HX elimination from $Ir(H)_2X(PBu^t_2Ph)_2$ promoted by CO coordination: assessment of X ligand influence†

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The coordinatively unsaturated complexes $Ir(H)_2X(PBu^t_2Ph)_2$ [X = Cl, Br, I, N_3, N=C=NSiMe$_3$, NHC(O)CH$_3$, OC(O)CF$_3$, OSO$_2$CF$_3$, OC(O)CH$_3$, SPh, OPh, F] all react within the mixing time in arene solvents to bind carbon monoxide. Subsequent reactivity of these CO adducts reductively to eliminate HX is dependent on the magnitude of the inherent destabilization caused by filled-filled repulsions between the ligand p_π orbitals and metal d_π orbitals. This destabilization is *not* sufficient to promote the loss of HX when X = Cl, Br, I, N_3, N=C=NSiMe$_3$, NHC(O)CH$_3$ or OC(O)CF$_3$. When X = OC(O)CH$_3$ or SPh, metastable CO adducts are formed that ultimately lose HX. The complexes containing OPh or F quickly lose HX upon reaction with CO. The unusual iridium(I) complexes $IrH(CO)_2(PBu^t_2Ph)$ and $IrH(CO)(PBu^t_2Ph)_2$ have been characterized by multinuclear NMR and IR spectroscopy. The reaction of $Ir(H)_2(F)(PBu^t_2Ph)_2$ with CO in a glass vessel yields crystalline $[Ir(H)_2(CO)_2(PBu^t_2Ph)_2][SiF_5]$ and $[Ir(CO)_2(PBu^t_2Ph)_2][SiF_5] \cdot C_6D_6$, both characterized by X-ray diffraction. The latter, although approximately square planar, has a C—Ir—C angle of only 162.7°. Crystallographic data (*Pc* at −165 °C) for $[Ir(H)_2(CO)_2(PBu^t_2Ph)_2][SiF_5]$, $a = 8.293(2)$, $b = 12.462(5)$, $c = 16.333(7)$ Å, $\beta = 98.21(2)°$ with $Z = 2$. Crystallographic data (*P2₁/n* at −172 °C) for $[Ir(CO)_2(PBu^t_2Ph)_2][SiF_5] \cdot C_6D_6$, $a = 13.041(7)$, $b = 12.998(5)$, $c = 22.553(13)$ Å, $\beta = 97.50(2)°$ with $Z = 4$.

The synthesis and reactivity of iridium dihydride complexes of the general formula $Ir(H)_2XL_2$ (X = halide or pseudohalide, L = bulky phosphine) have been extensively investigated since the earliest reports of the synthesis of these complexes.[1] These coordinatively unsaturated complexes react with a variety of Lewis bases[2] and π-acid ligands including dihydrogen[3] and ethylene.[4] Their reactivity towards alkynes has been used recently to synthesize a number of new alkynyl and vinylidene complexes.[5] Studies have also shown that these complexes may be used as catalysts or catalyst precursors for a number of catalytic processes including hydrogenation.[6]

While the investigations of the reactivity of these complexes have been extensive, the influence of the identity of the X ligand on the reactivity has been overlooked in many cases. It has been proposed[7] that coordinatively unsaturated transition metal complexes may be stabilized by donation of lone pair electron density from halide and pseudohalide ligands, provided that there is effective d_π–p_π orbital overlap between an empty d_π orbital and a filled (nonbonding) p_π ligand orbital. Thus, the reactivity (Lewis acidity) of $Ir(H)_2XL_2$ should be highly dependent on the ability of the X ligand to stabilize coordinative unsaturation. Indeed, we have observed that the rate of catalytic olefin isomerization activity of an $Ir(H)_2XL_2$ complex is dependent on the donating ability of the X ligand.[8]

However, the same properties of a ligand with strong 'net donating ability' (*i.e.*, combined σ and π electron donation) to stabilize coordinative unsaturation also serve to *destabilize* a coordinatively saturated complex *via* filled-filled d_π–p_π repulsions.[7] This destabilization is often manifested as a unimolecular reaction to remove the destabilizing repulsive interactions. These reactions can include ionization of the complex to expel the X ligand to the outer coordination sphere,[9] insertion into the M—X bond to replace the π-donor ligand X with a non-π-donating ligand,[10] or for complexes in a suitably high valence state, reductive elimination of the X

ligand and another ligand (L′) to release free L′X.[11] Therefore, the relative net donating ability of an X ligand can be revealed not only in the stabilization of coordinatively unsaturated complexes/intermediates, but also in the *destabilization* (and subsequent reactivity to remove such destabilization) of coordinatively saturated complexes and the formation of strong H—X bonds. Towards this end, the characterization of the reactions of a number of $Ir(H)_2X(PBu^t_2Ph)_2$ complexes with the strongly binding ligand, CO, have been performed. This study has been enhanced by a recently developed synthetic methodology that has been used to synthesize a large number of new $Ir(H)_2X(PBu^t_2Ph)_2$ encompassing a wide range of expected X ligand π-donor abilities.[12]

Experimental

General procedures

All manipulations were carried out using standard Schlenk and glovebox techniques under argon. Toluene, benzene and THF were dried and deoxygenated over sodium or potassium–benzophenone and distilled under argon. C_6D_6 and C_7D_8 were dried over sodium metal and vacuum distilled before use in a glovebox. CDCl$_3$ was dried over CaH$_2$ and vacuum distilled before use in a glovebox. ^{1}H (referenced to residual solvent impurity), ^{13}C{^{1}H}, ^{31}P{^{1}H} (referenced to external 85% H$_3$PO$_4$) and ^{19}F (referenced to external CFCl$_3$) NMR spectra were collected on Varian Gemini-300 and Inova-400 spectrometers. Ethylene (CP grade, Air Products), carbon monoxide (CP grade, Air Products) and ^{13}C (99% ^{13}C, Monsanto Research Corp.) were used without further purification. Triethylamine (Aldrich) was degassed and dried over 4 Å molecular sieves. Lithium 2,2,6,6-tetramethyl-piperidide was prepared by the reaction of 2,2,6,6-tetramethyl-piperidine with Bu^{n}Li in pentane at −78 °C. Compounds **1–3**[8], **4–7, 15, 18–20**,[12] and **21**[27] were synthesized according to literature procedures.

Preparations and reactions

Ir(H)$_2$Cl(CO)(PBu$^t_2$Ph)$_2$ (8). In a 100 mL Schlenk flask was dissolved Ir(H)$_2$Cl(PBu$^t_2$Ph)$_2$ (500 mg, 0.74 mmol) in 15 mL THF. This solution was degassed three times (freeze–pump–thaw method) and 1 atm CO introduced into the flask. Upon stirring, the solution rapidly (<2 min) changed from orange to colorless. The volatiles were removed *in vacuo* to yield an off-white solid (488 mg, 94%). ^{1}H NMR (C$_6$D$_6$, 25 °C): 8.45 (m), 7.20–7.01 (m), 1.49 (vt, J_{PH} = 7.2 Hz), 1.40 (vt, J_{PH} = 6.6 Hz), −8.20 (td, J_{PH} = 18.0 Hz, J_{HH} = 5.7 Hz), −20.31 (td, J_{PH} = 14.4 Hz, $J_{HH'}$ = 5.7 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 25 °C): 53.6 (s). IR (C$_6$D$_6$): ν(CO) 1985 cm^{-1}.

Ir(H)$_2$Br(CO)(PBu$^t_2$Ph)$_2$ (9). In an NMR tube was dissolved Ir(H)$_2$Br(PBu$^t_2$Ph)$_2$ (20 mg, 0.028 mmol) in 0.6 mL C$_6$D$_6$ to form an orange solution. This solution was degassed three times (freeze–pump–thaw) and 1 atm CO introduced. Upon mixing, the solution immediately became colorless. ^{1}H NMR (C$_6$D$_6$, 25 °C): 8.48 (m), 7.20–7.01 (m), 1.50 (vt, J_{PH} = 7.2 Hz), 1.41 (vt, J_{PH} = 6.6 Hz), −8.55 (td, J_{PH} = 18.0 Hz, $J_{HH'}$ = 5.4 Hz), −19.31 (td, J_{PH} = 14.4 Hz, $J_{HH'}$ = 5.4 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 25 °C): 48.4 (s). IR (C$_6$D$_6$): ν(CO) 1985 cm^{-1}.

Ir(H)$_2$I(CO)(PBu$^t_2$Ph)$_2$ (10). In an NMR tube was dissolved Ir(H)$_2$I(PBu$^t_2$Ph)$_2$ (20 mg, 0.026 mmol) in 0.6 mL C$_6$D$_6$ to form an orange solution. This solution was degassed three times (freeze–pump–thaw) and 1 atm CO introduced. Upon mixing, the solution immediately became colorless. ^{1}H NMR (C$_6$D$_6$, 25 °C): 8.38 (m), 7.19–7.01 (m), 1.51 (vt, J_{PH} = 7.2 Hz), 1.40 (vt, J_{PH} = 6.9 Hz), −9.95 (td, J_{PH} = 18.0 Hz, $J_{HH'}$ = 5.4 Hz), −17.56 (td, J_{PH} = 15.3 Hz, $J_{HH'}$ = 5.4 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 25 °C): 47.3 (s). IR (C$_6$D$_6$): ν(CO) 1985 cm^{-1}.

Ir(H)$_2$(N$_3$)(CO)(PBu$^t_2$Ph)$_2$ (11). In an NMR tube was dissolved Ir(H)$_2$(N$_3$)(PBu$^t_2$Ph)$_2$ (20 mg, 0.029 mmol) in 0.6 mL C$_6$D$_6$ to form an orange solution. This solution was degassed three times (freeze–pump–thaw) and 1 atm CO introduced. Upon mixing, the solution immediately became colorless. ^{1}H NMR (C$_6$D$_6$, 25 °C): 8.30 (m), 7.22–7.03 (m), 1.40 (vt, J_{PH} = 7.2 Hz), 1.34 (vt, J_{PH} = 6.9 Hz), −8.08 (td, J_{PH} = 18.0 Hz, $J_{HH'}$ = 5.4 Hz), −20.2 (td, J_{PH} = 14.4 Hz, $J_{HH'}$ = 5.4 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 25 °C): 59.4 (s). IR (C$_6$D$_6$): ν(CO) 1983 cm^{-1}.

Ir(H)$_2$(N=C=NSiMe$_3$)(CO)(PBu$^t_2$Ph)$_2$ (12). In an NMR tube was dissolved Ir(H)$_2$(N=C=NSiMe$_3$)(PBu$^t_2$Ph)$_2$ (20 mg, 0.027 mmol) in 0.6 mL C$_6$D$_6$ to form an orange solution. This solution was degassed three times (freeze–pump–thaw) and 1 atm CO introduced. Upon mixing the solution immediately became colorless. ^{1}H NMR (C$_6$D$_6$, 25 °C): 8.39 (m), 7.19–6.99 (m), 1.32 (vt, J_{PH} = 7.2 Hz), 1.27 (vt, J_{PH} = 6.8 Hz), 0.31 (s), −8.41 (td, J_{PH} = 18.0 Hz, $J_{HH'}$ = 5.6 Hz), −19.37 (td, J_{PH} = 14.4 Hz, $J_{HH'}$ = 5.6 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 25 °C): 48.5 (s). IR (C$_6$D$_6$): ν(CO) 1973 cm^{-1}.

Ir(H)$_2$[NHC(O)CH$_3$](CO)(PBu$^t_2$Ph)$_2$ (13). In an NMR tube was dissolved Ir(H)$_2$[NHC(O)CH$_3$](PBu$^t_2$Ph)$_2$ (15 mg, 0.022 mmol) in 0.6 mL C$_6$D$_6$. This yellow solution was degassed three times (freeze–pump–thaw) and 1 atm CO introduced. Upon mixing, the solution immediately became colorless. ^{1}H NMR (C$_6$D$_6$, 25 °C): 8.36 (m), 7.29–7.04 (m), 3.53 (br s, 1H), 1.89 (s, 3H), 1.39 (vt, J_{PH} = 6.9 Hz), 1.36 (vt, J_{PH} = 6.6 Hz), −10.2 (td, J_{PH} = 18.9 Hz, $J_{HH'}$ = 4.2 Hz), −18.3 (td, J_{PH} = 16.5 Hz, $J_{HH'}$ = 4.2 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 25 °C): 53.3 (s). IR (C$_6$D$_6$): ν(CO) 1962 cm^{-1}.

Ir(H)$_2$[OC(O)CF$_3$](CO)(PBu$^t_2$Ph)$_2$ (14). In an NMR tube was dissolved Ir(H)$_2$[OC(O)CF$_3$](PBu$^t_2$Ph)$_2$ (40 mg, 0.053 mmol) in 0.6 mL C$_6$D$_6$. This light yellow solution was degassed three times (freeze–pump–thaw) and 1.5 atm CO introduced. Upon mixing, the solution immediately became colorless. ^{1}H NMR (C$_6$D$_6$, 25 °C): 8.20 (m), 7.24–7.02 (m), 1.32 (vt, J_{PH} = 6.9 Hz), 1.28 (vt, J_{PH} = 6.9 Hz), −7.58 (td, J_{PH} = 18.3 Hz, $J_{HH'}$ = 6.0 Hz), −23.92 (td, J_{PH} = 14.4 Hz, $J_{HH'}$ = 6.0 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 25 °C): 54.3 (s). ^{19}F NMR (C$_6$D$_6$, 25 °C): −77.2 (s). IR (C$_6$D$_6$): ν(CO) 1960 cm^{-1}.

[Ir(H)$_2$(CO)$_2$(PBu$^t_2$Ph)$_2$][OSO$_2$CF$_3$] (16). In 10 mL toluene was dissolved Ir(H)$_2$(OSO$_2$CF$_3$)(PBu$^t_2$Ph)$_2$ (100 mg, 0.128 mmol) to form a yellow solution. This solution was transferred to a 100 mL flask where the solution was degassed three times (freeze–pump–thaw) and 1.5 atm CO introduced. Upon stirring, a white precipitate began to form in the solution. After stirring for 30 min at room temperature, the precipitate was filtered away from the colorless mother liquor and washed with toluene (2 × 5 mL). The solid was dried *in vacuo* to yield a white powder (97 mg, 90%). Anal. calcd for C$_{31}$H$_{48}$F$_3$IrO$_5$P$_2$S: C, 44.11; H, 5.74. Found: C, 44.21; H, 5.49%. ^{1}H NMR (CDCl$_3$, 25 °C): 8.14 (m), 7.8–7.66 (m), 1.60 (vt, J_{PH} = 7.8 Hz), −10.9 (t, J_{PH} = 15.0 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): 170.9 (ddt, J_{CH} = 43.1 Hz, $J_{CH'}$ = 5.5 Hz, J_{PC} = 5.5 Hz), 135.4 (vt, J_{PC} = 4.2 Hz), 132.3 (vt, J_{PC} = 7.0 Hz), 129.3 (vt, J_{PC} = 2.8 Hz), 128.4 (br s), 120.8 (q, J_{CF} = 321 Hz), 38.9 (vt, J_{PC} = 7.8 Hz), 30.6 (br s). ^{31}P{^{1}H} NMR (CDCl$_3$, 25 °C): 57.3 (s). IR (CDCl$_3$): ν(CO) 2078, 2039 cm^{-1}.

[Ir(H)$_2$(C$_2$H$_4$)(PBu$^t_2$Ph)$_2$][OSO$_2$CF$_3$] (17). In an NMR tube was dissolved Ir(H)$_2$(OSO$_2$CF$_3$)(PBu$^t_2$Ph)$_2$ (25 mg, 0.032 mmol) in 0.6 mL C$_6$D$_6$ to form a yellow solution. This solution was degassed three times (freeze–pump–thaw) and 1.5 atm C$_2$H$_4$ introduced. Upon mixing, yellow precipitate began to form in the solution. After 30 min at room temperature, the solution had become nearly colorless. ^{1}H NMR assay detected only dissolved C$_2$H$_4$. The C$_6$D$_6$ was decanted and CDCl$_3$ (0.6 mL) added to dissolve the precipitate. ^{1}H NMR (CDCl$_3$, 25 °C): 8.05 (m), 7.59–7.42 (m), 3.90 (br s, 4H), 1.32 (vt, 36 H, J_{PH} = 6.9 Hz), −24.4 (br s, 2H). ^{31}P{^{1}H} NMR (CDCl$_3$, 25 °C): 59.8 (s).

Reaction of Ir(H)$_2$[OC(O)CH$_3$](PBu$^t_2$Ph)$_2$ with CO. In an NMR tube was dissolved Ir(H)$_2$[OC(O)CH$_3$](PBu$^t_2$Ph)$_2$ (25 mg, 0.036 mmol) in 0.6 mL C$_6$D$_6$. This light yellow solution was degassed three times (freeze–pump–thaw) and 1.5 atm CO introduced. Upon mixing, the solution immediately became colorless. After 1 h at room temperature, the sample color had changed back to yellow. ^{1}H and ^{31}P{^{1}H} NMR assay at 30 min showed signals consistent with two iridium species in solution: Ir(H)$_2$[OC(O)CH$_3$](CO)(PBu$^t_2$Ph)$_2$ and IrH(CO)$_2$(PBu$^t_2$Ph) (in a *ca.* 1:1 ratio). NMR spectra for Ir(H)$_2$[OC(O)CH$_3$](CO)(PBu$^t_2$Ph)$_2$: ^{1}H NMR (C$_6$D$_6$, 25 °C): 8.62 (m), 7.18–6.98 (m), 2.04 (s), 1.53 (vt, J_{PH} = 7.2 Hz), 1.43 (vt, J_{PH} = 6.4 Hz), −7.85 (td, J_{PH} = 18.4 Hz, J_{HH} = 5.6 Hz), −23.45 (td, J_{PH} = 15.2 Hz, J_{HH} = 5.6 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 25 °C): 48.5 (s). Upon mixing for 18 h at room temperature, the yellow color remained. ^{1}H and ^{31}P{^{1}H} NMR showed only signals for IrH(CO)$_2$(PBu$^t_2$Ph), free phosphine and CH$_3$COOH (in a 1:1:1 ratio). ^{1}H NMR (C$_6$D$_6$, 25 °C): 11.8 (br s, CH$_3$COOH), 7.98 (m, free phosphine), 7.74 (m), 7.14–6.98 (m), 1.52 (s, CH_3COOH), 1.18 (d, J_{PH} = 11.7 Hz, free phosphine), 1.08 (d, J_{PH} = 14.4 Hz), −11.41 (d, J_{PH} = 43.2 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 25 °C): 57.9 (s), 40.0 (s, free phosphine). IR (C$_6$D$_6$): ν(CO) 1966 cm^{-1}.

Reaction of Ir(H)$_2$(SPh)(PBu$^t_2$Ph)$_2$ with CO. In an NMR tube was dissolved Ir(H)$_2$(SPh)(PBu$^t_2$Ph)$_2$ (25 mg, 0.033 mmol) in 0.6 mL C$_6$D$_6$. This light yellow solution was degassed three times (freeze–pump–thaw) and 1.5 atm CO introduced. Upon mixing, the solution immediately became colorless. After 1 h at room temperature, the sample color had changed back to yellow. ^{1}H and ^{31}P{^{1}H} NMR assay at 1 h showed signals consistent with two iridium species in solution:

$Ir(H)_2(SPh)(CO)(PBu^t_2Ph)_2$ and $IrH(CO)_2(PBu^t_2Ph)$ (in a *ca.* 1:1 ratio). NMR spectra for $Ir(H)_2(SPh)(CO)(PBu^t_2Ph)_2$: ^1H NMR (C_6D_6, 25 °C): 8.38 (m), 7.13–7.01 (m), 6.95–6.80 (m), 1.48 (vt, $J_{PH} = 7.2$ Hz), 1.37 (vt, $J_{PH} = 6.4$ Hz), −9.30 (td, $J_{PH} = 18.4$ Hz, $J_{HH} = 5.2$ Hz), 16.38 (td, $J_{PH} = 16.4$ Hz, $J_{HH} = 5.2$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 48.5 (s). Upon mixing for 18 h at room temperature, the yellow color remained. ^1H and $^{31}P\{^1H\}$ NMR show only signals for $IrH(CO)_2(PBu^t_2Ph)$, free phosphine and PhSH (in a 1:1:1 ratio). ^1H NMR (C_6D_6, 25 °C): 7.98 (m, free phosphine), 7.74 (m), 7.14–6.98 (m), 6.94 (m, *Ph*SH), 6.82 (m, *Ph*SH), 4.46 (br s, PhS*H*), 1.18 (d, $J_{PH} = 11.7$ Hz, free phosphine), 1.08 (d, $J_{PH} = 14.4$ Hz), −11.41 (d, $J_{PH} = 43$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 57.9 (s), 40.0 (s, free phosphine). IR (C_6D_6): ν(CO) 1966 cm^{-1}.

Reaction of $Ir(H)_2(OPh)(PBu^t_2Ph)_2$ with CO. In an NMR tube was dissolved $Ir(H)_2(OPh)(PBu^t_2Ph)_2$ (25 mg, 0.034 mmol) in 0.6 mL C_6D_6. This light yellow solution was degassed three times (freeze–pump–thaw) and 1.5 atm CO introduced. Upon mixing, the solution immediately became colorless. After <2 min at room temperature, the sample color had changed back to yellow. ^1H and $^{31}P\{^1H\}$ NMR assay showed only signals for $IrH(CO)_2(PBu^t_2Ph)$, free phosphine and PhOH (in a 1:1:1 ratio). ^1H NMR (C_6D_6, 25 °C): 7.98 (m, free phosphine), 7.74 (m), 7.14–6.98 (m), 6.71 (m, *Ph*OH), 6.56 (m, *Ph*OH), 4.62 (br s, PhO*H*), 1.18 (d, $J_{PH} = 11.7$ Hz, free phosphine), 1.08 (d, $J_{PH} = 14.4$ Hz), −11.41 (d, $J_{PH} = 43$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 57.9 (s), 40.0 (s, free phosphine). IR (C_6D_6): ν(CO) 1966 cm^{-1}.

$IrH(^{13}CO)_2(PBu^t_2Ph)$. In an NMR tube was dissolved $Ir(H)_2[OC(O)CH_3](PBu^t_2Ph)_2$ (25 mg, 0.036 mmol) in 0.6 mL C_6D_6. This light yellow solution was degassed three times (freeze–pump–thaw) and 1.0 atm ^{13}CO introduced. Upon mixing, the solution immediately became colorless. After 4 h at room temperature, the sample color had changed to yellow. ^1H NMR (C_6D_6, 25 °C): 7.74 (m), 7.14–6.98 (m), 1.08 (d, $J_{PH} = 14.4$ Hz), −11.41 (d, $J_{PH} = 43$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C, carbonyl): 178.45 (d, $J_{PC} = 2.3$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 57.9 (t, $J_{PC} = 2.3$ Hz).

Reaction of $Ir(H)_2(F)(PBu^t_2Ph)_2$ with CO in a Teflon-lined NMR tube. In a Teflon-lined NMR tube was dissolved $Ir(H)_2(F)(PBu^t_2Ph)_2$ (25 mg, 0.038 mmol) in 0.6 mL C_6D_6. This orange solution was degassed three times (freeze–pump–thaw) and 1.5 atm CO introduced. Upon mixing, the solution immediately became colorless. After <2 min at room temperature, the sample color had changed back to yellow. ^1H and $^{31}P\{^1H\}$ NMR assay showed only signals for $IrH(CO)_2(PBu^t_2Ph)$ and free phosphine. Free HF was undetected by ^1H NMR. ^1H NMR (C_6D_6, 25 °C): 7.98 (m, free phosphine), 7.74 (m), 7.14–6.98 (m), 1.18 (d, $J_{PH} = 11.7$ Hz, free phosphine), 1.08 (d, $J_{PH} = 14.4$ Hz), −11.41 (d, $J_{PH} = 43$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 57.9 (s), 40.0 (s, free phosphine).

Reaction of $Ir(H)_2(F)(PBu^t_2Ph)_2$ with CO and NEt_3. In a 100 mL Schlenk flask was dissolved $Ir(H)_2(F)(PBu^t_2Ph)_2$ (250 mg, 0.38 mmol) in 20 mL THF. To this orange solution was added NEt_3 (53 μL, 0.38 mmol). The solution was degassed three times (freeze–pump–thaw) and 1.0 atm CO introduced. Upon stirring, the solution rapidly became colorless. After 5 min at room temperature, the solution color had changed back to yellow. After stirring for 30 min, the volatiles were removed *in vacuo* to yield a bright yellow solid that was dried overnight. NMR and IR assay of the solid showed quantitative conversion to a single product with signals that were consistent with the formula $IrH(CO)(PBu^t_2Ph)_2$.^1H NMR (THF-d_8, 25 °C): 8.20 (m), 7.40–7.34 (m), 1.45 (vt, $J_{PH} = 6.6$ Hz), −0.73 (t, $J_{PH} = 23.7$ Hz). $^{31}P\{^1H\}$ NMR (THF-d_8, 25 °C): 79.3 (s). No ^{19}F NMR resonances were detected between +25

and −350 ppm. IR (C_6D_6): ν(CO) 2006(s), 1949(m), 1892(s) cm^{-1}.

$IrH(^{13}CO)(PBu^t_2Ph)_2$. In an NMR tube was dissolved $Ir(H)_2Cl(PBu^t_2Ph)_2$ (25 mg, 0.037 mmol) in 0.6 mL THF-d_8. This orange solution was degassed three times (freeze–pump–thaw) and 1.0 atm ^{13}CO introduced into the tube. Upon mixing, the solution rapidly became colorless. The solution was frozen in liquid N_2 and the headspace above the frozen solution evacuated and filled with argon. To the colorless solution of $Ir(H)_2Cl(^{13}CO)(PBu^t_2Ph)_2$ was added lithium 2,2,6, 6-tetramethylpiperidide (5.5 mg, 0.037 mmol). Upon mixing for 2 h, the homogeneous solution turned yellow and a fine precipitate was formed. ^1H NMR (THF-d_8, 25 °C): 8.20 (m), 7.40–7.34 (m), 1.45 (vt, $J_{PH} = 6.6$ Hz), −0.73 (dt, $J_{CH} = 28.2$ Hz, $J_{PH} = 23.7$ Hz). $^{13}C\{^1H\}$ NMR (THF-d_8, 25 °C, carbonyl): 192.45 (t, $J_{PC} = 7.3$ Hz). $^{31}P\{^1H\}$ NMR (THF-d_8, 25 °C): 79.3 (d, $J_{PC} = 7.3$ Hz).

Reaction of $IrH(CO)(PBu^t_2Ph)_2$ with CO. In an NMR tube was dissolved $IrH(CO)(PBu^t_2Ph)_2$ (15 mg, 0.023 mmol) in 0.6 mL C_6D_6. This orange solution was degassed three times (freeze–pump–thaw) and 1.5 atm CO introduced. Upon mixing, the orange solution immediately became light yellow. ^1H and $^{31}P\{^1H\}$ NMR assay showed only signals for $IrH(CO)_2(PBu^t_2Ph)$ and free phosphine. The sample was degassed five times (freeze–pump–thaw) and the NMR tube charged with argon. During the degassing process, the light yellow color darkened to become orange. ^1H and $^{31}P\{^1H\}$ NMR assay after degassing showed only signals for $IrH(CO)(PBu^t_2Ph)_2$.

Reaction of $Ir(H)_2(F)(PBu^t_2Ph)_2$ with CO in a glass vessel. In a 50 mL Schlenk flask was dissolved $Ir(H)_2(F)(PBu^t_2Ph)_2$ (200 mg, 0.3 mmol) in 10 mL C_6H_6. This orange solution was degassed three times (freeze–pump–thaw) and 1.0 atm CO introduced. Upon stirring, the solution rapidly became colorless. After <5 min at room temperature, the sample color had changed back to yellow. This solution was allowed to stand under a CO atmosphere overnight, forming a number of colorless crystals in the flask. The presence of several red-orange crystals was also noted. The crystals were separated from the solution and washed with C_6H_6 (2 × 2 mL). The colorless and red-orange (air stable) crystals were manually separated. A small number of the colorless crystals were dissolved in $CDCl_3$ and established to be $[Ir(H)_2(CO)(PBu^t_2Ph)_2][SiF_5]$ by ^1H, $^{31}P\{^1H\}$ and ^{19}F NMR. ^1H NMR ($CDCl_3$, 25 °C): 7.99 (m), 7.65–7.55 (m), 1.49 (vt, $J_{PH} = 8.4$ Hz), −11.02 (t, $J_{PH} = 14.8$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): 57.4 (s). ^{19}F NMR ($CDCl_3$, 25 °C): −141.7 (s). One of the red-orange crystals was dissolved in a minimal amount of $CDCl_3$ and assayed by ^{19}F NMR. ^{19}F NMR ($CDCl_3$, 25 °C): −142.3 (s).

X-Ray structure determinations

A small, well-formed crystal was selected and affixed to the end of a glass fiber using silicone grease. The mounted sample was then transferred to the goniostat where it was cooled for characterization (Table 1) and data collection. Standard inert atmosphere handling techniques were used throughout the investigation. Data were collected using a standard moving crystal-moving detector technique with fixed background counts at each extreme of the scan. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELXTL) and Fourier techniques.

$[Ir(H)_2(CO)_2(PBu^t_2Ph)_2][SiF_5]$. A systematic search of a limited hemisphere of reciprocal space located a set of data with monoclinic symmetry and systematic absences corresponding to either the centrosymmetric space group $P2/c$ or

	$[Ir(H)_2(CO)_2(PBu^t_2Ph)_2][SiF_5]$	$[Ir(CO)_2(PBu^t_2Ph)_2][SiF_5]\cdot C_6D_6$
Formula	$C_{30}H_{48}F_5IrO_2P_2Si$	$C_{32}H_{52}F_5IrO_2P_2Si$
M	817.95	894.05
Crystal system	Monoclinic	Monoclinic
Space group	Pc	$P2_1/n$
a/Å	8.293(2)	13.041(7)
b/Å	12.462(5)	12.998(5)
c/Å	16.333(7)	22.553(13)
β/°	98.21(2)	97.50(2)
U/Å^3	1670.6	3790.12
Z	2	4
ρ_{calcd}/g cm^{-3}	1.626	1.567
T/°C	-165	-172
λ/Å	0.710 69	0.710 69
Monochromator	Graphite	Graphite
μ/cm^{-1}	41.638	36.776
No. reflections		
total	3417	5978
independent	2935	4703
$R(F_o)^a$	0.039	0.0435
$R_w(F_o)^b$	0.042	0.0408

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\ddagger}$ where $w = 1/\sigma^2(|F_o|)$.

to the non-centrosymmetric space group Pc. Intensity statistics favored the non-centrosymmetric space group. Subsequent solution and refinement of the structure confirmed the proper space group to be Pc. Hydrogen atoms were placed at calculated positions and refined with the use of a riding model. Fluorine and lighter atoms were refined isotropically; all heavier atoms were refined anisotropically. The SiF_5 anion is disordered over two orientations in a ratio of *ca.* 3:2. A final difference Fourier map is relatively clean, with the largest peak having an intensity of 1.71 e Å^{-3}. The four largest difference peaks are all located near the iridium and all other peaks are lower than 0.75 e Å^{-3}.

$[Ir(CO)_2(PBu^t_2Ph)_2][SiF_5]\cdot C_6D_6$. A systematic search of a limited hemisphere of reciprocal space was used to determine that the crystal possessed monoclinic symmetry with systematic absences corresponding to the unique space group $P2_1/n$. A slight splitting was apparent within the crystal. Hydrogen atoms were placed in fixed calculated positions for the final cycles of refinement. A final difference Fourier map featured three peaks of intensity 2.2 e Å^{-3} lying in the vicinity of the Ir position. All remaining peaks were less than 1.0 e Å^{-3}.

CCDC reference number 440/033.

Results and Discussion
Reactions

Reaction of $Ir(H)_2X(PBu^t_2Ph)_2$ complexes with CO to form stable $Ir(H)_2X(CO)(PBu^t_2Ph)_2$. Iridium complexes $Ir(H)_2X(PBu^t_2Ph)_2$ [X = Cl, Br, I, N$_3$, N=C=NSiMe$_3$, NHC(O)CH$_3$, OC(O)CF$_3$, **1–7**] react within the mixing time in C_6D_6 with an excess of CO to form the coordinatively saturated compounds $Ir(H)_2X(CO)(PBu^t_2Ph)_2$ (**8–14**, eqn. 1).

(1)

L = PBu$^t_2$Ph
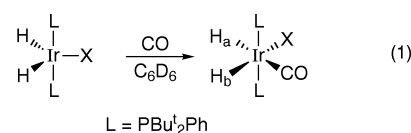
X	Reactant	Product
Cl	1	8
Br	2	9
I	3	10
N$_3$	4	11
NCNSiMe$_3$	5	12
NHC(O)CH$_3$	6	13
OC(O)CF$_3$	7	14

These reactions are readily observed by the loss of the yellow to orange color (characteristic of coordinative unsaturation) of solutions containing **1–7** upon exposure to an excess of CO, ultimately forming colorless solutions.

The products have been characterized by ^{1}H, ^{31}P$\{^1$H$\}$ NMR and IR spectroscopy (Table 2). These compounds are stable for periods of >1 week in benzene solution under either CO or argon atmosphere and do not lose CO under vacuum in solution or in the solid state. The rates of reaction of these compounds with CO appear to be remarkably similar given that the acetate and acetamide ligands have been shown by IR spectroscopy and X-ray crystallography to bind in an η^2 fashion to the iridium center.[12]

Reaction of $Ir(H)_2(OSO_2CF_3)(PBu^t_2Ph)_2$ with CO or C_2H_4. Upon reaction of $Ir(H)_2(OSO_2CF_3)(PBu^t_2Ph)_2$ (**15**) with an excess of CO in C_6D_6, the yellow solution rapidly begins to precipitate a colorless solid. After mixing for 1 min, the yellow color had faded to yield a colorless solution with a

Table 2 Selected ^{1}H, ^{31}P$\{^1$H$\}$ NMR and IR data (in C_6D_6) for compounds **8–14**, $Ir(H)_2X(CO)(PBu^t_2Ph)_2$

X	δH_a	δH_b	δL	J_{PH_a}/Hz	J_{PH_b}/Hz	J_{HH}/Hz	$\nu(CO)$/cm^{-1}
Cl	-8.20	-20.31	53.6	18.0	14.4	5.7	1985
Br	-8.55	-19.31	48.4	18.0	14.4	5.4	1985
I	-9.95	-17.56	47.3	18.0	15.3	5.4	1985
N$_3$	-8.08	-20.20	59.4	18.0	14.4	5.4	1983
NCNSiMe$_3$	-8.41	-19.37	48.5	18.0	14.4	5.6	1973
NHC(O)CH$_3$	-10.20	-18.30	53.3	18.9	16.5	4.2	1962
O$_2$CCF$_3$	-7.58	-23.92	54.3	18.3	14.4	6.0	1960

large amount of colorless precipitate. ^{1}H and ^{31}P{^{1}H} NMR assay of this colorless solution fails to show any resonances. If the C_6D_6 is decanted and CDCl$_3$ added, the precipitate rapidly dissolves to form a colorless solution. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR and IR spectroscopy show the formation of a single product, [Ir(H)$_2$(CO)$_2$(PBu$^t_2$Ph)$_2$][OSO$_2$CF$_3$] (**16**). If the reaction of **15** and an excess of CO is performed in CDCl$_3$, a rapid homogeneous reaction occurs to produce **16** in quantitative yield.

In a similar reaction, treatment of **15** with an excess of ethylene in C_6D_6 results in the precipitation of a colorless solid that may be dissolved in CDCl$_3$. ^{1}H and ^{31}P{^{1}H} NMR suggest that the product formed is [Ir(H)$_2$(C$_2$H$_4$)-(PBu$^t_2$Ph)$_2$][OSO$_2$CF$_3$] (**17**).

Thus, the reaction of **15** with CO is similar to the reactions of **1**–**7** with CO, except the characteristics of the triflate anion facilitate the ionization of an Ir(H)$_2$(OSO$_2$CF$_3$)(CO)(PBu$^t_2$Ph)$_2$ intermediate to form [Ir(H)$_2$(CO)(PtBu$^t_2$Ph)$_2$][OSO$_2$CF$_3$], which quickly adds a second equivalent of CO to form the final product, **16**. While the coordination of the triflate ligand to the metal in **15** has not been confirmed by an X-ray diffraction study, the solubility of **15** in nonpolar C_6D_6 suggests that it is a neutral species in which the triflate ligand is coordinated to the iridium. Therefore, ionization (and precipitation from benzene) does not occur until after CO binding.

Formation of 'metastable' Ir(H)$_2$X(CO)(PtBu$^t_2$Ph)$_2$ complexes. Reaction of Ir(H)$_2$(X)(PtBu$^t_2$Ph)$_2$ [X = OC(O)CH$_3$ (**18**) or SPh (**19**)] with an excess of CO in C_6D_6 results initially in a colorless solution. However, after a period of 30 min to 1 h, the colorless solution begins to turn yellow. ^{1}H and ^{31}P{^{1}H} NMR assay of these samples soon after the reappearance of coloration shows the presence of two iridium species in solution: Ir(H)$_2$X(CO)(PBu$^t_2$Ph)$_2$ and the same compound (independent of X) with a single upfield ^{1}H NMR resonance at -11.4 ppm. This resonance is a doublet ($J = 43$ Hz), suggestive of a monophosphine complex. Accordingly, the ^{31}P{^{1}H} NMR spectrum shows, in addition to a singlet assigned to Ir(H)$_2$X(CO)(PBu$^t_2$Ph)$_2$, two signals of equal intensity. One of these can be assigned, based upon the chemical shift, as free PBu$^t_2$Ph. The ^{1}H NMR of these solutions also shows the presence of free HX in solution. These data suggest that HX elimination and loss of a phosphine occur from Ir(H)$_2$X(CO)(PBu$^t_2$Ph)$_2$ to give a complex with the formula IrH(CO)$_n$(PBu$^t_2$Ph) (eqn. 2).
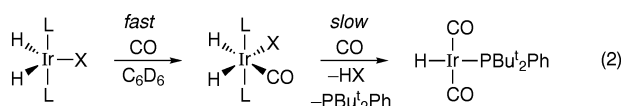
L = PBu$^t_2$Ph
X = OC(O)CH$_3$, SPh

If the reactions are allowed to proceed at room temperature for >12 h, quantitative formation of this complex is observed; IrH(CO)$_n$(PBu$^t_2$Ph), PBu$^t_2$Ph and HX are observed in a 1:1:1 ratio (by ^{1}H integration). The rates of formation of IrH(CO)$_n$(PBu$^t_2$Ph) from **18** and **19** are similar, with $t_{1/2} = 30$ min for **18** and $t_{1/2} = 1$ h for **19**.

Reaction of 18 with ^{13}CO. In an effort to verify the number of CO ligands present in the IrH(CO)$_n$(PBu$^t_2$Ph) product, the reaction of **18** with ^{13}CO was performed. The ^{31}P{^{1}H} NMR spectrum of the reaction mixture shows that the resonance for the coordinated PBu$^t_2$Ph of IrH(^{13}CO)$_n$(PBu$^t_2$Ph) has triplet splitting ($J_{PC} = 2.3$ Hz), indicating the presence of two equivalent CO ligands in the product. Accordingly, the ^{13}C{^{1}H} NMR spectrum shows only a single resonance in the carbonyl region at 178.5 ppm (doublet, $J = 2.3$ Hz). This data, coupled with the observation of only *one* CO stretch in the solution IR

spectrum of IrH(CO)$_n$(PBu$^t_2$Ph), suggest that the complex is *trans*-IrH(CO)$_2$(PBu$^t_2$Ph). The value of J_{PH} (43 Hz) is significantly larger than that expected for the coupling of *cis* hydride and phosphine ligands [$^2J_{PH}$ (*cis*) are 9–20 Hz in square planar *trans*-MH(CO)(PR$_3$)$_2$].[13] However, this $^2J_{PH}$ (*trans*) is not as large as those observed for complexes such as *fac*-Ir(H)$_3$(CO)(PPh$_3$)$_2$ (123 Hz).[14] An explanation for the smaller $^2J_{PH}$ in *trans*-IrH(CO)$_2$(PBu$^t_2$Ph) is that contraction of the C—Ir—C angles due to strong backbonding into the CO π^* orbitals by the electron-rich Ir^I (*vide infra*) causes a corresponding decrease in the H—Ir—P angle from 180° (the geometry moves towards T_d symmetry), decreasing the magnitude of the coupling between the hydride and phosphine ligands. Several complexes with the formula IrX(CO)$_2$(PR$_3$) have been reported recently,[15] but they have been characterized as *cis* dicarbonyl compounds based upon the observation of two CO stretches in the IR spectrum.

Reactions of Ir(H)$_2$(OPh)(PBu$^t_2$Ph)$_2$ and Ir(H)$_2$-(F)(PBu$^t_2$Ph)$_2$ with CO. A solution of Ir(H)$_2$(OPh)(PBu$^t_2$Ph)$_2$ (**20**) in C_6D_6 was allowed to react with an excess of CO in a sealed NMR tube. The orange solution quickly changed color to light yellow. The ^{1}H and ^{31}P{^{1}H} NMR spectra, after 5 min at room temperature, show complete conversion of **20** to IrH(CO)$_2$(PBu$^t_2$Ph). Equimolar amounts of PBu$^t_2$Ph and PhOH are also present in the solution.

A solution of Ir(H)$_2$(F)(PBu$^t_2$Ph)$_2$ (**21**) in C_6D_6 was allowed to react with an excess of CO in a sealed NMR tube. Due to the possibility of HF formation, this reaction was performed using a Teflon liner inside the NMR tube. Upon agitation, the solution changed color from orange to colorless and quickly (<2 min) back to yellow. ^{1}H and ^{31}P{^{1}H} NMR spectra recorded shortly after the appearance of the yellow color indicate a quantitative conversion of **21** to IrH(CO)$_2$(PBu$^t_2$Ph) and free phosphine. HF was not detected in the ^{1}H NMR spectrum. However, if the same reaction is performed without the Teflon liner in the NMR tube, visible etching of the inner surface of the NMR tube is apparent, indicating a reaction of the glass surface with HF.

Reaction of Ir(H)$_2$(F)(PBu$^t_2$Ph)$_2$ with CO and NEt$_3$. In an effort to neutralize reactive HF in a larger scale reaction of **21** with CO, NEt$_3$ was employed as an HF scavenger. A 1:1 mixture of **21** and NEt$_3$ was stirred under 1 atm CO in THF. Upon exposure to CO, this solution rapidly became colorless and turned yellow over *ca.* 5 min. Removal of the volatiles *in vacuo* yielded a bright yellow solid. ^{1}H and ^{31}P{^{1}H} NMR spectra show that this solid was not the expected IrH(CO)$_2$(PBu$^t_2$Ph), but instead was IrH(CO)(PBu$^t_2$Ph)$_2$, formed in essentially quantitative yield. This compound has a hydride resonance in the ^{1}H NMR spectrum at -0.73 ppm (triplet, $J_{PH} = 24$ Hz). This unusually low-field hydride chemical shift is characteristic of H *trans* to CO.[13,16] The triplet splitting indicates the presence of two equivalent phosphine ligands. Accordingly, the ^{31}P{^{1}H} NMR spectrum of this solution shows only one signal, a singlet at 79.3 ppm. In order to verify this assignment, IrH(CO)(PBu$^t_2$Ph)$_2$ was prepared *via* an independent route. The reaction of Ir(H)$_2$Cl(^{13}CO)(PBu$^t_2$Ph)$_2$ with one equivalent of lithium 2,2,6,6-tetramethylpiperidide in THF-d_8 results in the precipitation of LiCl and quantitative formation of IrH(^{13}CO)(PBu$^t_2$Ph)$_2$. The ^{31}P{^{1}H} NMR spectrum displays a doublet due to coupling with the ^{13}CO ligand and the ^{13}C{^{1}H} NMR spectrum shows a triplet ($J_{PC} = 7.3$ Hz) in the carbonyl region. The hydride is present in the ^{1}H NMR spectrum as a doublet of triplets ($J_{CH} = 28$ Hz, $J_{PH} = 24$ Hz) at -0.73 ppm.

Reaction of IrH(CO)(PBu$^t_2$Ph)$_2$ with CO. A solution of IrH(CO)(PBu$^t_2$Ph)$_2$ in C_6D_6 was allowed to react with an excess of CO, changing color from orange to light yellow

upon mixing. ^{1}H and ^{31}P$\{^1$H$\}$ NMR assays show equimolar IrH(CO)$_2$(PBu$^t_2$Ph) and PBu$^t_2$Ph in the solution. If this solution is degassed thoroughly, the solution color returns to orange. ^{1}H and ^{31}P$\{^1$H$\}$ NMR spectra verify a complete regeneration of IrH(CO)(PBu$^t_2$Ph)$_2$. These results, coupled with the dependence of the identity of the Ir^I products of the reactions of **21** and CO on the conditions employed (*i.e.*, removal of volatiles *in vacuo*), suggest that the initial product of the elimination of HX from Ir(H)$_2$X(CO)(PBu$^t_2$Ph)$_2$ is IrH(CO)(PBu$^t_2$Ph)$_2$. The mono-CO species reacts quickly with an excess of CO to dissociate one phosphine and form IrH(CO)$_2$(PBu$^t_2$Ph). While IrH(CO)$_2$(PBu$^t_2$Ph) appears to be stable under a CO atmosphere, removing CO *in vacuo* in the presence of free phosphine results in the loss of one CO ligand and recoordination of phosphine.

Reaction of Ir(H)$_2$(F)(PtBu$^t_2$Ph)$_2$ with CO in a glass vessel. We have found that NEt$_3$ is effective in scavenging HF formed in the reaction of **21** with CO. If this reaction is performed in a glass vessel without added base, the scavenging of HF can occur *via* the following reaction: 5HF + SiO$_2$ → 2H$_2$O + H$^+$ + SiF$_5^-$.

In a glass Schlenk flask, a benzene solution of **21** was allowed to stand overnight under a CO atmosphere. During this time, a number of colorless and red-orange crystals formed from the solution. The colorless crystals were assayed by ^{1}H and ^{31}P$\{^1$H$\}$ NMR and found to have spectra essentially identical to those of [Ir(H)$_2$(CO)$_2$-(PBu$^t_2$Ph)$_2$][OSO$_2$CF$_3$] (**16**). In addition, the ^{19}F NMR spectrum displayed a single resonance at −141.7 ppm. ^{19}F NMR assay of a red-orange crystal also showed a resonance at *ca.* −142 ppm. This chemical shift is intermediate between those of SiF$_4$ (−163.6 ppm) and [SiF$_6$]$^{2-}$ (−127.0 ppm)[17] and suggestive of the presence of a SiF$_5$ anion in the crystalline products. Despite the similarity of SiF$_5^-$ to commonly used, weakly coordinating anions such as BF$_4^-$ and PF$_6^-$, the pentafluorosilicate anion has been rarely used as a weakly coordinating counter ion.[18] There has been only one structural determination of a cationic organometallic complex with a pentafluorosilicate counter ion[19] and very few structural determinations of organic salts of the pentafluorosilicate anion.[20]

An X-ray crystal structure determination of the colorless crystals (Fig. 1) confirms the assignment of the product as [Ir(H)$_2$(CO)$_2$(PBu$^t_2$Ph)$_2$][SiF$_5$]. Selected bond distances and angles are shown in Table 3. While the hydride ligands were not located by X-ray diffraction, their positions may be inferred as *trans* to the CO ligands in an octahedral geometry. The carbonyl ligands are mutually *cis* [C—Ir—C angle 97.1(5)°] and the bulky phosphine ligands in the expected *trans* orientation. Unfortunately, the SiF$_5$ anion exhibited conformational disorder, ultimately being refined in two orientations in a 3 : 2 ratio, preventing further investigation of the anion. The formation of this complex from the reaction of **21** and CO in a glass vessel can be rationalized by the following sequence of reactions: The primary Ir-containing product of the reaction of **21** with CO, in the presence of HF, is

Fig. 1 ORTEP drawing of Ir(H)$_2$(CO)$_2$(PBu$^t_2$Ph)$_2$$^+$; hydrogens were not located

IrH(CO)$_2$(PBu$^t_2$Ph). Eventual reaction of HF with the glass surface produces HSiF$_5$, which can protonate IrH-(CO)$_2$(PBu$^t_2$Ph) to yield an [Ir(H)$_2$(CO)$_2$(PBu$^t_2$Ph)][SiF$_5$] intermediate that should readily react with free PBu$^t_2$Ph present in the solution (released in the primary reaction).

While the coordinatively saturated complex [Ir(H)$_2$-(CO)$_2$(PBu$^t_2$Ph)$_2$][SiF$_5$] is not informative as to the coordinating ability of the SiF$_5$ anion, the crystal structure of a red-orange crystal from this reaction shows this complex to be coordinatively unsaturated *trans*-[Ir(CO)$_2$-(PBu$^t_2$Ph)$_2$][SiF$_5$] with a noncoordinating SiF$_5$ anion and one molecule of C$_6$D$_6$ in the crystal lattice (Fig. 2).

The pentafluorosilicate anion is free from disorder and adopts the expected trigonal bipyramidal geometry. The P—Ir—P and C—Ir—C angles are both close to 180° (Table 4), indicating an approximate square-planar geometry for the Ir cation. However, there is a significant narrowing of the

Table 3 Selected bond distances (Å) and angles (deg.) for [Ir(H)$_2$(CO)$_2$(PBu$^t_2$Ph)$_2$][SiF$_5$]

Ir(1)—P(2)	2.406(3)	Ir(1)—C(34)	1.912(11)
Ir(1)—P(17)	2.386(3)	C(32)—O(33)	1.17(2)
Ir(1)—C(32)	1.910(13)	C(34)—O(35)	1.16(2)
P(2)—Ir(1)—P(17)	159.67(11)	P(17)—Ir(1)—C(34)	100.7(3)
P(2)—Ir(1)—C(32)	102.3(3)	Ir(1)—C(32)—O(33)	174.0(10)
P(2)—Ir(1)—C(34)	91.9(3)	Ir(1)—C(34)—O(35)	177.6(10)
P(17)—Ir(1)—C(32)	92.0(3)	C(32)—Ir(1)—C(34)	97.1(5)

Table 4 Selected bond distances (Å) and angles (deg.) for [Ir(CO)$_2$(PBu$^t_2$Ph)$_2$][SiF$_5$] · C$_6$D$_6$

Ir(1)—P(6)	2.376(6)	Ir(1)—C(4)	1.8821(11)
Ir(1)—P(21)	2.378(6)	C(2)—O(3)	1.125(7)
Ir(1)—C(2)	1.916(5)	C(4)—O(5)	1.1629(26)
F(37)—H(23)	2.526(7)	F(37)—H(50)	2.557(7)
F(41)—H(22)	2.619(8)		
Si—F(axial)	1.608(16)	Si—F(equatorial)	1.557(18)
	1.611(14)		1.582(17)
			1.608(20)
P(6)—Ir(1)—P(21)	173.70(11)	P(21)—Ir(1)—C(4)	93.0(6)
P(6)—Ir(1)—C(2)	88.4(7)	Ir(1)—C(2)—O(3)	176.3(13)
P(6)—Ir(1)—C(4)	91.7(6)	Ir(1)—C(4)—O(5)	174.2(14)
P(21)—Ir(1)—C(2)	88.4(8)	C(2)—Ir(1)—C(4)	162.7(8)

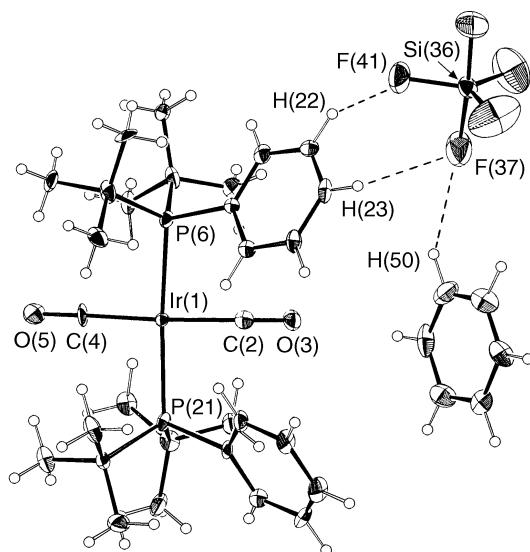**Fig. 2** ORTEP drawing of Ir(CO)$_2$(PBu$_2^t$Ph)$_2^+$, showing short contacts with SiF$_5^-$ and C$_6$D$_6$ in the solid lattice

C—Ir—C angle (162.7°) from 180°. This deviation from rigorous planarity may be indicative of strong backbonding into the CO π^* orbitals by the low-valent Ir^I, despite the 16 electron count at the metal. This phenomenon has been observed for other unsaturated low-valent dicarbonyl and carbonyl/nitrosyl complexes.[21]

While the SiF$_5$ anion is found to have no interactions with the metal, there are several contacts between aryl hydrogens and fluorine atoms of the SiF$_5$ anion (2.526–2.619 Å) that are close to the sum of the van der Waals radii of H and F (2.55 Å).[22] These contacts involve both the lattice benzene and the phenyl group of one phosphine ligand and appear to be quite weak as there is no perceptible lengthening of the Si—F bonds of the fluorine atoms involved in the interactions (average Si—F distance 1.593 Å).[23]

Assessment of the relative X ligand donor abilities

The magnitude of X-dependent 'π-stabilization of unsaturation' in d^6 RuH(X)(CO)(PBu$_2$Me)$_2$ has been determined by analysis of the ν(CO) values.[24] The degree of stabilization is found to vary according to the energy and spatial distribution of the ligand nonbonding electrons and is ordered as follows: H < I < Br < CCPh < Cl < SPh < OPh < NHPh < OH < OCH$_2$CF$_3$ < F < OSiPh$_3$ < OSiMe$_3$ < OEt. More recently, anisotropic frozen solution EPR spectra were analyzed to determine the π-donor series for X in (Me$_5$C$_5$)$_2$TiX as H < I < Br < Cl < N(Me)Ph < F ≈ OPh < OMe ≈ NH$_2$ ≈ N(Me)H.[25]

In the present study, we seek to measure the same property of X ligands using the inherent destabilization created by filled-filled d$_\pi$–d$_\pi$ repulsions in a coordinatively unsaturated metal complex containing an X ligand capable of π-donation. In this situation, nonbonding orbitals of the X ligand are interacting with the filled metal d$_\pi$ orbitals of the saturated complex. Our findings show that Ir(H)$_2$X(PBu$_2^t$Ph)$_2$ complexes containing X ligands expected to have relatively weak donating ability can achieve coordinative saturation, via the addition of a CO ligand, with no subsequent reaction to release the filled-filled repulsions. The X ligands that fall into this classification include Cl, Br, I, N$_3$, N=C=NSiMe$_3$, NHC(O)CH$_3$, OC(O)CF$_3$ and OSO$_2$CF$_3$. While X ligands with oxygen and nitrogen atom donors have been considered to be among the strongest π-donors,[24,25] the ligands used here all experience an electron-withdrawing effect from substituents. Trifluoroacetate and acetamide both donate

to the metal via heteroatoms that have a bond to an electron-withdrawing acyl carbon. The triflate ligand has a strongly electron-withdrawing SO$_2$CF$_3$ moiety on the donating oxygen atom. The β-nitrogen atoms of the azide ligand have a strong positive charge that serves to lower the electron-donating ability of the α-nitrogen atom. The initial reaction of Ir(H)$_2$[OC(O)CF$_3$](PBu$_2^t$Ph)$_2$ and Ir(H)$_2$[OC(O)CH$_3$](PBu$_2^t$Ph)$_2$ with CO is the same, to form Ir(H)$_2$(X)(CO)(PBu$_2^t$Ph)$_2$, but the enhanced donating power of acetate vs. trifluoroacetate promotes the elimination of acetic acid from Ir(H)$_2$[OC(O)CH$_3$](CO)(PBu$_2^t$Ph)$_2$. This is clearly evidence of the powerful influence of the CF$_3$ group to withdraw electron density from the acyl carbon, and ultimately the oxygen that forms the Ir—O bond. The factors that determine whether HX elimination from Ir(H)$_2$X(CO)(PBu$_2^t$Ph)$_2$ is exothermic are not only the destabilization of the six-coordinate species but also the driving force for formation of the H—X bond. Relatively strong electron-donating substituents (CH$_3$ vs. CF$_3$) contribute to the destabilization of the reactant by increasing σ and π donation, and favor HX formation (i.e., the product is a weak acid). Thus, the donating ability of X influences both reactants and products to achieve reaction.

A trend that has been observed previously is the decrease in π-donating ability upon moving down the periodic table. Among the halide group, the π-donating ability is found to decrease in the following order: I < Br < Cl ≪ F.[8,24,25] This trend is also apparent among oxygen/sulfur donor ligands. While Ir(H)$_2$(SPh)(PBu$_2^t$Ph)$_2$ reacts with CO to form a metastable Ir(H)$_2$(SPh)(CO)(PBu$_2^t$Ph)$_2$ complex, the reaction of Ir(H)$_2$(OPh)(PBu$_2^t$Ph)$_2$ with CO forms Ir(H)(CO)$_2$(PBu$_2^t$Ph), free phosphine and PhOH within two min at room temperature. The fluoride ligand has long been considered to have special properties among the group of halide ligands.[26] The strong π-donating ability of fluoride has been found to promote reactivity that is not observed in the analogous complexes with the heavier halide ligands.[26] During the reaction of Ir(H)$_2$(F)(PBu$_2^t$Ph)$_2$ with CO, the strong donating ability of fluoride distinguishes it from the heavier halides by promoting the facile elimination of HF upon CO coordination.

Conclusions

The coordinatively unsaturated complexes Ir(H)$_2$X(PBu$_2^t$Ph)$_2$ (X = Cl, Br, I, N$_3$, N=C=NSiMe$_3$, NHC(O)CH$_3$, OC(O)CF$_3$, OSO$_2$CF$_3$, OC(O)CH$_3$, SPh, OPh, F) all react within the mixing time with CO. Subsequent reactivity of these CO adducts to eliminate HX is dependent on the magnitude of the inherent destabilization caused by filled-filled repulsions between the ligand p$_\pi$ orbitals and filled d$_\pi$ orbitals and the formation of HX (i.e., the H—X bond strength). These factors are not sufficient to promote the loss of HX when X = Cl, Br, I, N$_3$, N=C=NSiMe$_3$, NHC(O)CH$_3$, OC(O)CF$_3$. When X = OC(O)CH$_3$ or SPh, metastable CO adducts are formed that ultimately lose HX. The iridium complexes containing phenoxide or fluoride ligands quickly lose HX upon reaction with CO. A coordination number of six alone is not sufficient to promote the loss of HX, since the acetamide and acetate complexes are six-coordinate before CO addition due to the η^2 binding modes of these ligands. Apparently, a π-acid ligand like CO is needed to make the hydrides of six-coordinate complexes more Brønsted acidic (facilitating HX elimination) and also to stabilize the resulting Ir^I product.

The qualitative ranking of donating ability of the X ligands based upon the reaction of Ir(H)$_2$X(PBu$_2^t$Ph)$_2$ with CO may be summarized in the following order: [Cl, Br, I, N$_3$, NCNSiMe$_3$, NHC(O)CH$_3$, OC(O)CF$_3$, OSO$_2$CF$_3$] < [OC(O)CH$_3$, SPh] < [OPh, F]. This order of donating ability, based upon reactivity, compares well with spectroscopic evaluations of donating ability published to date and

includes X ligands that have not been evaluated in these previous studies.

Acknowledgements

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