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

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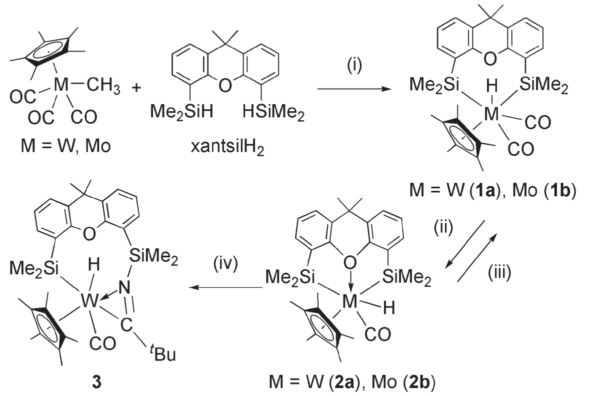
**The synthesis and characterization of tungsten and molybdenum complexes of the xanthene-based bis(silyl) ligand (xantsil) with a $\kappa^3$(*Si,Si,O*) coordination mode are reported, where an insertion of $^{t}$BuCN into a tungsten–silicon bond leads to formation of an $\eta^2$-iminoacyl complex.**

Transition metal bis(silyl) and silyl hydrido complexes have received considerable attention as key intermediates in the transition metal-catalysed dehydrogenative double silylation and hydrosilylation of unsaturated organic compounds.[1,2] In these catalytic reaction sequences, generation of coordinatively unsaturated species is essential for binding the substrates. Our group has recently developed a bis(silyl) chelating ligand, (9,9-dimethylxanthene-4,5-diyl)bis(dimethylsilyl) "xantsil".[3] Because of the weak coordination ability of an ether oxygen in the xanthene backbone, we observed that xantsil can be coordinated to a ruthenium centre in either $\kappa^2$(*Si,Si*) or $\kappa^3$(*Si,Si,O*) fashion.[3] We focused on this hemilabile nature[4] of the xantsil ligand to exploit *in situ* generation of coordinatively unsaturated bis(silyl) and silyl hydrido complexes. Here we describe the synthesis of group 6 metal bis(silyl) hydrido complexes having a $\kappa^2$- or $\kappa^3$-xantsil ligand. The lability of the oxygen coordination in $\kappa^3$-xantsil complexes results in an insertion of $^{t}$BuCN into a tungsten–silicon bond.

Ultraviolet irradiation of a 1 : 1 mixture of $\mathrm{Cp^*M(CO)_3Me}$ (M = W, Mo) and xantsil$\mathrm{H_2}$ in pentane for 20 min at 7 °C afforded the xantsil complexes $\mathrm{Cp^*M}\{\kappa^2$(*Si,Si*)-xantsil$\}$-$\mathrm{(CO)_2(H)}$ [M = W (**1a**), Mo (**1b**)] in 80 and 78% isolated yields, respectively (Scheme 1). The products are characterised by analytical and spectroscopic methods. Two $\mathrm{SiMe_2}$ moieties of complex **1** are equivalent in the NMR spectra in $\mathrm{C_6D_6}$ solution. The $^1$H NMR spectrum exhibits one singlet of a hydrido ligand at $\delta$ –3.95 (**1a**) and –5.65 (**1b**) with silicon satellites [$^2J_{\mathrm{SiH}}$ = 24 (**1a**) and 37 (**1b**) Hz]. These $^2J_{\mathrm{SiH}}$ values suggest the presence of non-classical Si–H interaction.[2] The $^{29}$Si{$^1$H} NMR spectrum shows one signal at $\delta$ 10.8 (**1a**) and 15.2 (**1b**) which is downfield shifted from that of xantsil$\mathrm{H_2}$ ($\delta$ –22.2) due to the coordination to tungsten. The IR spectrum of **1a** exhibits two CO stretching bands in the terminal CO region (1901 and 1844 cm$^{-1}$). We could not get crystals of **1** suitable for a full X-ray analysis, but a tentative analysis using a poor-quality crystal of **1a** revealed the piano-stool structure with mutually cis arrangements of two carbonyl and also two silyl ligands.



**Scheme 1** Reagents and conditions: (i) *hν*, –CO, –$\mathrm{CH_4}$, pentane, 7 °C, 20 min; (ii) *hν*, –CO, toluene, 7 °C, 50 min; (iii) + CO, $\mathrm{C_6D_6}$, rt, 1 month; (iv) + $^{t}$BuCN, toluene, rt, 90 min.

Further irradiation of a toluene solution of **1a** and **1b** for 50 min resulted in dissociation of another carbonyl ligand, and $\mathrm{Cp^*M}\{\kappa^3$(*Si,Si,O*)-xantsil$\}$(CO)(H) [M = W (**2a**) and Mo (**2b**)] were obtained in 92 and 88% yields, respectively. The IR spectrum of **2a** shows one CO vibration at 1813 cm$^{-1}$ which is shifted to a lower wavenumber region compared to those of **1a**. The $^1$H NMR spectra show the resonances of hydrido ligands at unusually low field [0.78 (**2a**) and –2.30 (**2b**) ppm] presumably due to the large magnetic anisotropy around the metal centre. In the $^{29}$Si{$^1$H} NMR spectrum for **2b**, the downfield-shift of the signal ($\delta$ 32.7) compared to that of **1b** suggests the presence of a stronger $\sigma$-donation of the silyl ligands in **2b**. This strong $\sigma$-donating ability of xantsil probably accelerates the photochemical dissociation of a carbonyl ligand in **1**.

The molecular structure of **2a** was determined by X-ray analysis (Fig. 1).‡ The W–O bond length [2.330(5) Å] indicates the coordination of xanthene oxygen to the metal centre. The W–Si bond distances [2.553(3) and 2.582(3) Å] are within the range of those (2.533–2.633 Å) observed in related Cp-containing silyltungsten complexes.[5] Thus, the xantsil ligand is in a tridentate $\kappa^3$(*Si,Si,O*) coordination mode to satisfy the 18-electron rule. Although the hydrido ligand of **2a** could not be located in the Fourier difference electron density map, it might be positioned within the widened Cp(centroid)–W–Si(2) angle 144.7°.

The photo-induced CO dissociation from **1** is reversible. In a sealed NMR tube, standing a $\mathrm{C_6D_6}$ solution of **2** in the presence of one equivalent of CO, which had been quantitatively formed *via*

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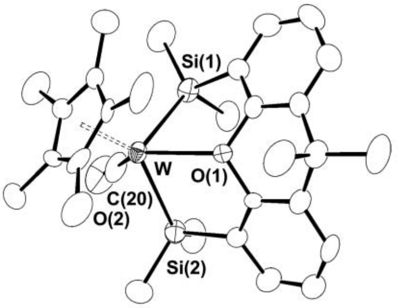

**Fig. 1** Molecular structure of **2a**. Selected bond distances (Å) and angles (°): W–Si(1) 2.553(3), W–Si(2) 2.582(3), W–O(1) 2.330(5), W–C(20) 1.93(1), O(2)–C(20) 1.15(1), Si(1)–W–Si(2) 98.76(9), Si(1)–W–O(1) 71.6(2), Si(2)–W–O(1) 76.3(2), Si(1)–W–C(20) 81.1(4), Si(2)–W–C(20) 65.6(3).

photolysis of **1**, led to slow conversion of **2** into **1** at room temperature almost quantitatively after 1 month. This observation indicates that the xantsil ligand in **2** is hemilabile due to the facile dissociation of metal–oxygen(xantsil) bond.

To confirm further the hemilability of the xantsil ligand in **2**, the reaction of **2a** with $^t$BuCN was investigated. Thus, treatment of a toluene solution of **2a** with $^t$BuCN at room temperature gave the nitrile-insertion product Cp*W{$\kappa^3$(*Si,N,C*)-xantsil(N=C$^t$Bu)}(CO)(H) (**3**) in 85% isolated yield.[6] The IR spectrum of **3** exhibits a band at 1606 cm$^{-1}$, assignable to the CN stretching mode of the $\eta^2$-iminoacyl ligand. Although the diamagnetic nature of **3** indicates the existence of a hydrido ligand, we could not assign the hydrido signal by $^1$H-NMR spectroscopy because there is no characteristic signal in the usual hydrido region (below 0 ppm). Thermal instability of **3** in a $C_6D_6$ solution even at room temperature made it difficult for us to characterise **3** further in solution.

On the other hand, the crystal structure of **3** has been determined by X-ray diffraction study (Fig. 2).‡ **3** has a novel 9-membered chelate ring, and the tungsten centre bears an $\eta^2$-iminoacyl, a silyl, a Cp* and a CO ligand. The W–N(1) and W–C(1) bond distances [2.235(5) and 2.063(6) Å, respectively] confirm the $\eta^2$-iminoacyl structure. The C(1)–N(1) bond length of 1.257(9) Å is comparable to those of previously reported tungsten $\eta^2$-iminoacyl complexes.[7] The puckered angle between the least-squares planes of two aromatic rings of the xantsil moiety [30.9 (3)°] is substantially smaller than that of oxygen-coordinated **2a** [44.0 (3)°].

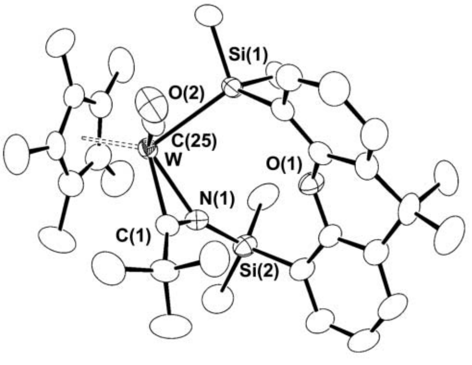

**Fig. 2** Molecular structure of **3**. Selected bond distances (Å) and angles (°): W–Si(1) 2.651(2), W–N(1) 2.235(5), W–C(1) 2.063(6), W–C(25) 1.916(6), Si(2)–N(1) 1.744(6), O(2)–C(25) 1.173(8), N(1)–C(1) 1.257(9), Si(1)–W–N(1) 93.7(2), Si(1)–W–C(25) 63.9(2), N(1)–W–C(1) 33.7(2), C(1)–W–C(25) 89.9(3), W–N(1)–Si(2) 147.3(3), W–N(1)–C(1) 65.6(3), W–C(1)–N(1) 80.6(4), C(1)–N(1)–Si(2) 146.5(5).

A plausible formation mechanism for **3** involves the initial coordination of nitrile to the tungsten centre of **2a** having a hemilabile xantsil ligand, followed by a 1,2-silyl migration to the nitrogen of the nitrile ligand. This type of migratory insertion of a nitrile C≡N bond into a metal–silyl bond to give an $\eta^2$-iminoacyl complex has been only recently reported by Bergman *et al.* for rhodium complexes[8] and by Nakazawa *et al.* for an iron complex.[9] In these reactions, the resulting $\eta^2$-iminoacyl complexes act as intermediates in the C–C bond activation of nitriles. On the other hand, in our case, the produced $\eta^2$-iminoacyl complex **3** is relatively stable and no C–C bond activation product has been observed.

In conclusion, we synthesised and characterised the first tungsten and molybdenum xantsil complexes. The hemilability of the $\kappa^3$-xantsil ligand in tungsten complex **2a** was confirmed by the reaction with CO giving the CO addition product **1a**, and by the reaction with $^t$BuCN giving the product **3** with the C≡N bond insertion into a W–Si bond. Further investigation into the reactivity of **2** is currently in progress.

## Notes and references

‡ *Crystal data* for **2a**: $C_{30}H_{40}O_2Si_2W$, $M$ = 672.65, orthorhombic, space group $Pca2_1$ (no. 29), $a$ = 9.5123(3), $b$ = 18.0026(6), $c$ = 16.9940(7) Å, $V$ = 2910.2(2) Å$^3$, $Z$ = 4, $T$ = 150 K, $\mu$(Mo–K$\alpha$) = 4.08 mm$^{-1}$, 23638 reflections measured, 6401 unique ($R_{int}$ = 0.058), $R1$ = 0.049 and $wR2$ = 0.113 (all data). For **3**: $C_{35}H_{49}NO_2Si_2W$, $M$ = 755.78, orthorhombic, space group $P2_12_12_1$ (no. 19), $a$ = 11.3139(5), $b$ = 14.8370(5), $c$ = 20.5961(7) Å, $V$ = 3457.4(2) Å$^3$, $Z$ = 4, $T$ = 150 K, $\mu$(Mo–K$\alpha$) = 3.44 mm$^{-1}$, 32360 reflections measured, 7893 unique ($R_{int}$ = 0.083), $R1$ = 0.040 and $wR2$ = 0.111 (all data). 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**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512759a.

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