Monatshefte für Chemie 117, 177—183 (1986)

Monatshefte für Chemie
Chemical Monthly

Reactions of Bis(trimethylsilyl)amine and -amide with $MoOCl_4$

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(Received 5 November 1984. Revised 16 December 1984. Accepted 17 December 1984)

Oxo-Mo(VI) imido-chloride, $[MoOCl_2(NH)(Et_2O)]_n$ and nitrido-chloride, $[Mo_2O_2Cl_2(N)_2(Et_2O)]_n$ have been synthesized by equimolar reactions of $MoOCl_4$ with $HN(SiMe_3)_2$ and $LiN(SiMe_3)_2$, respectively. Higher molar reactions of $HN(SiMe_3)_2$ lead to imido-silylamido derivatives, $[Mo_2OCl_3(NH)_3(NHSiMe_3)]_n$, whereas those of $LiN(SiMe_3)_2$ give silylimido bridged compounds, $Mo_4O_4Cl_4(NSiMe_3)_6$ and $Mo_4O_4(NSiMe_3)_8$. Elemental analyses, redox titration, magnetic moment, molecular weight, molar conductance, infrared, ^1H-NMR and TG-DTG-DTA studies are reported.

[Keywords: Imido-chloride; Nitrido-chloride, Silylimides of $O=Mo(VI)$*]*

Reaktionen von Bis(trimethylsilyl)amin und -amid mit $MoOCl_4$

Durch equimolare Reaktionen von $MoOCl_4$ mit $HN(SiMe_3)_2$ und $LiN(SiMe_3)_2$ wurden die Oxo-Mo(VI) Imido-chloride $[MoOCl_2(NH)(Et_2O)]_n$ und die Nitrido-chloride $[Mo_2O_2Cl_2(N)_2(Et_2O)]_n$ dargestellt. Höhermolekulare Reaktionen von $HN(SiMe_3)_2$ führen zu Imido-silylamido Derivaten $[Mo_2OCl_3(NH)_3(NHSiMe_3)]_n$, währenddessen die von $LiN(SiMe_3)_2$ silylimido-überbrückte Verbindungen ergeben: $Mo_4O_4Cl_4(NSiMe_3)_6$ und $Mo_4O_4(NSiMe_3)_8$. Die Strukturen sind mit Elementaranalysen, Redoxtitrationen, Messung der magnetischen Momente, Molekulargewichten, molarer Leitfähigkeit, Infrarot, ^1H-NMR und TG-DTG-DTA-Untersuchungen charakterisiert.

Introduction

The use of silylated amines and alkalimetal silylamides is well known in the synthesis of silylated amides of main group metals and metalloids and the complete series of first row transition metals and some lanthanides[1,2]. In continuation of our study on silyl-nitrogens[3], we describe here reactions of bis(trimethylsilyl)amine and lithium bis(trimethylsilyl)amide with $MoOCl_4$.

Results and Discussion

Oxomolybdenum(VI) halides are readily reduced compounds and undergo easy reduction with organic reagents and silylamines to provide O=Mo(V) or Mo(IV) compounds[4,5]. Bis(trimethylsilyl)amine and -amide are now being shown to form oxo-Mo(VI) derivatives containing simple and silylated imido or amido groups and nitrido linkages.

Equimolar amounts of $MoOCl_4$ and bis(trimethylsilyl)amine undergo cleavage to form a black solid, $[MoOCl_2(NH)(Et_2O)]_n$, (**1**), as:

$$MoOCl_4 + (Me_3Si)_2NH \xrightarrow{+Et_2O} \underset{(\mathbf{1})}{[MoOCl_2(NH)(Et_2O)]} + 2\,Me_3SiCl \qquad (1)$$

It appears that the simple replacement of one Cl atom by the monosilylamido group is followed by an intramolecular or intermolecular elimination of Me_3SiCl to form a polymeric structure containing NH bridges. A similar reaction between $TiCl_4$ and $(Me_3Si)_2NH$ was already reported[6] to yield $[TiCl_2(NH)]$.

Although reactions of alkalimetal bis(silyl)amides lead to disilylamido or silylimido derivatives, a 1:1 reaction of $MoOCl_4$ with $(Me_3Si)_2NLi$ leads to a O=Mo(VI)-nitride, $[Mo_2O_2Cl_2(N)_2(Et_2O)]_n$ (**2**):

$$2\,MoOCl_4 + 2(Me_3Si)_2NLi \xrightarrow{+Et_2O} \underset{(\mathbf{2})}{[Mo_2O_2Cl_2(N)_2(Et_2O)]} + 2\,LiCl + 4\,Me_3SiCl \qquad (2)$$

Preliminary elimination of LiCl is followed by both intramolecular as well as intermolecular cleavage of Me_3SiCl. Molybdenum(VI) nitrides of the type $MoNCl_3$ are already known but the methods of preparation from azides are not very convenient because of their explosive nature[7].

A 1:2 reaction between $MoOCl_4$ and $(Me_3Si)_2NH$ shows that initially about three moles of Me_3SiCl are formed; however, as the reaction proceeds (3 h), it leads to 2.5 mol of Me_3SiCl and 0.5 mol of $(Me_3Si)_2O$ (with no further change) per 1 mol of $MoOCl_4$. A light brown solid, $[Mo_2OCl_3(NH)_3(NHSiMe_3)]_n$ (**3**), is formed as:

$$2\,MoOCl_4 + 4(Me_3Si)_2NH \rightarrow \underset{(\mathbf{3})}{[Mo_2OCl_3(NH)_3(NHSiMe_3)]} + 5\,Me_3SiCl + (Me_3Si)_2O \qquad (3)$$

The possibility of hydrolysis of Me_3SiCl as source of siloxane is excluded on the basis of control experiments. It appears that Me_3SiCl interacts with O=Mo(VI) species to cause an oxygen atom transfer reaction.

Quantitative isolation of $(Me_3Si)_2O$ under moisture free reaction conditions and the absence of νMo = O and the presence of νMo—O—Mo[4] at 720 and 420 cm^{-1} in the infrared spectrum of **3** support the cleavage of the Mo = O bond. A 1 : 3 reaction of $MoOCl_4$ with $(Me_3Si)_2NH$ (even in 1,2-dimethoxyethane at reflux temperature for 12 h) gave the same results as the preceding 1 : 2 reaction.

Simultaneous salt elimination and release of Me_3SiCl are also observed in the reaction of two equivalents of $(Me_3Si)_2NLi$ with $MoOCl_4$. Tris(trimethylsilyl)amine is formed due to a secondary reaction of Me_3SiCl and $(Me_3Si)_2NLi$. The filtrate provides a chocolate brown cyclic silylimido derivative, $Mo_2O_2Cl_2(NSiMe_3)_3$ (**4**):

$$2\,MoOCl_4 + 4(Me_3Si)_2NLi \rightarrow \underset{(\mathbf{4})}{Mo_2O_2Cl_2(NSiMe_3)_3} + 4\,LiCl + 2\,Me_3SiCl + (Me_3Si)_3N \qquad (4)$$

A 1 : 3 reaction between $MoOCl_4$ and $(Me_3Si)_2NLi$ is accompanied by total chlorine elimination and a chocolate brown [bis-μ-(trimethylsilyl)imido]oxomolybdenum(VI) complex, $MoO(NSiMe_3)_2$ (**5**), is formed:

$$MoOCl_4 + 3(Me_3Si)_2NLi \rightarrow \underset{(\mathbf{5})}{MoO(NSiMe_3)_2} + 3\,LiCl + Me_3SiCl + (Me_3Si)_3N \qquad (5)$$

Compounds **1**–**3** are insoluble in nonpolar and less polar organic solvents whereas **4** and **5** are soluble in nonpolar solvents. Cryoscopic molecular weight determinations of **4** and **5** in benzene correspond to molecular formulae $Mo_4O_4Cl_4(NSiMe_3)_6$ and $Mo_4O_4(NSiMe_3)_8$, respectively. Molar conductance measurements at millimolar concentration in *DMSO* or acetone indicate their nonelectrolytic nature[8] (Table 1). The oxidation state of Mo(VI) is derived from Ce(IV) titrations and supported by magnetic susceptibility measurements indicating the diamagnetic character of **1**–**5**.

Infrared assignments characteristic for νMo = O[9], νMo—Cl[10], νMo = N[4,7], νMo—N, νSi—N[11] and νNH are given in Table 1. Compounds **1** and **2** show infrared bands around 1 170 and 1 070 cm^{-1} due to νOC_2 modes of the ether. Compounds **3**, **4**, and **5** contain bands typical for Me_3Si[11,12].

The semiquantitative ^{1}H NMR spectra (see Exp.) of $[MoOCl_2(NH)(Et_2O)]_n$ (**1**), and $[Mo_2O_2Cl_2(N)_2(Et_2O)]_n$ (**2**) in d_6-*DMSO* (plus known amount of toluene) agree with the number of ether molecules shown in the corresponding formulations. The ^{1}H NMR spectra of **1** and **2** consist of quartets at 3.43 and 3.3 ppm and a triplet at 1.10 ppm (with

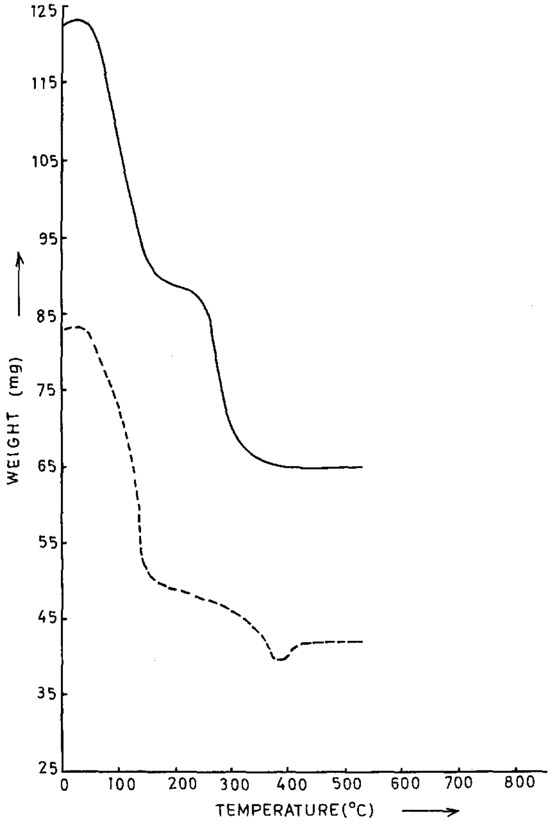

Fig. 1. TG curves for $MoOCl_2(NH)(Et_2O)$ (————) and $Mo_4O_4(NSiMe_3)_8$ (- - - - - - -)

relative areas 2 : 3). The ^1H NMR spectrum of $[Mo_2OCl_3(NH)_3(NHSiMe_3)]_n$ (**3**), indicates half a Me_3Si group per Mo atom appearing as a singlet at 0.14 ppm. This is also supported by its reaction with CH_3OH in CCl_4: the silyl signal at 0.14 ppm in **3** disappears completely and an equivalent silyl singlet at 0.06 ppm due to the formation of $Me_3Si—O—Me$ appears at 3.4 ppm. The ^1H NMR spectra of $Mo_2O_2Cl_2(NSiMe_3)_3$ (**4**), and $MoO(NSiMe_3)_2$ (**5**) in known amounts of toluene confirm the number of silyl groups indicated per Mo atom appearing as singlets at 0.27 ppm and 0.28 ppm, respectively.

TG-DTG-DTA measurements of **1** in air show a loss equivalent to Et_2O (actually trapped by heating **1** at 150°/10^{-3} Torr) in the range of 50–180° in an exothermic way due to the burning of organic matter (wt. loss obs.: 26.9, calc.: 27.2%) (Fig. 1). The residue $[MoOCl_2(NH)]$ loses chloro and imido groups (perhaps in the form of HCl, NH_3, N_2 and Cl_2) in the range of 180–370° to leave behind white MoO_3 (wt. loss obs.: 47.3, calc.: 47.0%).

Thermal analysis of $MoO(NSiMe_3)_2$ shows that it loses a weight equivalent to five Me_3SiN groups (probably in the form of N_2), silyl-amines and -hydrazines in the temperature range of 45–150° (wt. loss obs.: 38.2, calc.: 38.0%). The residue decomposes exothermally due to the burning of organic matter in the range of 150–380° to form violet Mo_2O_5 (wt. loss obs.: 52.2, calc.: 52.4%) which gains weight equivalent to an oxygen atom to form MoO_3 in the temperature range of 380–425° (wt. loss obs.: 50.5, calc.: 49.6%) (Fig. 1).

Compounds **1** and **2** appear to be higher polymers. **1** possesses imido as well as chloro bridges, whereas **2** has an unsymmetrical Mo—N=Mo linkage similar to $MoNCl_3$[13]. The compounds **4** and **5** seem to possess silylimido bridges.

Experimental

All preparations or manipulations were done on vacuum line or under dry nitrogen. Diethylether and 1,2-dimethoxyethane were dried over Na wire and distilled from sodium benzophenoneketyl prior to use. $(Me_3Si)_2NH$ (Fluka) was used after distillation and $(Me_3Si)_2NLi$ was prepared by the action of BuLi on $(Me_3Si)_2NH$. $MoOCl_4$ was prepared by heating MoO_3 with $SOCl_2$[4] and purified by resublimation at 70–80°/10^{-3} Torr. Molybdenum as $MoO_2(oxine)_2$ and chloride as AgCl were estimated from the complex after fusion. Carbon, hydrogen and nitrogen were analysed microanalytically. ^1H NMR assignments were done after comparison with authentic probes of $(Me_3Si)_2NH$, $(Me_3Si)_2NLi$, $(Me_3Si)_2NLi$, $(Me_3Si)_3N$, Me_3SiCl and $(Me_3Si)_2O$ in different solvents. Chemical shift in ppm from *TMS* in benzene and ether for silyl proton singlets are 0.09 and 0.5 for $(Me_3Si)_2NH$, 0.13 and —0.042 for $(Me_3Si)_2NLi$ and 0.23 and 0.21 for $(Me_3Si)_3N$, respectively. Me_3SiCl and $(Me_3Si)_2O$ show singlets at about 0.4 ppm and 0.06 ppm, respectively, in Et_2O or CCl_4. Semiquantitative ^1H NMR of pure complex (or reaction mixture) was done by adding a known amount of toluene or cyclohexane (analytical standard) to a solution of known concentration. From the integration of the proton signals in the complex (or reaction mixture), the number of trimethylsilyl groups (or different silyl products) or ether molecules were calculated per mole of the complex. ^1H NMR was done on a Varian EM-390 spectrometer and infrared spectra measured on a Perkin Elmer 621 grating spectrophotometer. Molecular weights were determined cryoscopically in benzene. *Gouy*'s method was applied for magnetic moment measurements at room temperature. Thermal analysis was done on the derivatograph MOM, Budapest. Oxidation states were determined by treating a known weight of the compound with a known volume of standard Ce(IV) solution excess, which was titrated against standard Fe(II) using *N*-phenylanthranilic acid as indicator.

General Procedure for Reactions of $MoOCl_4$ *with* $(Me_3Si)_2NH$ *or* $(Me_3Si)_2NLi$

A known weight of $MoOCl_4$ was dissolved in Et_2O, cooled in an ice bath and the required equivalent of bis(trimethylsilyl)amine (in Et_2O) or lithium

Table 1. *Molar conductance,* IR *and elemental analysis*

Compound	Λ_m*	Characteristic IR Bands (cm^{-1})				Found (Calc.) %				
		νMo=O	νMo—Cl	νMo—N	Others	C	H	N	Cl	Mo
$MoOCl_2(NH)(Et_2O)$	18.7	1 005	300	430	3 240 (νNH)	16.9 (17.6)	3.5 (4.0)	4.8 (5.1)	25.8 (26.1)	35.4 (35.3)
$Mo_2O_2Cl_2(N)_2(Et_2O)$	17.9	1 000	305	435	1 040 (νMo=N)	11.8 (12.1)	2.3 (2.5)	6.8 (7.0)	17.8 (17.9)	48.0 (48.4)
$Mo_2OCl_3(NH)_3(NHSiMe_3)$	28.5	—	360, 320	460	3 120 (νNH), 945 (νSi—N)	7.4 (7.3)	2.6 (2.6)	10.7 (11.3)	21.3 (21.5)	38.6 (38.8)
$Mo_2O_2Cl_2(NSiMe_3)_3$	6.0**	1 015	300	420	955 (νSi—N)	19.6 (19.4)	4.7 (4.8)	7.2 (7.5)	12.4 (12.8)	33.9 (34.5)
$MoO(NSiMe_3)_2$	2.5**	1 005	—	400	940 (νSi—N)	24.8 (25.2)	6.2 (6.3)	9.6 (9.8)	— —	33.2 (33.6)

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* $cm^2\,ohm^{-1}\,mol^{-1}$ in *DMSO*, ** In acetone.

bis(trimethylsilyl)amide (in benzene) was added dropwise to it with constant stirring. The volatiles were then carefully evacuated into liquid nitrogen cooled traps. Chlorine in the form of Me_3SiCl was estimated quantitatively from the trapped material and in certain bulk reactions the trapped material was fractionated carefully to distil out silyl products, such as Me_3SiCl, $(Me_3Si)_2O$ or $(Me_3Si)_2NH$. The residue was treated with ether (benzene for **4** and **5**) and the filtrate was concentrated *in vacuo*, treated with petroleum ether and cooled to isolate the solid compound.

Acknowledgement

One of the authors (*G. S.*) thanks CSIR, New Delhi for a senior research fellowship.

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