Physical Measurements. Infrared spectra were recorded as Nujol mulls on polyethylene sheets using a Nicolet 550 spectrometer. C, H, N analyses were carried out with a Perkin-Elmer 2400 CHNS/O analyzer. Conductivities were measured in ca. $5x10^{-4}$ M solutions using a Philips PW 9501/01 conductometer. NMR spectra were recorded on a Varian UNITY, a Varian Gemini 2000 and a Bruker ARX 300 MHz instruments. ^{1}H (300 MHz), ^{2}H (46.05 MHz) and ^{13}C (75.19 MHz) NMR chemical shifts were measured relative to partially deuterated solvent peaks but are reported in ppm relative to tetramethylsilane. ^{31}P NMR (121 MHz) chemical shifts were measured relative to H_3PO_4 (85%). Coupling constants are given in Hertz. Generally, spectral assignments were achieved by ^{1}H COSY and NOESY, and ^{13}C DEPT experiments. MS data were recorded on a VG Autospec double-focusing mass spectrometer operating in the positive mode; ions were produced with the Cs^{+} gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix. The crystallographic data for complex **4** were collected on a Siemens P4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å).

Synthesis. All reactions were carried out with exclusion of air by using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon prior to use. The complex $[Ir(\mu\text{-OMe})(cod)]_2$[1] was prepared by published methods.

The salt $[HP^{i}Pr_3]BF_4$ was prepared in quantitative yields by slow addition of a solution of HBF_4 (54% in diethylether) to a diethylether solution of $P^{i}Pr_3$. The white solid obtained was filtered, washed with ether and dried in vacuo. ^{1}H NMR ($CDCl_3$, 293 K) δ 1.41 (dd, J_{HP} = 17.6, J_{HH} = 7.2, 18H, PCHCH_3), 2.75 (m. 3H, PCHCH$_3$), 5.71 (dq, J_{HP} = 468.4, J_{HH} = 4.2, 1H, PH); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 293 K) δ 42.37 (s).

Preparation of $[(\eta^{6}\text{-}C_6H_6)IrH_2(P^{i}Pr_3)]BF_4$ (1): A suspension of $[Ir(\mu\text{-OMe})(cod)]_2$ (300 mg, 0.45 mmol) in acetone/benzene (20/1, 10 mL) was treated with $[HP^{i}Pr_3]BF_4$ (223 mg, 0.90 mmol), and the resulting orange solution was stirred under hydrogen atmosphere (P = 1 atm) for 1 h. The dark

solution obtained was filtered through celite and dried in vacuo. After treatment of the resulting residue with a mixture of diethylether/thf (4/1) a white solid precipitated. The solution was decanted and the solid washed with ether and dried in vacuo: yield 327 (70 %). IR (Nujol mull): 2237, 2208 ν(Ir-H); ^{1}H NMR ($CDCl_3$, 293 K) δ -16.66 (d, J_{HP} = 27. 2, 2H, Ir-H), 1.08 (dd, J_{HP} = 15.6, J_{HH} = 7.2, 18H, PCHCH_3), 2.14 (m, 3H, PCHCH_3), 6.71 (s, 6H, C_6H_6); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 51.23 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ 19.78 (d, J_{CP} = 1.3, PCHCH$_3$), 28.16 (d, J_{CP} = 34.4, PCHCH$_3$), 97.99 (d, J_{CP} = 2.3, C_6H_6); MS (FAB+, *m/z* (%)) 433 (100) [M$^+$]; Λ_M (acetone) = 135 Ω^{-1} cm^2 mol^{-1} (1:1). Anal. Calcd for $C_{15}H_{29}BF_4IrP$: C, 34.69; H, 5.63. Found: C, 34.28; H, 5.87.

[IrH$_2$(P^{i}Pr$_3$)(OC(CH$_3$)$_2$)$_3$]BF$_4$ (2): The NMR spectra of acetone-d_6 (0.5 mL) solutions of complex **1** (26 mg, 0.05 mmoL) at 293 K showed the presence of complex [IrH$_2$(P^{i}Pr$_3$)(OC(CD$_3$)$_2$)$_3$]BF$_4$ as the mayor species in solution, in equilibrium with **1**. Our attempts to isolate compound **4** by following the same procedure described for **1**, but in the absence of benzene, were unsuccessful. Data for [IrH$_2$(P^{i}Pr$_3$)(OC(CD$_3$)$_2$)$_3$]BF$_4$: ^{1}H NMR (acetone-d_6, 253 K) δ -31.08 (d, J_{HP} = 23.7, 2H, Ir-H), 1.15 (dd, J_{HP} = 13.5, J_{HH} = 6.8, 18H, PCHCH_3), 2.12 (m, 3H, PCHCH$_3$); ^{31}P{^{1}H} NMR (acetone-d_6, 253 K) δ 31.32 (s); ^{13}C{^{1}H} NMR(acetone-d_6, 253 K) δ 16.49 (s, PCHCH$_3$), 22.53 (d, J_{CP} = 35.2, PCHCH$_3$). The equilibrium constant for the formation of **2** (K = [**2**][C_6H_6] / [**1**]) was determined by integration of the ^{1}H NMR signals corresponding to the hydrido ligands of **1** and **2** and that of free benzene, in acetone-d_6 solutions ([**1**]$_0$ = 0.16 M) at 293 K. The value of 0.45 mol is the mean of the values obtained at different concentrations of added benzene (the values ranged from 0.44 to 0.47).

Preparation of [(η^6-C$_6$H$_5$Me)IrH$_2$(P^{i}Pr$_3$)]BF$_4$ (3): A solution of **1** (100 mg, 0.19 mmol) in acetone (5 mL) was treated with toluene (ca. 0.5 mL) and stirred during 1h. The resulting solution was concentrated to ca. 0.5 mL and treated with a mixture of diethylether / thf (4/1) to give a white solid which was filtered, washed with ether and dried in vacuo: yield 91 mg (90 %). IR (Nujol mull): 2245, 2201 ν(Ir-H); ^{1}H NMR ($CDCl_3$, 293 K) δ -16.81 (d, J_{HP} = 27. 3, 2H, Ir-H), 1.07 (dd, J_{HP} = 15.3, J_{HH} = 7.2, 18H, PCHCH_3), 2.13 (m, 3H, PCHCH_3), 2.64 (s, 3H, CH_3), 6.54 (d, J_{HH} = 6.0, 2H, CH),

6.59 (t, J_{HH} = 6.0, 1H, CH), 6.77 (t, J_{HH} = 6.0, 2H, CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 50.93 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 19.61 (d, J_{CP} = 1.0, PCH*C*H_3), 20.85 (s, CH_3), 27.90 (d, J_{CP} = 35.1, P*C*HCH$_3$), 95.53 (d, J_{CP} = 3.2, CH), 95.62, 100.11 (both s, CH), 116.54 (d, J_{CP} = 3.0, C); MS (FAB+, *m/z* (%)) 447 (100) [M^+]; Anal. Calcd for $C_{16}H_{31}BF_4IrP$: C, 36.03; H, 5.86. Found: C, 36.37; H, 5.76

Preparation of [(η^6-1,3,5-$C_6H_3(Me)_3$)$IrH_2(P^iPr_3)$]BF_4 (4): The compound was prepared following the procedure described for **3**, by using an excess of 1,3,5-$C_6H_3(Me)_3$) (ca. 0.3 mL): yield 98 mg (92 %). IR (Nujol mull): 2220 (br) ν(Ir-H); ^1H NMR ($CDCl_3$, 293 K) δ -17.72 (d, J_{HP} = 28.5, 2H, Ir-H), 1.07 (dd, J_{HP} = 15.3, J_{HH} = 6.9, 18H, PCHC*H*$_3$), 2.03 (m, 3H, PC*H*CH$_3$), 2.64 (s, 9H, CH_3), 6.39 (s, CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 48.16 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 19.57 (d, J_{CP} = 1.3, PCH*C*H$_3$), 20.48 (s, CH_3), 26.74 (d, J_{CP} = 35.0, P*C*HCH$_3$), 94.30 (d, J_{CP} =1.9, CH), 118.41 (d, J_{CP} = 1.8, C); MS (FAB+, *m/z* (%)) 475 (100) [M^+]; Anal. Calcd for $C_{18}H_{35}BF_4IrP$: C, 38.50; H, 6.28. Found: C, 38.62; H, 6.24.

The crystals used for the X-ray structural determination were obtained by slow diffusion of diethylether into a solution of **4** in acetone.

Preparation of [(η^6-1,2,4-$C_6H_3(Me)_3$)$IrH_2(P^iPr_3)$]BF_4 (5): The compound was prepared following the procedure described for **3**, by using an excess of 1,2,4-$C_6H_3(Me)_3$) (ca. 0.3 mL): yield 98 mg (92 %). IR (Nujol mull): 2241, 2210 ν(Ir-H); ^1H NMR (CD_2Cl_2, 293 K) δ -17.38 (A part of a ABX spin system (X = ^{31}P): J_{HP} = 27. 9, J_{HH} = 5.1, 1H, Ir-H), -17.36 (B part of a ABX spin system (X = ^{31}P): J_{HP} = 27. 9, J_{HH} = 5.1, 1H, Ir-H), 1.11, 1.12 (both dd, J_{HP} = 15.3, J_{HH} = 6.9, 9H, PCHC*H*$_3$), 2.11 (m, 3H, PC*H*CH$_3$), 2.48 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 6.40 (d, J_{HH} = 6.0, 1H, CH), 6.44 (s, 1H, CH), 6.60 (d, J_{HH} = 6.0, 1H, CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 49.86 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 18.42, 19.47 (both s, CH_3), 19.61, 19.69 (both d, J_{CP} = 1.5, PCH*C*H$_3$), 20.09 (s, CH_3), 28.11 (d, J_{CP} = 34.8, P*C*HCH$_3$), 95.13 (d, J_{CP} = 5.8, CH), 97.11, 101.33

(both s, CH), 100.57 (s, C), 113.69 (d, J_{CP} = 4.52, C), 114.88 (s, C); MS (FAB+, *m/z* (%)) 475 (100) [M^+]; Anal. Calcd for $C_{18}H_{35}BF_4IrP$: C, 38.50; H, 6.28. Found: C, 38.66; H, 6.23.

Preparation of $[(\eta^6\text{-}C_6(Me)_6)IrH_2(P^iPr_3)]BF_4$ (6): The compound was prepared following the procedure described for **3**, by using an excess of hexamethylbenzene (ca. 200 mg): yield 101 mg (88 %). IR (Nujol mull): 2220 (br) ν(Ir-H); ^{1}H NMR ($CDCl_3$, 293 K) δ -18.91 (d, J_{HP} = 29.7, 2H, Ir-H), 1.02 (dd, J_{HP} = 15.0, J_{HH} = 7.2, 18H, PCHC*H*$_3$), 1.98 (m, 3H, PC*H*CH$_3$), 2.50 (s, 18H, CH_3); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 45.41 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ 17.65 (s, CH_3), 19.50 (d, J_{CP} = 1.3, PCH*C*H$_3$), 27.33 (d, J_{CP} = 34.3, P*C*HCH$_3$), 110.29 (d, J_{CP} = 2.2, C); MS (FAB+, *m/z* (%)) 517 (100) [M^+]; Anal. Calcd for $C_{21}H_{41}BF_4IrP$: C, 41.79; H, 6.85. Found: C, 41.39; H, 6.73.

Preparation of $[(\eta^6\text{-}C_6H_5(C(Me)=CH_2)IrH_2(P^iPr_3)]BF_4$ (7): The compound was prepared following the procedure described for **3**, by using an excess of 1-methylstyrene (ca. 0.3 mL): yield 95 mg (90 %). IR (Nujol mull): 2222 (br) ν(Ir-H); ^{1}H NMR ($CDCl_3$, 293 K) δ -16.80 (d, J_{HP} = 27. 0, 2H, Ir-H), 1.09 (dd, J_{HP} = 15.3, J_{HH} = 6.9, 18H, PCHC*H*$_3$), 2.09 (d, J_{HH} = 1.5, 3H, CH_3), 2.15 (m, 3H, PC*H*CH$_3$), 5.41 (q, J_{HH} = 1.5, 1H, =CH_2), 5.66 (s, 1H, =CH_2), 6.75 (m, 3H, CH), 6.84 (m, 2H, CH); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 51.07 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ 19.80 (d, J_{CP} = 4.3, PCH*C*H$_3$), 21.73 (s, CH_3), 28.44 (d, J_{CP} = 34.8, P*C*HCH$_3$), 92.81 (d, J_{CP} = 3.2, CH), 98.17 (d, J_{CP} = 1.9, CH), 99.31 (d, J_{CP} = 1.2, CH), 118.29 (d, J_{CP} = 3.3, C), 120.68 (s, CH_2), 137.20 (s, C); MS (FAB+, *m/z* (%)) 473 (30) [M^+]; Anal. Calcd for $C_{18}H_{33}BF_4IrP$: C, 38.64; H, 5.94. Found: C, 38.33; H, 6.00.

Preparation of $[(\eta^6\text{-}C_6H_5(NH_2))IrH_2(P^iPr_3)]BF_4$ (8): The compound was prepared following the procedure described for **3**, by using the stoichiometric amount of aniline (18 μL): yield 83 mg (82 %). IR (Nujol mull): 3364, 3259 ν(N-H), 2177, 2226 ν(Ir-H); ^{1}H NMR ($CDCl_3$, 293 K) δ -18.25 (d, J_{HP} = 27. 6, 2H, Ir-H), 1.09 (dd, J_{HP} = 15.0, J_{HH} = 6.9, 18H, PCHC*H*$_3$), 2.10 (m, 3H, PC*H*CH$_3$), 5.67 (dd, J_{HH} = 6.9, 5.7, 1H, CH), 5.72 (br, 2H, NH_2), 6.09 (d, J_{HH} = 6.9, 2H, CH), 6.28 (t, J_{HH} = 5.7, 2H, CH);

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 45.62 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 19.47 (d, J_{CP} = 1.2, $PCHCH_3$), 26.73 (d, J_{CP} = 34.5, $PCHCH_3$), 76.14 (s, CH), 99.92 (d, J_{CP} = 1.7, CH), 129.5 (br, CH), 146.28 (d, J_{CP} = 2.4, C); MS (FAB+, *m/z* (%)) 448 (100) [M^+]; Anal. Calcd for $C_{15}H_{30}NBF_4IrP$: C, 33.71; H, 5.66; N, 2.62 Found: C, 33.88 H, 6.00; N, 2.70.

$[IrH_2(NH_2Ph)_3(P^iPr_3)]BF_4$ (9): A solution of complex **8** (80 mg, 0.15 mmol) in acetone (5 mL) was treated with an excess of aniline (100 μL, 1.1 mmol) and stirred during 30 min at room temperature. The resulting solution was concentrated to ca. 0. 5 mL and diethylether was slowly added to give a white solid. The solid was filtered, washed with ether and dried in vacuo. The spectroscopic analysis of $CDCl_3$ solutions of this solid reveals the presence of complexes **9** and **8**, and aniline in a ca. 5:2:1 molar ratio. This ratio shows that the solid still contains a 20 % of the starting complex **8**, which is consistent with the obtained elemental analysis. The solids obtained by this procedure using larger excess of aniline did not show contents in **9** above 80 %. Data for **9**: IR (Nujol mull): 3442, 3344, 3292, 3242 ν(N-H), 2206 (br) ν(Ir-H); ^1H NMR ($CDCl_3$, 253 K) δ -26.37 (d, J_{HP} = 22.5, 2H, Ir-H), 1.13 (dd, J_{HP} = 13.5, J_{HH} = 6.9, 18H, $PCHCH_3$), 2.07 (m, 3H, $PCHCH_3$), 3.71 (d, J_{HP} = 3.0, 2H, NH_2Ph), 5.18 (d, J_{HH} = 10.2, 2H, NH_2Ph), 5.75 (d, J_{HH} = 10.2, 2H, NH_2Ph), 5.99 (d, J_{HH} = 7.8, 2H, CH), 6.84 (t, J_{HH} = 7.8, 1H, CH), 6.97 (t, J_{HH} = 7.8, 2H, CH), 7.07 (t, J_{HH} = 7.5, 2H, CH), 7.17 (d, J_{HH} = 7.5, 4H, CH), 7.36 (t, J_{HH} = 7.5, 4H, CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 253 K) δ 26.65 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 253 K) δ 19.33 (s, $PCHCH_3$), 24.92 (d, J_{CP} = 32.5, $PCHCH_3$), 119.98, 120.54, 124.20, 124.80, 128.51, 130.12 (all s, CH), 142.47, 145.66 (both s, C).

Preparation of $[(\eta^6\text{-}C_6H_5Et)Ir(\eta^2\text{-}CH_2{=}CHPh)(P^iPr_3)]$ (10): A solution of **1** (100 mg, 0.19 mmol) in acetone (5 mL) was treated with styrene (ca. 500 μL) and stirred during 30 min at room temperature. The resulting solution was concentrated and diethylether was added to give a pale yellow solid, which was filtered, washed with ether and dried in vacuo: yield 100 mg (81%). ^1H NMR ($CDCl_3$, 293 K) δ 1.09 (t, J_{HH} = 7.5, 3H, CH_3), 1.15, 1.18 (both dd, J_{HP} = 14.4, J_{HH} = 7.8, 9H, $PCHCH_3$), 1.88 (ddd, J_{HH} = 8.4, 3.6, J_{HP} = 5.1, 1H, $=CH_2$), 2.00 (m, 3H, $PCHCH_3$), 2.16, 2.17 (both q,

J_{HH} = 7.5, 1H, CH_2), 3.14 (dd, J_{HH} = 10.8, 3.6, 1H, =CH_2), 3.75 (ddd, J_{HH} = 10.8, 8.4, J_{HP} = 6.0, 1H, =CH), 5.26 (d, J_{HH} = 6.3, 1H, CH), 5.49 (td, J_{HH} = 6.3, 1.2, 1H, CH), 5.71 (d, J_{HH} = 6.3, 1H, CH), 6.41 (td, J_{HH} = 6.3, 1.2, 1H, CH), 6.78 (t, J_{HH} = 6.3, 1H, CH), 7.02 (tt, J_{HH} = 7.2, 1.2, 1H, CH), 7.07, 7.22 (both m, 2H, CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 20.41 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 14.12 (s, CH_3), 17.38 (s, CH_2), 19.32, 19.44 (both s, PCH*C*H_3), 24.27 (d, J_{CP} = 30.7, P*C*HCH$_3$), 25.66 (s, =CH_2), 41.35 (s, =CH), 93.58 (d, J_{CP} = 4.2, CH), 93.79 (s, CH), 94.83 (d, J_{CP} = 3.0, CH), 95.39 (d, J_{CP} = 1.0, CH), 100.61 (d, J_{CP} = 1.0, CH), 123.31 (d, J_{CP} = 2.7, C), 126.14, 126.82, 128.77 (all s, CH), 144.48 (s, C); MS (FAB+, *m/z* (%)) 563 (20) [M^+], 457 (50) [M^+- C_6H_5Et]; Anal. Calcd for $C_{25}H_{39}BF_4IrP$: C, 46.22; H, 6.05. Found: C, 46.06; H, 5.77.

Preparation of [(η^6-C_6H_6)Ir(η^2-C_2H_4)(P^iPr_3)] (11): Ethylene was bubbled through a solution of of **1** (100 mg, 0.19 mmol) in acetone (5 mL) during 30 min at room temperature. The resulting solution was concentrated and diethylether was added to give a pale yellow solid, which was filtered, washed with ether and dried in vacuo: yield 88 mg (85 %). ^1H NMR ($CDCl_3$, 293 K) δ 1.60 (dd, J_{HP} = 14.1, J_{HH} = 7.2, 18H, PCHCH_3), 2.07 (part A of a AA'MM'X spin system (X = ^{31}P): $J_{AA'}$ = 8.5, J_{AM} = 11.3, $J_{AM'}$ = 2.3, J_{AX} = 4.9, 2H, CH_2), 2.39 (m, 3H, PC*H*CH$_3$), 3.32 (part M of a AA'MM'X spin system (X = ^{31}P): $J_{MM'}$ = 8.5, J_{MX} = 0.8, 2H, CH_2), 7.01 (s, 6H, C_6H_6); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 22.43 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 19.31 (d, J_{CP} = 1.4, PCH*C*H$_3$), 19.53 (d, J_{CP} = 2.2, C_2H_4), 24.43 (d, J_{CP} = 32.2, P*C*HCH$_3$), 95.89 (d, J_{CP} = 2.2, C_6H_6); MS (FAB+, *m/z* (%)) 459 (100) [M^+]; Λ_M (acetone) = 129 Ω^{-1} cm^2 mol^{-1} (1:1). Anal. Calcd for $C_{17}H_{31}BF_4IrP$: C, 37.37; H, 5.90. Found: C, 37.02 H, 5.55.

Preparation of [(η^6-1,3,5-$C_6H_3(Me)_3$)Ir(η^2-C_2H_4)(P^iPr_3)] (12): A solution of complex **4** (150 mg, 0.27 mmol) in acetone (5 mL) was stirred in atmosphere of ethylene (1 atm) during 12 h at 313 K. The resulting yellow solution was dried in vacuo and the residue was dissolved in CH_2Cl_2 and filtered through celite. The solution was then concentrated to ca. 0.5 mL and treated with diethylether to give a pale yellow solid, which was filtered, washed with ether and dried in vacuo: yield 125 mg (80 %).^1H

NMR ($CDCl_3$, 293 K) δ 1.15 (dd, J_{HP} = 14.1, J_{HH} = 7.2, 18H, PCHC*H*$_3$), 1.82 - 1.90 (m, 5H, CH_2 and PC*H*CH_3), 2.22 (part M of a AA'MM'X spin system (X = ^{31}P): J_{AM} = 11.1, $J_{AM'}$ = 2.2, $J_{MM'}$ = 8.1, J_{MX} = 0.9, 2H, CH_2), 2.47 (s, 9H, CH_3), 6.10 (s, 3H, CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 19.69 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 19.28 (d, J_{CP} = 1.4, PCH*C*H_3), 19.47 (s, CH_3), 22.68 (d, J_{CP} = 30.9, P*C*HCH_3), 23.58 (d, J_{CP} = 2.3, C_2H_4), 94.41 (d, J_{CP} = 2.3, CH), 114.35 (d, J_{CP} = 2.3, C); MS (FAB+, *m/z* (%)) 501 (100) [M^+]. Anal. Calcd for $C_{20}H_{37}BF_4IrP$: C, 40.84; H, 6.53. Found: C, 40.77; H, 6.38.

X-ray Structure Análisis of 4. See Table 1 to Table 5 in the following pages.

References:

(1) Usón, R.; Oro, L.A.; Cabeza, J.A. *Inorg. Synth.* **1985**, *23*, 126.

Table 1. Crystal data and structure refinement for compound **4**.

Identification code	compound4
Empirical formula	C_{18} H_{35} B F_4 Ir P
Formula weight	561.44
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1$
Unit cell dimensions	a = 8.1477(7) Å
	b = 13.8943(12) Å β = 109.454(10)°
	c = 10.1659(9) Å
Volume	1085.14(16) $Å^3$
Z, Calculated density	2, 1.718 Mg/m^3
Absorption coefficient	6.258 mm^{-1}
F(000)	552
Crystal size	0.36 x 0.24 x 0.18 mm
Theta range for data collection	2.12 to 25.07°
Limiting indices	-9<=h<=9, -16<=k<=16, -12<=l<=12
Reflections collected / unique	4286 / 3842 [R(int) = 0.0200]
Completeness to theta = 25.07	99.6 %
Absorption correction	Psi-scans
Max. and min. transmission	0.3988 and 0.2116
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3842 / 1 / 255
Goodness-of-fit on F^2	1.079
Final R indices [I>2σ(I)]	R1 = 0.0345, wR2 = 0.0816
R indices (all data)	R1 = 0.0367, wR2 = 0.0833
Absolute structure parameter	-0.026(14)
Extinction coefficient	0.0059(5)
Largest diff. peak and hole	0.690 and -0.668 e.$Å^3$

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for compound **4**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ir	2311(1)	8564(1)	1348(1)	23(1)
P	2234(3)	9200(2)	-727(2)	20(1)
C(1)	546(11)	8453(11)	2695(8)	26(2)
C(2)	2039(13)	7920(7)	3291(10)	28(2)
C(3)	3728(12)	8364(8)	3681(9)	31(3)
C(4)	3827(13)	9372(8)	3412(10)	30(2)
C(5)	2302(13)	9905(7)	2783(10)	30(2)
C(6)	674(13)	9440(6)	2444(9)	26(2)
C(7)	-1208(13)	7970(7)	2360(11)	35(2)
C(8)	5345(14)	7793(9)	4403(11)	42(3)
C(9)	2410(18)	10976(8)	2603(13)	47(3)
C(10)	2679(12)	8272(6)	-1867(9)	27(2)
C(11)	2129(13)	8550(20)	-3430(8)	44(2)
C(12)	4556(14)	7923(8)	-1390(12)	41(2)
C(13)	3689(11)	10251(7)	-557(10)	26(2)
C(14)	5560(13)	10065(8)	450(11)	40(2)
C(15)	3769(13)	10670(7)	-1928(11)	34(2)
C(16)	68(12)	9668(7)	-1792(10)	30(2)
C(17)	-1284(13)	8864(8)	-2122(12)	46(3)
C(18)	-534(14)	10521(8)	-1132(12)	41(3)
B	-1661(16)	10762(8)	-5638(12)	36(3)
F(1)	-1701(9)	9759(4)	-5687(7)	50(2)
F(2)	-1515(12)	11116(5)	-6871(7)	66(2)
F(3)	-248(10)	11082(6)	-4568(7)	59(2)
F(4)	-3162(11)	11114(6)	-5492(12)	88(3)

Table 3. Bond lengths (Å) and angles (°) for compound **4**.

Ir-C(2)	2.246(9)
Ir-P	2.270(2)
Ir-C(3)	2.282(8)
Ir-C(1)	2.297(8)
Ir-C(4)	2.337(9)
Ir-C(6)	2.343(9)
Ir-C(5)	2.367(9)
Ir-H(0)	1.4903
Ir-H(1)	1.5030
P-C(10)	1.849(9)
P-C(13)	1.852(9)
P-C(16)	1.854(9)
C(1)-C(2)	1.380(15)
C(1)-C(6)	1.404(17)
C(1)-C(7)	1.512(13)
C(2)-C(3)	1.438(14)
C(2)-H(2)	0.9500
C(3)-C(4)	1.434(17)
C(3)-C(8)	1.504(15)
C(4)-C(5)	1.405(15)
C(4)-H(4)	0.9666
C(5)-C(6)	1.411(14)
C(5)-C(9)	1.506(14)
C(6)-H(6)	0.8597
C(7)-H(7A)	0.8823
C(7)-H(7B)	0.8823
C(7)-H(7C)	0.8823
C(8)-H(8A)	0.9591
C(8)-H(8B)	0.9591
C(8)-H(8C)	0.9591
C(9)-H(9A)	1.0501
C(9)-H(9B)	1.0501
C(9)-H(9C)	1.0501
C(10)-C(12)	1.521(14)
C(10)-C(11)	1.550(14)
C(10)-H(10)	1.0000
C(11)-H(11A)	0.9331
C(11)-H(11B)	0.9331
C(11)-H(11C)	0.9331
C(12)-H(12A)	0.9660

C(12)-H(12B)	0.9660
C(12)-H(12C)	0.9660
C(13)-C(15)	1.532(13)
C(13)-C(14)	1.549(13)
C(13)-H(13)	0.9767
C(14)-H(14A)	0.9691
C(14)-H(14B)	0.9691
C(14)-H(14C)	0.9691
C(15)-H(15A)	0.9348
C(15)-H(15B)	0.9348
C(15)-H(15C)	0.9348
C(16)-C(18)	1.522(14)
C(16)-C(17)	1.525(14)
C(16)-H(16)	0.8502
C(17)-H(17A)	0.9715
C(17)-H(17B)	0.9715
C(17)-H(17C)	0.9715
C(18)-H(18A)	0.9848
C(18)-H(18B)	0.9848
C(18)-H(18C)	0.9848
B-F(3)	1.368(13)
B-F(4)	1.371(14)
B-F(2)	1.388(15)
B-F(1)	1.395(13)

C(2)-Ir-P	173.1(3)
C(2)-Ir-C(3)	37.0(4)
P-Ir-C(3)	149.5(3)
C(2)-Ir-C(1)	35.3(4)
P-Ir-C(1)	138.7(3)
C(3)-Ir-C(1)	64.7(3)
C(2)-Ir-C(4)	65.1(4)
P-Ir-C(4)	119.4(3)
C(3)-Ir-C(4)	36.1(4)
C(1)-Ir-C(4)	75.3(4)
C(2)-Ir-C(6)	63.3(3)
P-Ir-C(6)	113.3(2)
C(3)-Ir-C(6)	74.9(4)
C(1)-Ir-C(6)	35.2(4)
C(4)-Ir-C(6)	62.5(4)
C(2)-Ir-C(5)	75.5(3)
P-Ir-C(5)	105.1(2)

C(3)-Ir-C(5)	63.9(4)
C(1)-Ir-C(5)	63.5(4)
C(4)-Ir-C(5)	34.7(4)
C(6)-Ir-C(5)	34.9(3)
C(2)-Ir-H(0)	99.9
P-Ir-H(0)	75.1
C(3)-Ir-H(0)	132.7
C(1)-Ir-H(0)	89.2
C(4)-Ir-H(0)	164.0
C(6)-Ir-H(0)	106.6
C(5)-Ir-H(0)	139.4
C(2)-Ir-H(1)	119.6
P-Ir-H(1)	63.3
C(3)-Ir-H(1)	110.6
C(1)-Ir-H(1)	144.3
C(4)-Ir-H(1)	123.4
C(6)-Ir-H(1)	174.0
C(5)-Ir-H(1)	149.3
H(0)-Ir-H(1)	68.0
C(10)-P-C(13)	110.8(4)
C(10)-P-C(16)	103.1(4)
C(13)-P-C(16)	103.5(4)
C(10)-P-Ir	111.1(3)
C(13)-P-Ir	113.7(3)
C(16)-P-Ir	113.9(3)
C(2)-C(1)-C(6)	119.7(9)
C(2)-C(1)-C(7)	119.3(12)
C(6)-C(1)-C(7)	120.9(10)
C(2)-C(1)-Ir	70.3(5)
C(6)-C(1)-Ir	74.2(5)
C(7)-C(1)-Ir	128.9(7)
C(1)-C(2)-C(3)	120.9(9)
C(1)-C(2)-Ir	74.4(5)
C(3)-C(2)-Ir	72.9(5)
C(1)-C(2)-H(2)	119.6
C(3)-C(2)-H(2)	119.6
Ir-C(2)-H(2)	124.8
C(4)-C(3)-C(2)	118.4(9)
C(4)-C(3)-C(8)	120.8(9)
C(2)-C(3)-C(8)	120.7(10)
C(4)-C(3)-Ir	74.0(5)
C(2)-C(3)-Ir	70.1(5)

C(8)-C(3)-Ir	129.0(7)
C(5)-C(4)-C(3)	120.2(9)
C(5)-C(4)-Ir	73.8(5)
C(3)-C(4)-Ir	69.8(5)
C(5)-C(4)-H(4)	119.9
C(3)-C(4)-H(4)	119.9
Ir-C(4)-H(4)	128.7
C(4)-C(5)-C(6)	119.1(9)
C(4)-C(5)-C(9)	119.8(9)
C(6)-C(5)-C(9)	120.8(10)
C(4)-C(5)-Ir	71.5(5)
C(6)-C(5)-Ir	71.6(5)
C(9)-C(5)-Ir	133.7(7)
C(1)-C(6)-C(5)	121.5(9)
C(1)-C(6)-Ir	70.6(5)
C(5)-C(6)-Ir	73.5(5)
C(1)-C(6)-H(6)	119.2
C(5)-C(6)-H(6)	119.2
Ir-C(6)-H(6)	129.1
C(1)-C(7)-H(7A)	109.5
C(1)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(1)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(3)-C(8)-H(8A)	109.5
C(3)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(3)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(5)-C(9)-H(9A)	109.5
C(5)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(5)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(12)-C(10)-C(11)	108.9(8)
C(12)-C(10)-P	114.1(7)
C(11)-C(10)-P	114.7(11)
C(12)-C(10)-H(10)	106.2
C(11)-C(10)-H(10)	106.2

P-C(10)-H(10)	106.2
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(15)-C(13)-C(14)	109.5(8)
C(15)-C(13)-P	115.8(7)
C(14)-C(13)-P	112.9(7)
C(15)-C(13)-H(13)	106.0
C(14)-C(13)-H(13)	106.0
P-C(13)-H(13)	106.0
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(18)-C(16)-C(17)	110.6(9)
C(18)-C(16)-P	113.5(7)
C(17)-C(16)-P	110.5(7)
C(18)-C(16)-H(16)	107.3
C(17)-C(16)-H(16)	107.3
P-C(16)-H(16)	107.3
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5

H(17B)-C(17)-H(17C)	109.5
C(16)-C(18)-H(18A)	109.5
C(16)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(16)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
F(3)-B-F(4)	110.0(9)
F(3)-B-F(2)	107.5(10)
F(4)-B-F(2)	108.6(10)
F(3)-B-F(1)	110.9(9)
F(4)-B-F(1)	110.5(10)
F(2)-B-F(1)	109.2(9)

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for compound **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Ir	34(1)	20(1)	17(1)	1(1)	12(1)	-1(1)
P	22(1)	22(1)	17(1)	1(1)	8(1)	0(1)
C(1)	33(4)	29(7)	20(3)	1(5)	12(3)	-10(5)
C(2)	41(5)	22(5)	24(5)	-1(4)	17(4)	0(4)
C(3)	32(4)	48(11)	12(4)	7(4)	5(3)	8(5)
C(4)	30(5)	39(6)	23(5)	-13(4)	11(4)	-19(5)
C(5)	46(6)	27(5)	27(5)	-12(4)	24(4)	-11(4)
C(6)	42(6)	21(5)	21(4)	1(3)	19(4)	7(4)
C(7)	30(5)	31(5)	47(6)	-1(4)	17(5)	-5(4)
C(8)	33(6)	62(7)	28(5)	7(5)	6(5)	3(5)
C(9)	71(8)	28(5)	47(7)	-8(5)	27(6)	-11(5)
C(10)	32(5)	27(5)	25(4)	-1(3)	14(4)	1(3)
C(11)	65(6)	48(5)	26(4)	-12(10)	25(4)	-10(11)
C(12)	46(6)	44(6)	40(6)	-9(5)	22(5)	4(5)
C(13)	23(4)	27(4)	28(5)	0(4)	10(4)	-6(4)
C(14)	32(5)	47(6)	38(6)	3(5)	8(5)	-6(5)
C(15)	36(5)	33(5)	37(6)	11(4)	16(4)	-3(4)
C(16)	24(5)	38(5)	24(5)	10(4)	3(4)	6(4)
C(17)	23(5)	51(7)	54(7)	5(5)	-1(4)	-6(4)
C(18)	36(6)	41(6)	47(6)	13(5)	15(5)	16(5)
B	39(6)	30(6)	32(6)	-9(5)	1(5)	3(5)
F(1)	60(4)	32(3)	62(4)	-4(3)	26(3)	-1(3)
F(2)	107(6)	47(4)	37(4)	4(3)	15(4)	15(4)
F(3)	54(4)	57(4)	44(4)	-3(4)	-13(3)	-7(3)
F(4)	58(5)	65(5)	155(9)	-55(6)	55(6)	-16(4)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for compound4.

	x	y	z	U(eq)
H(0)	1056	7950	275	20(20)
H(1)	3190	7997	513	20(20)
H(2)	1949	7251	3446	50(20)
H(4)	4950(160)	9690(50)	3670(40)	50(20)
H(6)	-260(150)	9770(50)	2080(60)	50(20)
H(7A)	-1200(50)	7590(70)	3050(80)	100(20)
H(7B)	-1430(70)	7630(70)	1590(90)	100(20)
H(7C)	-2020(80)	8410(40)	2240(110)	100(20)
H(8A)	5430(80)	7690(70)	5360(90)	100(20)
H(8B)	6350(90)	8140(50)	4370(100)	100(20)
H(8C)	5290(70)	7190(60)	3940(80)	100(20)
H(9A)	2270(140)	11330(30)	3470(90)	100(20)
H(9B)	1410(120)	11200(20)	1700(100)	100(20)
H(9C)	3620(110)	11150(19)	2510(110)	100(20)
H(10)	1956	7701	-1815	50(20)
H(11A)	2410(90)	9190(50)	-3510(10)	49(8)
H(11B)	930(70)	8470(60)	-3840(30)	49(8)
H(11C)	2710(90)	8160(40)	-3880(30)	49(8)
H(12A)	4650(20)	7370(50)	-1930(60)	49(8)
H(12B)	4910(40)	7750(50)	-420(70)	49(8)
H(12C)	5300(50)	8430(40)	-1520(60)	49(8)
H(13)	3210(60)	10760(70)	-130(60)	50(20)
H(14A)	6180(50)	9670(50)	-10(40)	49(8)
H(14B)	5507(13)	9740(50)	1280(70)	49(8)
H(14C)	6160(50)	10670(40)	710(60)	49(8)
H(15A)	4290(100)	11280(50)	-1760(20)	49(8)
H(15B)	2640(80)	10720(50)	-2570(50)	49(8)
H(15C)	4430(90)	10260(40)	-2290(50)	49(8)
H(16)	148(17)	9860(30)	-2560(120)	50(20)
H(17A)	-1470(70)	8660(40)	-1270(50)	49(8)
H(17B)	-870(50)	8320(40)	-2530(80)	49(8)
H(17C)	-2370(70)	9100(20)	-2780(70)	49(8)
H(18A)	-1650(90)	10760(40)	-1770(50)	49(8)
H(18B)	340(70)	11040(40)	-950(70)	49(8)
H(18C)	-680(90)	10320(20)	-250(70)	49(8)