

Easy Oxidatively Induced Silicon-Carbon Bond Activation in Organoplatinum Chemistry

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Electronic Supporting Information

Synthetic procedures

The complex $[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2]$, $[\text{Pt}_2(\text{CD}_3)_4(\mu\text{-SMe}_2)_2]$ and ligand $\text{Me}_2\text{Si}(2\text{-C}_5\text{H}_4\text{N})_2$, bps, were prepared according to the literature.^{1,2}

[PtMe₂(bps)], 1. To a stirring solution of bps (0.75 g, 3.48 mmol) in ether (10 mL) was added $[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2]$ (1.0 g, 1.74 mmol). After 1h, the product precipitated from solution as a pale brown solid, which was separated, washed with ether (3 x 2 mL) and pentane (3 x 2 mL), and dried under vacuum. Yield: 88%. Anal. Calcd. for $\text{C}_{14}\text{H}_{20}\text{N}_2\text{PtSi}$: C, 38.26; H, 4.59; N, 6.37. Found: C, 38.53; H, 4.85; N, 6.33 %. NMR in CDCl_3 : $\delta(^1\text{H}) = 0.71$ [s, 6H, $^2J_{\text{PtH}} = 80$ Hz, PtMe]; 0.77 [s, 3H, SiMe]; 1.11 [s, 3H, SiMe]; 7.21 [dd, 2H, $^3J_{\text{HH}} = 7, 5$ Hz, H⁵]; 7.55 [d, 2H, $^3J_{\text{HH}} = 7$ Hz, H³]; 7.67 [t, 2H, $^3J_{\text{HH}} = 7$ Hz, H⁴]; 8.97 [d, 2H, $^3J_{\text{HH}} = 5$ Hz, $^3J_{\text{PtH}} = 25$ Hz, H⁶]; $\delta(^{13}\text{C}) = -18.5$ [PtMe]; -3.9 [SiMe]; -1.7 [SiMe]; 125.4 [C5]; 130.4 [C3]; 133.7 [C4]; 152.4 [C6]; 163.1 [C2]. Complex **1-d₆** was prepared similarly from $[\text{Pt}_2(\text{CD}_3)_4(\mu\text{-SMe}_2)_2]$. The ¹H NMR spectrum was the same except that the methylplatinum resonance at $\delta(^1\text{H}) = 0.71$ was absent.

[Me(bps)Pt-OSiMe(2-C₅H₄N)₂PtMe₃][B(OCH₂CF₃)(C₆F₅)₃],

2[B(OCH₂CF₃)(C₆F₅)₃]. To a solution of **1** (0.09 g, 0.45 mmol) in $\text{CF}_3\text{CH}_2\text{OH}$ (5 mL) was added a solution of $\text{B}(\text{C}_6\text{F}_5)_3$ (0.11 g, 0.45 mmol) in $\text{CF}_3\text{CH}_2\text{OH}$ (5 mL). The mixture was stirred for 2 d, then the volume of the solution was reduced to 2 mL, and the mixture was stored at 0 °C for 2 d., to give the product as colourless crystals, which were separated and dried under vacuum. Yield 37 %. Anal. Calcd. for $\text{C}_{47}\text{H}_{39}\text{BF}_{18}\text{N}_4\text{O}_2\text{Pt}_2\text{Si}_2 \cdot 2\text{H}_2\text{O}$: C, 36.97; H, 2.84; N, 3.67. Found: C, 36.77; H, 2.32; N, 3.62 %. NMR in acetone-*d*₆: $\delta(^1\text{H}) = 0.15$ [s, 3H, $^2J_{\text{PtH}} = 69$ Hz, MePt^{IV} *trans* N]; 0.64 [s, 3H, $^2J_{\text{PtH}} = 75$ Hz, MePt^{II} *trans* N]; 0.95 [s, 3H, bps SiMe]; 1.17 [s, 3H, $^2J_{\text{PtH}} = 68$ Hz, MePt^{IV} *trans* N]; 1.22 [s, 3H, OSiMe]; 1.23 [s, 3H, $^2J_{\text{PtH}} = 78$ Hz, MePt^{IV} *trans* O]; 1.63 [s, 3H, bps SiMe]; 3.57 [q, 2H, $^3J_{\text{HF}} = 12$ Hz, CH₂]; 7.01 [m, 1H, H^{5d}]; 7.38 [m, 1H, H^{5a}]; 7.61 [m, 1H, H^{5c}]; 7.64 [m, 1H, H^{5b}]; 7.74 [m, 1H, H^{3a}]; 7.83 [m, 1H, H^{4d}]; 7.88 [m, 1H, H^{3d}]; 7.96 [m, 1H, H^{4a}]; 8.07 [m, 2H, H^{3b}, H^{4b}]; 8.11 [m, 1H, H^{4c}]; 8.15 [m, 1H, H^{3c}]; 8.49 [m, 1H, $^3J_{\text{PtH}} = 20$ Hz, H^{6d}]; 8.60 [m, 1H, $^3J_{\text{PtH}} = 20$ Hz, H^{6c}]; 8.72 [m, 1H, $^3J_{\text{PtH}} = 21$ Hz, H^{6b}]; 8.96 [m, 1H, $^3J_{\text{PtH}} = 65$ Hz, H^{6a}]. $\delta(^{19}\text{F}) = -75$ [br, 3F, CF₃]; -133 [br m, 6F, F², F⁶]; -164 [m, 3F, F⁴]; -168 [br, 6F, F³, F⁵].

[Me₃Pt(HOSiMe(2-C₅H₄N)₂)[PhCO₂], 3c. To a solution of complex **1** (0.05 g, 0.12 mmol) in acetone (10 mL) was added dibenzoyl peroxide (0.03 g, 0.12 mmol). The mixture was stirred for 2 h., the volume was reduced to 1 mL, and pentane (5 mL) was added to precipitate the product as a white solid, which was separated, washed with ether (3 x 2 mL) and pentane (3 x 2 mL), and dried under vacuum. NMR in CD_2Cl_2 : $\delta(^1\text{H}) =$

1.04 [s, 3H, Si-Me]; 1.05 [s, 6H, $^2J_{\text{PtH}} = 70$ Hz, MePt *trans* N]; 1.14 [s, 3H, $^2J_{\text{PtH}} = 75$ Hz, MePt *trans* O]; 2.12 [s, 1H, OH]; 7.37 [m, 4H, H⁵, H^m]; 7.46 [m, 1H, H^p]; 7.75 [m, 2H, H³]; 7.80 [m, 2H, H⁴]; 7.95 [m, 2H, H^o]; 8.58 [m, 2H, $^3J_{\text{PtH}} = 20$ Hz, H⁶].

Monitoring of reactions by ^1H NMR and ESI-MS.

In a typical reaction, complex **1** (1 mg) was dissolved in CD₃OD (1 mL), and then excess hydrogen peroxide (0.01 mL) was added to the solution to give [Me₃Pt(HOSiMe(2-C₅H₄N)₂)[OH], **3b**. The ^1H NMR spectrum was recorded immediately and then at intervals for several days. NMR in CD₃OD after 4 min.: $\delta(^1\text{H}) = 0.94$ [s, 3H, SiMe]; 0.98 [s, 6H, $^2J_{\text{PtH}} = 69$ Hz, MePt *trans* N]; 1.15 [s, 3H, $^2J_{\text{PtH}} = 75$ Hz, MePt *trans* O]; 7.43 [m, 2H, H⁵]; 7.80 [m, 2H, H³]; 7.86 [m, 2H, H⁴]; 8.62 [m, 2H, $^3J_{\text{PtH}} = 20$ Hz, H⁶]; $\delta(^{13}\text{C}) = -10.7$ [PtMe]; -10.4 [PtMe]; -4.6 [SiMe]; 123.4 [C5]; 129.1 [C3]; 136.5 [C4]; 146.5 [C6]; 165.8 [C2]. The similar reaction with **1-d₆** to give **3b*** gave identical ^1H NMR data except that the resonance at $\delta(^1\text{H}) = 0.98$ was absent. The complexes decomposed slowly over several days.

Similar reactions in MeOH were monitored by ESI-MS: Complexes **3b** and **3b*** gave an envelope of peaks at $m/z = 456$ and 462 respectively, as expected for [Me₃Pt(HOSiMe(2-C₅H₄N)₂)⁺ and [Me₃Pt(HOSiMe(2-C₅H₄N)₂)⁺-d₆, and also at 911 and 923 respectively, as expected for [H{Me₃Pt(OSiMe(2-C₅H₄N)₂)₂}⁺ and [H{Me₃Pt(OSiMe(2-C₅H₄N)₂)₂}⁺-d₁₂.

[PtI₂Me₂(bps)], 4. To a stirred solution of **1** (0.02 g, 0.455 mmol) in CH₂Cl₂ (5 mL) was added excess iodine (0.012 g). The mixture was stirred for 2 h., the solvent was removed under vacuum, and the red product was washed with pentane (3 x 3 mL) and ether (3 x 3 mL) and dried under vacuum. Yield 84%. NMR in CD₂Cl₂: $\delta(^1\text{H}) = 0.81$ [s, 6H, Si-Me]; 2.39 [s, 6H, $^2J_{\text{PtH}} = 71$ Hz, PtMe]; 7.42 [m, 2H, H⁵]; 7.78 [m, 2H, H³]; 7.86 [m, 2H, H⁴]; 9.36 [m, 2H, $^3J_{\text{PtH}} = 25$ Hz, H⁶].

Structure Determinations: Data were collected at low temperature (150 K) using a Nonius Kappa-CCD area detector diffractometer. Details are in the cif files. Figures are shown with 25% thermal ellipsoids.

Crystal data:

1: C₁₄H₂₀N₂PtSi, fw = 439.50, monoclinic, C2/c, a = 15.2967(7), b = 12.8601(6), c = 15.8369(8) Å, $\beta = 102.191(3)^\circ$, V = 3045.1(3) Å³, Z = 8, d(calc) = 1.917 Mg m⁻³, R1 = 0.0469, wR2 = 0.1124 [I > 2s(I)].

2: C₄₇H₃₉BF₁₈N₄O₂Pt₂Si₂, fw = 1490.99, triclinic, P-1, a = 11.812(2), b = 13.535(3), c = 16.700(3) Å, $\alpha = 79.94(3)$, $\beta = 80.78(3)$, $\gamma = 79.76(3)^\circ$, V = 2564.0(9) Å³, Z = 2, d(calc.) = 1.931 Mg m⁻³, R1 = 0.0437, wR2 = 0.0972 [I > 2s(I)].

3c: C₂₁H₂₆N₂O₃PtSi, fw = 577.62, monoclinic, P2₁/n, a = 14.305(3), b = 10.130(2), c = 14.985(3) Å, $\beta = 99.04(3)^\circ$, V = 2144.6(7) Å³, Z = 4, d(calc) = 1.789 Mg m⁻³, R1 = 0.0298, wR2 = 0.0732 [I > 2s(I)].

4: C₁₄H₂₀I₂N₂PtSi, fw = 693.30, monoclinic, P2₁/n, a = 9.3692(3), b = 13.7960(5), c = 14.4724(5) Å, $\beta = 100.964(2)^\circ$, V = 1836.52(11) Å³, Z = 4, d(calc) = 2.507 Mg m⁻³, R1 = 0.0507, wR2 = 0.1369 [I > 2s(I)].

References

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