Synthesis, characterization, and X-ray structures of three iridium(III)-hydrido-cyclometallated-imine complexes, including the first reported hydrido-(η^1-imine)-Ir complex

Fabio Lorenzini, Paolo Marcazzan, Brian O. Patrick, and Brian R. James

Abstract: Reactions of *cis*,*trans*,*cis*-[Ir(H)$_2$(PPh$_3$)$_2$(solv)$_2$]PF$_6$ (solv = MeOH or Me$_2$CO) with the imines HN=CPh$_2$, (*o*-HOC$_6$H$_4$)C(Me)=NCH$_2$Ph, and PhC(H)=N(*p*-F-C$_6$H$_4$) in MeOH or acetone under Ar give the complexes [IrH{NH=C(Ph)(*o*-C$_6$H$_4$)}(NH=CPh$_2$)(PPh$_3$)$_2$]PF$_6$ (**3**), [IrH{PhCH$_2$N=C(Me)(*o*-C$_6$H$_3$OH)}(solv)(PPh$_3$)$_2$]PF$_6$, where solv = MeOH (**4**) or Me$_2$CO (**4a**), and [IrH{N(*p*-F-C$_6$H$_4$)=CH(*o*-C$_6$H$_4$)}(Me$_2$CO)(PPh$_3$)$_2$]PF$_6$ (**5a**), which have been isolated and characterized. The imine (C$_6$F$_5$)C(H)=NPh is unreactive toward the Ir precursors. The X-ray structures of **3**, **4**·2MeOH, and **5a**·1/2Me$_2$CO show an η^2-*N*,*C*-imine moiety coordinated via the N atom and an orthometallated-C atom. Complex **3**, which contains both an orthometallated imine and an η^1-imine, is the first structurally characterized hydrido-(η^1-imine)-Ir complex. Comparisons are made with data for the corresponding Rh systems.

Key words: iridium, hydride complexes, imines, fluoroimines, phosphine complexes, orthometallation, crystallography, NMR spectroscopy.

Résumé : Les réactions du *cis*,*trans*,*cis*-[Ir(H)$_2$(PPh$_3$)(solv)$_2$]PF$_6$ (solv = MeOH ou Me$_2$CO) avec les imines HN=CPh$_2$, (*o*-HOC$_6$H$_4$)C(Me)=NCH$_2$Ph et PhC(H)=N(*p*-F-C$_6$H$_4$), en solution dans le MeOH ou l'acétone, sous une atmosphère d'argon, conduit à la formation des complexes [IrH{NH=C(Ph)(*o*-C$_6$H$_4$)}(NH=CPh$_2$)(PPh$_3$)$_2$]PF$_6$ (**3**), [IrH{PhCH$_2$N=C(Me)(*o*-C$_6$H$_3$OH)}(solv)(PPh$_3$)$_2$]PF$_6$ dans lequel solv = MeOH (**4**) ou Me$_2$CO (**4a**) et [IrH{N(*p*-F-C$_6$H$_4$)=CH(*o*-C$_6$H$_4$)}(Me$_2$CO)(PPh$_3$)$_2$]PF$_6$ (**5a**) qui ont été isolés et caractérisés. L'imine (C$_6$F$_5$)CH=NPh n'est pas réactive vis-à-vis les précurseurs Ir. Les structures des composés **3**, **4**·2MeOH et **5a**·1/2Me$_2$CO telles que déterminées par diffraction des rayons X ont permis de montrer la présence d'une portion η^2-*N*,*C*-imine coordinée par le biais de l'atome d'azote et d'un atome de carbone orthométallé. Le complexe **3** qui comporte une imine orthométallée ainsi qu'une η^1-imine est le premier complexe hydrido-(η^1-imine)-Ir à être caractérisée d'un point de vue structural. On a effectué des comparaisons avec des données pour les systèmes correspondants du rhodium.

Mots-clés : iridium, complexes d'hydrure, imines, fluoroimines, complexes de phosphine, organométallation, cristallographie, spectroscopie RMN.

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Introduction

Since 2003, we have published 10 papers (1), including one review (2), on the hydrogenation of imines catalyzed by the Rh- and Ir-bis(triphenylphosphine) precursor complexes [M(cod)(PPh$_3$)$_2$]PF$_6$ (M = Rh, Ir; cod = 1,5-cyclooctadiene). Much diverse imine-coordination chemistry has been unveiled, important parameters being the structure and physical nature (solid or liquid) of the imine, the imine:metal stoichiometry, the presence of trace water, the nature of the solvent, use of an inert or an H_2 atmosphere, and catalyst poisoning by the amine product. The studies on the Ir systems, because of their lack of catalytic activity, have been more limited than those on the Rh systems. With imines containing an aryl moiety at the imine-C atom, the Ir precursor has generally formed (at 1:1 imine/Ir stoichiometries) monohydrido-Ir^{III} species via orthometallation at an ortho-C atom of an assumed [*trans*-Ir(PPh$_3$)$_2$(η^1-imine)(solv)]$^+$ intermediate, where solv = MeOH or Me$_2$CO (3); this 'standard' chemistry is illustrated in Scheme 1. With use of excess of the imine PhCH$_2$N=CHPh, the presence of trace water results in Ir-promoted hydrolysis of the imine and the generated benzylamine simply replaces the coordinated solvent of the orthometallated species (3). This new paper reports on the reactions of the Ir precursor with three imines, HN=CPh$_2$ (**Im^1**), (*o*-HOC$_6$H$_4$)C(Me)=NCH$_2$Ph (**Im^2**), and PhC(H)=N(*p*-F-C$_6$H$_4$) (**Im^3**) (see Scheme 2), and notes the non-reactivity of (C$_6$F$_5$)C(H)=NPh (**Im^4**). The imines **Im^1** and **Im^2** were chosen for comparison with their known reactivity toward the corresponding Rh precursor species (1), while the fluoro-substituted imines were used in the hope

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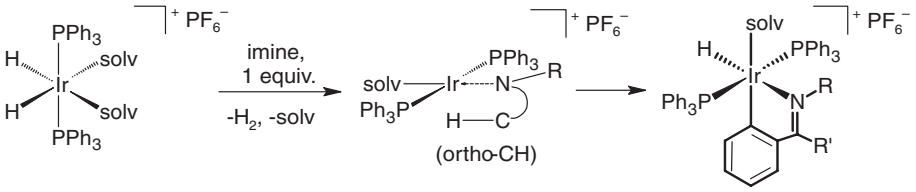
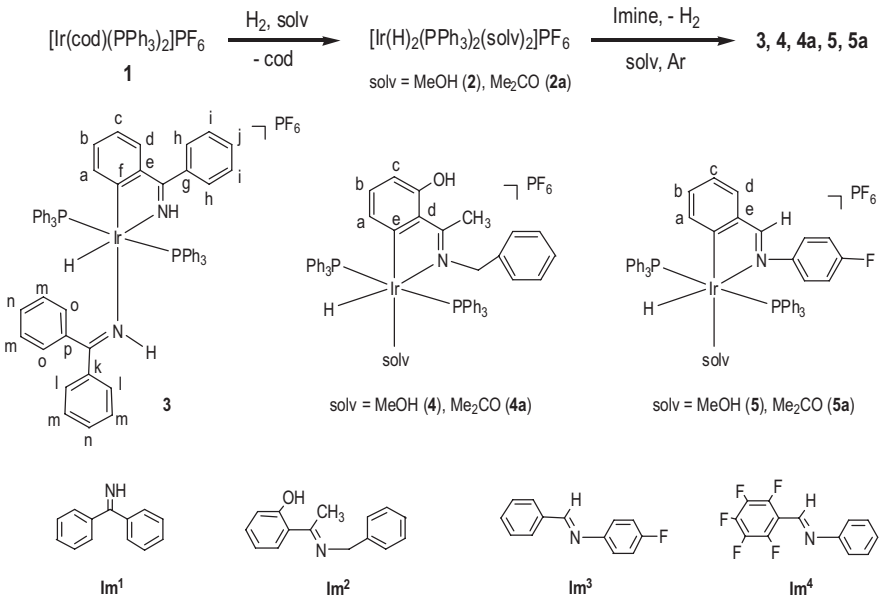
Scheme 1. Formation of Ir^{III}-cyclometallated-imine complexes (R, R′ = aryl or alkyl). $[Ir(cod)(PPh_3)_2]^+$ under H_2 is known to generate *cis*,*trans*,*cis*-$[Ir(H)_2(PPh_3)_2(solv)_2]^+$ (solv = Me_2CO or MeOH (refs. 3, 4)).



Scheme 2. Reactions of *cis*,*trans*,*cis*-$[Ir(H)_2(PPh_3)_2(solv)_2]PF_6$ (solv = MeOH (**2**) or Me_2CO (**2a**)) with the imines **Im[1]**, **Im[2]**, and **Im[3]** to form the complexes $[IrH\{NH=C(Ph)(o\text{-}C_6H_4)\}(\eta^1\text{-}NH=CPh_2)(PPh_3)_2]PF_6$ (**3**), $[IrH\{PhCH_2N=C(Me)(o\text{-}C_6H_3OH)\}(solv)(PPh_3)_2]PF_6$ (solv = MeOH (**4**) or Me_2CO (**4a**)), and $[IrH\{N(p\text{-}C_6H_4\text{-}F)=CH(o\text{-}C_6H_4)\}(solv)(PPh_3)_2]PF_6$ (solv = MeOH (**5**) or Me_2CO (**5a**)). **Im[4]** showed no reactivity.



that the product might be a monometallic η^2-C=N (π-bonded) species because electron-withdrawing substituents appear to favour side-on bonding of imines (5). Such species have not been detected in metal complex-catalyzed hydrogenation of imines and whether they play a mechanistic role (as do π-bonded olefins in catalyzed olefin hydrogenations) is an important, unanswered question (6). We find, in fact, that **Im[1]**, **Im[2]**, and **Im[3]** all form hydrido-orthometallated species akin to those shown in Scheme 1, although in the **Im[1]** product the solvent has been replaced by a second η^1-bonded **Im[1]**. The product from the **Im[1]** reaction corresponds to that found earlier for the Rh system (1*b*); however, the structure presented is the first reported for a hydrido-η^1-imine complex of Ir. The product from the **Im[2]** reaction is different from that of the corresponding Rh system, which does not give an orthometallated product (1*a*). Comparisons between the Ir and Rh reactions with **Im[3]** and **Im[4]** systems are also mentioned.

Experimental

All manipulations and synthetic procedures were performed at room temperature (rt, ~20 °C) under an atmosphere of dry Ar or extra-dry H_2 (from Praxair, Edmonton, Alta.) as stated, using standard Schlenk techniques. The liquid imine $HN=CPh_2$ was a Sigma-Aldrich product, while the solid imines $(o\text{-}HOC_6H_4)C(Me)=NCH_2Ph$, $PhC(H)=N(p\text{-}F\text{-}C_6H_4)$, and $(C_6F_5)C(H)=NPh$ were synthesized previously in this laboratory (7*a*); recent papers by other groups have also described the syntheses of the solid imines, which involve condensation of the ketones or aldehydes with the appropriate amine (7*b*, 7*c*).

The $[Ir(cod)(PPh_3)_2]PF_6$ complex (**1**) was prepared according to a literature procedure (8) using $IrCl_3{\cdot}3H_2O$ purchased from Colonial Metals Inc. Acetone and MeOH (Fisher Scientific) were dried over K_2CO_3 and Mg/I_2, respectively, and distilled under N_2. Acetone-d_6, CD_2Cl_2, and CD_3OD (Cambridge Isotope Laboratory) were used as received for measuring $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectra at rt on a Bruker AV400 spectrometer. When necessary, atom assignments were made by means of ^1H-$^{13}C\{^1H\}$ (HSQC and HMBC) and ^1H-$^{31}P\{^1H\}$ (HSQC and HMBC) NMR correlation spectroscopies. Residual protonated species in the deuterated solvents were used as internal references (δ: 2.05 q for acetone-d_6; δ: 5.32 t for CD_2Cl_2; and δ: 3.31 q and 4.87 s for CD_3OD). All shifts are reported in ppm (s = singlet, d = doublet, t = triplet, q = quintet, spt = septet, m = multiplet, br = broad), relative to external $SiMe_4$ or 85% aq. H_3PO_4, with *J* values in Hz. Solid samples of the synthesized complexes were stored at rt under Ar; elemental

analyses were performed on a Carlo Erba 1108 analyzer. ESI-MS were acquired in the positive ion mode on a Bruker Esquire LC ion-trap mass spectrometer equipped with an electrospray ion source; solvents used were acetone/MeOH or CH_2Cl_2/MeOH, and the sample solution of concentration ~25–50 μmol/L was infused into the ion source by a syringe pump at a flow-rate of 700 μL/h. MALDI-MS were obtained on a Bruker Biflex IV MALDI-TOF spectrometer equipped with a nitrogen laser. The samples were dissolved in acetone/MeOH or CH_2Cl_2/MeOH and dithranol was used as matrix. The sample solutions (~1 mg/mL) and the matrix (20 mg/mL) were mixed in a ratio of 1:1 to 1:10, and 1 μL of the mixture was deposited onto the sample target; these spectra were acquired in the positive reflection mode with delay extraction by averaging 100 laser shots, and were calibrated externally using peptides. MS data are reported as *m*/*z* values. IR spectra were measured with a Thermo Nicolet FT-IR Nexus spectrometer using either a KBr pellet or a solution, as stated.

[IrH{NH=C(Ph)(*o*-C_6H_4)}(HN=CPh_2)(PPh_3)$_2$]PF_6 (3)

A red suspension of [Ir(cod)(PPh_3)$_2$]PF_6 (**1**) (61 mg, 0.063 mmol) in MeOH (1.8 mL) was reacted with 1 atm H_2 at rt to generate immediately a brown solution containing *cis*,*trans*,*cis*-[Ir(H)$_2$(PPh_3)$_2$(MeOH)$_2$]PF_6 (**2**) (3, 4). HN=CPh_2 (**Im^1**) (22.0 μL, 0.127 mmol) in MeOH (0.5 mL) was then added under H_2. Stirring the mixture at rt for 90 min resulted in precipitation of a yellow solid that was collected, washed with Et_2O (3 × 5 mL), and dried in vacuo (63 mg, 82% yield). IR (KBr, cm^{-1}): 3429 (ν_{N-H}), 2132 (ν_{Ir-H}), 1589, 1560 ($\nu_{C=N}$). IR (CH_2Cl_2, cm^{-1}): 3340 (ν_{N-H}), 2195 (ν_{Ir-H}), 1583, 1568 ($\nu_{C=N}$). ^{1}H NMR (CD_2Cl_2) (see Scheme 2 for atom-labeling) δ: –15.80 (t, 1H, $^2J_{HP}$ = 14.1, Ir*H*), 10.21 (s, *H*N=C(*o*-C_6H_4)), 9.98 (s, *H*N=CPh_2), 7.58 (t, 1H, $^3J_{HHi}$ ~ 7.6, H_j), 7.43 (d, 1H, $^3J_{HH}$ = 7.3, H_d), 7.39–7.06 (m, 38H, PC_6H_5, H_i, H_m, H_n), 6.86 (d, 2H, $^3J_{HH}$ = 7.7, H_l or H_o), 6.75 (t, 1H, $^3J_{HHa}$ ~ $^3J_{HHc}$ ≅ 7.3, H_b), 6.65 (t, 1H, $^3J_{HHb}$ ~ $^3J_{HHd}$ ~ 7.2, H_c), 6.56 (d, 1H, $^3J_{HH}$ = 7.5, H_a), 6.37 (d, 2H, $^3J_{HH}$ = 7.6, H_h), 6.28 (d, 2H, $^3J_{HH}$ = 7.5, H_l or H_o). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ: 189.40 (s, NH=*C*(*o*-C_6H_4)), 179.32 (s, HN=*C*Ph_2), 151.59 (s, C_f), 147.32 (s, C_e), 142.04 (s, C_d), 137.97 (s, C_k or C_p), 137.01 (s, C_k or C_p), 134.69 and 131.88-127.93 (m, PC_6H_5, C_i, C_m, C_n), 133.82 (s, C_a), 131.18 (s, C_c), 129.86 (s, C_j), 129.43 (s, C_l or C_o), 128.65 (s, C_h), 128.64 (s, C_l or C_o), 121.23 (s, C_b); the C_g signal could not be assigned. ^{31}P{^{1}H} NMR (CD_2Cl_2) δ: 16.93 (s, *P*Ph), –143.70 (spt, $^1J_{PF}$ = 712.0, *P*F_6). ESI-MS: 1080 [M$^+$], 899 [M$^+$-NH=C(Ph)(*o*-C_6H_4)]. Anal. calcd. for $C_{62}H_{52}N_2F_6P_3Ir$: C 60.83, H 4.28, N 2.29; found: C 60.87, H 4.30, N 2.18.

Yellow, X-ray quality tablet crystals of **3** were grown at rt by diffusion of Et_2O into a CH_2Cl_2 solution (1.5 mL) of the complex (25 mg, 20.4 mmol).

[IrH{$PhCH_2$N=C(Me)(*o*-C_6H_3OH)}(solv)(PPh_3)$_2$]PF_6; solv = MeOH (4), Me_2CO (4a)

A red suspension of **1** (60 mg, 0.062 mmol) in acetone (1.0 mL) was reacted with 1 atm H_2 at rt to form a brown solution of *cis*,*trans*,*cis*-[Ir(H)$_2$(PPh_3)$_2$(Me_2CO)$_2$]PF_6 (**2a**).[2] Addition under Ar of (*o*-HOC_6H_4)C(Me)=NCH_2Ph (**Im^2**) (16 mg, 0.069 mmol) in acetone (1.0 mL) and subsequent stirring of the mixture at rt for 1 h generated a yellow solution. Addition of Et_2O (20.0 mL) precipitated a yellow powder that was collected, washed with Et_2O (2 × 10 mL), and dried in vacuo; the product is **4a** (51 mg, 72% yield). IR (KBr, cm^{-1}): 3057 (ν_{O-H}), 2195 (ν_{Ir-H}), 1587, 1579 ($\nu_{C=N}$). IR (acetone, cm^{-1}): 2034 (ν_{Ir-H}), 1581 ($\nu_{C=N}$). ^{1}H NMR (acetone-d_6) (see Scheme 2 for atom-labeling) δ: –15.48 (t, 1H, $^2J_{HP}$ = 17.6, Ir*H*), 8.94 (br s, 1H, O*H*), 7.51 (m, 5H, $CH_2C_6H_5$), 7.39 (m, 15H, PC_6H_5), 7.27 (t, 1H, $^3J_{HHa}$ ~ $^3J_{HHc}$ ~ 7.3, H_b), 7.04 (m, 15H, PC_6H_5), 6.49 (d, 1H, $^3J_{HHb}$ ~ 7.2, H_c), 6.28 (d, 1H, $^3J_{HHb}$ ~ 7.4, H_a), 5.50 (br s, 2H, NCH_2), 2.09 (br s, 3H, CH_3), 2.09 (br m, 6H, (CH_3)$_2$CO). ^{13}C{^{1}H} NMR (acetone-d_6) δ: 183.26 (s, *C*(H)=N), 159.20 (s, C_d), 136.52 (s, *C*-OH), 134.25 (m, PC_6H_5), 133.31 (s, C_a), 132.71 (m, $CH_2C_6H_5$), 128.59 (m, PC_6H_5), 127.94 (s, C_b), 110.83 (s, C_c), 56.99 (s, *C*H_2Ph) 20.66 (s, *C*H_3); the C_e signal could not be assigned. ^{31}P{^{1}H} NMR (acetone-d_6) δ: 17.91 (s, *P*Ph), –142.64 (spt, $^1J_{PF}$ = 707.3, *P*F_6). MALDI-MS: 942 [M-PF_6-Me_2CO]$^+$, 679 [M – H-PF_6-Me_2CO-PPh_3]$^+$.

X-ray quality, yellow prism crystals of **4**·2MeOH, as well as a yellow precipitate of **4**, were obtained at ~273 K from a saturated MeOH (2.0 mL) solution of **4a**; **4** was washed with Et_2O and dried in vacuo. Anal. calcd. for $C_{52}H_{49}N_4O_2F_6P_3Ir$ (**4**): C 55.81, H 4.41, N, 1.25; found: C 55.89, H 4.94, N 1.22.

[IrH{N(*p*-F-C_6H_4)=CH(*o*-C_6H_4)}(Me_2CO)(PPh_3)$_2$]PF_6 (5a)

A red solution of **1** (25 mg, 0.026 mmol) in acetone-d_6 (or acetone) (1.0 mL) was treated as above with H_2 to form a solution of **2a**. Addition under Ar of PhC(H)=N(*p*-F-C_6H_4) (**Im^3**) (6 mg, 0.030 mmol) in acetone-d_6 (or acetone) (0.5 mL) at rt resulted in a yellow solution into which slow diffusion of Et_2O generated overnight a yellow, crystalline powder (**5a**) and X-ray quality, yellow plate crystals of **5a**·1/2Me_2CO. The powder (**5a**) was collected, washed with Et_2O (3 × 5 mL), and dried in vacuo (24 mg, 83% yield). IR (KBr, cm^{-1}): 2206 (ν_{Ir-H}), 1599 ($\nu_{C=N}$). IR (CH_2Cl_2, cm^{-1}): 2217 (ν_{Ir-H}), 1599, 1587 ($\nu_{C=N}$). ^{1}H NMR (acetone-d_6) (see Scheme 2 for atom-labeling) δ: –16.98 (t, 1H, $^2J_{HP}$ = 15.8, Ir*H*), 8.15 (br s, 1H, C(*H*)=N), 7.49 (m, 6H, C_6H_4F, H_a, H_d), 7.40–7.30, 7.19–7.09 (m, 30H, PC_6H_5), 6.87 (br t, 1H, H_b or H_c), 6.55 (dt, 1H, $^3J_{HH}$ ~ 7.6, $^4J_{HH}$ ~ 1.2, H_b or H_c). ^{13}C{^{1}H} NMR (acetone-d_6) δ: 175.07 (s, *C*(H)=N), 146.88 (s, C_e), 131.43 (m, PC_6H_5), 129.42 (s, C_b or C_c), 128.84 (m, C_6H_4F, C_a, C_d), 126.69 (m, PC_6H_5), 119.39 (s, C_b or C_c). ^{31}P{^{1}H} NMR (acetone-d_6) δ: 17.69 (s, *P*Ph), –142.64 (spt, $^1J_{PF}$ = 707.3, *P*F_6). MALDI-MS: 917 [M-H-PF_6-Me_2CO]$^+$. Anal. calcd. for $C_{52}H_{48}NOF_7P_3Ir$: C 55.71, H 4.32, N 1.25; found: C 55.37, H 4.18, N, 1.25.

Attempted reactions with (C_6F_5)C(H)=NPh (Im^4)

Solutions of **2** and **2a** (and the corresponding species with solv = CD_3OD and acetone-d_6, see Scheme 2) were made in the appropriate solvents as described above, but using a smaller quantity of **1** (15 mg, 0.016 mmol) in 0.5 mL of the respective solvents. No rt reactions over several hours were seen on addition of **Im^4** (5 mg, 0.017 mmol), the NMR spec-

[2] All the complexes labelled with an 'a' have coordinated acetone.

Table 1. Crystal data for complexes **3**, **4**·2MeOH, and **5a**·1/2Me_2CO.

Crystal	**3**	**4**·2MeOH	**5a**·1/2Me_2CO
Empirical formula	$C_{62}H_{52}N_2F_6P_3Ir$	$C_{54}H_{57}N_4O_4F_6P_3Ir$	$C_{53.5}H_{49}NO_{1.5}F_7P_3Ir$
Formula weight	1224.17	1183.12	1148
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$Pna2_1$ (no. 33)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
Crystal size (mm^3)	0.10 × 0.18 × 0.35	0.12 × 0.20 × 0.50	0.05 × 0.20 × 0.40
a (Å)	27.947(1)	12.1301(5)	23.6030(10)
b (Å)	18.5418(7)	13.4827(7)	14.8451(7)
c (Å)	12.0971(5)	31.115(2)	28.2107(14)
α (°)	90.0	90.00	90.00
β (°)	90.0	95.718(2)	92.489(2)
γ (°)	90.0	90.00	90.00
Volume ($Å^3$)	6268.6(4)	5063.4(4)	9875.4(8)
Z	4	4	8
$D_{calcd.}$ (mg m^{-3})	1.297	1.552	1.544
Abs. μ (mm^{-1})	2.260	2.800	2.868
F(000)	2456.00	2384.00	4592.00
Reflections collected	40 584	64 532	129 567
Unique reflections [R(int)]	13 043 [0.051]	12 067 [0.051]	15 224 [0.097]
No. of variables	673	643	1212
GoF on F^2	1.05	1.03	1.20
Final R indices ($I > 2\sigma(I)$)	R_1 0.064,[a] wR_2 0.126[b]	R_1 0.048,[a] wR_2 0.065[b]	R_1 0.111,[a] wR_2 0.195[b]
Max. diff. peak/hole (e $Å^{-3}$)	3.84, –2.87	0.99, –1.12	3.87, –5.27

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$.

tra revealing the presence of only **2** or **2a**. ^{1}H NMR (CD_3OD) δ: –29.46 (t, 1H, $^2J_{HP}$ = 17.1, Ir*H*). ^{31}P{^{1}H} NMR (CD_3OD) δ: 27.16 (s, *P*Ph), –143.32 (spt, $^1J_{PF}$ = 707.5, *P*F_6). ^{1}H NMR (acetone-d_6) δ: –27.68 (t, 1H, $^2J_{HP}$ = 15.9, Ir*H*). ^{31}P{^{1}H} NMR (acetone-d_6) δ: 28.89 (s, *P*Ph), –142.62 (spt, $^1J_{PF}$ = 707.4, *P*F_6). These NMR data are in accord with literature values (3, 4).

X-ray crystallographic analyses of 3, 4·2MeOH, and 5a·1/2Me_2CO

Measurements were made at 173(1) K on a Bruker X8 APEX diffractometer using graphite-monochromated Mo-K α radiation (λ = 0.71073 Å); data were collected and integrated using the Bruker SAINT software package (9) and were corrected for absorption effects using the multi-scan technique (SADABS) (10) with minimum and maximum transmission coefficients of 0.551 and 0.798, respectively, for **3**, 0.434 and 0.715 for **4**·2MeOH, and 0.549 and 0.866 for **5a**·1/2Me_2CO. The data were corrected for Lorentz and polarization effects, and the structures were solved by direct methods (11). For **3**, one phenyl ring appears to be disordered over 2 sites; the 2 rings were thus refined using mild restraints with the major fragment refined anisotropically and the minor fragment isotropically. Located in difference maps and refined isotropically were the imine-H of the orthometallated imine of **3**, and the hydride and the H-atoms of the OH groups of the coordinated MeOH and the C_6H_3 ring of **4**. The hydrides of **3** and **5a** were not located and were thus not included in the models. All other H-atoms of the complexes were placed in calculated positions and were not refined. Some of the crystallographic data are given in Table 1, while selected bond lengths and angles are given in Table 2.

Results and discussion

The new complexes [IrH{NH=C(Ph)(*o*-C_6H_4)}(HN=CPh_2)-(PPh_3)$_2$]PF_6 (**3**), [IrH{$PhCH_2N$=C(Me)(*o*-C_6H_3OH)}(solv)-(PPh_3)$_2$]PF_6, where solv = MeOH (**4**) or Me_2CO (**4a**), and [IrH{N(*p*-F-C_6H_4)=CH(*o*-C_6H_4)}(Me_2CO)(PPh_3)$_2$]PF_6 (**5a**), were obtained by reaction of *cis*,*trans*,*cis*-[Ir(H)$_2$(PPh_3)$_2$(solv)$_2$]PF_6 (solv = MeOH (**2**) or Me_2CO (**2a**)) with the imine, with co-production of H_2 (Scheme 2); the complexes are of the well-documented hydrido-orthometallated-imine type (Scheme 1). Such complexes have been characterized for many metals (certainly for all the platinum metals; see following and ref. 12), and continue to attract attention because of their wide range of applicability in areas that include asymmetric synthesis, functionalization of C–H bonds, C-C coupling reactions, and biological systems (13).

Complex **3** was readily obtained in 82% yield from reaction in MeOH of **2** with 2 equiv. of benzophenone imine (HN=CPh_2, **Im^1**), and was fully characterized by X-ray analysis, elemental analysis, and NMR, IR, and MS data. Our group recently isolated the analogous Rh complex with essentially the same structure (see later), but the Rh species was formed more slowly via *cis*-[Rh(PPh_3)$_2$(η^1-NH=CPh_2)$_2$]PF_6 in which one imine ligand subsequently undergoes orthometallation (1*b*). No intermediates were detected in the Ir system, the stronger Ir-H bond (vs. Rh-H) presumably promoting the metallation step (14).

The reaction of **2** with (*o*-HOC_6H_4)C(Me)=NCH_2Ph (**Im^2**) in MeOH resulted in a mixture of products that could not be separated. However, a successful isolation of complex **4** was achieved by carrying out a 1:1 reaction of **2a** with **Im^2** in acetone and then recrystallizing the resulting isolated acetone analogue (**4a**) from MeOH. Complex **4a**, obtained in

Table 2. Selected bond lengths and angles for **3**, **4**·2MeOH, and **5a**·1/2Me_2CO.

3		**4**·2MeOH		**5a**·1/2Me_2CO[a]	
Bond lengths (Å)					
Ir(1)—C(1)	2.018(7)	Ir(1)—C(1)	1.998(3)	Ir(2)—C(53)	2.082(15)
Ir(1)—N(1)	2.138(6)	Ir(1)—H(1)	1.27(4)	Ir(2)—N(2)	2.157(12)
Ir(1)—N(2)	2.132(6)	Ir(1)—N(1)	2.151(3)	Ir(2)—O(2)	2.154(10)
Ir(1)—P(1)	2.3308(19)	Ir(1)—O(2)	2.237(2)	Ir(2)—P(3)	2.332(4)
Ir(1)—P(2)	2.331(2)	Ir(1)—P(1)	2.3320(8)	Ir(2)—P(4)	2.316(4)
N(1)—C(7)	1.296(9)	Ir(1)—P(2)	2.3310(8)	C(59)—N(2)	1.294(18)
C(14)—N(2)	1.265(9)	C(7)—N(1)	1.299(4)		
Bond angles (°)					
C(1)-Ir(1)-N(1)	78.7(3)	C(1)-Ir(1)-H(1)	95.9(16)	C(53)-Ir(2)-N(2)	79.3(5)
C(1)-Ir(1)-N(2)	177.1(3)	C(1)-Ir(1)-N(1)	78.27(11)	C(53)-Ir(2)-O(2)	170.4(5)
C(1)-Ir(1)-P(1)	87.3(2)	C(1)-Ir(1)-O(2)	178.07(10)	C(53)-Ir(2)-P(3)	87.3(4)
C(1)-Ir(1)-P(2)	89.6(2)	C(1)-Ir(1)-P(1)	88.04(8)	C(53)-Ir(2)-P(4)	88.3(4)
N(1)-Ir(1)-N(2)	98.6(2)	C(1)-Ir(1)-P(2)	88.95(8)	N(2)-Ir(2)-O(2)	91.1(4)
N(1)-Ir(1)-P(1)	92.21(16)	H(1)-Ir(1)-N(1)	173.8(16)	N(2)-Ir(2)-P(3)	94.6(3)
N(1)-Ir(1)-P(2)	92.40(17)	H(1)-Ir(1)-O(2)	84.6(16)	N(2)-Ir(2)-P(4)	97.2(3)
N(2)-Ir(1)-P(1)	91.70(16)	H(1)-Ir(1)-P(1)	88.6(15)	O(2)-Ir(2)-P(3)	94.5(3)
N(2)-Ir(1)-P(2)	91.58(16)	H(1)-Ir(1)-P(2)	76.7(15)	O(2)-Ir(2)-P(4)	92.0(3)
P(1)-Ir(1)-P(2)	173.88(7)	N(1)-Ir(1)-O(2)	101.26(10)	P(3)-Ir(2)-P(4)	166.37(14)
C(14)-N(2)-Ir(1)	134.7(5)	N(1)-Ir(1)-P(1)	93.26(7)	Ir(2)-O(2)-C(102)	137.6(13)
C(7)-N(1)-H(1n)	127(4)	N(1)-Ir(1)-P(2)	100.84(7)		
Ir(1)-N(1)-H(1n)	118(4)	O(2)-Ir(1)-P(1)	90.12(6)		
		O(2)-Ir(1)-P(2)	92.98(6)		
		P(1)-Ir(1)-P(2)	164.67(3)		
		C(34)-O(2)-Ir(1)	122.7(2)		

[a]Data for one of the two molecules in the asymmetric unit.

72% yield, was well characterized by NMR, MS, and IR data, but a satisfactory elemental analysis could not be obtained, possibly because of the variable acetone solvate content; complex **4** as a yellow powder gave a good elemental analysis for a non-solvated species, while the crystal contained two MeOH solvates per molecule as determined by X-ray analysis (see later).

Of note, the rate of formation of **4a** appears to be dependent on the water content of the solvent (acetone or methanol); in the synthetic work carried out in dried solvents, reaction was complete in ~1 h, but the reaction of **2a** with **Im²**, as monitored by $^{31}P\{^1H\}$ NMR spectroscopy in non-dried acetone-d_6, took ~13 d for completion (Fig. S1, δ_P: 28.89 for **2a** and 17.91 for **4a**).[2] Presumably, water competes with the solvent for a coordination site in **2a** and (or) **4a** and somehow impedes the reaction, although there was no direct evidence for the presence of any aquo species.

Reaction of **2a** with PhC(H)=N(*p*-F-C_6H_4) (**Im³**) at ~1:1 stoichiometry in acetone led to the isolation of **5a** in 83% yield as a mixture of a yellow powder and crystals after slow diffusion of Et_2O into the solution of **5a**; higher yields were obtained when a 2:1 ratio of **Im³**/Ir was used. Elemental analysis of the powder corresponded to unsolvated **5a**, while X-ray analysis of the crystal revealed one-half an acetone solvate per molecule (see below). NMR, MS, and IR data were in accord with the solid state structure. The formation of **5a** is apparently a reversible process as evidenced by monitoring under H_2 an acetone-d_6 solution of isolated **5a** by $^{31}P\{^1H\}$ NMR spectroscopy (Fig. S2)[3]: the δ_P 17.69 resonance of **5a** decays over a week and is partially replaced by the δ_P 28.89 signal of the Ir-dihydride (**2a**, where solv = acetone-d_6). Of note, no formation of **5** (the MeOH/CD_3OD analogue of **5a**) was evident when **2** (solv = CD_3OD) was reacted with ~1 mol equiv. of **Im³** in CD_3OD at rt; in situ $^{31}P\{^1H\}$ NMR spectra over several hours revealed only the δ_P 27.16 resonance of **2**, although over the period of a week this was replaced completely by broad singlets at δ_P 21.00 and 19.68 due to unidentified species (at an **Im³**:Ir ratio of 2, ~15% of **5** was formed over a week as evidenced by a resonance at δ_P 17.66). The complications detected by the NMR experiments may again be symptomatic of water impurity in the deuterated solvents and stresses the need for dry solvents in the synthetic procedures.

As monitored by $^{31}P\{^1H\}$ NMR spectroscopy, there was no reaction at rt of **2** or **2a** with (C_6F_5)C(H)=NPh (**Im⁴**) in the respective solvents at imine:Ir ratios up to 2.

The X-ray structures of the cations of **3**, **4**·2MeOH, and **5a**·1/2Me_2CO are shown in Figs. 1–3, and some geometrical

[2] Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 3710. For more information on obtaining material refer to cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC numbers 670430–670432 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via 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 336033; or deposit@ccdc.cam.ac.uk).

Fig. 1. Structure of the $[IrH\{NH{=}C(Ph)(o\text{-}C_6H_4)\}(HN{=}CPh_2)(PPh_3)_2]^+$ cation of **3**, with 50% probability ellipsoids.

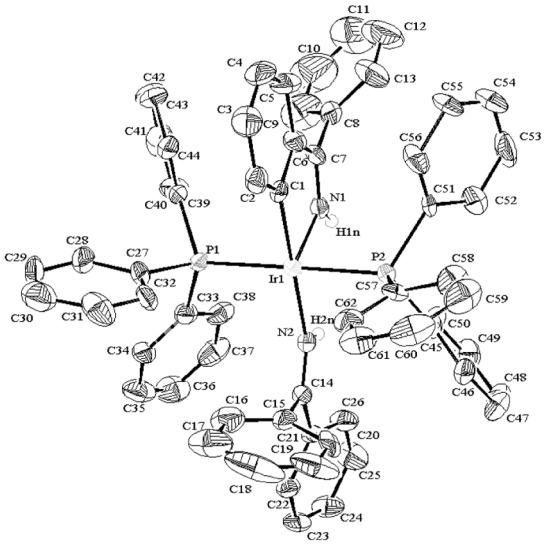
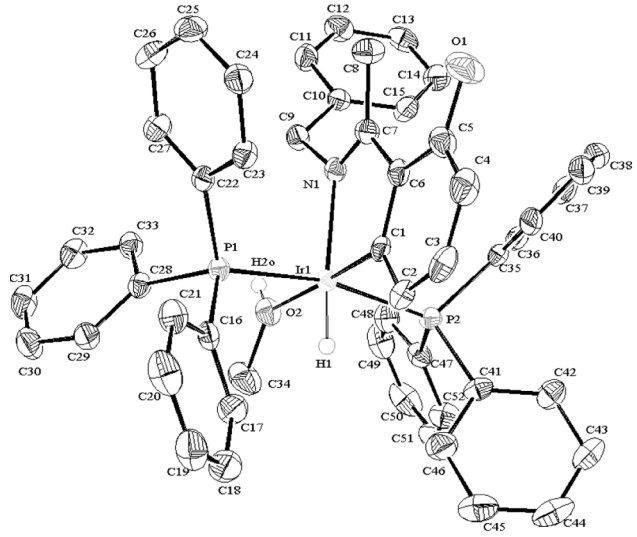
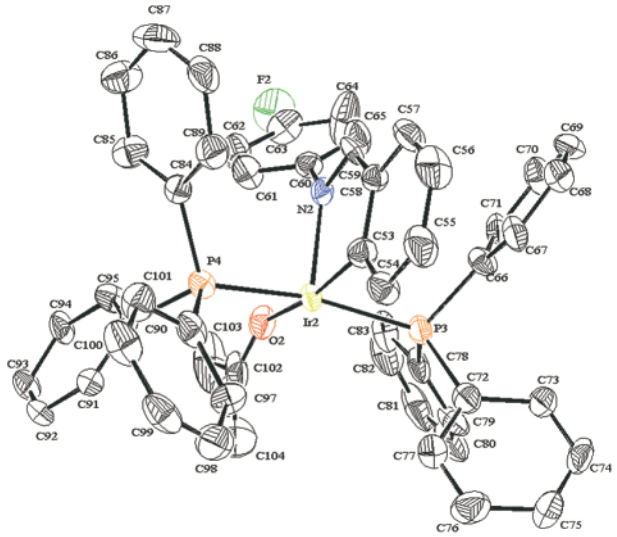


Fig. 2. Structure of the $[IrH\{PhCH_2N{=}C(Me)(o\text{-}C_6H_3OH)\}(MeOH)(PPh_3)_2]^+$ cation of **4**, with 50% probability ellipsoids.



parameters are listed in Table 2. Complexes **3** and **4**·2MeOH crystallize with one molecule in the asymmetric unit, while **5a**·1/2Me_2CO crystallizes as two almost identical, crystallographically independent molecules with one molecule of free acetone in the asymmetric unit. The structures of the three distorted octahedral Ir^{III} cations exhibit similar features, all having five coordination sites occupied by the same arrangement of ligands: an η^2-imine moiety coordinated via the imine-N atom and the orthometallated-C atom (C_{ortho}), a hydride trans to the N-atom, and *trans*-PPh_3 ligands cis to the hydride (cf. Scheme 1), and, while **4** and **5a** respectively have MeOH or Me_2CO coordinated trans to C_{ortho}, **3** has a second imine, η^1-coordinated. The hydride attached to the heavy metal centre was successfully located by X-ray analysis only for **4**, but ^1H NMR data (a high-field triplet at δ_H –17 to –15 with $^2J_{HP}$ ~ 14–18 Hz, and IR data

Fig. 3. Structure of one of the two almost identical molecules of the $[IrH\{N(p\text{-}C_6H_4\text{-}F){=}CH(o\text{-}C_6H_4)\}(Me_2CO)(PPh_3)_2]^+$ cation of **5a**, with 50% probability ellipsoids.



showing $\nu_{Ir\text{-}H}$ 2034–2217 cm^{-1}) unequivocally establish its presence in all three complexes. (Solid state and solution IR data for $\nu_{C=N}$ for **3**–**5**, $\nu_{N\text{-}H}$ for **3**, and $\nu_{O\text{-}H}$ for **4** are also noted). The hydride resonances are very similar to those we found earlier for an analogue of **5a** synthesized in the same manner but using $PhC(H){=}NCH_2Ph$ (**3**). The imine-N*H* proton singlets for **3**, at δ 9.98 (for the η^1-imine) and 10.21 (for the η^2-imine), are close to the values reported for the same imine (**Im^1**) similarly coordinated at Ru^{II} and Os^{II} (15) but are ~3 ppm to lower field than those of the Rh analogue $[RhH\{NH{=}C(Ph)(o\text{-}C_6H_4)\}(HN{=}CPh_2)(PPh_3)_2]PF_6$ (1*b*). Measurements of 2D HSQC, HMBC $^{31}P\{^1H\}/^1H$, and 2D HSQC, HMBC $^{13}C\{^1H\}/^1H$ NMR spectra have allowed for assignment of all the ^1H NMR resonances of **3**, **4**, and **5a**. The $^{31}P\{^1H\}$ NMR spectra of **3**, **4a**, and **5a** each show a sharp singlet in the δ 18–17 region for the *trans*-phosphines, and a septet at δ ~–143 for the PF_6^- anion. Mass spectral data for complex **3** show the mass fragment of the intact cation, while the highest fragments seen for **4a** and **5a** correspond to $[IrH\{N(CH_2Ph){=}C(Me)(o\text{-}C_6H_3OH)\}(PPh_3)_2]^+$ and $[Ir\{N(p\text{-}F\text{-}C_6H_4){=}CH(o\text{-}C_6H_4)\}(PPh_3)_2]^+$, respectively.

The five-membered planar metallocycle ring within the complexes is essentially coplanar with the η^1-N atom of the second imine in **3**, the O-C of the MeOH in **4**·2MeOH, and the O-C-C_2 unit of the Me_2CO in **5a**. The N-Ir-C angle of the metallocycle of all three structures (79.3°–78.3°) is very similar to those found in other cyclometallated imine complexes of Ir^{III} (3) and also, for example, of Rh^{III} (16) and Os^{II} (17). The *trans*-PPh_3 ligands are bent slightly towards the hydride as indicated by P-Ir-P angles of 164.7° to 173.9° and other angles at the Ir centre (Table 2); all such hydridobis(phosphine)-orthometallated-imine complexes of Ir (3) and Rh (1*b*, 16) systems display such bending. The Ir-O-C angles of the coordinated MeOH in **4** and coordinated acetone in **5a** are 122.7° and 137.6°, respectively.

The Ir—P, Ir—N, and Ir—C_{ortho} bond lengths (and the C=N bond lengths for the η^2-*C*,*N*-imine) for the three complexes are in the range found previously for the closely re-

lated orthometallated-imine species [IrH{$PhCH_2N$=CH(*o*-C_6H_4)}(PPh_3)$_2$L]PF_6, where L = Me_2CO or $PhCH_2NH_2$ (3). The geometry of the orthometallated benzophenone ligand of **3** is also very similar to that of the same ligand within the Rh analogue of **3** (1*b*) and within complexes of Ru^{II} (15*d*) and Os^{II} (17). The C=N bond length of the η^1-NH=CPh_2 of **3** is about 0.2 Å shorter than that of the corresponding Rh complex (1*b*) and those found in other Rh^{I}- and Rh^{III}-(η^1-imine) complexes (18).

As far as we are aware, complex **3** is the first structurally characterized Ir(η^1-imine) complex, where the imine is a 'standard one', i.e., containing only alkyl, aryl, or hydrogen substituents at the imine-C and -N atoms; however, other such Ir(η^1-imine) complexes have been isolated, including benzophenone systems (19). Complex **3** is also a relatively rare example of a hydrido-η^1-imine species; except for the Rh analogue of **3** mentioned above (1*b*), all the other examples are η^1-benzophenone derivatives of Ru or Os (15). There is, of course, a vast literature on Ir complexes with 'non-standard' η^1-N=C < moieties within a range of ligands such as imine-ethers, iminols, and amidines (20), diimines (21), pyrazoles (22), imidazoles (22), oxazolines (23), oxazolones (24), anthranil (25), and creatinine (26).

The ketimine **Im^2**, containing an *o*-OH substituent in the imine-C phenyl group, forms complex **4**, a typical hydrido-orthometallated species akin to those we report here and elsewhere (3); however, this is the first type of such a complex derived from this ketimine. In complexes of Cu^{II} (27), Ru^{II} (28), and V^{IV} (29), the ketimine is chelated via the N-atom and the alkoxy-O atom from the hydroxy group. In recent work, on an analogous study of this imine with *cis*,*trans*,*cis*-[$Rh(H)_2(PPh_3)_2(MeOH)_2$]PF_6 (or *cis*-[$Rh(PPh_3)_2(MeOH)_2$]PF_6), we isolated an unique type of zwitterionic complex, namely [Rh{η^4-$(C_6H_4O)^{(-)}$C(Me)=$N^{(+)}$(H)CH_2Ph}-(PPh_3)$_2$]PF_6, in which the ketimine is coordinated via the C_4 part of the *o*-hydroxy-arene moiety in a quinoid form; this tautomer is generated via proton transfer from the O-atom to the N-atom within the molecular, benzenoid form. Presumably, the strength of the Ir–H bond again promotes the orthometallation.

Complex **5a** formed from **Im^3** is again a typical hydrido-orthometallated species, but we are unaware of any other such structures with this fluorinated imine. Of note, however, a recent structure with this imine, Ni[^{i}Pr_2P(CH_2)$_2$P^iPr_2]-[PhC(H)=N(*p*-F-C_6H_4)], reveals the π-bonded **Im^3** (5), and indeed this report prompted us to investigate the reactivity of this particular imine toward Ir. The strength of the Ir–H bond again likely favours formation of **5a**. Of major interest, in a cursory study we have found that the reaction of **Im^3** with the Rh analogue of **2a** forms only a trace of a hydrido-orthometallated species, and the major product has yet to be identified.[3] The fluoro-aldimine (C_6F_5)C(H)=NPh (**Im^4**) was unreactive toward **2**, **2a**, or the corresponding Rh species; the reactivity of **Im^4** toward the Ni precursor used for the **Im^3** reaction, [Ni{^{i}Pr_2P(CH_2)$_2$P^iPr_2}]$_2$(μ-H)$_2$, was not reported (5). We continue studies with variation of the fluoroimine and the phosphine ligand in the hope of achieving an appropriate electronic and steric environment for formation of a π-bonded imine-Ir or -Rh complex.

Our previous studies have shown that isolated Ir-cyclometallated-imine complexes are stable toward H_2 in acetone or MeOH solution at ambient conditions and are not effective for catalytic hydrogenation of the imine (3, 30), and this has been confirmed recently by the Zaragosa group (31). The new complexes **3**–**5** are similarly inactive. In general, cyclometallated-imine Rh complexes can become active catalysts in MeOH, when they undergo partial reductive elimination of the cyclometallated imine (the reverse of orthometallation — cf. the intermediate shown in Scheme 1) to generate a solvated η^1-imine species that does react with H_2 (2, 16*a*). The Rh analogues of **3** (1*b*) and **5a**[4] are inactive toward H_2, while the Rh analogue of **4** (or **4a**) is unknown (see earlier), and the Ir and Rh complexes derived from **Im^3** in MeOH are not characterized.

Conclusions

Following our earlier work on the reactions between imines and *cis*,*trans*,*cis*-[$Rh(H)_2(PPh_3)_2(solv)_2$]$^+$ (solv = MeOH or Me_2CO), this article describes reactions of the imines with the corresponding Ir precursor species. The selected imines are HN=CPh_2, (*o*-HOC_6H_4)C(Me)=NCH_2Ph, and PhC(H)=N(*p*-F-C_6H_4), the last one being chosen with the aim of possibly favouring formation of an η^2-C=N (π-bonded) species. However, in each case, the product is a hydrido species containing an η^2-*N*,*C*-imine moiety coordinated via the N atom and an orthometallated-C atom. With benzophenone imine, the product contains also a second imine that is η^1-N coordinated, the product proving to be the first reported, structurally characterized hydrido-(η^1-imine)-Ir complex. The Ir complexes are inactive as precursor hydrogenation catalysts for the imines. Comparisons are made with the products formed in the corresponding Rh systems and significant differences are noted.

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