Cyanosilylation of a Molybdenum(VI) Dioxo Complex

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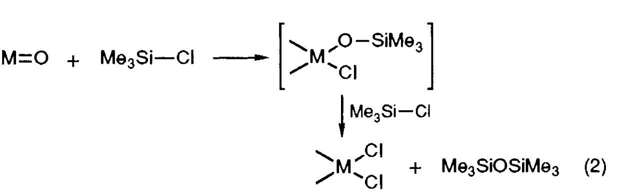
Dioxobis(*N,N*-diethyldithiocarbamato)molybdenum(VI) reacts with trimethylcyanosilane in a 1 : 1 ratio to give a stable adduct which is fully characterized by X-ray analysis.

Transition metal oxo chemistry has encountered increasing interest in the last few years on account of the importance of the M=O function in many aspects of catalysis and coordination chemistry.[1,2] Thus, it has been shown to be essential not only in most oxidation processes but also in several other transition metal catalysed reactions.[3–6] Metal oxo complexes have furthermore been widely studied as models for metal oxide surfaces used in heterogeneous catalysis.[7] In a different domain, this function has also been compared with the carbonyl group in organic chemistry.[8]

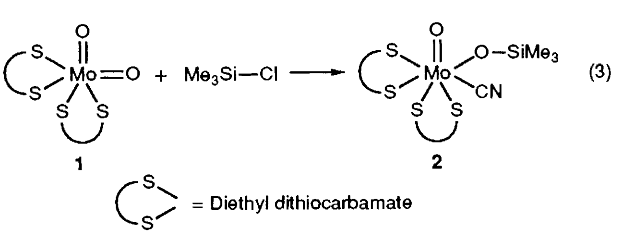
Silylation of transition metal oxo compounds can also be considered as an important facet of this field since the control of this reaction should not only give a better insight at the molecular level on how metal oxides are adsorbed on silanes or polysiloxanes, but it could also constitute an excellent way to fix cleanly any transition metal complex bearing an M=O group on a functionalized silyl species [eqn. (1)].

The reactions of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{W=O}$,[9] $\text{Me}_3\text{Re=O}$[10] and CrO_3[11] with Me_3SiCl have been reported. In all cases the initial adduct could not be observed since it immediately underwent further electrophilic attack by a second mole of Me_3SiCl resulting in the formation of the dichloro complex and elimination of hexamethyldisiloxane [eqn. (2)].†



Trialkylcyanosilanes on the other hand have never been reported as silylating agents of metal oxo compounds, although they have been widely used in organic chemistry on aldehydes,[12,13] ketones[14] and epoxides.[15]

We report the reaction of a molybdenum(VI) dioxo complex with trimethylcyanosilane which underwent cleanly a 1 : 1 addition yielding a stable and crystalline product **2** [eqn. (3)] even in the presence of excess cyanosilane.



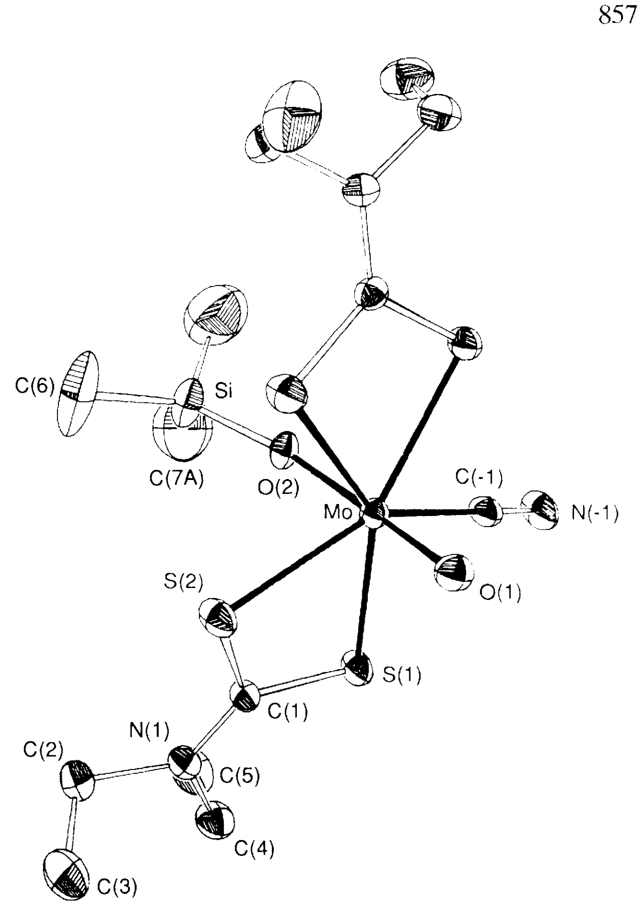


Fig. 1 ORTEP view of **2**. Selected bond distances (Å) and bond angles (°): Mo–O(1) 1.684(5), Mo–O(2) 1.945(5), Mo–S(1) 2.507(1), Mo–S(2) 2.520(2), Mo–C(-1) 2.157(9), O(2)–Si 1.165(6), Si–C(6) 1.71(1), Si–C(7A) 1.81(1), Si–C(7B) 2.12(1), C(-1)–N(-1) 1.13(1); O(1)–Mo–O(2) 177.4(3), O(1)–Mo–S(1) 93.04(7), O(1)–Mo–S(2) 92.2(2), O(1)–Mo–C(-1) 93.7(3), S(1)–Mo–S(2) 68.61(5), S(1)–Mo–O(2) 87.71(6), S(1)–Mo–C(-1) 73.05(4), S(2)–Mo–C(-1) 141.44(5), Mo–O(2)–Si 159.9(3), Mo–O(2)–S(2) 85.7(1), C(-1)–Mo–O(2) 88.9(3), Mo–C(-1)–N(-1) 180.0(8), O(2)–Si–C(6) 116.0(5), O(2)–Si–C(7A) 113.2(5), O(2)–Si–C(7B) 101.(14). For clarity, only the position C(7A) is represented for the disordered methyl group.

A mixture of Me_3SiCN (0.5 cm^3, 0.37 g, 3.75 mmol) and $\text{MoO}_2(\text{S}_2\text{CNEt}_2)_2$[16] **1** (1.59 g, 3.75 mmol) in CH_2Cl_2 (15 cm^3) was stirred under an inert atmosphere for 3 h at 20 °C. Evaporation of the solvent gave a light brown solid in nearly quantitative yield. Recrystallization from CH_2Cl_2–diethyl ether (50 : 50) afforded air-stable yellow prisms. Elemental analysis, IR data and ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy were well in accord with the addition product **2**.‡ This was confirmed by a single crystal X-ray diffraction analysis.§ The structure given in Fig. 1 shows that the plane of symmetry includes the molybdenum atom, the cyano and oxo groups and the O–Si–Me moiety. This plane bisects the molecule with the two diethyl dithiocarbamate ligands and two of the methyl groups on silicon lying on each side of the plane. The methyl group C(7) is equally distributed over two positions C(7A) and C(7B); this disorder had no effect on the determination of the rest of the structure.

Dioxo(diethyl dithiocarbamato)molybdenum(VI) is a well known oxo transfer agent, and has been widely studied.[1] It was of interest to see what would be the effect of introducing a siloxy group upon its ability to transfer an oxygen atom to a substrate. The comparative reactivity study performed on the stoichiometric oxidation of PPh_3 with **1** and **2** showed that the

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† More interestingly the use of triphenylchlorosilane with CrO_3 afforded a relatively more stable addition product; the presence of excess chlorosilane, however, leads to the formation of hexaphenyldisiloxane in a manner analogous to the scheme shown in eqn. (1) above.[11]

‡ IR ν(KBr)/cm^{-1} 2018w (C≡N), 871s (Mo=O), 958s (Mo–OSi), 1241m (O–SiMe$_3$), 836s and 748w; ^{1}H NMR (CDCl$_3$) δ 0.16 (s, CH$_3$Si); ^{13}C NMR (CDCl$_3$) δ 1.18 (CH$_3$Si) and 143.1 (CN); ^{29}Si NMR (CDCl$_3$) δ 11.18 (SiOMo). ^{29}Si NMR was recorded using INEPT with refocusing sequence. Unlike ^{1}H NMR, this allowed an easy and quantitative measurement of all silylated structures [*e.g.* Me$_3$SiCN: −11.45; (Me$_3$Si)$_2$O : 7.38; Me$_3$SiOH : 17.09; Me$_3$SiC$_6$H$_5$ (internal standard): −4.14].

§ *Crystal data*: $\text{C}_{14}\text{H}_{29}\text{MoN}_3\text{O}_2\text{S}_4\text{Si}$, $M = 523.67$, orthorhombic, space group *Pnma*, $a = 13.437(3)$, $b = 14.582(4)$, $c = 12.409(3)$ Å, $V = 2431$ Å^3, $D_c = 1.43$ g cm^{-3}, $Z = 8$, crystal size 0.2 × 0.4 × 0.5 mm, μ(Mo-Kα) = 9.18 cm^{-1}, 1987 unique data collected at room temperature on an Enraf Nonius CAD 4 diffractometer. 1250 reflections with $I > 3\sigma$ were used to solve the structure to $R = 0.038$ and $R_w = 0.050$. All atoms were refined anisotropically; hydrogen atoms, except for those on C(7), were placed on their geometrically calculated position. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

silylated complex was still able to transfer an oxo group to a phosphine but at a considerably lower rate (k for **1** = 7.1×10^{-2},[17] k for **2** = 1.33×10^{-4} l mol^{-1} s^{-1}). The silylated reduced form could be reoxidized with either O_2, dimethyl sulfoxide or N_2O without loss of the siloxy or the cyano group, but was not structurally fully characterized.

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