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

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Synthesis of Cp*W{κ²(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 ºC. 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, νCO), 1844 (m, νCO),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), 1.06 (s, 6 H, SiMe₂), 1.25 (s, 15 H, C₅Me₅), 1.10 (s, 6 H, SiMe₂). 13C{¹H} NMR (75.5 MHz, toluene-d₈): 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-d₈), 102.7 (C₅Me₅), 36.5 (CMe₂), 31.1 (CMe₂), 22.9 (CMe₂), 10.2 (C₅Me₅), 9.1 (SiMe₂), 2.7 (SiMe₂). ²⁰Si{¹H} NMR (59.6 MHz, toluene-d₈): 10.8 (¹J_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 xantsilH (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 C_{31}H_{40}O_{3}Si_{2}Mo: 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, 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, CMe_2), 1.27 (s, 3 H, CMe_2), 1.11 (s, 3 H, C_5Me_5), 1.10 (s, 3 H, SiMe_2), 0.81 (s, 3 H, SiMe_2), –5.65 (s, 1 H, J_{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 (C_5Me_5), 36.4 (CMe_2), 31.0 (CMe_2), 22.8 (CMe_2), 10.2 (C_5Me_5), 8.3 (SiMe_2), 4.1 (SiMe_2). 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 ºC. 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 C_{30}H_{40}O_{2}Si_{2}W: C, 53.57; H, 5.99. IR (KBr): 1813 (s, ν(CO)) cm^{-1}. 1H NMR (300 MHz, C_6D_6): δ 7.37-7.50 (m, 2 H, ArH), 6.84-7.01 (m, 4 H, ArH), 1.69 (s, 15 H, C_5Me_5), 1.38 (s, 3 H, CMe_2), 1.24 (s, 3 H, CMe_2), 0.98 (s, 6 H, SiMe_2), 0.91 (br s, 6 H, SiMe_2), 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 (C_5Me_5), 35.7 (CMe_2), 33.1 (CMe_2), 24.4 (CMe_2), 11.3 (C_5Me_5), 10.6 (SiMe_2), 5.6 (br, SiMe_2). MS (EI): m/z 672 (M^+), 644 (M^{2+}–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$_2$Si$_2$Mo: C, 61.62; H, 6.89. IR (KBr): 1819 (s, $\nu_{\text{CO}}$), cm$^{-1}$. $^1$H NMR (300 MHz, toluene-$d_8$): $\delta$ 7.26-7.34 (m, 2 H, ArH), 6.74-6.89 (m, 4 H, ArH), 1.62 (s, 15 H, C$_5$Me$_5$), 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 {$^1$H} 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$_5$Me$_5$), 35.5 (CMe$_2$), 33.2 (CMe$_2$), 24.1 (CMe$_2$), 11.2 (C$_5$Me$_5$), 10.3 (SiMe$_2$), 5.2 (SiMe$_2$). $^{29}$Si {$^1$H} NMR (59.6 MHz, toluene-$d_8$): 32.7.

**Synthesis of Cp*W{Si,N,C}-xantsil(N=CtBu)}(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$_2$Si$_2$W: C, 55.62; H, 6.53; N, 1.85. IR (KBr): 1790 (s, $\nu_{\text{CO}}$), 1606 (m, $\nu_{\text{CN}}$) cm$^{-1}$. $^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ 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$_5$Me$_5$), 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$_6$D$_6$ at room temperature prevents us from measuring the $^{13}$C {$^1$H} and $^{29}$Si {$^1$H} 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. 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.\textsuperscript{2} The structure of 3 was solved as a racemic twin (BASF = 0.318) in the acentric space group \textit{P}2\textsubscript{1}2\textsubscript{1}2\textsubscript{1}. Crystallographic data are available as CIF files.

References