

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

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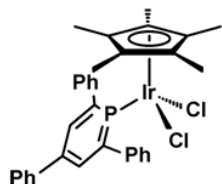
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Supplementary Material

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)¹ and 2,4,6-triphenylpyridine (6)² were prepared according to the literature. [Cp*IrCl₂]₂ and [Cp*RhCl₂]₂ were obtained from Aldrich. The solvents were dried and deoxygenated using custom-made solvent purification columns filled with Al₂O₃. The ¹H, ¹³C{¹H} and ³¹P{¹H} 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.

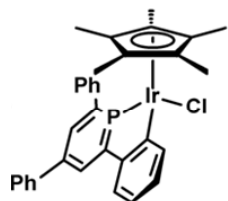
Chloro(η⁵-pentamethylcyclopentadienyl)(2,4,6-triphenylphosphinine-P)iridium(III) (**2**)



A mixture of [Cp*IrCl₂]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 CD₂Cl₂ (0.5 mL) and transferred to a Young NMR-Tube under argon. **2** was formed immediately at room temperature. δ_H(400.16 MHz; CD₂Cl₂) 1.35 (15 H, s, Me), 7.35-7.41 (7 H, m, H_{arom}), 7.44 (2 H, t, ³J_(H,H) = 7.4 Hz, H_{arom}), 7.59-7.64 (6 H, m, H_{arom}), 8.03 (2 H, d, ³J_(H,P) = 19.2 Hz, H_β); δ_C(100.63 MHz; CD₂Cl₂) 8.9 (C₅Me₅), 94.3 (C₅Me₅),

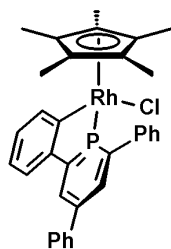
127.8 (d, $J_{(C,P)} = 3.1$ Hz), 127.9 (br s), 128.4, 129.2, 130.7 (br s), 139.4 (br s), 140.3, 140.5, 140.7 (d, $J_{(C,P)} = 4.7$ Hz), 142.2 (d, $J_{(C,P)} = 12.1$ Hz), 163.2 (d, $J_{(C,P)} = 17.2$ Hz); δ_P (161.00 MHz; CD_2Cl_2) 133.0. MALDI-TOF (m/z): 722.12 g/mol [M^+].

***rac*-Chloro(η^5 -pentamethylcyclopentadienyl)(2-phenyl-C_o-4,6-diphenylphosphinine-P)iridium(III) (3)**



A mixture of $[Cp^*IrCl_2]_2$ (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 $T = 80^\circ C$ for 6 h and monitored by means of $^{31}P\{^1H\}$ 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%). δ_H (400.16 MHz; CD_2Cl_2) 1.59 (15 H, d, $^4J_{(H,P)} = 3.2$ Hz, Me), 7.05-7.12 (2 H, m, H_{arom}), 7.39-7.43 (1 H, m, H_{arom}), 7.45-7.56 (5 H, m, H_{arom}), 7.65-7.70 (3 H, m, H_{arom}), 7.79-7.83 (1 H, m, H_{arom}), 7.84-7.86 (1 H, m, H_{arom}), 7.86-7.88 (1 H, m, H_{arom}), 8.01 (1 H, dd, $^3J_{(H,P)} = 21.6$ Hz, $^4J_{(H,H)} = 1.6$ Hz, H_β), 8.35 (1 H, dd, $^3J_{(H,P)} = 22.4$ Hz, $^4J_{(H,H)} = 1.6$ Hz, H_β); δ_C (50.27 MHz; CD_2Cl_2) 9.1 (C_5Me_5), 96.6 (d, $^2J_{(C,P)} = 3.3$ Hz, C_5Me_5), 120.1 (d, $J_{(C,P)} = 19.1$ Hz), 123.2, 127.8, 128.2, 128.5, 128.6, 128.7, 129.2, 129.5, 134.9 (d, $J_{(C,P)} = 11.4$ Hz), 139.8 (d, $J_{(C,P)} = 25.3$ Hz), 140.3 (d, $J_{(C,P)} = 11.2$ Hz), 140.6, 142.7 (d, $J_{(C,P)} = 5.3$ Hz), 144.5 (d, $J_{(C,P)} = 30.8$ Hz), 152.6 (d, $J_{(C,P)} = 28.0$ Hz), 154.0, 165.4 (d, $^1J_{(C,P)} = 42.9$ Hz, C_α), 177.0; δ_P (161.00 MHz; CD_2Cl_2) 170.8.

***rac*-Chloro(η^5 -pentamethylcyclopentadienyl)(2-phenyl-C_o-4,6-diphenylphosphinine-P)rhodium(III) (5)**



A mixture of $[Cp^*RhCl_2]_2$ (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 $T = 80^\circ C$ for 18 h and monitored by means of $^{31}P\{^1H\}$ 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%). δ_H (400.16 MHz; CD_2Cl_2) 1.49 (15 H, d,

$^4J_{(H,P)} = 4.4$ 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, $^3J_{(H,P)} = 18.8$ Hz, H_{β}) and 8.34 (1 H, d, $^3J_{(H,P)} = 21.2$ Hz, H_{β}). δ_{C} (100.63 MHz; CD_2Cl_2) 9.5 (C_5Me_5), 102.2 (d, $^2J_{(C,Rh)} = 9.3$ Hz, C_5Me_5), 120.8 (d, $^2J_{(C,Rh)} = 20.6$ 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, $^2J_{(C,Rh)} = 13.5$ Hz), 140.2 (d, $^2J_{(C,Rh)} = 12.4$ Hz), 140.7, 141.0, 141.2, 142.6 (d, $^1J_{(C,Rh)} = 5.3$ Hz), 145.3 (d, $^1J_{(C,Rh)} = 36.1$ Hz), 160.5 (dd, $^2J_{(C,Rh)} = 9.5$ Hz, $^2J_{(C,P)} = 3.2$ Hz), 163.2 (dd, $^1J_{(C,P)} = 30.7$ Hz, $^2J_{(C,Rh)} = 4.9$ Hz), 172.8 (dd, $^1J_{(C,P)} = 30.9$ Hz, $^2J_{(C,Rh)} = 13.3$ Hz); δ_{P} (162.01 MHz; CD_2Cl_2) 208.8 (d, $^1J_{(P,Rh)} = 187.8$ Hz).

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

A mixture of $[\text{Cp}^*\text{IrCl}_2]_2$ (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_2Cl_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 $T = 80^\circ\text{C}$ and the composition was followed by means of ^{31}P NMR (Figure S-1).

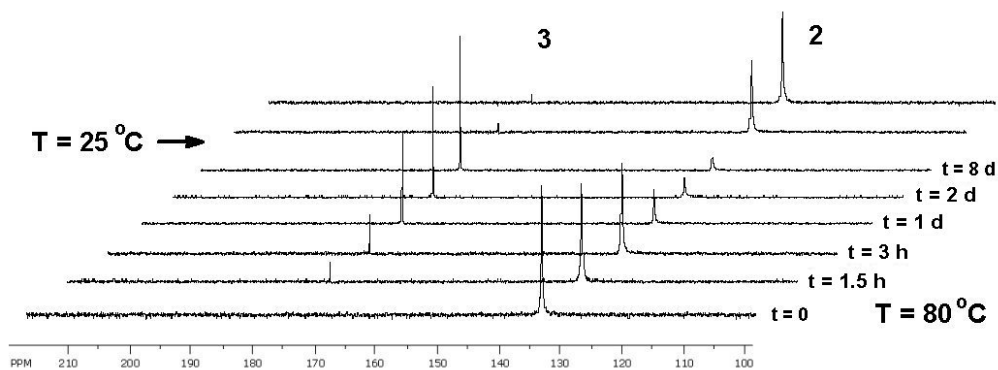


Figure S-1: Time-dependent $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for the reaction of **1** with $[\text{Cp}^*\text{IrCl}_2]_2$ in the absence of NaOAc at $T = 80^\circ\text{C}$.

Reaction of 2,4,6-triphenylpyridine with $[\text{Cp}^*\text{IrCl}_2]_2$:

Attempt 1: A mixture of $[\text{Cp}^*\text{IrCl}_2]_2$ (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_2Cl_2 (0.5 mL) and heated to $T = 80^\circ\text{C}$ for 5 days under argon. The yellow reaction mixture

was analyzed by means of ^1H NMR spectroscopy. No signals of the cyclometalated product **7** could be detected.

Attempt 2: A mixture of $[\text{Cp}^*\text{IrCl}_2]_2$ (25.3 mg, 0.032 mmol, 1.0 equiv), 2,4,6-triphenylpyridine (20.2 mg, 0.066 mmol, 2.1 equiv), and $\text{NaOAc}\cdot 3\cdot\text{H}_2\text{O}$ (11.3 mg, 0.083 mmol, 2.6 equiv) was suspended in CD_2Cl_2 (0.5 mL) and heated to $T = 80^\circ\text{C}$ for 5.5 days under argon. The yellow reaction mixture was analyzed by means of ^1H NMR spectroscopy. No signals of the cyclometalated product **7** could be detected.

Reaction of 2,4,6-triphenylpyridine with $[\text{Cp}^*\text{RhCl}_2]_2$:

Attempt 1: A mixture of $[\text{Cp}^*\text{RhCl}_2]_2$ (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_2Cl_2 (0.5 mL) and heated to $T = 80^\circ\text{C}$ for 8 days under argon. The yellow reaction mixture was analyzed by means of ^1H NMR spectroscopy. No signals of the cyclometalated product **8** could be detected.

Attempt 2: A mixture of $[\text{Cp}^*\text{RhCl}_2]_2$ (20.3 mg, 0.033 mmol, 1.0 equiv), 2,4,6-triphenylpyridine **6** (20.2 mg, 0.066 mmol, 2.0 equiv), and $\text{NaOAc}\cdot 3\cdot\text{H}_2\text{O}$ (20.0 mg, 0.147 mmol, 4.5 equiv) was suspended in CD_2Cl_2 (0.5 mL) and heated to $T = 80^\circ\text{C}$ for 8 days under argon. The yellow reaction mixture was analyzed by means of ^1H NMR spectroscopy. No signals of the cyclometalated product **8** could be detected.

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

$\text{C}_{33}\text{H}_{31}\text{ClIrP}$, $F_w = 686.20$, orange needle, $0.23 \times 0.06 \times 0.04 \text{ mm}^3$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 7.1991(8)$, $b = 14.1332(15)$, $c = 25.829(3) \text{ \AA}$, $V = 2628.0(5) \text{ \AA}^3$, $Z = 4$, $D_x = 1.734 \text{ g/cm}^3$, $\mu = 5.26 \text{ mm}^{-1}$. 31203 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator ($\lambda = 0.71073 \text{ \AA}$) up to a resolution of $(\sin \theta/\lambda)_{\text{max}} = 0.65 \text{ \AA}^{-1}$ at a temperature of $150(2) \text{ K}$. Intensity data were integrated with the SAINT software.³ An analytical absorption correction was performed with SADABS⁴ (0.34-0.86 correction range). 6014 Reflections were unique ($R_{\text{int}} = 0.0531$), of which 5582 were observed [$I > 2\sigma(I)$]. The structure was solved with Direct Methods using the program SHELXS-97⁵ and refined with SHELXL-97⁵ 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 > 2 σ (I)]: 0.0261 / 0.0584. R1/wR2 [all refl.]: 0.0314 / 0.0610. S = 1.051. Flack parameter⁶ $x = -0.016(6)$. Residual electron density between -1.33 and 1.98 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, $\beta = 98.867(1)^\circ$, V = 2719.14(8) Å³, Z = 4, D_x = 1.458 g/cm³, $\mu = 0.81$ mm⁻¹. 49748 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator ($\lambda = 0.71073$ Å) up to a resolution of $(\sin \theta/\lambda)_{\max} = 0.65$ 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 (R_{int} = 0.0265), of which 5694 were observed [I > 2 σ (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 > 2 σ (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:

- 1) G. Märkl, *Angew. Chem.* **1966**, 78, 907.
- 2) K. Dimroth, *Angew. Chem.* **1960**, 72, 331.
- 3) SAINT (Version 7.68A). Bruker AXS Inc., Madison, Wisconsin, USA.
- 4) Sheldrick, G. M. (1999). SADABS: Area-Detector Absorption Correction, v2.10, Universität Göttingen, Germany.

- 5) G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.
- 6) H. D. Flack, *Acta Cryst.* **1983**, *A39*, 876-881.
- 7) A.L. Spek, *Acta Cryst.* **2009**, *D65*, 148-155.
- 8) A.M.M. Schreurs, X. Xian, L.M.J. Kroon-Batenburg, *J. Appl. Cryst.* **2010**, *43*, 70-82.