C-H Activation of 2,4,6-Triphenylphosphinine: Unprecedented Formation of Cyclometalated [(P^C)Ir(III)] and [(P^C)Rh(III)] Complexes

Leen E.E. Broeckx\textsuperscript{a}, Martin Lutz\textsuperscript{b}, Dieter Vogt\textsuperscript{a}, and Christian Müller\textsuperscript{*a}

\textsuperscript{a} Schuit Institute of Catalysis, Laboratory for Homogeneous Catalysis, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands. Fax: +31 40-2455054; Tel: +31-40-2474679; E-mail: c.mueller@tue.nl

\textsuperscript{b} Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, 3584 CH Utrecht, The Netherlands

Supplementary Material

General remarks:
All experiments were performed under an inert argon atmosphere, using modified Schlenk techniques or in a MBraun dry box, unless otherwise stated. All glassware was dried prior to use by heating under vacuum to remove traces of water. 2,4,6-triphenylphosphinine (1)\textsuperscript{1} and 2,4,6-triphenylpyridine (6)\textsuperscript{2} were prepared according to the literature. [Cp*IrCl\textsubscript{2}] and [Cp*RhCl\textsubscript{2}] were obtained from Aldrich. The solvents were dried and deoxygenated using custom-made solvent purification columns filled with Al\textsubscript{2}O\textsubscript{3}. The \textsuperscript{1}H, \textsuperscript{13}C{\textsuperscript{1}H} and \textsuperscript{31}P{\textsuperscript{1}H} NMR spectra were recorded on a Varian Mercury 200 or 400 MHz spectrometer. The mass characterization of 2 has been performed by positive mode reflection MALDI-TOF using a Voyager-DE PRO instrument.

Chloro(η\textsuperscript{5}-pentamethylcyclopentadienyl)(2,4,6-triphenylphosphinine-P)iridium(III) (2)

A mixture of [Cp*IrCl\textsubscript{2}] (24.6 mg, 0.031 mmol, 1.0 equiv) and 2,4,6-triphenylphosphinine 1 (20.9 mg, 0.064 mmol, 2.1 equiv) was suspended in CD\textsubscript{2}Cl\textsubscript{2} (0.5 mL) and transferred to a Young NMR-Tube under argon. 2 was formed immediately at room temperature. δ\textsuperscript{H}(400.16 MHz; CD\textsubscript{2}Cl\textsubscript{2}) 1.35 (15 H, s, Me), 7.35-7.41 (7 H, m, H\textsubscript{arom}), 7.44 (2 H, t, \textsuperscript{3}J_{(H,H)} = 7.4 Hz, H\textsubscript{arom}), 7.59-7.64 (6 H, m, H\textsubscript{arom}), 8.03 (2 H, d, \textsuperscript{3}J_{(H,P)} = 19.2 Hz, H\textsubscript{p}); δ\textsuperscript{C}(100.63 MHz; CD\textsubscript{2}Cl\textsubscript{2}) 8.9 (C\textsubscript{3}Me\textsubscript{3}), 94.3 (C\textsubscript{3}Me\textsubscript{3}),
rac-Chloro(η⁵-pentamethylcyclopentadienyl)(2-phenyl-C₆-4,6-diphenylphosphinine-P)iridium(III) (3)

A mixture of [Cp*IrCl₂]₂ (24.6 mg, 0.031 mmol, 1.0 equiv), 2,4,6-triphenylphosphinine 1 (20 mg, 0.062 mmol, 2.0 equiv), and NaOAc (5.7 mg, 0.070 mmol, 2.3 equiv) was suspended in dichloromethane (0.5 mL) and transferred to a Young NMR-tube under argon. The suspension was heated to T = 80°C for 6 h and monitored by means of ³¹P{¹H} NMR spectroscopy. The orange reaction mixture was filtered over celite and recrystallized by diffusion of diethyl ether into the dichloromethane solution. 3 was obtained as dark orange crystals (40.9 mg, 96.7%). δH(400.16 MHz; CD₂Cl₂) 1.59 (15 H, d, ³J(H,P) = 3.2 Hz, Me), 7.05-7.12 (2 H, m, Hₐrøm), 7.39-7.43 (1 H, m, Hₐrøm), 7.45-7.60 (5 H, m, Hₐrøm), 7.65-7.70 (3 H, m, Hₐrøm), 7.79-7.83 (1 H, m, Hₐrøm), 7.84-7.86 (1 H, m, Hₐrøm), 7.86-7.88 (1 H, m, Hₐrøm), 8.01 (1 H, dd, ³J(H,P) = 21.6 Hz, ⁴J(H,H) = 1.6 Hz, Hβ), 8.35 (1 H, dd, ³J(H,P) = 22.4 Hz, ⁴J(H,H) = 1.6 Hz, Hβ); δC(50.27 MHz; CD₂Cl₂) 9.1 (C₅Me₅), 96.6 (d, ²J(C,P) = 3.3 Hz, C₅Me₅), 120.1 (d, ³J(C,P) = 19.1 Hz), 123.2, 127.8, 128.2, 128.5, 128.6, 128.7, 129.2, 129.5, 134.9 (d, ³J(C,P) = 11.4 Hz), 139.8 (d, ³J(C,P) = 25.3 Hz), 140.3 (d, ³J(C,P) = 11.2 Hz), 140.6, 142.7 (d, ³J(C,P) = 5.3 Hz), 144.5 (d, ³J(C,P) = 30.8 Hz), 152.6 (d, ³J(C,P) = 28.0 Hz), 154.0, 165.4 (d, ¹J(C,P) = 42.9 Hz, Cα), 177.0; δp(161.00 MHz; CD₂Cl₂) 170.8.

rac-Chloro(η⁵-pentamethylcyclopentadienyl)(2-phenyl-C₆-4,6-diphenylphosphinine-P)rhodium(III) (5)

A mixture of [Cp*RhCl₂]₂ (22.3 mg, 0.036 mmol, 1.0 equiv), 2,4,6-triphenylphosphinine 1 (23.2 mg, 0.072 mmol, 2.0 equiv), and NaOAc (6.2 mg, 0.076 mmol, 2.1 equiv) was suspended in dichloromethane (0.5 mL) and transferred to a Young NMR-tube under argon. The suspension was heated to T = 80°C for 18 h and monitored by means of ³¹P{¹H} NMR spectroscopy. The dark brown solution was filtered over celite and recrystallized by diffusion of diethyl ether in the filtrate to obtain 5 as red crystals (18.9 mg, 44.3%). δH(400.16 MHz; CD₂Cl₂) 1.49 (15 H, d,
$^{4}J_{(H,P)} = 4.4$ Hz, Me), 7.09–7.13 (2 H, m, H$_{arom}$), 7.39–7.44 (1 H, m, H$_{arom}$), 7.46–7.56 (5 H, m, H$_{arom}$), 7.68 (3 H, d, $J_{(H,P)} = 6.8$ Hz, H$_{arom}$), 7.75–7.78 (1 H, m, H$_{arom}$), 7.90 (2 H, d, $J_{(H,P)} = 7.6$ Hz, H$_{arom}$), 8.03 (1 H, d, $^{3}J_{(H,P)} = 18.8$ Hz, H$_{\beta}$) and 8.34 (1 H, d, $^{3}J_{(H,P)} = 21.2$ Hz, H$_{\beta}$). $\delta_{C}(100.63$ MHz; CD$_{2}$Cl$_{2}$) 9.5 (C$_{5}$Me$_{5}$), 102.2 (d, $^{2}J_{(C,Rh)} = 9.3$ Hz, C$_{5}$Me$_{5}$), 120.8 (d, $^{2}J_{(C,Rh)} = 20.6$ Hz), 123.6, 127.8, 128.1, 128.4 (d, $J_{(C,Rh)} = 11.1$ Hz), 128.6, 128.9, 129.2, 129.5, 134.4 (d, $^{2}J_{(C,Rh)} = 13.5$ Hz), 140.7, 141.0, 141.2, 142.6 (d, $^{1}J_{(C,Rh)} = 5.3$ Hz), 145.3 (d, $^{1}J_{(C,Rh)} = 36.1$ Hz), 160.5 (dd, $^{2}J_{(C,Rh)} = 9.5$ Hz, $^{2}J_{(C,P)} = 3.2$ Hz), 163.2 (dd, $^{1}J_{(C,P)} = 30.7$ Hz, $^{2}J_{(C,Rh)} = 4.9$ Hz), 172.8 (dd, $^{1}J_{(C,P)} = 30.9$ Hz, $^{2}J_{(C,Rh)} = 13.3$ Hz); $\delta_{P}(162.01$ MHz; CD$_{2}$Cl$_{2}$) 208.8 (d, $^{1}J_{(P,Rh)} = 187.8$ Hz).

**Reaction of 2,4,6-triphenylphosphinine (1) with [Cp*IrCl$_2$]$_2$ in the absence of NaOAc:**

A mixture of [Cp*IrCl$_2$]$_2$ (17.6 mg, 0.022 mmol, 1.0 equiv) and 2,4,6-triphenylphosphinine 1 (14.5 mg, 0.045 mmol, 2.0 equiv) was suspended in CD$_2$Cl$_2$ (0.5 mL) and transferred to a Young NMR-Tube under argon. 2 was formed immediately at room temperature. The mixture was heated to T = 80°C and the composition was followed by means of $^{31}$P NMR (Figure S-1).

**Figure S-1:** Time-dependent $^{31}$P{1H} NMR spectra for the reaction of 1 with [Cp*IrCl$_2$]$_2$ in the absence of NaOAc at T = 80°C.

**Reaction of 2,4,6-triphenylpyridine with [Cp*IrCl$_2$]$_2$:**

Attempt 1: A mixture of [Cp*IrCl$_2$]$_2$ (42.9 mg, 0.054 mmol, 1.0 equiv), 2,4,6-triphenylpyridine 6 (33.0 mg, 0.107 mmol, 2.0 equiv), and NaOAc (8.8 mg, 0.107 mmol, 2.0 equiv) was suspended in CD$_2$Cl$_2$ (0.5 mL) and heated to T = 80°C for 5 days under argon. The yellow reaction mixture
was analyzed by means of $^1$H NMR spectroscopy. No signals of the cyclometalated product 7 could be detected.

Attempt 2: A mixture of [Cp*IrCl$_2$]$_2$ (25.3 mg, 0.032 mmol, 1.0 equiv), 2,4,6-triphenylpyridine (20.2 mg, 0.066 mmol, 2.1 equiv), and NaOAc·3·H$_2$O (11.3 mg, 0.083 mmol, 2.6 equiv) was suspended in CD$_2$Cl$_2$ (0.5 mL) and heated to T = 80°C for 5.5 days under argon. The yellow reaction mixture was analyzed by means of $^1$H NMR spectroscopy. No signals of the cyclometalated product 7 could be detected.

**Reaction of 2,4,6-triphenylpyridine with [Cp*RhCl$_2$]$_2$:**

Attempt 1: A mixture of [Cp*RhCl$_2$]$_2$ (19.7 mg, 0.032 mmol, 1.0 equiv), 2,4,6-triphenylpyridine (19.9 mg, 0.065 mmol, 2.0 equiv), and NaOAc (5.3 mg, 0.065 mmol, 2. equiv) was suspended in CD$_2$Cl$_2$ (0.5 mL) and heated to T = 80°C for 8 days under argon. The yellow reaction mixture was analyzed by means of $^1$H NMR spectroscopy. No signals of the cyclometalated product 8 could be detected.

Attempt 2: A mixture of [Cp*RhCl$_2$]$_2$ (20.3 mg, 0.033 mmol, 1.0 equiv), 2,4,6-triphenylpyridine 6 (20.2 mg, 0.066 mmol, 2.0 equiv), and NaOAc·3·H$_2$O (20.0 mg, 0.147 mmol, 4.5 equiv) was suspended in CD$_2$Cl$_2$ (0.5 mL) and heated to T = 80°C for 8 days under argon. The yellow reaction mixture was analyzed by means of $^1$H NMR spectroscopy. No signals of the cyclometalated product 8 could be detected.

**X-ray crystal structure analysis of 3:**

C$_{33}$H$_{31}$ClIrP, Fw = 686.20, orange needle, 0.23 x 0.06 x 0.04 mm$^3$, orthorhombic, P2$_1$2$_1$2$_1$ (no. 19), a = 7.1991(8), b = 14.1332(15), c = 25.829(3) Å, V = 2628.0(5) Å$^3$, Z = 4, D$_x$ = 1.734 g/cm$^3$, μ = 5.26 mm$^{-1}$. 31203 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) up to a resolution of (sin θ/λ)$_{\text{max}}$ = 0.65 Å$^{-1}$ at a temperature of 150(2) K. Intensity data were integrated with the SAINT software.$^3$ An analytical absorption correction was performed with SADABS$^4$ (0.34-0.86 correction range). 6014 Reflections were unique (R$_{\text{int}}$ = 0.0531), of which 5582 were observed [I>2σ(I)]. The structure was solved with Direct Methods using the program SHELXS-97$^5$ and refined with SHELXL-97$^5$ against F$^2$ of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated
positions and refined with a riding model. 330 Parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0216 / 0.0549. R1/wR2 [all refl.]: 0.0251 / 0.0574. S = 1.040. Residual electron density between -0.23 and 0.47 e/Å³. Geometry calculations and checking for higher symmetry was performed with the PLATON program.⁷

**X-ray crystal structure analysis of 5:**

C₃₃H₃₁ClPRh, Fw = 596.91, red block, 0.39 x 0.29 x 0.17 mm³, monoclinic, P2₁/c (no. 14), a = 7.3342(1), b = 16.3287(4), c = 22.9799(3) Å, β = 98.867(1)°, V = 2719.14(8) Å³, Z = 4, Dₓ = 1.458 g/cm³, μ = 0.81 mm⁻¹. 49748 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) up to a resolution of (sin θ/λ)max = 0.65 Å⁻¹ at a temperature of 150(2) K. Intensity data were integrated with the Eval15 software.⁸ An absorption correction based on multiple measured reflections was performed with SADABS⁴ (0.67-0.75 correction range). 6249 Reflections were unique (Rₑₐₓ = 0.0265), of which 5694 were observed [I>2σ(I)]. The symmetry of a pseudo-orthorhombic C-cell is not fulfilled by the intensities and pseudo-orthorhombic twinning was not detected. The structure was solved with Direct Methods using the program SHELXS-97⁵ and refined with SHELXL-97⁵ against F² of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and refined with a riding model. 330 Parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0216 / 0.0549. R1/wR2 [all refl.]: 0.0251 / 0.0574. S = 1.040. Residual electron density between -0.23 and 0.47 e/Å³. Geometry calculations and checking for higher symmetry was performed with the PLATON program.⁷

**References:**