and $\Delta f''$[35] and the mass attenuation coefficients[36] were those of Creagh and coworkers. All calculations were performed using teXsan[37] crystallographic software. The final reliability factors for **3** were R_1 = 0.027 (based on 7787 reflections with $I > 3\sigma(I)$) and wR_2 = 0.077 (on F^2, all data), with the corresponding numbers for **4** being R_1 = 0.031 (8723 reflections) and wR_2 = 0.087.

* These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk.

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