

Group 6 metal complexes with a hemilabile tridentate xantsil ligand and facile insertion of ^tBuCN into a W–Si bond [xantsil = (9,9-dimethylxanthene-4,5-diyl)bis(dimethylsilyl)]

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Synthesis of Cp*W{ κ^2 (Si,Si)-xantsil}(CO)₂(H) (1a). A Pyrex sample tube (10 mm o.d.) with a Teflon vacuum stopcock was charged with a solution of Cp*W(CO)₃Me (20 mg, 0.047 mmol) and xantsilH₂ (16 mg, 0.049 mmol) in pentane (*ca.* 2 mL) and degassed under vacuum. The mixture was irradiated with a 450 W medium pressure Hg lamp for 20 minutes at 7 °C. During the photoreaction, the mixture was degassed at 5 minutes intervals by a freeze-pump-thaw cycle on a vacuum line. After removal of the volatiles, the residue was washed with pentane several times and dried. Compound **1a** was obtained as a white powder (27 mg, 0.038 mmol, 80%). Found: C, 53.16; H, 5.89. Calc. for C₃₁H₄₀O₃Si₂W: C, 53.14; H, 5.75. IR (KBr): 1901 (s, ν_{CO}), 1844 (m, ν_{CO}), cm⁻¹. ¹H NMR (300 MHz, C₆D₆): δ 7.43 (dd, 2 H, $J = 7.4$, 1.4 Hz, ArH), 7.24 (dd, 2 H, $J = 7.4$, 1.4 Hz, ArH), 7.06 (t, 2 H, $J = 7.4$ Hz, ArH), 1.57 (s, 3 H, CMe₂), 1.35 (s, 3 H, CMe₂), 1.23 (s, 6 H, SiMe₂), 1.21 (s, 15 H, C₅Me₅), 1.10 (s, 6 H, SiMe₂), -3.95 (s, 1 H, $^1J_{\text{WH}} = 83$ Hz, $^1J_{\text{SiH}} = 24$ Hz, W–H). ¹³C {¹H} NMR (75.5 MHz, toluene-*d*₈): δ 223.4 (CO), 160.2, 133.0, 129.1, 125.3, 123.3 (ArC, one of the signals is overlapped with those of toluene-*d*₈), 102.7 (C₅Me₅), 36.5 (CMe₂), 31.1 (CMe₂), 22.9 (CMe₂), 10.2 (C₅Me₅), 9.1 (SiMe₂), 2.7 (SiMe₂). ²⁹Si {¹H} NMR (59.6 MHz, toluene-*d*₈): 10.8 ($^1J_{\text{WSi}} = 14$ Hz). MS (EI): m/z 700 (M⁺), 672 (M⁺–CO), 644 (M⁺–2CO).

Synthesis of Cp*Mo{ κ^2 (Si,Si)-xantsil}(CO)₂(H) (1b): A mixture of Cp*Mo(CO)₃Me (20 mg, 0.060 mmol) and xantsilH₂ (20 mg, 0.061 mmol) in pentane (*ca.* 2 mL) was irradiated as described for **1a**. Workup similar to that used for **1a** yielded **1b** as a white powder (29 mg, 0.047 mmol, 78%). Found: C, 60.77; H, 6.74. Calc. for C₃₁H₄₀O₃Si₂Mo: C, 60.76; H, 6.58. IR (KBr): 1909 (s, ν_{CO}), 1851 (m, ν_{CO}) cm⁻¹. ¹H NMR (300 MHz, toluene-*d*₈): δ 7.32 (dd, 2 H, $J = 7.4, 1.4$ Hz, ArH), 7.14 (dd, 2 H, $J = 7.4, 1.4$ Hz, ArH), 6.96 (t, 2 H, $J = 7.4$ Hz, ArH), 1.49 (s, 3 H, CMe₂), 1.27 (s, 3 H, CMe₂), 1.11 (s, 15 H, C₅Me₅), 1.10 (s, 6 H, SiMe₂), 0.81 (s, 6 H, SiMe₂), -5.65 (s, 1 H, $^2J_{\text{SiH}} = 37$ Hz, Mo-H). ¹³C{¹H} NMR (75.5 MHz, toluene-*d*₈): δ 232.7 (CO), 160.2, 134.6, 133.0, 129.4, 123.4 (ArC, one of the signals is overlapped with those of toluene-*d*₈), 103.7 (C₅Me₅), 36.4 (CMe₂), 31.0 (CMe₂), 22.8 (CMe₂), 10.2 (C₅Me₅), 8.3 (SiMe₂), 4.1 (SiMe₂). ²⁹Si{¹H} NMR (59.6 MHz, toluene-*d*₈): δ 15.2. MS (EI): m/z 614 (M⁺).

Synthesis of Cp*W{ κ^3 (Si,Si,O)-xantsil}(CO)(H) (2a). A solution of **1a** (33 mg, 0.047 mmol) in toluene (*ca.* 1 mL) was placed in a Pyrex sample tube (10 mm o.d.) with a Teflon vacuum stopcock and was irradiated with a 450 W medium pressure Hg lamp for 50 minutes at 7 °C. The reaction mixture was degassed at 20 minutes intervals by a freeze-pump-thaw cycle on a vacuum line. After removal of the volatiles, the residue was washed with hexane and dried. Compound **2a** was obtained as an orange powder (29 mg, 0.043 mmol, 92%). Found: C, 53.67; H, 6.07. Calc. for C₃₀H₄₀O₂Si₂W: C, 53.57; H, 5.99. IR (KBr): 1813 (s, ν_{CO}) cm⁻¹. ¹H NMR (300 MHz, C₆D₆): δ 7.37-7.50 (m, 2 H, ArH), 6.84-7.01 (m, 4 H, ArH), 1.69 (s, 15 H, C₅Me₅), 1.38 (s, 3 H, CMe₂), 1.24 (s, 3 H, CMe₂), 0.98 (s, 6 H, SiMe₂), 0.91 (br s, 6 H, SiMe₂), 0.78 (s, 1 H, W-H). ¹³C{¹H} NMR (75.5 MHz, toluene-*d*₈): δ 231.5 (CO), 162.3, 141.1, 133.6, 130.8, 125.7, 123.9 (ArC), 99.9 (C₅Me₅), 35.7 (CMe₂), 33.1 (CMe₂), 24.4 (CMe₂), 11.3 (C₅Me₅), 10.6 (SiMe₂), 5.6 (br, SiMe₂). MS (EI): m/z 672 (M⁺), 644 (M⁺-CO).

Synthesis of Cp*Mo{ κ^3 (Si,Si,O)-xantsil}(CO)(H) (2b). Complex **2b** was prepared by the photoreaction of **1b** (17 mg, 0.027 mmol) in a manner similar to that used for **2a**. The product was isolated as an orange powder (14 mg, 0.023 mmol, 88%).

Found: C, 61.27; H, 6.88. Calc. for $C_{30}H_{40}O_2Si_2Mo$: C, 61.62; H, 6.89. IR (KBr): 1819 (s, ν_{CO}), cm^{-1} . 1H NMR (300 MHz, toluene- d_8): δ 7.26-7.34 (m, 2 H, ArH), 6.74-6.89 (m, 4 H, ArH), 1.62 (s, 15 H, C_5Me_5), 1.38 (s, 3 H, CMe_2), 1.23 (s, 3 H, CMe_2), 0.90 (s, 6 H, $SiMe_2$), 0.82 (s, 6 H, $SiMe_2$), -2.30 (s, 1 H, Mo-H). $^{13}C\{^1H\}$ NMR (75.5 MHz, toluene- d_8): 236.3 (CO), 160.5, 138.6, 133.3, 130.5, 125.2, 123.8 (ArC), 101.3 (C_5Me_5), 35.5 (CMe_2), 33.2 (CMe_2), 24.1 (CMe_2), 11.2 (C_5Me_5), 10.3 ($SiMe_2$), 5.2 ($SiMe_2$). $^{29}Si\{^1H\}$ NMR (59.6 MHz, toluene- d_8): 32.7.

Synthesis of $Cp^*W\{\kappa^3(Si,N,C)\text{-xantsil}(N=C^tBu)\}(CO)(H)$ (3**).** A toluene (3 mL) solution of **2a** (20 mg, 0.029 mmol) and $tBuCN$ (12 mg, 0.14 mmol) was stirred at room temperature under an atmosphere of dinitrogen. The solution immediately turned from orange-red to purple. After stirring for 90 minutes, volatiles were removed under reduced pressure. Washing the residue with pentane and drying under vacuum gave a purple powder of **3** (19 mg, 0.025 mmol, 85%). Found: C, 55.51; H, 6.49; N, 1.74. Calc. for $C_{35}H_{49}NO_2Si_2W$: C, 55.62; H, 6.53; N, 1.85. IR (KBr): 1790 (s, ν_{CO}), 1606 (m, ν_{CN}) cm^{-1} . 1H NMR (300 MHz, C_6D_6): δ 7.71-7.77 (m, 1 H, ArH), 7.25-7.32 (m, 2 H, ArH), 6.97-7.09 (m, 3 H, ArH), 1.89 (s, 15 H, C_5Me_5), 1.53 (s, 3 H, CMe_2), 1.30 (s, 3 H, CMe_2), 1.20 (s, 3 H, $SiMe_2$), 1.05 (s, 3 H, $SiMe_2$), 0.83 (s, 3 H, $SiMe_2$), 0.81 (s, 9 H, tBu), 0.46 (s, 3 H, $SiMe_2$), the W-H signal could not be observed probably due to the overlap with other signals. Thermal instability of **3** in C_6D_6 at room temperature prevents us from measuring the $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra. MS (EI): m/z 755 (M^+), 727 (M^+-CO).

X-ray Crystal Structure Determination of **2a and **3**.** X-ray quality single crystals were obtained from toluene/hexane at -20 °C for **2a** as orange crystals and **3** as purple crystals. Intensity data for the analysis were collected on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) under a cold nitrogen stream ($T = 150$ K). Both structures were solved by direct methods using the SHELXS-97 program and refined by full matrix least-squares techniques on all F^2 data with SHELXL-97.¹ Anisotropic refinement was

applied to all non-hydrogen atoms, and all the hydrogen atoms except a hydrido ligand were put at calculated positions. The metal-hydrido hydrogens were not located in the difference map and were not included in the refinement. CCDC reference numbers 284200 (**2a**) and 284201 (**3**). Refinement of the Flack parameter for **2a** yielded 0.02(1), confirming the correct polarity.² The structure of **3** was solved as a racemic twin (BASF = 0.318) in the acentric space group $P2_12_12_1$. Crystallographic data are available as CIF files.

References

1. G. M. Sheldrick, *SHELXS-97, Programs for Solving X-ray Crystal Structures*, University of Göttingen, 1997; G. M. Sheldrick, *SHELXL-97, Programs for Refining X-ray Crystal Structures*, University of Göttingen, 1997.
2. H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876.