Rhodium and Iridium Complexes of Bulky Tertiary Phosphine Ligands. Searching for Isolable Cationic M(III) Alkylidenes

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- Supporting Information -

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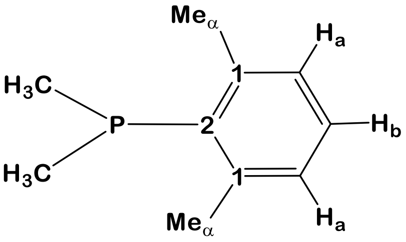
1. General experimental details.

All operations were performed under an argon atmosphere using standard Schlenk techniques, employing dry solvents and glassware. HRMS data were obtained using a Jeol JMS-SX 102A mass spectrometer at the Analytical Services of the Universidad de Sevilla (CITIUS). Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). Infrared spectra were recorded on a Bruker Vector 22 spectrometer. The NMR instruments were Bruker DRX-500, DRX-400 and DRX-300 spectrometers. Spectra were referenced to external $SiMe_4$ (δ 0 ppm) using the residual proton solvent peaks as internal standards (^1H NMR experiments), or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments), while ^{31}P was referenced to external H_3PO_4. Spectral assignments were made by routine one- and two-dimensional NMR experiments where appropriate. Dimer $[(\eta^5-C_5Me_5)IrCl_2]_2$[1] and $NaBAr_F$[2] were prepared according to literature procedures. In the ^1H NMR spectra all aromatic couplings are of *ca*. 7.5 Hz. The ^1H and $^{13}C\{1H\}$ NMR spectral data for the BAr_F^- anion (BAr_F = $B[3,5-(CF_3)_2C_6H_3)]$) in CD_2Cl_2 are identical for all complexes and therefore are not repeated below. BAr_F^-: ^1H RMN: δ 7.75 (s, 8 H, *o*-Ar), 7.58 (s, 4 H, *p*- Ar). $^{13}C\{1H\}$ RMN: δ 162.1 (q, 37 Hz, *ipso*-Ar), 135.3 (*o*-Ar), 129.2 (q, 31 Hz, *m*-Ar), 124.9 (q, 273 Hz, CF_3), 117.8 (*p*-Ar).

2. General synthesis of phosphine ligands.

a) $PMe_2(Xyl)$



Preparation of PXX'(Xyl), X, X' = Cl, Br

A solution of PCl_3 (1 mL, 11.5 mmol) in THF (20 mL) placed in a three-neck round-bottom flask was cooled down to -78 ºC. Using a dropping funnel a THF solution of $(2,6\text{-}Me_2C_6H_3)MgBr$[3] (15.5 mL, 0.71 M, 11.0 mmol) was added to the former solution at this temperature, resulting in the formation of a white precipitate. The reaction mixture was allowed to warm to room temperature and additionally stirred for 12 h. The solvent was removed under reduced pressure and the crude product extracted with pentane (4 x 30 mL). The volatiles were evaporated under vacuum to give a mixture of $PCl_2(Xyl)$, PBrCl(Xyl) and $PBr_2(Xyl)$ in a *ca.* ratio of 40:45:15.

$PCl_2(Xyl)$: $^{31}P\{^1H\}$ RMN (162 MHz, C_6D_6, 25 ºC) δ: 166.1.

PBrCl(Xyl): $^{31}P\{^1H\}$ RMN (162 MHz, C_6D_6, 25 ºC) δ: 159.8.

$PBr_2(Xyl)$: $^{31}P\{^1H\}$ RMN (162 MHz, C_6D_6, 25 ºC) δ: 151.4.

Preparation of $PMe_2(Xyl)$

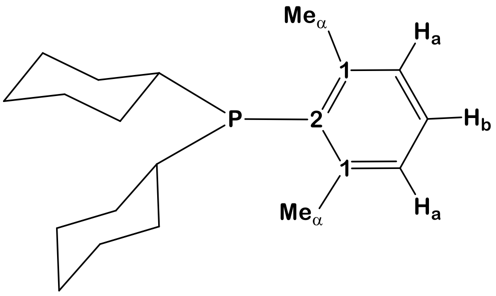
The above mixture of halophosphines $PCl_2(Xyl)$, PBrCl(Xyl) and $PBr_2(Xyl)$ (*ca.* 40:45:15; 800 mg, *ca.* 2.70 mmol) was placed in a three-necked round-bottom flask and dissolved in diethyl ether (30 mL). MeMgBr (2.7 mL, 3 M in Et_2O, 8 mmol) was added dropwise at -78 ºC using a dropping funnel, then the reaction mixture was slowly warmed (2h) to 25 ºC and additionally stirred for 12 h. The solvent was removed at 0 ºC under vacuum and the residue extracted with pentane. The volatiles was evaporated at 0 ºC under reduced pressure to yield $PMe_2(Xyl)$ as a colorless oil (290 mg, *ca.* 65 %). **^1H NMR** (400 MHz, C_6D_6, 25 ºC) δ: 7.00 (t, 1 H, H_b), 6.83 (dd, 2 H, $^4J_{HP}$ = 2.2 Hz, H_a), 2.50 (s, 6 H, Me_α), 1.24 (d, 6 H, $^2J_{HP}$ = 5.3 Hz, PMe). All aromatic couplings are of *ca.* 7.5 Hz. **$^{13}C\{^1H\}$ NMR** (100 MHz, C_6D_6, 25 ºC) δ: 144.2 (d, $^2J_{CP}$ = 15 Hz, C_1), 136.5 (d,

${}^{1}J_{CP}$ = 24 Hz, C_2), 129.4 (d, ${}^{3}J_{CP}$ = 4 Hz, CH_a), 129.3 (CH_b), 23.4 (d, ${}^{3}J_{CP}$ = 20 Hz, Me_α), 12.4 (d, ${}^{1}J_{CP}$ = 15 Hz, PMe). **${}^{31}P\{{}^{1}H\}$ NMR** (160 MHz, C_6D_6, 25 ºC) δ: -54.0.

b) General procedure for the synthesis of PR_2(Xyl) (R = Ph, ^{i}Pr, Cy).

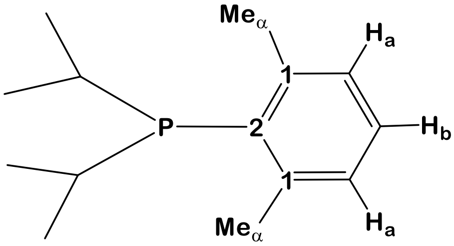
A freshly prepared THF solution of 2,6-dimethylphenylmagnesium bromide[3] was added dropwise to a stirred solution of an equimolar amount of the corresponding chlorophosphine ($PClR_2$) (13.5 mmol) in 20 mL of THF at -78 °C. After addition was completed, the reaction mixture was allowed to reach room temperature and stirred overnight. All the volatiles were then removed under reduced pressure and the pale yellow solid residue was extracted with pentane (3 × 20 mL). Evaporation of the organic solvent *in vacuo* afforded a yellow oil (PPh_2(Xyl)[4] and P(^{i}Pr)$_2$(Xyl)) or a white solid (P(Cy)$_2$Xyl), which was characterized as the corresponding phosphine. For P(^{i}Pr)$_2$Xyl all evaporation steps were carried out at 0 ºC in order to avoid partial evaporation of the phosphine.

P(Cy)$_2$(Xyl)



${}^{1}H$ NMR (400 MHz, CD_2Cl_2, 25 ºC) δ: 7.10 (t, 1 H, H_b), 6.99 (br. d, 2 H, H_a), 2.58, 2.47 (br. s, 3 H each, Me_α), 2.23 (m, 2 H, 2 PCH), 1.97 (m, 2 H, CH_2(Cy)), 1.78 (m, 2 H, CH_2(Cy)), 1.62 (m, 4 H, CH_2(Cy)), 1.34 (m, 4 H, CH_2(Cy)), 1.23 (m, 6 H, CH_2(Cy)), 0.95 (m, 2 H, CH_2(Cy)). All aromatic couplings are of *ca*. 7.5 Hz. **${}^{13}C\{{}^{1}H\}$ NMR** (100 MHz, CD_2Cl_2, 25 ºC) δ: 128.9 (CH_b), 128.3 (br. s, CH_a), 35.5 (d, ${}^{1}J_{CP}$ = 14 Hz, PCH), 34.0 (*C*H_2(Cy)), 33.8 (*C*H_2(Cy)), 30.9 (d, J_{CP} = 10 Hz, *C*H_2(Cy)), 27.5 (d, J_{CP} = 8 Hz, *C*H_2(Cy)), 27.2 (d, J_{CP} = 14 Hz, *C*H_2(Cy)), 26.7 (*C*H_2(Cy)), 24.8, 23.3 (br. s, Me_α). Signals due to C_1 and C_2 were not located due to their broadening. **${}^{31}P\{{}^{1}H\}$ NMR** (160 MHz, CD_2Cl_2, 25 ºC) δ: -5.6.

P(^{i}Pr)$_2$(Xyl)

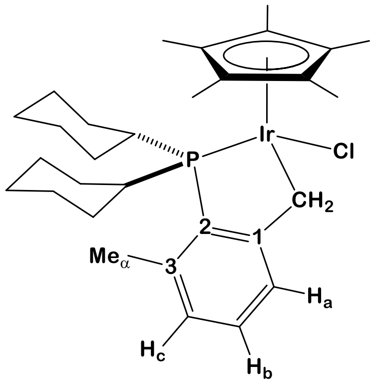


^{1}H NMR (500 MHz, CDCl$_3$, 60 ºC) δ: 7.09 (t, 1 H, H$_b$), 7.00 (d, 2 H, H$_a$), 2.58 (br s, 6 H, Me$_\alpha$), 2.46 (sept, 2 H, $^3J_{HH}$ = 7.0 Hz, C*H*(^{i}Pr)), 1.23 (dd, 6 H, $^3J_{HH}$ = 7.0, $^3J_{HP}$ = 16.7 Hz, *Me*($^{\mathrm{i}}$Pr)), 0.85 (dd, 6 H, $^3J_{HH}$ = 7.0, $^3J_{HP}$ = 13.2 Hz, *Me*(^{i}Pr)). All aromatic couplings are of *ca*. 7.5 Hz. **^{13}C{^{1}H} NMR** (125 MHz, CDCl$_3$, 60 ºC) δ: 144.9 (br s, C$_1$), 134.6 (d, $^1J_{CP}$ = 24 Hz, C$_2$), 128.8 (CH$_b$), 128.5 (br s, CH$_a$), 24.9 (d, $^1J_{CP}$ = 14 Hz, *Me*(^{i}Pr)), 23.8 (br s, Me$_\alpha$), 22.8 (d, $^2J_{CP}$ = 28 Hz, *Me*(^{i}Pr)), 21.2 (d, $^2J_{CP}$ = 14 Hz, *Me*(^{i}Pr)). **^{31}P{^{1}H} NMR** (200 MHz, CDCl$_3$, 60 ºC) δ: 7.2.

3. Synthesis and characterization of iridium and rhodium compounds

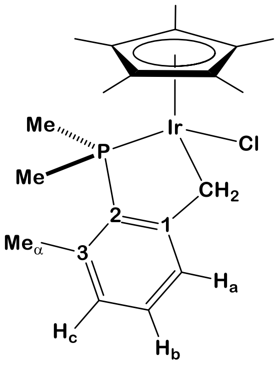
Synthesis and spectroscopic characterization of iridium chloride compounds.

[(η^5-C_5Me_5)Ir(Cl){P(Cy)$_2$(2,6-CH_2(Me)C_6H_3)}] (1b)



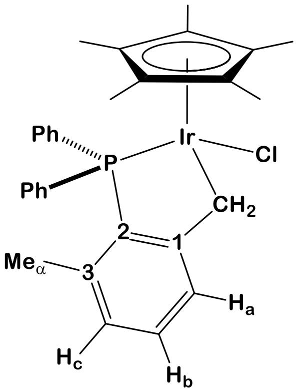
^{1}H NMR (400 MHz, CD_2Cl_2, 25 ºC) δ: 7.19 (d, 1 H, H_a), 7.04 (td, 1 H, $^5J_{HP}$ = 2.0 Hz, H_b), 6.83 (d, 1 H, H_c), 3,67 (d, 1 H, $^2J_{HH}$ = 13.8 Hz, IrC*H*H), 2.98 (m, 2 H, IrCH*H*, PC*H*CH), 2,49 (s, 3 H, Me_α), 2.13 – 1.78 (m, 7 H, CH_2(Cy), PCHC*H*), 1.72 (d, 15 H, $^4J_{HP}$ = 1.4 Hz, C_5Me_5), 1.67 – 1.40 (m, 7 H, CH_2(Cy)), 1.34 – 1.05 (m, 6 H, CH_2(Cy)), 0.60 (m, 1 H, CH_2(Cy)). All aromatic couplings are of *ca*. 7.5 Hz. **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2, 25 ºC) δ: 163.0 (d, $^2J_{CP}$ = 26 Hz, C_1), 140.6 (C_3), 133.4 (d, $^1J_{CP}$ = 48 Hz, C_2), 129.8 (CH_b), 127.9 (d, $^3J_{CP}$ = 7 Hz, CH_c), 127.5 (d, $^3J_{CP}$ = 12 Hz, CH_a), 91.9 (*C*$_5$Me$_5$), 41.1 (d, $^1J_{CP}$ = 29 Hz, PCH*C*H), 36.8 (d, $^1J_{CP}$ = 29 Hz, P*C*HCH), 31.3 (d, J_{CP} = 5 Hz, *C*H$_2$(Cy)), 29.8 (d, J_{CP} = 6 Hz, *C*H$_2$(Cy)), 29.2 (*C*H$_2$(Cy)), 28.1 (*C*H$_2$(Cy)), 28.0 (d, J_{CP} = 8 Hz, *C*H$_2$(Cy)), 27.7 (d, J_{CP} = 10 Hz, *C*H$_2$(Cy)), 27.5 (d, J_{CP} = 12 Hz, *C*H$_2$(Cy)), 27.2 (d, J_{CP} = 14 Hz, *C*H$_2$(Cy)), 26.7 (*C*H$_2$(Cy)), 26.6 (*C*H$_2$(Cy)), 22.9 (Me_α), 17.2 (d, $^2J_{CP}$ = 4 Hz, $IrCH_2$), 9.2 (C$_5$*Me*$_5$). **^{31}P{^{1}H} NMR** (160 MHz, CD_2Cl_2, 25 ºC) δ: 38.0. **Anal. Calcd.** for $C_{30}H_{45}ClIrP$: C, 54.24; H, 6.83. **Found**: C, 54.3; H, 6.9.

[(η^5-C_5Me_5)Ir(Cl){P(Me)$_2$(2,6-CH_2(Me)C_6H_3)}] (1c)



^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC) δ: 7.25 (d, 1 H, H$_a$), 7.04 (td, $^5J_{HP}$ = 1.6 Hz, H$_b$), 6.78 (dd, 1 H, $^4J_{HP}$ = 1.9 Hz, H$_c$), 3.50 (d, 1 H, $^2J_{HH}$ = 14.4 Hz, IrC*H*H), 3.29 (dd, 1 H, $^2J_{HH}$ = 14.4, $^3J_{HP}$ = 5.1 Hz, IrCH*H*), 2,45 (s, 3 H, Me), 2.06 (d, 3 H, $^2J_{HP}$ = 11.1 Hz, P*Me*Me), 1.79 (d, 3 H, $^2J_{HP}$ = 11.3 Hz, PMe*Me*), 1.78 (d, 15 H, $^4J_{HP}$ = 1.9 Hz, C$_5$Me$_5$). All aromatic couplings are of *ca*. 7.5 Hz. **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$, 25 ºC) δ: 160.8 (d, $^2J_{CP}$ = 30 Hz, C$_1$), 139.7 (C$_3$), 135.3 (d, $^1J_{CP}$ = 59 Hz, C$_2$), 130.2 (CH$_b$), 127.5 (d, $^3J_{CP}$ = 7 Hz, CH$_c$), 127.4 (d, $^3J_{CP}$ = 14 Hz, CH$_a$), 91.1 (*C*$_5$Me$_5$), 20.8 (d, $^3J_{CP}$ = 3 Hz, Me$_\alpha$), 15.2 (d, $^1J_{CP}$ = 36 Hz, P*Me*Me), 13.9 (d, $^1J_{CP}$ = 37 Hz, PMe*Me*), 16.4 (d, $^2J_{CP}$ = 3 Hz, IrCH$_2$), 8.8 (C$_5$*Me*$_5$). **^{31}P{^{1}H} NMR** (160 MHz, CDCl$_3$, 25 ºC) δ: 3.3. **Anal. Calcd.** for C$_{20}$H$_{29}$ClIrP: C, 45.49; H, 5.54. **Found**: C, 45.3; H, 5.4.

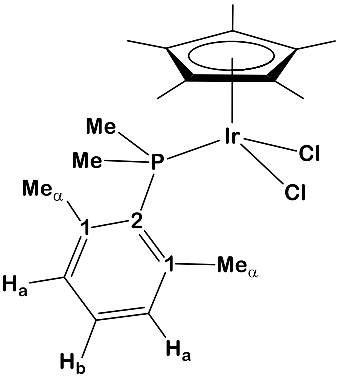
[(η^5-C$_5$Me$_5$)Ir(Cl){P(Ph)$_2$(2,6-CH$_2$(Me)C$_6$H$_3$)}] (1d)



^{1}H NMR (500 MHz, CDCl$_3$, 25 ºC) δ: 7.52 – 7.44 (m, 3 H, H$_a$, PPh$_2$), 7.43 – 7.33 (m, 4 H, PPh$_2$), 7.33 – 7.28 (m, 4 H, PPh$_2$), 7.17 (td, 1 H, $^5J_{HP}$ = 1.9 Hz, H$_b$), 6.83 (dd, 1 H, $^4J_{HP}$ = 3.2 Hz, H$_c$), 3.86 (d, 1 H, $^2J_{HH}$ = 14.6 Hz, IrC*H*H), 3.73 (dd, 1 H, $^2J_{HH}$ = 14.6, $^3J_{HP}$ = 4.1 Hz, IrCH*H*), 1.78 (s, 3 H, Me$_\alpha$), 1.56 (d, 15 H, $^4J_{HP}$ = 2.0 Hz, C$_5$Me$_5$). All aromatic couplings are of *ca*. 7.5 Hz. **^{13}C{^{1}H} NMR** (125 MHz, CDCl$_3$, 25 ºC) δ: 163.2 (d, $^2J_{CP}$ = 30 Hz, C$_1$), 141.4 (C$_3$), 134.7 (d, $^1J_{CP}$ = 42 Hz, *ipso*-Ph), 134.2 (d, $^1J_{CP}$ = 53 Hz, C$_2$), 133.1, 133.0, 132.0, 131.9, 131.0 (PPh$_2$), 130.9 (d, $^4J_{CP}$ = 2 Hz, CH$_b$), 130.7 (d, $^1J_{CP}$ = 57 Hz, *ipso*-Ph), 129.5, 129.3 (d, J_{CP} = 3 Hz, PPh$_2$), 128.0, 127.9 (PPh$_2$), 127.6 (CH$_c$), 127.5 (d, $^3J_{CP}$ = 8 Hz, CH$_a$), 127.2, 127.1 (PPh$_2$), 92.0 (*C*$_5$Me$_5$), 21.7 (d, $^3J_{CP}$ = 3 Hz, Me$_\alpha$), 16.7 (d, $^2J_{CP}$ = 3 Hz, IrCH$_2$), 8.6 (C$_5$*Me*$_5$). **^{31}P{^{1}H} NMR** (200 MHz, CDCl$_3$, 25 ºC) δ: 28.6. **Anal. Calcd.** for C$_{30}$H$_{32}$ClIrP: C, 55.33; H, 4.95. **Found**: C, 55.2; H, 5.1.

When the synthesis of **1d** was carried out at room temperature for 6 hours the final product was a mixture of the metalated chloride complex **1d** and the non-metalated bis-chloride species (η^5-C_5Me_5)$IrCl_2$(PPh_2(Xyl). in a *ca.* ratio of 65:35. To achieve the complete metalation of the phosphine ligand the reaction had to be carried out at 45 ºC. The non-metalated compound is characterized by ^{1}H NMR signals at 2.31 and 1.39 (d, $^4J_{HP}$ = 2.4 Hz) ppm, due to the methyl groups of the xylyl ring and the Cp* ligand, respectively. In the ^{31}P{^{1}H} NMR spectrum a broad singlet is recorded at -1.1 ppm.

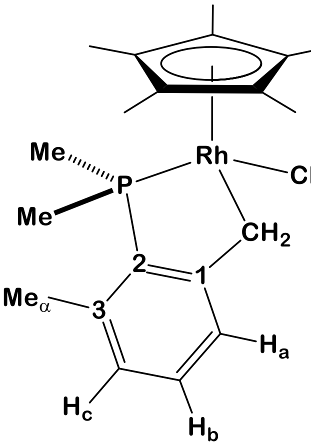
[(η^5-C_5Me_5)Ir(Cl)$_2${P(Me)$_2$(2,6-(Me)$_2C_6H_3$)}]



[Cp*$IrCl_2$]$_2$ (0.10 g, ca. 0.13 mmol) was dissolved in dry CH_2Cl_2 (5 mL) in a Schlenk flask. The dark solution was cooled to 0ºC and a dichloromethane solution of the phosphine (43 mg, 0.26 mmol) was added. The reaction mixture was stirred for 30 min at 0ºC and the solvent removed under reduced pressure. The crude was washed with pentane to afford the compound as a pale orange powder (160 mg, 88 %). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ºC) δ: 7.15 (td, $^5J_{HP}$ = 1.7 Hz, H_b), 7.01 (dd, 2 H, $^4J_{HP}$ = 3.2 Hz, H_a), 2,59 (s, 6 H, Me_α), 2.02 (d, 6 H, $^2J_{HP}$ = 10.4 Hz, PMe_2), 1.39 (d, 15 H, $^4J_{HP}$ = 2.2 Hz, C_5Me_5). All aromatic couplings are of *ca*. 7.5 Hz. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$, 25 ºC) δ: 141.8 (d, $^2J_{CP}$ = 9 Hz, C_1), 130.3 (d, $^3J_{CP}$ = 8 Hz, CH_a), 129.9 (CH_b), 129.3 (d, $^1J_{CP}$ = 45 Hz, C_2), 91.6 (d, $^2J_{CP}$ = 3 Hz, C_5Me$_5$), 24.7 (d, $^3J_{CP}$ = 5 Hz, Me_α), 16.8 (d, $^1J_{CP}$ = 40 Hz, PMe_2), 8.3 (C_5*Me*$_5$). **^{31}P{^{1}H} NMR** (160 MHz, $CDCl_3$, 25 ºC) δ: -20.2. **Anal. Calcd.** for $C_{20}H_{30}Cl_2IrP$: C, 42.6; H, 5.4. **Found**: C, 43.0; 5.2.

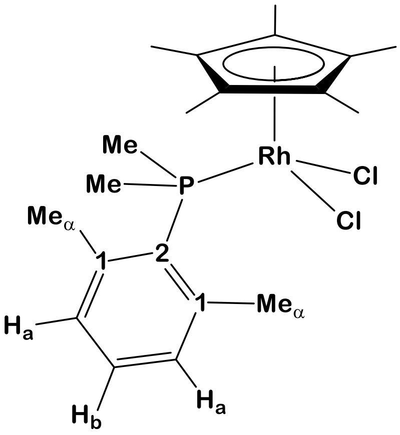
Spectroscopic characterization of rhodium chloride compounds.

$[(\eta^5\text{-}C_5Me_5)Rh(Cl)\{P(Me)_2(2,6\text{-}CH_2(Me)C_6H_3)\}]$ (2c)



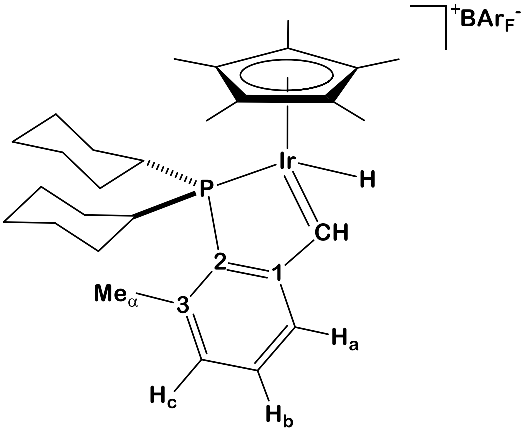
^{1}H NMR (500 MHz, CD_2Cl_2, 25 ºC) δ: 7.15 (d, 1 H, H_a), 7.09 (td, 1 H, $^5J_{HP} = 2.2$ Hz, H_b), 6.87 (dd, 1 H, $^4J_{HP} = 2.9$ Hz, H_c), 3.21 (m, 2 H, $RhCH_2$), 2.46 (s, 3 H, Me_α), 1.98 (d, 3 H, $^2J_{CP} = 11.5$ Hz, P*Me*Me), 1.74 (d, 3 H, $^2J_{CP} = 10.4$ Hz, PMe*Me*), 1.72 (d, 15 H, $^4J_{HP} = 2.7$ Hz, C_5Me_5). All aromatic couplings are of *ca*. 7.5 Hz. **^{13}C{^{1}H} NMR** (125 MHz, CD_2Cl_2, 25 ºC) δ: 159.5 (d, $^2J_{CP} = 31$ Hz, C_1), 139.8 (C_3), 134.4 (d, $^1J_{CP} = 51$ Hz, C_2), 129.8 (CH_b), 127.3 (d, $^4J_{CP} = 7$ Hz, CH_c), 126.0 (d, $^4J_{CP} = 26$ Hz, CH_a), 97.3 (C_5Me_5), 28.9 (dd, $^1J_{CRh} = 24$, $^2J_{CP} = 9$ Hz, $RhCH_2$), 20.8 (Me_α), 14.8 (d, $^1J_{CP} = 30$ Hz, P*Me*Me), 14.5 (d, $^1J_{CP} = 27$ Hz, PMe*Me*), 8.9 (C_5Me_5). **^{31}P{^{1}H} NMR** (200 MHz, CD_2Cl_2, 25 ºC) δ: 41.2 (d, $^1J_{RhP} = 158$ Hz). **Anal. Calcd.** for $C_{20}H_{29}ClPRh$: C, 54.8; H, 6.7. **Found**: C, 54.8; H, 6.7.

$(\eta^5\text{-}C_5Me_5)Rh(Cl)_2\{P(Me)_2(2,6\text{-}(Me)_2C_6H_3)\}$



^{1}H NMR (500 MHz, CDCl$_3$, 25 ºC) δ: 7.20 (td, 1 H, $^{5}J_{HP}$ = 1.8 Hz, H$_b$), 7.06 (dd, 2 H, $^{4}J_{HP}$ = 3.0 Hz, H$_a$), 2.63 (s, 6 H, Me$_{\alpha}$), 1.98 (d, 6 H, $^{2}J_{CP}$ = 10.7 Hz, PMe$_2$), 1.42 (d, 15 H, $^{4}J_{HP}$ = 3.5 Hz, C$_5$Me$_5$). All aromatic couplings are of *ca*. 7.5 Hz. **^{13}C{^{1}H} NMR** (125 MHz, CDCl$_3$, 25 ºC) δ: 142.7 (d, $^{2}J_{CP}$ = 8 Hz, C$_1$), 130.8 (d, $^{4}J_{CP}$ = 8 Hz, CH$_a$), 130.5 (d, $^{1}J_{CP}$ = 33 Hz, C$_2$), 130.3 (d, $^{4}J_{CP}$ = 3 Hz, CH$_b$), 98.6 (dd, $^{1}J_{CRh}$ = 7, $^{2}J_{CP}$ = 3 Hz, *C*$_5$Me$_5$), 25.5 (d, $^{3}J_{CP}$ = 6 Hz, Me$_{\alpha}$), 18.3 (d, $^{1}J_{CP}$ = 34 Hz, PMe$_2$), 9.1 (C$_5$*Me*$_5$). **^{31}P{^{1}H} NMR** (200 MHz, CDCl$_3$, 25 ºC) δ: 12.0 (d, $^{1}J_{RhP}$ = 143 Hz). **Anal. Calcd.** for $C_{20}H_{30}Cl_2PRh$: C, 50.55; H, 6.36. **Found**: C, 50.3; H, 6.5.

Spectroscopic characterization of iridium hydride-alkylidene 3b^{+}.

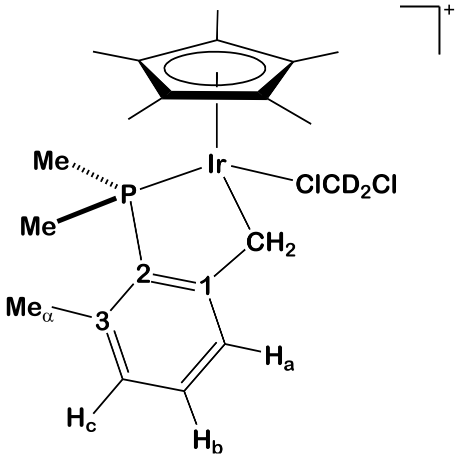


IR (Nujol): υ(IrH) 2150 cm^{-1}. **^{1}H NMR** (400 MHz, CD$_2$Cl$_2$, 25 ºC) δ: 7.68 (d, 1 H, H$_a$), 7.61 (dd, 1 H, $^{4}J_{HP}$ = 3.3 Hz, H$_c$), 7.33 (td, 1 H, $^{5}J_{HP}$ = 2.4 Hz, H$_b$), 2.69 (s, 3 H, Me$_{\alpha}$), 2.41 (m, 2 H, P(C*H*)$_2$), 2.17 (d, 15 H, $^{4}J_{HP}$ = 1.1 Hz, C$_5$Me$_5$), 1.88 – 1.69 (m, 8 H, CH$_2$(Cy)), 1.51 – 1.25 (m, 8 H, CH$_2$(Cy)), 1.14 (m, 2 H, CH$_2$(Cy)), 0.78 (m, 2 H, CH$_2$(Cy)). All aromatic couplings are of *ca*. 7.5 Hz. **^{1}H NMR** (500 MHz, CD$_2$Cl$_2$, -80 ºC) δ: 15.50 (s, 1 H, IrCH), -15.14 (d, 1 H, $^{2}J_{HP}$ = 27.3 Hz, Ir−H). Hydride and carbene signals are only detectable at temperatures below -50ºC.**^{13}C{^{1}H} NMR** (100 MHz, CD$_2$Cl$_2$, 25 ºC) δ: 263.1 (Ir=CH), 166.6 (C$_1$), 144.0 (C$_3$), 137.1 (d, $^{1}J_{CP}$ = 54 Hz, C$_2$), 137.0 (d, $^{3}J_{CP}$ = 8 Hz, CH$_c$), 133.9 (CH$_b$), 128.6 (d, $^{3}J_{CP}$ = 12 Hz, CH$_a$), 104.4 (*C*$_5$Me$_5$), 34.8 (d, $^{1}J_{CP}$ = 31 Hz, P(*C*H)$_2$), 29.0 (*C*H$_2$(Cy)), 28.9 (d, J_{CP} = 4 Hz, *C*H$_2$(Cy)), 26.7 (d, J_{CP} = 14 Hz, *C*H$_2$(Cy)), 26.6 (d, J_{CP} = 12 Hz, *C*H$_2$(Cy)), 26.2 (*C*H$_2$(Cy)), 22.1 (Me$_{\alpha}$), 10.3 (C$_5$*Me*$_5$).**^{31}P{^{1}H} NMR** (160 MHz, CD$_2$Cl$_2$, 25 ºC) δ: 62.1. **Anal. Calcd.** for $C_{62}H_{56}BF_{24}IrP$: C, 49.94; H, 3.79. **Found**: C, 50.1; H, 3.5.

Synthesis of dichloromethane adducts 4c·$CH_2Cl_2^+$ and 4d·$CH_2Cl_2^+$

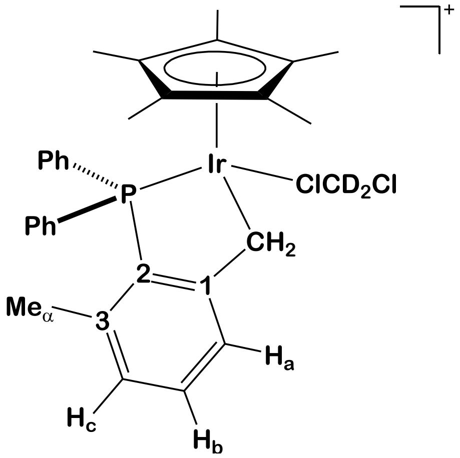
To a solid mixture of **1c** or **1d** (0.08 mmol) and $NaBAr_F$ (72 mg, 0.08 mmol) placed in a Schlenk flask was added 5 mL of CH_2Cl_2 at 0ºC. The resulting orange solution was stirred for 15 min at the same temperature and then filtered. $^{31}P\{^1H\}$ NMR monitoring of the reaction showed quantitative conversion of the chloride complex to the dichloromethane adduct. Spectroscopic analysis was undertaken with a sample of the complex directly prepared in CD_2Cl_2 without further purification. All attempts to obtain crystals suitable for X-ray analysis were unsuccessful due to the formation of dark orange oils. All dichloromethane adducts and those of other Lewis bases (see below) were isolated as their corresponding BAr_F^- salts.

$[(\eta^5\text{-}C_5Me_5)Ir(CH_2Cl_2)\{P(Me)_2(2,6\text{-}CH_2(Me)C_6H_3)\}]^+$(4c·$CH_2Cl_2^+$)



^{1}H NMR (500 MHz, CD_2Cl_2, 0 ºC) δ: 7.37 (d, 1 H, H_a), 7.24 (t, 1 H, H_b), 7.08 (m, 1 H, H_c), 2.90 (br. s, 2 H, $IrCH_2$), 2,49 (s, 3 H, Me_α), 2.00 (d, 6 H, $^2J_{HP}$ = 10.8 Hz, PMe_2), 1.88 (s, 15 H, C_5Me_5). All aromatic couplings are of *ca.* 7.5 Hz. **^{1}H NMR** (500 MHz, CD_2Cl_2, -90 ºC) δ: 3.55 (br. s, 1 H, IrC*H*H), 3.17 (br. s, 1 H, IrCH*H*). **$^{13}C\{^1H\}$ NMR** (100 MHz, CD_2Cl_2, 0 ºC) δ: 159.2 (d, $^2J_{CP}$ = 31 Hz, C_1), 142.0 (C_3), 135.3 (C_2, overlapped with BAr_F), 133.0 (CH_b), 131.0 (CH_c), 126.7 (d, $^3J_{CP}$ = 13 Hz, CH_a), 96.6 (C_5Me$_5$), 20.7 (Me_α), 18.0 (br. s, $IrCH_2$), 14.4 (d, $^1J_{CP}$ = 38 Hz, PMe_2), 8.8 (C_5Me_5). **$^{31}P\{^1H\}$ NMR** (160 MHz, CD_2Cl_2, 0 ºC) δ: 8.3 (br. s).

$[(\eta^5\text{-}C_5Me_5)\overline{Ir(CD_2Cl_2)\{P(Ph)_2(2,6\text{-}CH}_2(Me)C_6H_3)\}]^+$($4d\cdot CH_2Cl_2^+$)

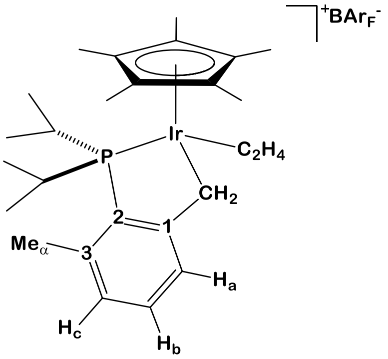


^{1}H NMR (500 MHz, CD_2Cl_2, -20 ºC) δ: 7.53 – 7.19 (m, 12 H, H_a, H_b, PPh_2), 6.64 (m, 1 H, H_c), 3.82 (d, 1 H, $^2J_{HH}$ = 15.6 Hz, IrC*H*H), 3.42 (d, 1 H, $^2J_{HH}$ = 15.6 Hz, IrCH*H*), 1.75 (s, 3 H, Me_α), 1.00 (s, 15 H, C_5Me_5). All aromatic couplings are of *ca*. 7.5 Hz. **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2, -20 ºC) δ: 163.5 (d, $^2J_{CP}$ = 34 Hz, C_1), 141.7 (C_3), 133.9 (d, $^1J_{CP}$ = 61 Hz, *ipso*-Ph), 132.3 (d, $^1J_{CP}$ = 56 Hz, C_2), 131.7, 131.4, 129.9, 129.6, 129.1, 128.8, 128.6, 128.3, 127.6, 127.4, 127.0, 126.8 (CH_a, CH_b, CH_c, PPh_2), 94.1 (*C*$_5$Me$_5$), 22.1 (Me_α), 18.3 ($IrCH_2$), 8.2 (C$_5$*Me*$_5$). **^{31}P{^{1}H} NMR** (160 MHz, CD_2Cl_2, -20 ºC) δ: 35.5.

Synthesis of cationic adducts $4\cdot L^+$ (L = NCMe, NC_5H_5, C_2H_4).

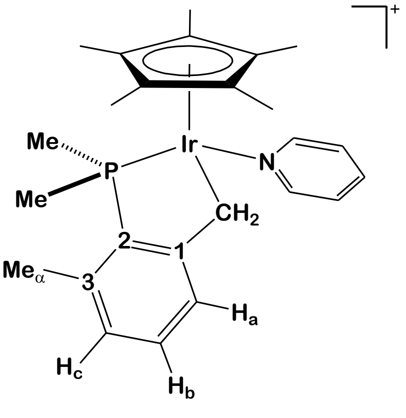
To a solid mixture of the iridium chloride complex (0.08 mmol) and $NaBAr_F$ (72 mg, 0.08 mmol) placed in a Schlenk flask was added 5 mL of CH_2Cl_2. The reaction mixture was stirred for 5 min at room temperature under 1 bar C_2H_4 (a thick-wall vessel instead of a conventional Schlenk flask was employed in this case), or alternatively treated with 100 μL of NCMe or pyridine (for corresponding NCMe or pyridine adducts, respectively). The solution was filtered and the solvent was then evaporated under reduced pressure to obtain a pale white (**$4\cdot NCMe^+$**, **$1\cdot C_2H_4^+$**) or a yellow powder (**$3\cdot NC_5H_5^+$**) in *ca*. 95% yield. These complexes can be recrystallized from a 1:2 mixture of CH_2Cl_2:pentane.

$[(\eta^5\text{-}C_5Me_5)Ir(C_2H_4)\{P(^iPr)_2(2,6\text{-}CH_2(Me)C_6H_3)\}]^+(4a\cdot C_2H_4)^+$



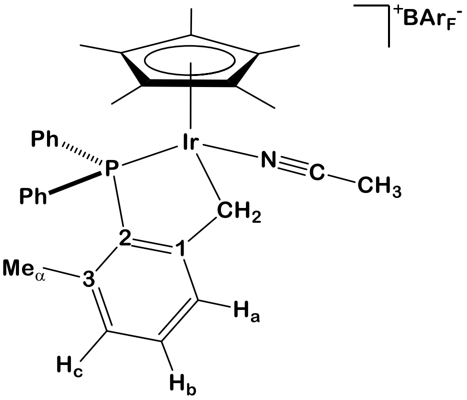
^{1}H NMR (400 MHz, CD_2Cl_2, 25 ºC) δ: 7.29 (d, 1 H, H_a), 7.20 (td, 1 H, $^5J_{HP}$ = 2.4 Hz, H_b), 6.99 (dd, 1 H, $^5J_{HP}$ = 3.5 Hz, H_c), 3,67 (d, 1 H, $^2J_{HH}$ = 12.5 Hz, IrC*H*H), 3.39 (dd, 1 H, $^2J_{HH}$ = 12.5, $^3J_{HP}$ = 3.3 Hz, IrCH*H*), 3.28 (dseptet, 1 H, $^2J_{HP}$ = 13.4, $^3J_{HH}$ = 7.4 Hz, 2.77 (br. s, 2 H, C_2H_4), 2.40 (s, 3 H, Me_α), 2.38 (m, 1 H, C*H*(^{i}Pr)), 2.29 (m, 2 H, C_2H_4), 1.77 (d, 15 H, $^4J_{HP}$ = 1.5 Hz, C_5Me_5), 1.31 (dd, 3 H, $^3J_{HP}$ = 13.7, $^3J_{HH}$ = 7.3 Hz, *Me*(^{i}Pr)}), 1.25 (dd, 3 H, $^3J_{HP}$ = 19.0, $^3J_{HH}$ = 7.1 Hz, *Me*(^{i}Pr)), 1.17 (dd, 3 H, $^3J_{HP}$ = 13.9, $^3J_{HH}$ = 7.2 Hz, *Me*(^{i}Pr)), 0.69 (dd, 3 H, $^3J_{HP}$ = 16.8, $^3J_{HH}$ = 7.2 Hz, *Me*(^{i}Pr)). All aromatic couplings are of *ca*. 7.5 Hz. **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2, 25 ºC) δ: 157.6 (d, $^2J_{CP}$ = 26 Hz, C_1), 141.4 (C_3), 129.5 (C_2, overlapped with BAr_F), 131.9 (CH_b), 130.6 (d, $^3J_{CP}$ = 8 Hz, CH_c), 126.8 (d, $^3J_{CP}$ = 14 Hz, CH_a), 100.7 ($C_5$$Me_5$), 46.8 (br. s, C_2H_4), 42.5 (br. s, C_2H_4), 30.9 (d, $^1J_{CP}$ = 29 Hz, *CH*(^{i}Pr)), 27.4 (d, $^1J_{CP}$ = 30 Hz, *CH*(^{i}Pr), 22.6 (Me_α), 20.5 (*Me*(^{i}Pr)), 20.2 (d, $^2J_{CP}$ = 6 Hz, *Me*(^{i}Pr)), 19.8 (*Me*(^{i}Pr)), 19.7 (d, $^2J_{CP}$ = 4 Hz, *Me*(^{i}Pr)), 11.9 (d, $^2J_{CP}$ = 2 Hz, $IrCH_2$), 8.4 (C_5*Me_5*). **^{31}P{^{1}H} NMR** (160 MHz, CD_2Cl_2, 25 ºC) δ: 42.7. **Anal. Calcd.** for $C_{58}H_{53}BF_{24}IrP$: C, 48.38; H, 3.71. **Found**: C, 48.3; H, 3.8.

$[(\eta^5\text{-}C_5Me_5)Ir(NC_5H_5)\{P(Me)_2(2,6\text{-}CH_2(Me)C_6H_3)\}][BAr_F]^+(4c\cdot py^+)$



^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) δ: 8.36 (d, 2 H, *o*-py), 7.73 (1 H, *p*-py, overlapped with BAr_F), 7.25 (d, 1 H, H_a), 7.19 (t, 2 H, *m*-py), 7.07 (td, 1 H, $^5J_{HP}$ = 1.9 Hz, H_b), 6.79 (dd, 1 H, $^4J_{HP}$ = 3.4 Hz, H_c), 3.57 (d, 1 H, $^2J_{HH}$ = 14.3 Hz, IrC*H*H), 2.70 (dd, 1 H, $^2J_{HH}$ = 14.3, $^3J_{HP}$ = 5.8 Hz, IrCH*H*), 2,32 (s, 3 H, Me_α), 2.90 (d, 3 H, $^2J_{HP}$ = 10.7 Hz, P*Me*Me), 1.82 (d, 3 H, $^2J_{HP}$ = 10.4 Hz, PMe*Me*), 1.63 (d, 15 H, $^4J_{HP}$ = 1.8 Hz, C_5Me_5). All aromatic couplings are of *ca*. 7.5 Hz. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$, 25 ºC) δ: 157.5 (d, $^2J_{CP}$ = 28 Hz, C_1), 155.2 (*o*-py), 140.5 (C_3), 139.0 (*p*-py), 133.2 (d, $^1J_{CP}$ = 51 Hz, C_2), 131.8 (CH_b), 129.5 (d, $^3J_{CP}$ = 8 Hz, CH_c), 127.2 (*m*-py), 126.8 (d, $^3J_{CP}$ = 13 Hz, CH_a), 93.4 (*C_5*Me_5), 21.2 (Me_α), 18.0 ($IrCH_2$), 15.3 (d, $^1J_{CP}$ = 37 Hz, P*Me*Me), 13.6 (d, $^1J_{CP}$ = 33 Hz, PMe*Me*), 8.7 (C_5*Me_5*). **^{31}P{^{1}H} NMR** (160 MHz, $CDCl_3$, 25 ºC) δ: -0.5. **Anal. Calcd.** for $C_{57}H_{46}BF_{24}IrNP$: C, 47.71; H, 3.23; N, 0.98. **Found**: C, 47.2; H, 3.3; N, 1.1.

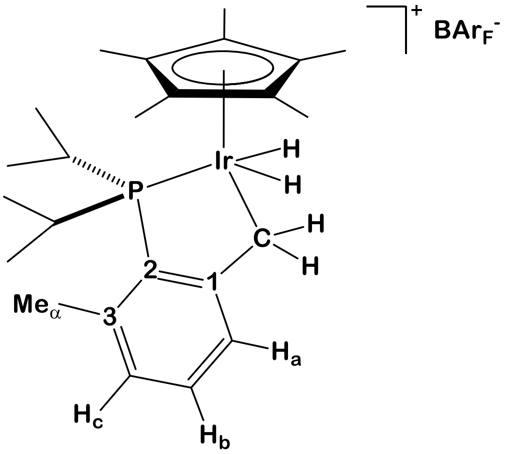
[(η^5-C_5Me_5)Ir(NCMe){P(Ph)$_2$(2,6-CH_2(Me)C_6H_3)}][BAr_F]$^+$(4d·NCMe$^+$)



IR (Nujol): υ(CN) 2290 cm^{-1}. **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 ºC) δ: 7.55 – 7.40 (m, 9 H, H_a, PPh_2), 7.36 (m, 3 H, H_b, PPh_2), 7.02 (dd, 1 H, $^4J_{HP}$ = 3.6 Hz, H_c), 3.61 (d, 1 H, $^2J_{HH}$ = 15.0 Hz, IrC*H*H), 3.27 (dd, 1 H, $^2J_{HH}$ = 15.0, $^3J_{HP}$ = 3.0 Hz, IrCH*H*), 1.79 (s, 3 H, Me_α), 1.74 (d, 3 H, $^5J_{HP}$ = 1.1 Hz, NCMe), 1.56 (d, 15 H, $^4J_{HP}$ = 1.9 Hz, C_5Me_5). All aromatic couplings are of *ca*. 7.5 Hz. **^{13}C{^{1}H} NMR** (125 MHz, CD_2Cl_2, 25 ºC) δ: 160.9 (d, $^2J_{CP}$ = 31 Hz, C_1), 142.5 (C_3), 132.3, 132.2, 132.1 (PPh_2), 131.7 (C_2, overlapped with other aromatic signals), 131.5, 131.3, 130.7 (PPh_2), 129.5 (d, $^1J_{CP}$ = 39 Hz, *ipso*-Ph), 129.1, 128.8, 128.7 (PPh_2), 128.1 (d, $^1J_{CP}$ = 45 Hz, *ipso*-Ph), 129.0 (d, $^3J_{CP}$ = 6 Hz, CH_c), 127.6 (d, $^3J_{CP}$ = 15 Hz, CH_a), 115.0 (N*C*Me), 94.7 (*C_5*Me_5), 21.4 (Me_α), 15.7 ($IrCH_2$), 8.1 (C_5*Me_5*), 1.6 (NC*Me*). **^{31}P{^{1}H} NMR** (200 MHz, CD_2Cl_2, 25 ºC) δ:

28.4. **Anal. Calcd.** for $C_{64}H_{47}BF_{24}IrNP$: C, 50.57; H, 3.12; N, 0.92. **Found**: C, 50.6; H, 3.4; N, 1.0.

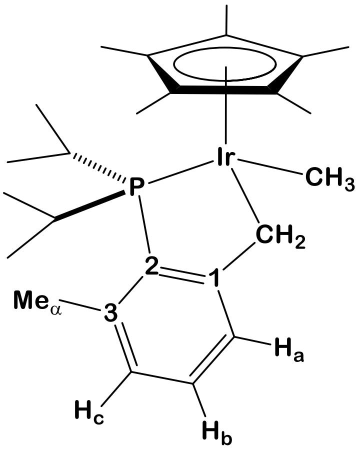
Synthesis of cationic iridium dihydride alkyl compound 8a$^+$.



A *J. Young* NMR tube was charged with **[3a]BAr$_F$** (30 mg, 0.021 mmol) and CD_2Cl_2 (0.6 mL). The tube was charged with H_2 (1 bar) and shaken. The solution rapidly turned from red to yellow and $^{31}P\{^1H\}$ NMR monitoring of the reaction showed clean and quantitative conversion to **8a**$^+$. Spectroscopic data were obtained without further purification. **^{1}H NMR** (400 MHz, CD_2Cl_2, 25 ºC) δ: 7.26 (d, 1 H, H$_a$), 7.21 (td, 1 H, $^5J_{HP}$ = 2.4 Hz, H$_b$), 6.97 (dd, 1 H, $^5J_{HP}$ = 4.0 Hz, H$_c$), 2.64 (br. s, 2 H, C*H*(^{i}Pr)), 2.45 (s, 3 H, Me$_\alpha$), 2.10 (d, 15 H, $^4J_{HP}$ = 1.3 Hz, C_5Me_5), 1.02 (dd, 6 H, $^3J_{HP}$ = 18.1, $^3J_{HH}$ = 6.8 Hz, *Me*(^{i}Pr)), 0.96 (dd, 3 H, $^3J_{HP}$ = 18.7, $^3J_{HH}$ = 7.0 Hz, *Me*(^{i}Pr)). All aromatic couplings are of *ca*. 7.5 Hz. Hydride and methylene signals are only detectable at temperatures below -20ºC. **^{1}H NMR** (400 MHz, CD_2Cl_2, -80 ºC) δ: 7.16 (m, 2 H, H$_a$, H$_b$), 6.87 (br. s, 1 H, H$_c$), 3.47 (d, 1 H, $^2J_{HH}$ = 13.0 Hz, IrC*H*H), 3.38 (d, 1 H, $^2J_{HH}$ = 13.0 Hz, IrCH*H*), 2.87 (br. s, 1 H, C*H*(^{i}Pr)), 2.35 (s, 3 H, Me$_\alpha$), 2.02 (br. s, 1 H, C*H*(^{i}Pr)), 1.92 (s, 15 H, C_5Me_5), 1.19 (dd, 3 H, $^3J_{HP}$ = 14.5, $^3J_{HH}$ = 6.9 Hz, *Me*(^{i}Pr)), 0.93 (dd, 3 H, $^3J_{HP}$ = 19.0, $^3J_{HH}$ = 6.3 Hz, *Me*(^{i}Pr)), 0.76 (dd, 3 H, $^3J_{HP}$ = 19.2, $^3J_{HH}$ = 6.2 Hz, *Me*(^{i}Pr)), 0.61 (dd, 3 H, $^3J_{HP}$ = 17.8, $^3J_{HH}$ = 6.7 Hz, *Me*(^{i}Pr)), -13.62 (s, 1 H, Ir–H), -13.97 (d, 1 H, $^2J_{HP}$ = 16.1 Hz). **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2, 25 ºC) δ: 158.0 (d, $^2J_{CP}$ = 23 Hz, C$_1$), 140.7 (d, $^2J_{CP}$ = 4 Hz, C$_3$), 132.0 (CH$_b$), 130.6 (d, $^3J_{CP}$ = 9 Hz, CH$_c$), 125.7 (d, $^3J_{CP}$ = 14 Hz, CH$_a$), 125.6 (C$_2$), 103.3 (*C*$_5$Me$_5$), 27.6 (br. d, $^1J_{CP}$ = 32 Hz, *C*H(^{i}Pr)), 22.6 (Me$_\alpha$), 18.6

(Me(^{i}Pr)), 18.4 (d, $^2J_{CP}$ = 2 Hz, Me(^{i}Pr)), 9.8 (C_5Me_5), 9.5 ($IrCH_2$). **^{31}P{^{1}H} NMR** (160 MHz, CD_2Cl_2, 25 ºC) δ: 60.7.

Synthesis of iridium methyl compound 9a.

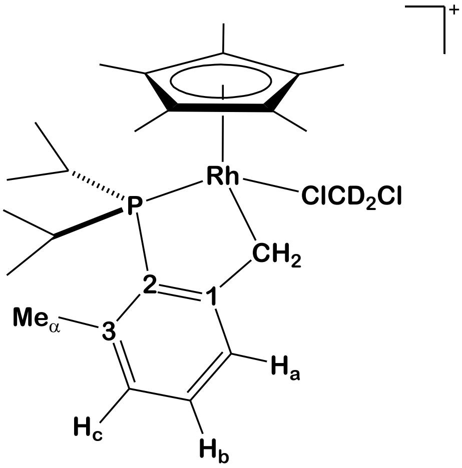


A solution of **1a** (50 mg, 0.086 mmol) in CH_2Cl_2 (5 mL) was cooled to 0ºC and a solution of $ZnMe_2$ in toluene (2M, 80 µL) was added dropwise. The yellow solution rapidly cleared up to become nearly colorless. The mixture was stirred at 20ºC for 3 h, quenched with H_2O (10 µL) and the solvent removed under reduced pressure to provide crude compound **9a** as a pale yellow solid. The product was extracted with pentane and the solvent removed under vacuum to yield the desired product as a pale yellow powder (38 mg, 79 %). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 ºC) δ: 7.17 (d, 1 H, H_a), 6.98 (td, 1 H, $^5J_{HP}$ = 1.8 Hz, H_b), 6.80 (d, 1 H, H_c), 3,16 (d, 1 H, $^2J_{HH}$ = 14.2 Hz, IrCHH), 3.05 (dseptet, 1 H, $^2J_{HP}$ = 11.5, $^3J_{HH}$ = 6.9 Hz, CH(^{i}Pr)), 2,48 (s, 3 H, Me_α), 2.23 (octet, 1 H, $^2J_{HP}$ = $^3J_{HH}$ = 7.1 Hz, CH(^{i}Pr)), 2.05 (dd, 1 H, $^2J_{HH}$ = 14.2, $^3J_{HP}$ = 3.4 Hz, IrCHH), 1.72 (d, 15 H, $^4J_{HP}$ = 1.5 Hz, C_5Me_5), 1.11 (dd, 3 H, $^3J_{HP}$ = 17.7, $^3J_{HH}$ = 6.8 Hz, Me(^{i}Pr)}), 1.03 (dd, 3 H, $^3J_{HP}$ = 13.4, $^3J_{HH}$ = 7.1 Hz, Me(^{i}Pr)), 0.91 (dd, 3 H, $^3J_{HP}$ = 13.8, $^3J_{HH}$ = 7.1 Hz, Me(^{i}Pr)), 0.81 (dd, 3 H, $^3J_{HP}$ = 15.3, $^3J_{HH}$ = 7.1 Hz, Me(^{i}Pr)), -0.20 (d, 3 H, $^3J_{HP}$ = 3.4 Hz, $IrCH_3$). All aromatic couplings are of *ca*. 7.5 Hz. **^{13}C{^{1}H} NMR** (125 MHz, CD_2Cl_2, 25 ºC) δ: 162.6 (d, $^2J_{CP}$ = 26 Hz, C_1), 140.3 (C_3), 134.7 (d, $^1J_{CP}$ = 45 Hz, C_2), 128.5 (CH_b), 128.0 (d, $^3J_{CP}$ = 7 Hz, CH_c), 127.5 (d, $^3J_{CP}$ = 12 Hz, CH_a), 90.9 (C_5Me_5), 31.3 (d, $^1J_{CP}$ = 29 Hz, CH(^{i}Pr)), 27.8 (d, $^1J_{CP}$ = 29 Hz, CH(^{i}Pr)), 22.3 (Me_α), 20.4 (d, $^2J_{CP}$ = 7 Hz, Me(^{i}Pr)), 19.6 (Me(^{i}Pr)), 18.8 (Me(^{i}Pr)), 18.1 (Me(^{i}Pr)), 13.1 ($IrCH_2$), 8.7

(C_5*Me*$_5$), -25.2 (d, $^2J_{CP}$ = 8 Hz, IrCH_3).**^{31}P{^{1}H} NMR** (200 MHz, CD_2Cl_2, 25 ºC) δ: 52.8. **Anal. Calcd.** for $C_{25}H_{40}IrP$: C, 53.26; H, 7.15. **Found**: C, 53.2; H, 7.2.

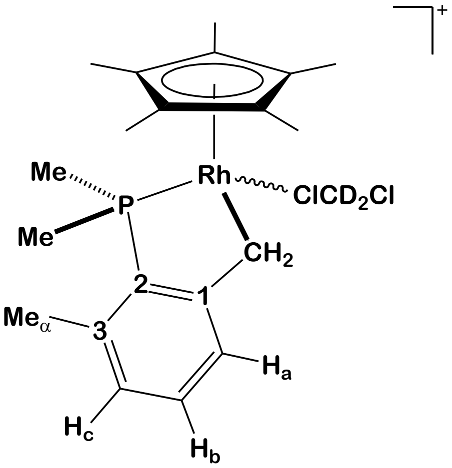
Synthesis of cationic rhodium dichloromethane adducts, 5a$^+$ and 5c$^+$. Once more, the above complexes were isolated as BAr$_F^-$ salts. A solid mixture of the rhodium chloride complex (**2a**, 49 mg, 0.1 mmol; **2c**, 44 mg, 0.1 mmol) and NaBAr$_F$ (88 mg, 0.1 mmol) placed in a Schlenk flask was dissolved in CH_2Cl_2 (3 mL) at -20 ºC. Monitoring of the reactions by ^{31}P{^{1}H} NMR showed quantitative conversion after 5 min into the dichloromethane adducts. The solution was filtered and the cationic adducts isolated as red crystals (107 mg, 76 % and 84 mg, 62 % for **[5a]BAr$_F$** and **[5c]BAr$_F$**, **r**espectively) by slow diffusion of pentane into the dichloromethane solution at -25 ºC.

[(η^5-C_5Me_5)Rh(ClCD$_2$Cl){P(^{i}Pr)$_2$(2,6-CH$_2$(Me)C$_6$H$_3$)]$^+$(5a·ClCD$_2$Cl$^+$)



^{1}H NMR (400 MHz, CD_2Cl_2, 25 ºC) δ: 7.26 (m, 2 H, H$_a$, H$_b$), 7.12 (d, 1 H, H$_c$), 3.49 (m, 2 H, RhCH_2), 2.74 (m, 2 H, C*H*(^{i}Pr)), 2.50 (s, 3 H, Me$_\alpha$), 1.68 (d, 15 H, $^4J_{HP}$ = 2.0 Hz, C_5Me_5), 1.20 (dd, 6 H, $^3J_{HH}$ = 7.1, *Me*(^{i}Pr)), 1.17 (d, 6 H, $^3J_{HH}$ = 7.0, *Me*(^{i}Pr)). All aromatic couplings are of *ca*. 7.5 Hz. **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2, 25 ºC) δ: 150.7 (br. d, $^2J_{CP}$ = 25 Hz, C$_1$), 141.1 (C$_3$), 132.0 (CH$_b$), 130.6 (d, $^4J_{CP}$ = 7 Hz, CH$_c$), 126.7 (d, $^4J_{CP}$ = 14 Hz, CH$_a$), 124.5 (d, $^1J_{CP}$ = 43 Hz, C$_2$), 101.2 (*C*$_5$Me$_5$), 33.9 (d, $^1J_{CRh}$ = 23 Hz, RhCH_2), 27.4 (d, $^1J_{CP}$ = 22 Hz, *C*H(^{i}Pr)), 22.4 (Me$_\alpha$), 19.2 (*Me*(^{i}Pr)), 19.1 (*Me*(^{i}Pr)), 9.6 (C_5*Me*$_5$). **^{31}P{^{1}H} NMR** (160 MHz, CD_2Cl_2, 25 ºC) δ: 77.3 (d, $^1J_{RhP}$ = 158 Hz). **Anal. Calcd.** for $C_{57}H_{51}BCl_2F_{24}PRh$: C, 48.64; H, 3.65. **Found**: C, 48.8; H, 3.3.

[(η^5-C$_5$Me$_5$)Rh(ClCD$_2$Cl){P(Me)$_2$(2,6-CH$_2$(Me)C$_6$H$_3$)}]$^-$(5c·CD$_2$Cl$_2$$^+$)



^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 25 ºC) δ: 7.25, 7.23 (d, 1 H each, Ha, H$_b$), 7.02 (m, 1 H, H$_c$), 3.40 (m, 2 H, RhCH$_2$), 2.46 (s, 3 H, Me$_\alpha$), 1.91 (d, 6 H, $^2J_{CP}$ = 10.1 Hz, P(Me)$_2$), 1.72 (d, 15 H, $^4J_{HP}$ = 2.7 Hz, C$_5$Me$_5$). All aromatic couplings are of *ca*. 7.5 Hz. **^{13}C{^{1}H} NMR** (100 MHz, CD$_2$Cl$_2$, 25 ºC) δ: 155.0 (C$_1$), 141.5 (C$_3$), 131.5 (C$_2$), 132.7 (d, $^5J_{CP}$ = 2 Hz, CH$_b$), 130.0 (d, $^4J_{CP}$ = 8 Hz, CH$_c$), 126.1 (d, $^4J_{CP}$ = 18 Hz, CH$_a$), 101.1 (*C*$_5$Me$_5$), 31.1 (dd, $^1J_{CRh}$ = 24, $^2J_{CP}$ = 6 Hz, RhCH$_2$), 21.2 (d, $^3J_{CP}$ = 4 Hz, Me$_\alpha$), 14.6 (d, $^1J_{CP}$ = 29 Hz, P(Me)$_2$), 9.4 (C$_5$*Me*$_5$). **^{31}P{^{1}H} NMR** (160 MHz, CD$_2$Cl$_2$, 25 ºC) δ: 36.0 (d, $^1J_{RhP}$ = 161 Hz).

4. Solution dynamic ^{1}H NMR spectroscopy of compounds 3a$^+$ and 8a$^+$

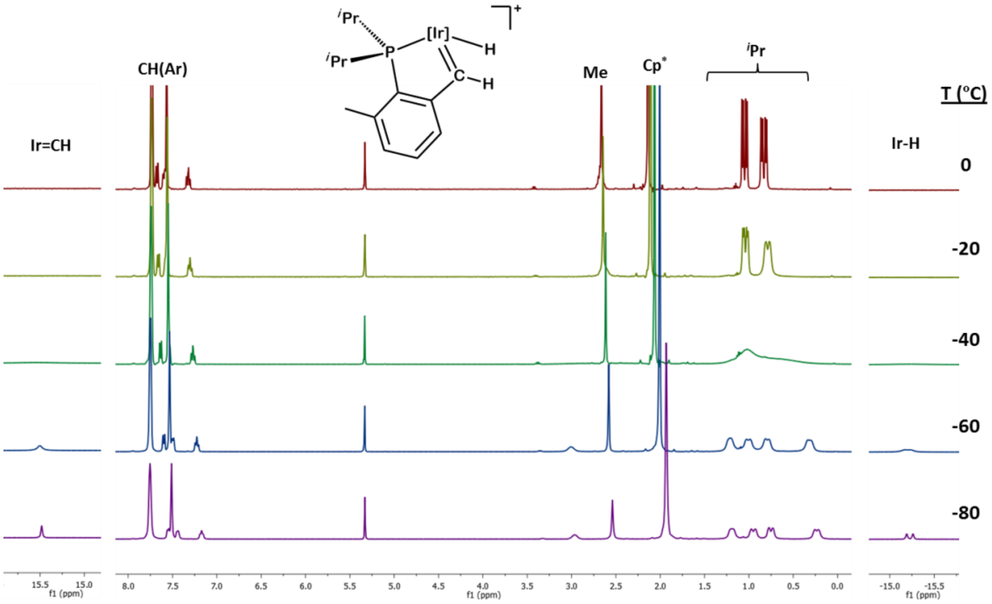


Figure S1. Solution dynamic behavior of **3a**$^+$ by ^{1}H NMR (CD_2Cl_2).

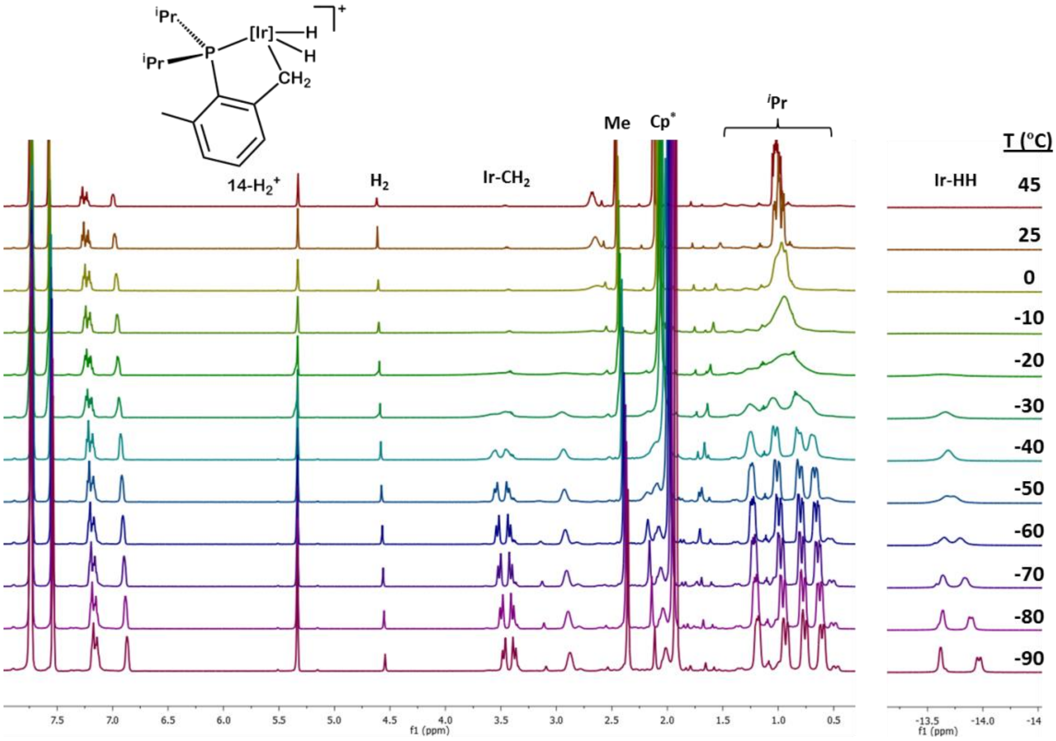


Figure S2. Solution dynamic behavior of **8a**$^+$ by ^{1}H NMR (CD_2Cl_2).

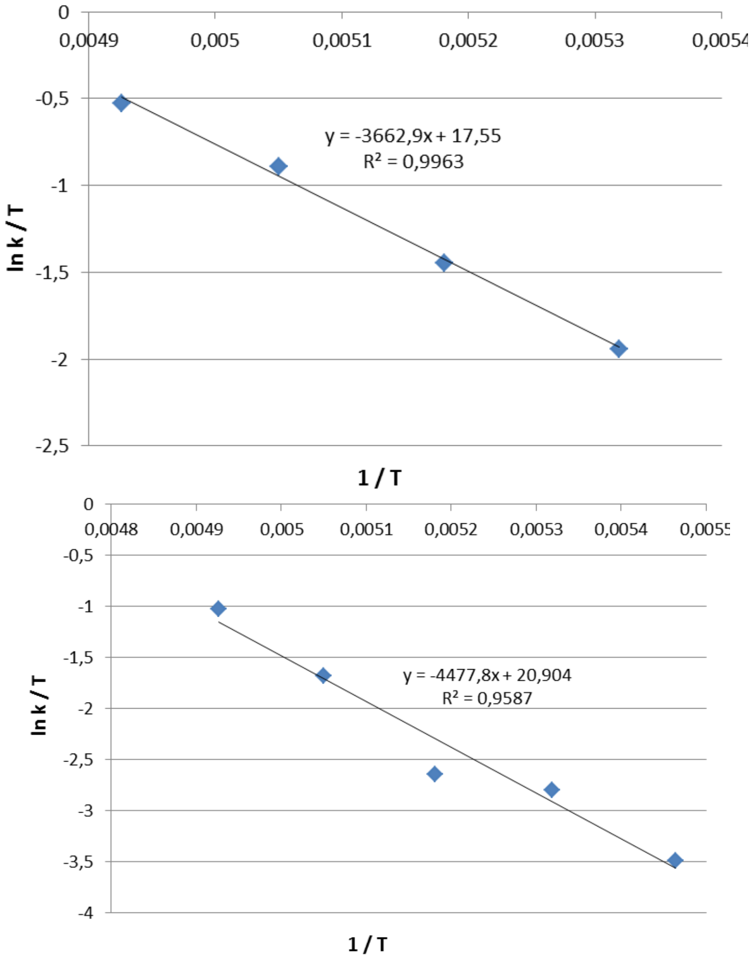


Figure S3. Eyring plots for the solution dynamic behavior of compounds (a) **3a**$^+$ and (b) **3b**$^+$ between -70 and -90 ºC.

5. Kinetic studies on the conversion of $7a^+$ into $4a{\cdot}PMe_3^+$

A screw-capped NMR tube was charged with compound **[3a]BAr$_F$** (20 mg, 0.014 mmol) and CD_2Cl_2 (0.6 mL) under argon. Then PMe_3 (1.6 µL, 0.015 mmol) was added at -40 ºC and the NMR tube rapidly shaken. The course of the reaction was monitored by $^{31}P\{^1H\}$ NMR and a first-order kinetic dependence on the concentration of **7a**$^+$ was measured. Representation of ln[**7a**$^+$] *vs.* time (Figure S4) allowed measuring a first-order kinetic rate constant of $3.4{\cdot}10^{-5}$ s^{-1}, which corresponds to a $\Delta G^{\ddagger} = 24.8 \pm 0.3$ $kcal{\cdot}mol^{-1}$.

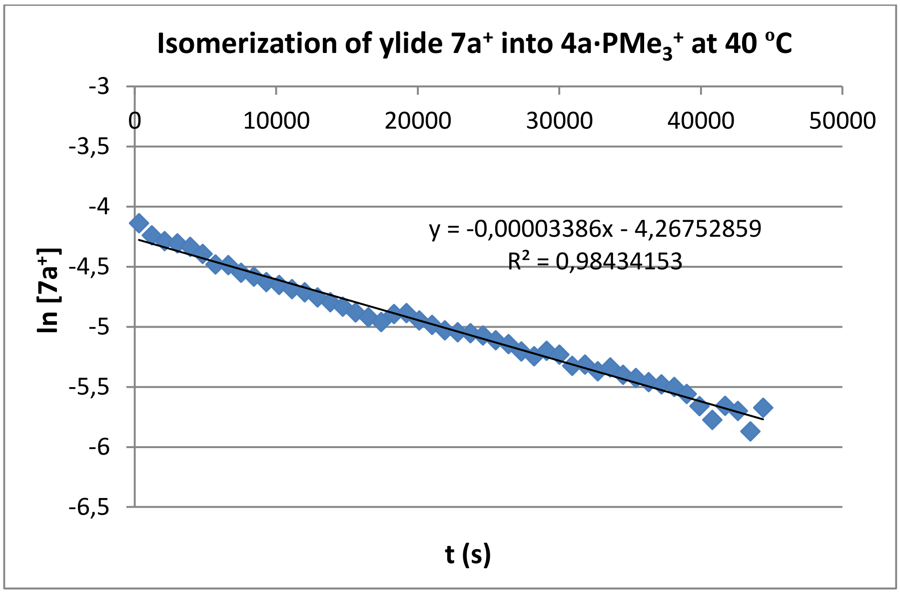


Figure S4. First-order representation of ln[**7a**$^+$] *vs.* time for the isomerization of **7a**$^+$ into **4a·PMe$_3$**$^+$.

6. X-Ray Structural Characterization

Crystallographic details.

A single crystal of suitable size, coated with dry perfluoropolyether was mounted on a glass fiber and fixed in a cold nitrogen stream [T = 173 K] to the goniometer head. Data collection was performed on a Bruker APEX-II CCD diffractometer using monochromatic radiation λ(Mo $K_{\alpha1}$) = 0.71073 Å generated by a fine-focus sealed tube by means of ω and φ scans at the Instituto de Investigaciones Químicas (IIQ, Sevilla). The data were reduced (SAINT) [5] and corrected for Lorentz polarization effects and absorption by multiscan method applied by SADABS.[6]The structure was solved by direct methods and refined against all F^2 data by full-matrix least-squares techniques using the SHELXTL package (v. 6.14).[7] All the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included from calculated positions (except the one directly bound to iridium in **3a**$^+$) and refined riding on their respective carbon atoms with C-H = 0.95 Å or C-H = 0.98 Å for methyl H atoms, and U_{iso}(H) = 1.2 U_{eq} (C) or U_{iso}(H) = 1.5 U_{eq} (C) for methyl H atoms. Structures **1c**, **3a** and **4d·NCMe**$^+$ contain two iridium molecules per unit cell, while the other seven compounds contain a single iridium species. The disorder of the BAr_F anion has been modeled over several positions in structures **3a**$^+$, **4c·NC$_5$H$_5$**$^+$, **4d·NCMe**$^+$ and **5a·CH$_2$Cl$_2$**$^+$, and their corresponding anisotropic displacement parameters restrained to be similar using instructions SIMU and DELU. Crystals of compound **4a·PMe$_3$**$^+$ were probably grown with a small amount of an impurity of an uncertain related species (*ca.* 3%). This disorder was modeled accordingly and similarity restrains and constraints were applied. The dichloromethane molecule in **5a·CH$_2$Cl$_2$**$^+$ was also modeled over two positions (73:27) and SIMU and DELU commands were used. CCDC-1022589 (**1a**), CCDC-1022590 (**1c**), CCDC-1022591 (**2a**), CCDC-1022592 (**3a**$^+$), CCDC-1022593 (**4a·PMe$_3$**$^+$), CCDC-1022594 (**4c·NC$_5$H$_5$**$^+$), CCDC-1022595 (**4d·NCMe**), CCDC-1022596 (**5a·CH$_2$Cl$_2$**$^+$), CCDC-1022597 (**6a**$^+$) and CCDC-1022598 (**9a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

ORTEP diagrams for compounds 1c, 4a·PMe$_3^+$, 9a, 4c·NC$_5$H$_5^+$ and 4d·NCMe+.

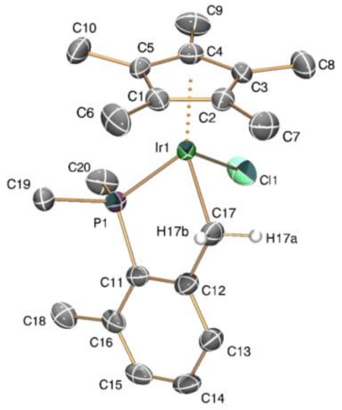


Figure S5. ORTEP diagram for compound **1c**. Thermal ellipsoids are drawn at the 50 % probability and most hydrogen atoms have been omitted for clarity.

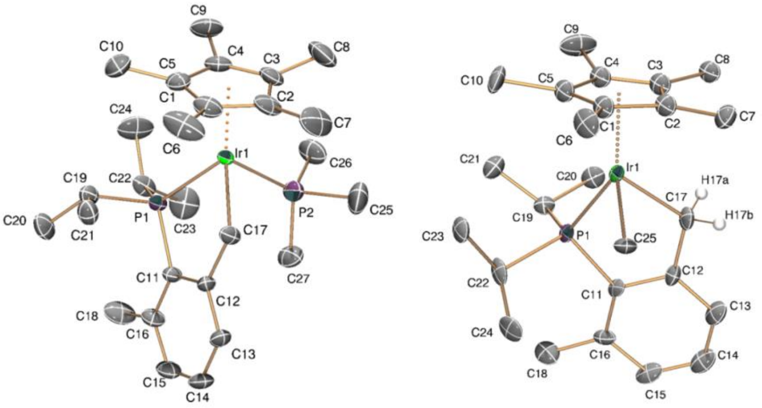


Figure S6. ORTEP diagram for compounds **4a·PMe$_3^+$** (Left) and **9a** (Right). Thermal ellipsoids are drawn at the 50 % probability and hydrogen atoms and the counterion of **4a·PMe$_3^+$** have been omitted for clarity.

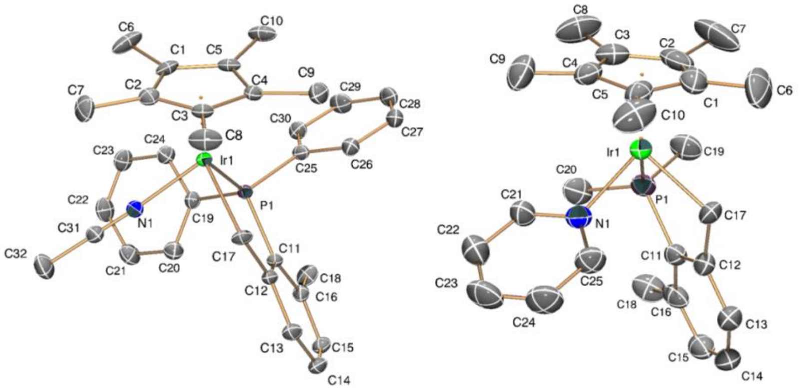


Figure S7. ORTEP diagram for compounds **4d·NCMe$^+$** (Left) and **4c·NC$_5$H$_5^+$** (Right). Thermal ellipsoids are drawn at the 50 % probability and hydrogen atoms and counterions have been omitted for clarity.

Table S1. Crystal data and structure refinement for compounds **1a**, **1c**, **2a**, **3a**$^+$ and **6a**$^+$.

	1a	**1c**	**2a**	**3a**$^+$	**6a**$^+$
formula	$C_{24}H_{37}ClIrP$	$C_{20}H_{29}ClIrP$	$C_{24}H_{37}ClPRh$	$C_{56}H_{49}BF_{24}IrP$	$C_{56}H_{48}BBrF_{24}IrP$
fw	584.18	528.07	494.87	1411.93	1490.83
cryst.size, mm	0.15 × 0.07 × 0.05	0.38 × 0.30 × 0.25	0.47 × 0.07 × 0.05	0.31 × 0.28 × 0.08	0.50 × 0.40 × 0.20
crystal system	Triclinic	triclinic	Triclinic	Triclinic	Triclinic
space group	*P* -1	*P*-1	*P* -1	*P* -1	*P* -1
a, Å	7.9728 (4)	8.6116 (2)	8.0055 (15)	18.1609 (9)	14.2344 (3)
b, Å	10.9488 (5)	14.9595 (4)	10.979 (2)	18.2151 (9)	14.3864 (3)
c, Å	14.2700 (8)	17.3050 (7)	14.170 (3)	19.2306 (10)	15.1992 (3)
α, deg	103.683 (2)	113.275 (2)	103.595 (5)	74.310 (2)	98.547 (1)
β, deg	94.758 (2)	101.941 (2)	94.881 (5)	68.576 (2)	102.499 (1)
γ, deg	100.316 (2)	94.921 (1).	99.872 (5)	81.856 (2)	109.285 (1)
V, Å^3	1180.47 (10)	1968.46 (11)	1182.3 (4)	5694.8 (5)	2785.23 (10)
T, K	173	173	173	173	173
Z	2	4	2	4	2
ρ_{calc}, g cm^{-3}	1.643	1.765	1.390	1. 647	1.778
μ, mm^{-1} (MoKα)	5.84	7.00	0.91	2.49	3.26
F(000)	580	1032	516	2792	1464
absorption corrections	multi-scan, 0.35-0.83	multi-scan, 0.29-0.43	multi-scan, 0.85–1.00	multi-scan, 0.51–0.83	multi-scan, 0.33–0.43
θ range, deg	1.5 – 27.5	2.4 – 25.2	2.0 – 27.5	1.2 – 25.2	1.8 – 25.1
no. of rflns measd	24184	47178	17264	98961	50695
R_{int}	0.039	0.027	0.036	0.036	0.023
no. of rflns unique	5409	7130	5339	20497	9892
no. of params / restraints	5409 / 0 / 254	7130 / 0 / 431	5339 / 0 / 254	20497/483 /1621	9892 / 0 / 777
R_1 ($I > 2\sigma(I)$) [a]	0.021	0.021	0.028	0.037	0.020
R_1 (all data)	0.022	0.023	0.043	0.051	0.020
wR_2 ($I > 2\sigma(I)$)	0.054	0.051	0.061	0.079	0.051
wR_2 (all data)	0.055	0.052	0.068	0.088	0.051
Diff.Fourier.peaks min/max, eÅ^{-3}	-2.17 / 2.27	-1.89 / 2.51	-0.81 / 0.91	-2.99/ 5.15	-0.72 / 2.01

Table S2. Crystal data and structure refinement for compounds **5c·CH$_2$Cl$_2$$^+$**, **4a·PMe$_3$$^+$**, **9a**, **4c·NC$_5H_5$$^+$** and **4d·NCMe**.

	5a·CH$_2$Cl$_2$$^+$	**4a·PMe$_3$$^+$**	**9a**	**4c·NC$_5$H$_5$$^+$**	**4d·NCMe**
formula	$C_{57}H_{51}BF_{24}Cl_2PRh$	$C_{59}H_{58}BF_{24}IrP_2$	$C_{25}H_{40}IrP$	$C_{57}H_{46}BF_{24}IrNP$	$C_{64}H_{45}BF_{24}IrNP$
fw	1407.57	1488.00	563.74	1434.95	1521.03
cryst.size, mm	0.36 × 0.18 × 0.17	0.30 × 0.30 × 0.20	0.35 × 0.25 × 0.20	0.65 × 0.40 × 0.15	0.35 × 0.15 × 0.14
crystal system	monoclinic	triclinic	Orthorhombic	Triclinic	monoclinic
space group	$P2_1/n$	P-1	$P\ 2_12_12_1$	P-1	$P2_1/c$
a, Å	12.835 (2)	12.3738 (1)	8.2676 (3)	12.1875 (6)	17.6209 (6)
b, Å	35.645 (5)	13.0143 (1)	9.1408 (3)	15.4248 (9)	18.8941 (6)
c, Å	13.161 (2)	18.6831 (2)	30.4909 (11)	17.4088 (9)	36.6859 (11)
α, deg	90	88.945 (1)°	90	104.366 (1)°	90
β, deg	92.468 (3)°	80.381 (1)°	90	107.736 (2)°	90.0072 (16)
γ, deg	90	86.717 (1)°	90	100.186 (1)°	90
V, Å^3	6015.7 (17)	2961.37 (5)	2304.27 (14)	2904.5 (3)	12213.9 (7)
T, K	173	173	100	173	173
Z	4	2	4	2	8
ρ_{calc}, g cm^{-3}	1.554	1.669	1. 625	1. 641	1.654
μ, mm^{-1} (MoKα)	0.51	2.42	5. 87	2.44	2.33
F(000)	2832	1480	1128	1416	6016
absorption corrections	multi-scan, 0.29-0.43	multi-scan, 0.35-0.44	multi-scan, 0.31–0.43	multi-scan, 0.30-0.43	multi-scan, 0.74–0.50
θ range, deg	1.1 – 25.2	1.9 – 30.0	2.3 – 25.2	1.8 – 25.2	2.2 - 30.0
no. of rflns measd	52988	93234	6468	56437	278216
R_{int}	0.046	0.021	0.058	0.027	0.068
no. of rflns unique	10855	17110	4102	10403	35593
no. of params / restraints	10855 / 7 / 808	17110 / 114 / 944	4102 / 36 / 255	10403 / 42 / 824	35593 / 29 / 1681
R_1 ($I > 2\sigma(I)$) [a]	0.014	0.031	0.043	0.031	0.031
R_1 (all data)	0.061	0.033	0.111	0.035	0.055
wR_2 ($I > 2\sigma(I)$)	0.016	0.076	0.043	0.082	0.061
wR_2 (all data)	0.096	0.077	0.111	0.086	0.066
Diff.Fourier.peaks min/max, eÅ^{-3}	-0.84 / 0.98	-0.83 / 1.46	-2.17 / 5.38	-0.92 / 2.50	-1.02 / 1.21

Selected geometric parameters

Table S3. Selected bond lengths [Å] and angles [°] for **1a**.

Bond lengths (Å)			
Ir1—C17	2.097 (3)	P1—C22	1.858 (3)
Ir1—P1	2.2733 (7)	P1—C19	1.865 (3)
Ir1—Cl1	2.4020 (7)	C11—C12	1.396 (4)
P1—C11	1.833 (3)	C12—C17	1. 1.505 (4)
Bond angles (º)			
C17—Ir1—P1	81.34 (9)	C11—P1—Ir1	105.33 (10)
C17—Ir1—Cl1	84.63 (10)	C22—P1—Ir1	118.03 (10)
P1—Ir1—Cl1	92.53 (3)	C19—P1—Ir1	111.87 (10)
C11—P1—C22	107.75 (14)	C11—C12—C17	120.6 (2)
C11—P1—C19	107.87 (13)	C13—C12—C17	120.1 (3)
C22—P1—C19	105.59 (14)		

Table S4. Selected bond lengths [Å] and angles [°] for **1c**

Bond lengths (Å)			
Ir1—C17	2.093 (4)	P1—C20	1.815 (4)
Ir1—P1	2.2362 (10)	P1—C11	1.817 (4)
Ir1—Cl1	2.3989 (11)	C12—C17	1.504 (6)
P1—C19	1.815 (4)		
Bond angles (º)			
C17—Ir1—P1	81.82 (12)	C20—P1—C11	110.1 (2)
C17—Ir1—Cl1	86.25 (14)	C19—P1—Ir1	117.05 (14)
P1—Ir1—Cl1	88.30 (4)	C20—P1—Ir1	114.46 (16)
C19—P1—C20	102.6 (2)	C11—P1—Ir1	106.35 (13)
C19—P1—C11	105.95 (19)		

Table S5. Selected bond lengths [Å] and angles [°] for **2a**.

Bond lengths (Å)			
Rh1—C17	2.079 (2)	Rh1—Cl1	2.4007 (7)
Rh1—C1	2.187 (2)	P1—C11	1.834 (2)
Rh1—C4	2.218 (2)	P1—C19	1.856 (2)
Rh1—C5	2.226 (2)	P1—C22	1.864 (2)
Rh1—C3	2.266 (2)	C12—C17	1.502 (3)
Rh1—P1	2.2776 (7)	C11—C12	1.404 (3)
Rh1—C2	2.281 (2)		

Bond angles (°)			
C17—Rh1—C1	107.38 (10)	C3—Rh1—P1	129.15 (7)
C17—Rh1—C4	112.03 (10)	C17—Rh1—C2	144.91 (10)
C1—Rh1—C4	62.79 (9)	C1—Rh1—C2	37.69 (8)
C17—Rh1—C5	91.90 (9)	C4—Rh1—C2	61.57 (8)
C1—Rh1—C5	38.06 (8)	C5—Rh1—C2	62.09 (8)
C4—Rh1—C5	36.74 (10)	C3—Rh1—C2	35.89 (8)
C17—Rh1—C3	149.63 (10)	P1—Rh1—C2	105.52 (6)
C1—Rh1—C3	62.29 (8)	C17—Rh1—Cl1	86.46 (8)
C4—Rh1—C3	37.65 (9)	C1—Rh1—Cl1	153.75 (6)
C5—Rh1—C3	61.97 (9)	C4—Rh1—Cl1	91.53 (6)
C17—Rh1—P1	80.96 (7)	C5—Rh1—Cl1	121.90 (7)
C1—Rh1—P1	110.36 (6)	C3—Rh1—Cl1	94.42 (6)
C4—Rh1—P1	166.36 (6)	P1—Rh1—Cl1	93.51 (2)
C5—Rh1—P1	143.51 (7)	C2—Rh1—Cl1	126.53 (6)

Table S6. Selected bond lengths [Å] and angles [°] for **3a**$^+$.

Bond lengths (Å)			
Ir1—C17	1.896 (5)	P1—C22	1.843 (6)
Ir1—P1	2.2774 (12)	P1—C19	1.855 (5)
Ir1—H1	1.3708	C11—C12	1.408 (7)
P1—C11	1.831 (5)	C12—C13	1.400 (7)

Bond angles (°)			
C17—Ir1—P1	80.53 (15)	C11—P1—Ir1	103.04 (17)
C17—Ir1—H1	94.8	C22—P1—Ir1	117.77 (18)

P1—Ir1—H1	79.2	C19—P1—Ir1	112.36 (19)
C11—P1—C22	109.6 (3)	C11—C12—C17	117.4 (4)
C11—P1—C19	106.0 (2)	C13—C12—C17	121.6 (5)
C22—P1—C19	107.5 (3)		

Table S7. Selected bond lengths [Å] and angles [°] for **4a·PMe$_3$$^+$**

Bond lengths (Å)			
Ir1—C17	2.118 (3)	Ir1—C5	2.305 (3)
Ir1—C2	2.232 (3)	P1—C11	1.828 (3)
Ir1—C1	2.267 (3)	P1—C22	1.858 (3)
Ir1—C3	2.281 (3)	P1—C19	1.868 (3)
Ir1—P2	2.2881 (9)	P2—C27	1.819 (4)
Ir1—P1	2.2978 (7)	P2—C25	1.821 (4)
Ir1—C4	2.302 (3)	P2—C26	1.824 (4)

Bond angles (º)			
C17—Ir1—C2	97.03 (12)	C17—Ir1—C4	154.45 (12)
C17—Ir1—C1	93.71 (12)	P2—Ir1—C4	113.22 (9)
C2—Ir1—C1	37.39 (14)	P1—Ir1—C4	113.93 (9)
C17—Ir1—C3	130.85 (12)	P2—Ir1—C5	149.48 (9)
C25—P2—Ir1	111.85 (17)	P1—Ir1—C5	101.08 (9)
C26—P2—Ir1	117.33 (15)	C11—P1—C22	112.58 (15)
C17—Ir1—P2	84.91 (9)	C11—P1—C19	103.21 (14)
C2—Ir1—P2	105.58 (11)	C22—P1—C19	101.59 (15)
C1—Ir1—P2	142.61 (10)	C11—P1—Ir1	105.48 (9)
C3—Ir1—P2	92.39 (10)	C22—P1—Ir1	119.62 (11)
C17—Ir1—P1	79.81 (8)	C19—P1—Ir1	113.33 (10)
C2—Ir1—P1	157.34 (11)	C27—P2—C25	98.5 (2)
C1—Ir1—P1	120.05 (10)	C27—P2—C26	101.79 (19)
C3—Ir1—P1	148.83 (10)	C25—P2—C26	101.7 (2)
P2—Ir1—P1	96.54 (3)	C27—P2—Ir1	122.35 (13)

Table S8. Selected bond lengths [Å] and angles [°] for **4c·NC$_5$H$_5^+$**

Bond lengths (Å)

Ir1—C17	2.115 (4)	Ir1—P1	2.2802 (11)
Ir1—N1	2.121 (3)	P1—C11	1.809 (4)
Ir1—C2	2.172 (4)	P1—C19	1.816 (5)
Ir1—C1	2.211 (4)	P1—C20	1.820 (5)
Ir1—C5	2.221 (4)	N1—C21	1.338 (6)
Ir1—C3	2.243 (4)	N1—C25	1.353 (5)
Ir1—C4	2.259 (4)		

Bond angles (°)

C17—Ir1—N1	88.63 (15)	C5—Ir1—C3	62.99 (17)
C17—Ir1—C2	110.9 (2)	C17—Ir1—C4	146.24 (17)
N1—Ir1—C2	155.93 (17)	N1—Ir1—C4	93.36 (15)
C17—Ir1—C1	91.74 (18)	C2—Ir1—C4	62.57 (18)
N1—Ir1—C1	131.78 (18)	C1—Ir1—C4	62.32 (17)
C2—Ir1—C1	38.1 (2)	C5—Ir1—C4	38.11 (16)
C17—Ir1—C5	108.22 (17)	C17—Ir1—P1	78.84 (13)
N1—Ir1—C5	97.69 (16)	N1—Ir1—P1	90.89 (10)
C2—Ir1—C5	63.59 (19)	C2—Ir1—P1	106.19 (15)
C1—Ir1—C5	37.29 (18)	C1—Ir1—P1	136.37 (15)
C17—Ir1—C3	149.46 (18)	C5—Ir1—P1	168.93 (12)
N1—Ir1—C3	120.77 (17)	C3—Ir1—P1	106.54 (13)
C2—Ir1—C3	38.5 (2)	C21—N1—Ir1	119.4 (3)
C1—Ir1—C3	63.24 (19)	C25—N1—Ir1	122.6 (3)

Table S9. Selected bond lengths [Å] and angles [°] for **4d·NCMe$^+$**.

Bond lengths (Å)

Ir1—N1	2.029 (2)	Ir1—P1	2.2713 (6)
Ir1—C17	2.118 (2)	P1—C11	1.810 (3)
Ir1—C4	2.178 (3)	P1—C25	1.817 (3)
Ir1—C3	2.224 (3)	P1—C19	1.819 (3)
Ir1—C2	2.236 (3)	N1—C31	1.136 (3)
Ir1—C5	2.239 (3)	C11—C12	1.393 (3)
Ir1—C1	2.260 (3)		

Bond angles (°)

N1—Ir1—C17	86.13 (10)	N1—Ir1—P1	87.26 (6)
N1—Ir1—C4	155.08 (9)	C17—Ir1—P1	82.04 (7)
C17—Ir1—C4	99.32 (10)	C4—Ir1—P1	117.50 (7)
N1—Ir1—C3	117.35 (9)	C3—Ir1—P1	154.86 (7)
C17—Ir1—C3	93.95 (10)	C2—Ir1—P1	156.09 (7)
C4—Ir1—C3	38.43 (9)	C5—Ir1—P1	102.65 (7)
N1—Ir1—C2	93.00 (9)	C11—P1—Ir1	106.63 (8)
C17—Ir1—C2	121.85 (10)	C25—P1—Ir1	118.58 (9)
C4—Ir1—C2	63.39 (10)	C19—P1—Ir1	109.65 (8)
C3—Ir1—C2	37.09 (9)	C31—N1—Ir1	176.4 (2)
N1—Ir1—C5	138.53 (10)	C12—C17—Ir1	117.44 (17)
C17—Ir1—C5	134.79 (10)	C30—C25—P1	124.7 (2)
N1—Ir1—C1	103.43 (10)	C26—C25—P1	116.1 (2)
C17—Ir1—C1	156.59 (10)	C24—C19—P1	118.7 (2)
C4—Ir1—C1	63.34 (10)	C20—C19—P1	121.7 (2)

Table S10. Selected bond lengths [Å] and angles [°] for **5a·CH$_2$Cl$_2$$^+$**.

Bond lengths (Å)

Rh1—C17	2.079 (5)	Rh1—Cl1	2.5222 (16)
Rh1—C5	2.131 (5)	P1—C11	1.828 (5)
Rh1—C4	2.211 (5)	P1—C22	1.853 (5)
Rh1—C3	2.228 (6)	P1—C19	1.861 (6)
Rh1—C1	2.258 (5)	Cl1—C25	1.769 (7)
Rh1—C2	2.267 (6)	Cl2A—C25	1.735 (9)
Rh1—P1	2.3202 (15)	Cl2B—C25	1.768 (18)

Bond angles (°)

C17—Rh1—C5	107.3 (2)	C17—Rh1—C2	149.6 (2)
C17—Rh1—C4	91.6 (2)	C5—Rh1—C2	62.1 (2)
C5—Rh1—C4	38.2 (2)	C4—Rh1—C2	62.07 (19)
C17—Rh1—C3	111.9 (2)	C3—Rh1—C2	37.8 (2)
C5—Rh1—C3	63.0 (2)	C1—Rh1—C2	35.1 (2)
C4—Rh1—C3	36.9 (2)	C17—Rh1—P1	79.70 (17)
C17—Rh1—C1	145.7 (2)	C5—Rh1—P1	111.76 (15)
C5—Rh1—C1	38.5 (2)	C4—Rh1—P1	144.39 (16)
C4—Rh1—C1	62.73 (19)	C3—Rh1—P1	168.04 (15)

C3—Rh1—C1	61.6 (2)	C1—Rh1—P1	107.32 (14)
C2—Rh1—P1	130.47 (15)	C3—Rh1—Cl1	88.52 (15)
C17—Rh1—Cl1	91.66 (17)	C1—Rh1—Cl1	120.45 (16)
C5—Rh1—Cl1	149.86 (16)	C2—Rh1—Cl1	89.67 (16)
C4—Rh1—Cl1	120.72 (16)	P1—Rh1—Cl1	94.20 (6)

Table S11. Selected bond lengths [Å] and angles [°] for **6a**$^+$

Bond lengths (Å)			
Ir1—C17	1.907 (2)	Ir1—Br1	2.4854 (3)
Ir1—C2	2.215 (2)	P1—C11	1.825 (2)
Ir1—C1	2.232 (2)	P1—C22	1.850 (3)
Ir1—C5	2.253 (2)	P1—C19	1.865 (3)
Ir1—P1	2.3060 (6)	C12—C17	1.441 (3)
Ir1—C4	2.333 (2)	C11—C16	1.397 (3)
Ir1—C3	2.336 (2)	C11—C12	1.419 (3)

Bond angles (º)			
C17—Ir1—C2	110.17 (10)	C22—P1—C19	106.23 (12)
C17—Ir1—C1	95.83 (10)	C11—P1—Ir1	102.75 (8)
C2—Ir1—C1	37.95 (9)	C22—P1—Ir1	120.94 (9)
C17—Ir1—C5	116.33 (9)	C19—P1—Ir1	109.79 (8)
C17—Ir1—P1	80.32 (7)	C16—C11—P1	130.4 (2)
P1—Ir1—C4	126.13 (6)	C12—C11—P1	109.16 (17)
C17—Ir1—Br1	93.78 (7)	C13—C12—C11	120.5 (2)
C2—Ir1—Br1	149.63 (6)	C13—C12—C17	121.6 (2)
C1—Ir1—Br1	124.01 (6)	C11—C12—C17	117.9 (2)
C5—Ir1—Br1	90.71 (6)	C12—C17—Ir1	125.58 (18)
P1—Ir1—Br1	89.135 (17)	C21—C19—P1	116.29 (19)
C4—Ir1—Br1	89.31 (6)	C20—C19—P1	110.01 (17)
C3—Ir1—Br1	118.83 (6)	C23—C22—P1	109.60 (18)
C11—P1—C22	111.27 (12)	C24—C22—P1	115.86 (19)
C11—P1—C19	104.83 (11)		

Table S12. Selected bond lengths [Å] and angles [°] for **9a**.

Bond lengths (Å)			
Ir1—C17	2.114 (9)	P1—C22	1.876 (10)
Ir1—P5	2.228 (2)	P1—C19	1.872 (10)
Ir1—C25	2.100 (11)	C11—C12	1.393 (14)
P1—C11	1.822 (9)	C12—C17	1.494 (14)

Bond angles (º)			
C17—Ir1—P5	81.3 (3)	C11—P1—Ir1	106.1 (3)
C25—Ir1—C17	80.9 (4)	C19—P1—Ir1	118.1 (3)
C25—Ir1—P5	87.4 (3)	C22—P1—Ir1	119.5 (3)
C11—P1—C19	100.7 (4)	C11—C12—C17	119.3 (8)
C11—P1—C22	107.0 (5)	C13—C12—C17	121.3 (9)
C19—P1—C22	103.5 (5)		

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