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REACTIONS OF CHLOROSILANES WITH DIOXOMOLYBDENUM(VI) COMPLEXES

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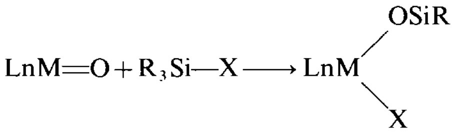
Abstract—Various trialkylchlorosilanes were reacted with a number of molybdenum–oxo complexes in order to establish the main factors which influence the process of addition of the Si—Cl function across the Mo═O bond. A novel intermolecular mode of hexaalkyldisiloxane formation was observed in one case.

The chemistry of transition metal–oxo compounds is an area of an ever wider domain of interest which includes many aspects of catalysis, coordination chemistry and biochemically related systems.[1–3] Thus, the presence of the M═O moiety has been shown to be essential in catalytic oxygen atom transfer reactions[4] and in several other transition metal catalysed reactions.[5] Metal–oxo complexes have furthermore been widely studied as models for metal oxide surfaces used in heterogeneous catalysis.[6]

Silylation of the M═O function is a relevant reaction to this field since it gives a better insight into how the metal oxides interact with silanes or polysiloxanes. Furthermore, this reaction constitutes a clean way to fix any metal–oxo complex to a functionalized silyl species.

Two kinds of behaviour have been reported so far for the reaction of an halosilane (R_3SiX) with a transition metal–oxo complex, the 1,2-monoaddition (1)



$$\mathrm{LnM{=}O + R_3Si{-}X \longrightarrow LnM}\begin{matrix}\diagup \mathrm{OSiR_3} \\ \diagdown \mathrm{X}\end{matrix} \qquad (1)$$

and the halogenation reaction (2).

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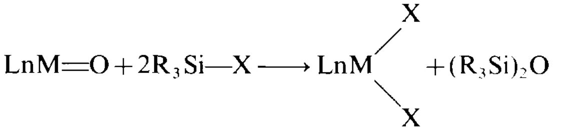


$$\mathrm{LnM{=}O} + 2\mathrm{R_3Si{-}X} \longrightarrow \mathrm{LnM}\begin{array}{l}\diagup \mathrm{X}\\ \diagdown \mathrm{X}\end{array} + (\mathrm{R_3Si})_2\mathrm{O} \qquad (2)$$

The reaction of CrO_3,[7] Me_3ReO_3,[8] $(\eta^5\text{-}C_5Me_5)_2W{=}O$,[9] $[(\eta^5\text{-}C_5Me_5)MoO_3]$[10] and $(\eta^5\text{-}C_5Me_5)ReO_3$[8] with Me_3SiCl are some examples of the second behaviour, while the reaction of $AgTcO_4$, $AgReO_4$ with Me_3SiCl,[9] Ag_2MoO_4 with Ph_3SiCl[11] and $[(\eta^5\text{-}C_5Me_5)WO_3]^-$ with a series of $RR'R''Si{-}Cl$ silanes bulkier than the trimethyl derivative[10] lead to the formation of the metal–siloxy complex with yields ranging from 30 to 90%. Therefore, in order to gain further insight into the factors which may control the nature of the silylation of transition metal–oxo compounds, we attempted a limited systematic study of the reaction of a series of chlorosilanes with molybdenum(VI)–oxo complexes which is the object of this report.

EXPERIMENTAL

General materials and equipment

All materials were commercial products and were used without further purification. All solvents were thoroughly degassed prior to use by repeated evacuation followed by admission of dry and oxygen-free nitrogen or argon. Diethyl ether was distilled from sodium wire immediately prior to use. Dichloromethane and *n*-hexane were dried over activated molecular sieves. NMR spectra were recorded on a Brucker WH 200 and a Brucker AMX 400 spectrometer. IR spectra were recorded on a Perkin–Elmer 1720 XFT spectrometer.

Preparation of dioxo-bis-diethyldithiocarbamato molybdenum(VI)

This was prepared according to the method described previously.[13] An aqueous solution (300 cm^3) containing $Na_2MoO_4 \cdot 2H_2O$ (14.5 g, 60 mmol) and $(C_2H_5)_2NCS_2Na \cdot 3H_2O$ (16 g, 71 mmol) was slowly acidified with HCl (0.6 N, 315 cm^3). The brown–orange solid formed was filtered and washed several times with water and dried under reduced pressure. It was recrystallized from warm diethyl ether/benzene. Yield 67%. IR(KBr): 2983(w), 2939(w), 1534(w), 1458(w), 1438(w), 1379(m), 1353(m), 1276(s), 1203(s), 1149(m), 1009(m), 912(vs), 879(vs), 847(m), 574(m) cm^{-1}.

Preparation of oxodichloro-bis-diethyldithiocarbamato molybdenum(VI)

This was prepared according to the method described previously.[14] It was also alternatively prepared by reacting dioxo-bis-diethyldithiocarbamato molybdenum(VI) with a three-fold excess of Me_3SiCl. IR(KBr): 2983(w), 2939(w), 1534(w), 1458(w), 1438(w), 1379(m), 1353(m), 1276(s), 1203(m), 1149(m), 1071(m), 1009(s), 947(vs), 847(m), 574(w), ^1H NMR ($CDCl_3$): d 3.9 (m, CH_2), d 1.4 (m, CH_3).

Preparation of oxo-bis-diethyldithiocarbamato molybdenum(IV)

This was prepared according to the method described previously[15] and characterized by comparison of its spectroscopic properties. An aqueous solution (50 cm^3) containing $Na_2S_2O_4 \cdot 2H_2O$ (20 g, 98 mmol) was slowly added (50 cm^3) containing $Na_2MoO_4 \cdot 2H_2O$ (4 g, 16.5 mmol) and $(C_2H_5)_2NCS_2Na \cdot 3H_2O$ (7.4 g, 33 mmol). The pink–red solid formed was filtered and washed several times with water and dried under reduced pressure. Yield: 80%. IR: 2978(w), 2935(w), 2871(w), 1526(s), 1438(s), 1458(m), 1355(m), 1296(s), 1551(m), 1095(m), 960(vs).

Preparation of $[Mo_2O_7][PPh_4]_2$

This was prepared according to the method described previously.[16] An aqueous solution of $Na_2MoO_4 \cdot 2H_2O$ (1.25 g, 5.2 mmol in 3 cm^3 of water) was slowly acidified with 1 cm^3 of 6 N HCl until the pH remained between 4 and 5. Tetraphenylphosphonium chloride (0.8 g, 2.1 mmol) was then added and the solid formed was filtered and washed several times with water, ethanol, acetone and diethyl ether. The solid $(Mo_8O_{26})(PPh_4)_4$ was recrystallized from acetonitrile and kept under inert atmosphere. Yield: 70%. To a stirred acetonitrile solution (250 cm^3) containing 5.0 g (2.3 mmol) of $(Mo_8O_{26})(PPh_4)_4$ was added 9.5 cm^3 of a 1 M methanolic solution of PPh_4OH. The suspension was filtered after 20 min and concentrated under reduced pressure to give a viscous oil. A solid is obtained by addition of 10 cm^3 of acetone followed by 100 cm^3 of diethyl ether. Yield: 4.4 g (60%). IR: 3051(w), 2360(w), 1885(s), 1792(s), 1585(m), 1483(m), 1107(s), 759(m), 723(m), 691(m), 528(s).

Reaction of R_3SiX *with* $Mo(O)_2(dtc)_2$

In a typical experiment, 1.6 mmol of R_3SiX were added to a stirred solution of 0.8 mmol (2 : 1) or 1.6

mmol (1 : 1) of the molybdenum–oxo complex in CH_2Cl_2 under nitrogen. After 2–24 h the reaction mixture was evaporated under reduced pressure and the solid formed was filtered and recrystallized.

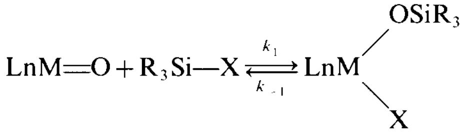
Reaction of $(CH_3)_2(CMe_3)SiCl$ *with* $Mo(O)_2(dtc)_2$

To a CH_2Cl_2 solution (20 cm^3) containing $Mo(O)_2(dtc)_2$ (0.58 g, 1.38 mmol) was added at 25°C under nitrogen while stirring 0.209 g (1.38 mmol) of $(CH_3)_2(C(CH_3)_3)SiCl$. After 3 h the volume of the solution was reduced to 10 cm^3 under reduced pressure and the amber precipitate filtered. IR(KBr): 2983(w), 2939(w), 1534(w), 1458(w), 1438(w), 1379(m), 1353(m), 1276(s), 1203(m), 1149(m), 1071(m), 1009(s), 847(m), 574(s) (dtc), 1242(s) (Si—O), 958(s) (Mo—O—Si), 879(s)(Mo=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ −0.20 (s, 6H, CH_3), δ 0.68 (s, 9H, $C(CH_3)_3$), δ 1.2–1.4 (m, 12H, CH_3 dtc), δ 3.6–3.9 (m, 8H, CH_2 dtc); ^{29}Si NMR ($CDCl_3$): δ 14.702 (Mo—O—*Si* $(Me)_3(CCH_3)$. Found: C, 33.2; H, 6.4; N, 5.0; Cl, 6.3; Mo, 16.4; Si, 4.5. Calc. for $C_{16}H_{35}N_2O_2ClS_4MoSi$: C, 33.4; H, 6.1; N, 4.9; Cl, 6.2; Mo, 16.7; Si, 4.9%.

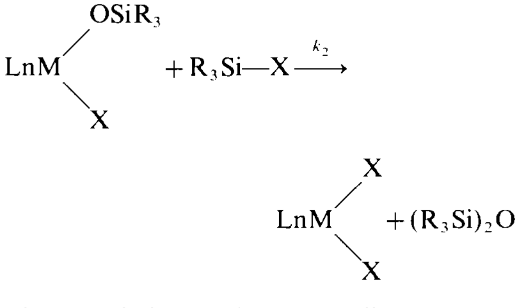
The reaction was left for 24 h and then its volume reduced to 10 cm^3 under reduced pressure and a red crystalline solid was isolated. IR($CDCl_3$): 2983(w), 2939(w), 1534(w), 1458(w), 1438(w), 1379(m), 1353(m), 1276(s), 1203'm), 1149(m), 109(s), 847(m), 574(s), (dtc); 956(s) (Mo=O); 799(s) (Mo—O—Mo) cm^{-1}.

RESULTS AND DISCUSSION

In order to have a common ground of discussion to both behaviours we will consider the halogenation (2) as a two step reaction.



$$\mathrm{LnM{=}O} + \mathrm{R_3Si{-}X} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{LnM}(\mathrm{OSiR_3})(\mathrm{X}) \tag{3}$$



$$\mathrm{LnM}(\mathrm{OSiR_3})(\mathrm{X}) + \mathrm{R_3Si{-}X} \xrightarrow{k_2} \mathrm{LnMX_2} + (\mathrm{R_3Si})_2\mathrm{O} \tag{4}$$

where steric interactions, as well as electronic factors such as M—O and Si—X bond energies and polarities, play a major role in the determination of the activation energy for each step. Thus, for a thermodynamically favoured silylation process, if $k_2 > k_1, k_{-1}$ a halogenation behaviour should be expected. Whereas, if $k_1 \gg k_2, k_{-1}$ the major reaction product will be the metal–siloxy complex if the reaction is stopped in its early stages.

When $Mo(O)_2(dtc)_2$ (dtc = diethyldithiocarbamate) was reacted for 2 h with an equimolar quantity of Me_3SiCl the products observed were $MoOCl_2(dtc)_2$ and $(Me_3Si)_2O$ while ~0.5 mol of $Mo(O)_2(dtc)_2$ were recovered at the end of the reaction. If a two-fold excess of chlorosilane was used the reaction proceeds faster to the same products and no dioxo complex was left unreacted.

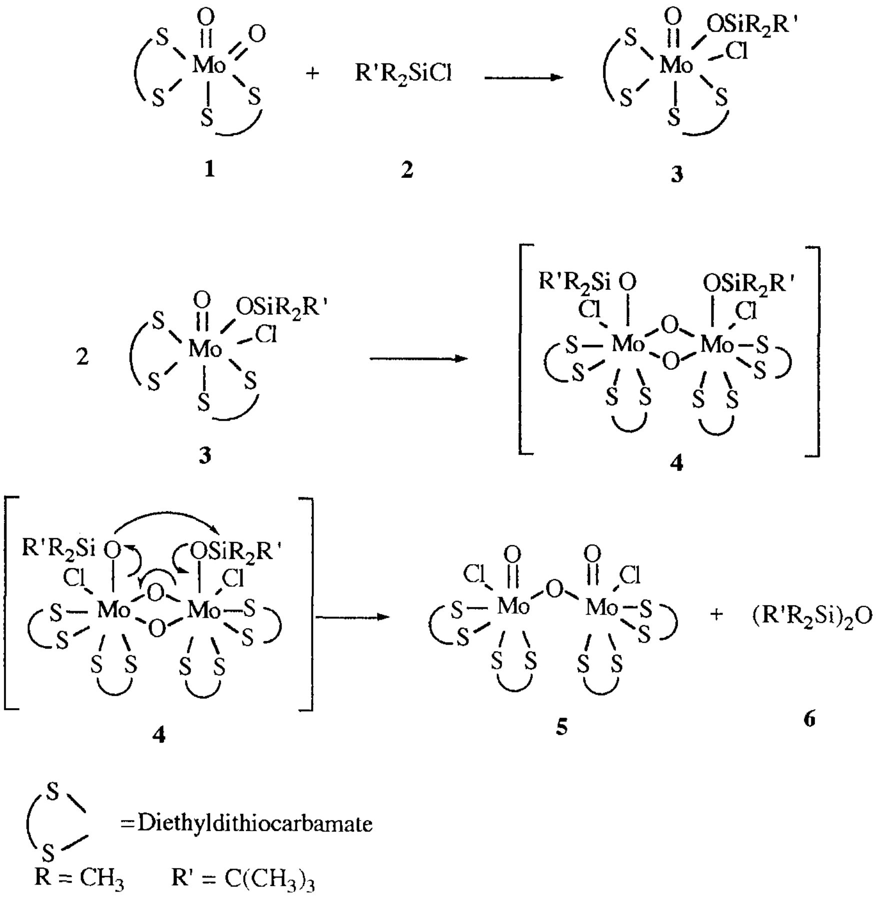
This reaction was followed at both Si/Mo molar ratios (1 : 1; 2 : 1) using ^{29}Si NMR at room temperature and at −40°C. In all cases a known quantity of Me_3SiPh was added to the reaction mixture as an internal standard. The results observed at the different temperatures and molar ratio were similar: a growing signal which corresponds to $(Me_3Si)_2O$ at 7.382 ppm correlated to a fast consumption of the Me_3SiCl, according to the reaction schemes (1) and (3). A transient signal at 9.929 ppm which disappeared at the end of the reaction was also observed. A definite assignment for this signal cannot be made although it appears where a molybdenum siloxy complex would be expected to resonate.

When a Si/Mo molar ratio of 10 was used the observed products were the same. Furthermore, addition of Me_3SiCl to $MoOCl_2(dtc)_2$ led to no reaction even when the reaction conditions (temperature, solvent, reaction time and Si/Mo ratio) were significantly varied over a wide range. It can, thus, be concluded from these experiences that the reaction between Me_3SiCl and $Mo(O)_2(dtc)_2$ proceeds with a stoichiometry shown in eq. (2).

The steric interactions which should be involved in a reaction between $MoOCl_2(dtc)_2$ and Me_3SiCl could explain the failure to silylate the mono-oxomolybdenum(VI) complex. However, the reaction between Me_3SiCl and $Mo^{IV}\,O(dtc)_2$ did not proceed at all which is against the steric argument and suggests instead an electronic influence between the two oxo groups in the reaction pattern.[12]

Supporting evidence for this is provided by the reaction of $(Mo_2O_7)(PPh_4)_2$ with Me_3SiCl. In this case the reaction is even faster and the isolated products were $(Me_3Si)_2O$ and an isopolymolybdate salt.

In order to better control this diaddition an increase of the steric interaction in eq. (3) and thus a decrease of k_2 was attempted by replacing Me_3Si Cl by Ph_3SiCl. Again, with either $Mo(O)_2(dtc)_2$ or $(Mo_2O_7)(PPh_4)_2$, only the formation of $(Ph_3Si)_2O$



Scheme 1.

(^{29}Si NMR: 7.32 ppm) was observed, indicating that the change in steric requirement was largely counterbalanced by the change in polarization and therefore strength of the Si—Cl bond when methyl was replaced by phenyl groups.

The substitution of only one methyl group in Me_3SiCl by a t-butyl group was considered. The reaction of $Me_2(Me_3C)Si—Cl$ with $Mo(O)_2(dtc)_2$ proceeds much slower than with any of the other halosilanes used before and allowed us to detect by ^{1}H and ^{29}Si NMR the formation of the corresponding metal siloxy intermediate as well as its unprecedented evolution pattern.

A three step reaction could clearly be observed by following it during 24 h at room temperature. At the start of the reaction (< 1 min), besides the signal pattern corresponding to the dtc complex (**1**), we could only observe a set of two singlets assigned to the starting silane (**2**) at 0.96 and 0.33 ppm. After 15 min, the set of signals corresponding to the 1,2 addition of the Si—Cl bond onto the oxo moiety started to appear at −0.18 (CH_3) and 0.70 (CMe_3). This complex was isolated and fully characterized in a separate experiment and corresponds to $Mo(O)Cl[OSiMe_2(CMe_3)](dtc)_2$ (**3**). After approximately 2 h a new set of signals appeared at 0.18 (CH_3) and 0.94 ppm (CMe_3) (**4**) accompanied after a while by the appearance of another set of signals [0.095 (CH_3) and 0.91 ppm (CMe_3)] corresponding to the disiloxane (**6**). With time, the former set slowly disappeared while the disiloxane signals increased. The final products after 24 h were isolated and characterized as $[(CH_3)_2(CMe_3)Si]_2O$ (**6**) and the dimer $Mo_2(O)_2O(dtc)_4Cl_2$ (**5**). All these observations can best be illustrated as is shown in Scheme 1 where the proposed silyloxy–oxo dimer intermediate (**4**) plays an important role in this unprecedented intermolecular hexaalkyldisiloxane formation yielding a new oxo–μ-oxo molybdenum(VI) complex (**5**).

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