

Preparation and Coordination Properties Including Catalytic Activities of a Bulky 2-Methyl-3-thioxo-1,3-diphosphapropene

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Experimental Details

4: A solution of **2** (0.54 g, 1.11 mmol) and sulfur (1.16 mmol as S) in toluene (10 mL) was refluxed for 20 h and subsequently cooled to room temperature. The solvent was removed in vacuo and the residue was purified by silica-gel column chromatography (hexane/toluene) to afford 0.52 g of **4** (91% yield). Colorless crystals, mp 67 °C; $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 314.8 (P=C), 50.9 (P=S), $^2J_{\text{PP}} = 123$ Hz; ^1H NMR (400 MHz, CDCl_3): δ 8.02–7.96 (m, 4H, Ph), 7.56–7.49 (m, 6H, Ph), 7.47 (brs, 2H, Mes*), 1.57 (dd, $^3J_{\text{PH}} = 17.6$ Hz, $^3J_{\text{PH}} = 14.4$ Hz, 3H, CH₃), 1.51 (s, 18H, *o*-*t*-Bu), 1.37 (s, 9H, *p*-*t*-Bu); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 171.6 (dd, $^1J_{\text{PC}} = 65.9$ Hz, $^1J_{\text{PC}} = 59.3$ Hz, P=C), 154.1 (s, *o*-Mes*), 151.2 (s, *p*-Mes*), 136.9 (dd, $^1J_{\text{PC}} = 67.4$ Hz, $^3J_{\text{PC}} = 19.0$ Hz, *ipso*-Mes*), 133.1 (d, $^2J_{\text{PC}} = 10.3$ Hz, *o*-Ph), 132.6 (pseudo-t, $^1J_{\text{PC}} = 10.6$ Hz, $^3J_{\text{PC}} = 10.6$ Hz, *ipso*-Ph), 129.6 (s, *p*-Ph), 128.8 (d, $^3J_{\text{PC}} = 2.8$ Hz, *m*-Ph), 122.7 (s, *m*-Mes*), 38.5 (s, *o*-CMe₃), 35.6 (s, *p*-CMe₃), 33.5 (d, $^4J_{\text{PC}} = 6.3$ Hz, *o*-CMe₃), 32.0 (s, *p*-CMe₃), 21.4 (dd, $^2J_{\text{PC}} = 14.3$ Hz, $^2J_{\text{PC}} = 7.5$ Hz, CH₃); IR (KBr): ν 656 cm⁻¹ (P=S). Anal. Calcd for C₃₂H₄₂P₂S: C, 73.81; H, 8.13%. Found: C, 73.24, H, 8.01%.

6 and **7:** To a solution of **4** (100 mg, 0.192 mmol) in THF (10 mL) was added W(CO)₅(thf) [ca. 0.20 mmol, prepared by irradiation of a solution of W(CO)₆ in THF (20 mL) with a medium-pressure Hg lamp (100W)] and the mixture was stirred for 16 h. The solution was concentrated in vacuo and the residue was purified by silica-gel column chromatography (hexane/toluene) to afford **6** including the desulfurized complex [Mes*P=C(Me)PPh₂][W(CO)₅] (69 mg, ca. 42%) and **7** (23 mg, 15%) together with the starting material **4** (33 mg, 33% recover). Attempted recrystallization of **6** was not successful due to the disproportionation to **4** and **7**. **7:** Brown solid, mp (dec): 143 °C; $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 324.6 ($^1J_{\text{PW}} = 278$ Hz, P=C), 56.9 (P=S), $^2J_{\text{PP}} = 123$ Hz; ^1H NMR (400 MHz, CDCl_3): δ 7.65–7.57 (m, 6H, Ph), 7.51–7.48 (m, 6H, Ph), 1.62 (s, 18H, *o*-*t*-Bu), 1.34 (s, 9H, *p*-*t*-Bu), 1.11 (dd, $^2J_{\text{PH}} = 20.8$ Hz, $^2J_{\text{PH}} = 15.2$ Hz, 3H, CH₃); IR (KBr): ν 2015, 1905, 1871 (CO), 602 (P=S). Anal. Calcd for C₃₆H₄₂O₄P₂SW: C, 52.95; H, 5.18%. Found: C, 52.82, H, 5.31%.

8: A solution of **4** (100 mg, 0.192 mmol) and PdCl₂(MeCN)₂ (0.192 mmol) in dichloromethane (10 mL) was stirred at room temperature for 30 min. Hexane (10 mL) was added to the reaction mixture and the precipitated complex was collected by filtration. The yellow solid was recrystallized in dichloromethane at 0 °C to afford **8** (0.113 g, 84%). Yellowish-brown solid, mp 218–220 °C; ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 277.5 (P=C), 55.5 (P=S), ²J_{PP} = 95 Hz; ¹H NMR (400 MHz, CDCl₃): δ 7.80–7.33 (m, 6H, Ph), 7.66–7.63 (m, 4H, Ph), 7.54 (d, ⁴J_{PH} = 4.0 Hz, 2H, Mes*), 1.63 (d, ⁵J_{PH} = 1.2 Hz, 18H, *o*-*t*-Bu), 1.41 (dd, ²J_{PH} = 27.2 Hz, ²J_{PH} = 15.2 Hz, 3H, CH₃), 1.31 (s, 9H, *p*-*t*-Bu); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 155.4 (d, ¹J_{PC} = 3.5 Hz, *o*-Mes*), 154.2 (dd, ¹J_{PC} = 62.4 Hz, ¹J_{PC} = 41.0 Hz, P=C), 134.7 (d, ⁴J_{PC} = 3.0 Hz, *p*-Mes*), 132.7 (d, ²J_{PC} = 11.1 Hz, *o*-Ph), 130.3 (d, ⁴J_{PC} = 13.1 Hz, *p*-Ph), 129.1 (dd, ¹J_{PC} = 71.1 Hz, ³J_{PC} = 12.4 Hz, *ipso*-Mes*), 125.3 (d, ³J_{PC} = 9.5 Hz, *m*-Ph), 124.7 (dd, ¹J_{PC} = 83.4 Hz, ³J_{PC} = 10.9 Hz, *ipso*-Ph), 120.2 (s, *m*-Mes*), 39.8 (s, *o*-CMe₃), 35.5 (s, *p*-CMe₃), 35.2 (s, *o*-CMe₃), 31.3 (s, *p*-CMe₃), 21.5 (dd, ²J_{PC} = 12.7 Hz, ²J_{PC} = 3.8 Hz, CH₃); IR (KBr): ν 654 cm⁻¹ (P=S). Anal. Calcd for C₃₂H₄₂Cl₂P₂PdS·1.5CH₂Cl₂: C, 48.74; H, 5.49%. Found: C, 49.14, H, 5.48%.

10: A solution of **4** (100 mg, 0.192 mmol), [(*η*³-allyl)PdCl]₂ (0.096 mmol), and silver(I) triflate (2.11 mmol) in dichloromethane (5 mL) was stirred at room temperature for 2 h. The solution was filtered through Celite and the solvent was removed in vacuo. The residual solid was washed with hexane to afford 0.148 g of **10** (94% yield). Yellow crystals, mp 125 °C; ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 289.2 (P=C), 61.0 (P=S), ²J_{PP} = 126 Hz; ¹H NMR (400 MHz, CDCl₃): δ 7.78–7.57 (m, 12H, arom), 5.91 (dddd, 1H, *J* = 13.2 Hz, *J* = 7.2 Hz, CH), 4.99 (dd, 1H, *J* = 7.2 Hz, CHH), 4.72 (d, 1H, *J* = 7.2 Hz, CHH), 3.85 (dd, 1H, *J* = 13.2 Hz, *J* = 13.2 Hz, CHH), 3.57 (d, 1H, *J* = 13.2 Hz, CHH), 1.51 (s, 9H, *o*-*t*-Bu), 1.49 (dd, ²J_{PH} = 14.8 Hz, ²J_{PH} = 10.0 Hz, 3H, CH₃), 1.43 (s, 9H, *o*-*t*-Bu), 1.34 (s, 9H, *p*-*t*-Bu); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 167.1 (dd, ¹J_{PC} = 61.6 Hz, ¹J_{PC} = 29.1 Hz, P=C), 155.8 (s, *p*-Mes*), 155.5 (d, ²J_{PC} = 1.3 Hz, *o*-Mes*), 155.5 (s, *o*-Mes*), 134.6 (pt, ⁴J_{PC} = ⁶J_{PC} = 2.9 Hz, *p*-Ph), 132.3 (d, ²J_{PC} = 8.4 Hz, *o*-Ph), 132.3 (d, ²J_{PC} = 8.4 Hz, *o*-Ph), 130.4 (d, ³J_{PC} = 8.4 Hz, *m*-Ph), 130.3 (d, ³J_{PC} = 8.4 Hz, *m*-Ph), 126.1 (dd, ¹J_{PC} = 16.4 Hz, ³J_{PC} = 8.0 Hz, *ipso*-Mes*), 125.7 (pt, ²J_{PC} = 14.3 Hz, CH), 125.3 (dd, ¹J_{PC} = 16.4 Hz, ³J_{PC} = 8.0 Hz, *ipso*-Ph), 124.4 (d, ³J_{PC} = 6.5 Hz, *m*-Mes*), 121.3 (q, ¹J_{FC} = 321.0 Hz, CF₃SO₃), 74.7 (d, ²J_{PC} = 4.8 Hz, CH₂), 74.5 (d, ²J_{PC} = 34.4 Hz, CH₂), 39.0 (s, *o*-CMe₃), 38.9 (s, *o*-CMe₃), 35.7 (s, *p*-CMe₃), 34.0 (d, ⁴J_{PC} = 1.9 Hz, *o*-CMe₃), 33.9 (d, ⁴J_{PC} = 1.8 Hz, *o*-CMe₃), 31.3 (s, *p*-CMe₃), 21.8 (dd, ²J_{PC} = 7.5 Hz, ²J_{PC} = 5.5 Hz, CH₃); IR (KBr): ν 640 cm⁻¹ (P=S). Anal. Calcd for C₃₆H₄₇F₃O₃P₂PdS₂: C, 52.91; H, 5.80%. Found: C, 53.01, H, 6.05%.

11: A solution of **2** (100 mg, 0.205 mmol), [η^3 -allyl]PdCl₂ (0.102 mmol), and silver(I) triflate (2.25 mmol) in dichloromethane (5 mL) was stirred at room temperature for 6 h. The solution was filtered through Celite and the solvent was removed in vacuo to afford practically pure **11** (0.16 g, 100%). Complex **11** decomposed in several hours in an argon atmosphere. NMR data for **11**: ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 249.8 (P=C), 12.4 (PPh₂), ²J_{PP} = 11 Hz; ¹H NMR (400 MHz, CDCl₃): δ 7.61 (m, 8H, arom), 7.53 (dm, *J* = 2.8 Hz, arom), 5.92 (m, 1H, CH), 4.93 (m, 2H, CHH), 3.78 (m, 2H, CHH), 1.73 (dd, ³J_{PH} = 29.4 Hz, ³J_{PH} = 12.6 Hz, CH₃), 1.55 (s, 18H, *o-t*-Bu), 1.35 (s, 9H, *p-t*-Bu).