Mixed Chloride/Amine Complexes of Dimolybdenum(II). 1. Preparation, Characterization, and Crystal Structure of Mo2Cl4(NHEt2)4: A Quadruply-Bonded Dimolybdenum Compound with Diethyl…

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Mixed Chloride/Amine Complexes of Dimolybdenum(II). 1. Preparation, Characterization, and Crystal Structure of Mo$_2$Cl$_4$(NHEt$_2$)$_4$: A Quadruply-Bonded Dimolybdenum Compound with Diethylamine Ligands

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Reaction of the molybdenum(III) complex Mo$_2$Cl$_6$(THF)$_3$ with diethylamine at room temperature causes reduction of the starting compound to produce the dimolybdenum(II) complex Mo$_2$Cl$_4$(NHEt$_2$)$_4$ (**1**). It was shown that the Cl$^-$ anions released by the substitution with amine can react with more of the starting material to give side products of molybdenum(III). Four such products were isolated and characterized: [NH$_2$Et$_2$][MoCl$_4$(NHEt$_2$)$_2$] (**2**), [NH$_2$Et$_2$][Mo$_2$Cl$_7$(NHEt$_2$)$_2$] (**3**), [NH$_2$Et$_2$]$_2$[MoCl$_5$(NHEt$_2$)] (**4**), and [NH$_2$Et$_2$]$_3$[Mo$_2$Cl$_8$(NEt$_2$)] (**5**). The crystal structures of all complexes **1**−**5** have been investigated by X-ray diffraction. The structure of **1** consists of two *trans*-MoCl$_2$(NHEt$_2$)$_2$ units joined by a quadruple Mo−Mo bond (2.1330(6) Å). The crystallographic parameters for compounds **1**−**5** are as follows: for **1**, monoclinic space group $C2/c$ with $a = 20.846(1)$ Å, $b = 7.044(1)$ Å, $c = 19.868(3)$ Å, $\beta = 118.72(2)°$, and $Z = 4$; for **2**, triclinic space group $P\bar{1}$ with $a = 9.820(3)$ Å, $b = 10.305(1)$ Å, $c = 11.510(1)$ Å, $\alpha = 95.779(8)°$, $\beta = 97.80(2)°$, $\gamma = 111.17(1)°$, and $Z = 2$; for **3**, monoclinic space group $P2_1/n$ with $a = 13.847(5)$ Å, $b = 10.448(4)$ Å, $c = 22.091(4)$ Å, $\beta = 96.68(2)°$, and $Z = 4$; for **4**, monoclinic space group $P2_1/c$ with $a = 11.710(2)$ Å, $b = 12.363(2)$ Å, $c = 30.272(7)$ Å, $\beta = 95.87(2)°$, and $Z = 8$; for **5**, monoclinic space group $P2_1/n$ with $a = 10.335(1)$ Å, $b = 18.061(1)$ Å, $c = 16.775(1)$ Å, $\beta = 95.558(8)°$, and $Z = 4$.

Introduction

It has been found that reactions between the tungsten(III) complex W$_2$Cl$_6$(THF)$_4$ and primary amines, NH$_2$R (R = Bu^t,[1] Bu^s, Cy[2]), proceed according to eq 1, without change in the oxidation state of the tungsten atoms.

$$[W_2Cl_6(THF)_4] + 6\,NH_2R \longrightarrow W_2Cl_4(NHR)_2(NH_2R)_2 + 2\,[NH_3R]Cl + 4\,THF \quad (1)$$
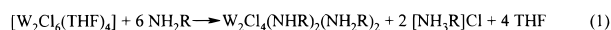
The resulting ditungsten(III) complexes contain one amido and one amine group in trans positions on each W atom (Chart 1a). With the secondary amine NHEt$_2$, this reaction gives the analogous species W$_2$Cl$_4$(NEt$_2$)$_2$(NHEt$_2$)$_2$,[3] but in this case, the amido and amino groups are cis to each other (Chart 1b). All these compounds have been used as precursors in reactions where the amine groups are replaced by monodentate[2−4] and bidentate[5] phosphines, and the isomerization processes of those derivatives have been investigated.

For molybdenum(III) species, the reaction between MoBr$_3$ and NHMe$_2$ was reported in 1962 as affording [MoBr$_2$(NMe$_2$)· NHMe$_2$]$_n$.[6] Later, the compound was reformulated[7] as Mo$_2$Br$_4$-(NHMe$_2$)$_4$ and the chloride analogue was also described. Despite the fact they are presumably quadruply-bonded Mo$_2^{4+}$ compounds, their crystal structures remain unknown. On the other hand, molybdenum(II) species of the type Mo$_2$X$_4$L$_4$ (X = Cl, Br, L = 4-picoline;[8] X = Br, L = 4-*tert*-butylpyridine[9]) are known, which have the exceptional D_{2h} geometry, where the trans amines are opposite to each other across the metal−metal bond (Chart 1c). These few, but interesting, observations inspired us to study further the interaction of Mo^{III} species with amines. In this article, we report the results of such an investigation with diethylamine, NHEt$_2$, which led to the isolation of the new complex Mo$_2$Cl$_4$(NHEt$_2$)$_4$ (**1**) with a quadruple bond between the metal atoms. Some other products of these complex reactions, isolated under differing conditions, are also described here: [NH$_2$Et$_2$][MoCl$_4$(NHEt$_2$)$_2$] (**2**), [NH$_2$-Et$_2$][Mo$_2$Cl$_7$(NHEt$_2$)$_2$] (**3**), [NH$_2$Et$_2$]$_2$[MoCl$_5$(NHEt$_2$)] (**4**), and [NH$_2$Et$_2$]$_3$[Mo$_2$Cl$_8$(NEt$_2$)] (**5**).

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of dry oxygen-free argon or nitrogen with standard Schlenk

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(7) (a) Edwards, D. A.; Maguire, J. J. *Inorg. Chim. Acta* **1977**, *25*, L47. (b) Armstrong, J. E.; Edwards, D. A.; Maguire, J. J.; Walton, R. A. *Inorg. Chem.* **1979**, *18*, 1172.

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Chart 1
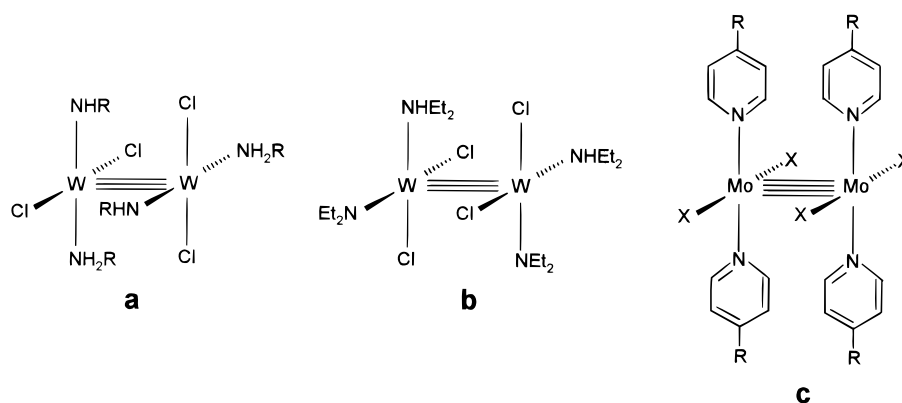
techniques. Solvents were dried and deoxygenated by refluxing over suitable reagents before use. $NHEt_2$, $NHEt_2 \cdot HCl$, and $Co(C_5H_5)_2$ were purchased from Aldrich, Inc. Benzene-d_6 (in ampules) and dichloromethane-d_2 were obtained from Cambridge Isotope Laboratories, Inc., and used as received. $MoCl_3(THF)_3$ and $Mo_2Cl_6(THF)_3$ were synthesized according to published procedures.[10] Sodium amalgam was prepared in a drybox by dissolving a weighed amount of metallic sodium in an approximately measured quantity of mercury that was pumped under vacuum for at least 1 h in a Schlenk flask.

(A1) Synthesis of $Mo_2Cl_4(NHEt_2)_4$ (1). A 1 mL (9.62 mmol) portion of $NHEt_2$ was added to a suspension of 0.20 g (0.32 mmol) of $Mo_2Cl_6(THF)_3$ in 20 mL of THF. After 20 h stirring at room temperature, the solvent was removed under vacuum from the red solution. $Mo_2Cl_4(NHEt_2)_4$ was extracted from the residue with 20 mL of toluene (45% yield based on the total amount of molybdenum).

Anal. Calcd for $Mo_2Cl_4N_4C_{16}H_{44}$: C, 30.68; H, 7.10; N, 8.95. Found: C, 30.82; H, 6.98; N, 8.90. IR data (KBr, cm^{-1}): 3219 (m), 2971 (vs), 2823 (s), 2771 (s), 2468 (m), 2373 (w), 1630 (br, m), 1460 (m), 1390 (m), 1262 (w), 1184 (m), 1064 (m), 1047 (m), 990 (s), 802 (m), 783 (m), 509 (br, w). ^1H NMR data (benzene-d_6, 22 °C): δ 4.50 (br, NH), 3.26 (br, CH_2), 0.89 (br, CH_3). ^1H NMR data (dichloromethane-d_2, 22 °C): δ 4.20 (br, 1H, NH), 3.15 (br, 4H, CH_2), 0.99 (br, 6H, CH_3). UV−vis (CH_2Cl_2 in the presence of $NHEt_2$; λ_{max}, nm): 534 (d−d* transition).

Red crystals of compound **1** were obtained by cooling the toluene solution in a dry ice/ethanol bath (25% yield). However, these crystals were not of X-ray quality. The crystals used for the crystal structure determination were formed by a very slow addition of hexanes over a toluene solution of the compound. Hexanes and the solution were placed in different sections of a modified U-tube separated by a very-fine-pore filter.

The portion of the residue insoluble in toluene contained several species: orange $[NH_2Et_2][MoCl_4(NHEt_2)_2]$ (**2**), yellow $[NH_2Et_2]_2[MoCl_5(NHEt_2)]$ (**4**), and red $[NH_2Et_2]_3[Mo_2Cl_8(NEt_2)]$ (**5**). The first one was definitely the major component, and the last one was present in less than 1% yield. Compound **2** could also be separated pure from the mixture by extraction with hot benzene (35% based on starting Mo).

Anal. Calcd for $MoCl_4N_3C_{12}H_{34}$: C, 31.45; H, 7.49; N, 9.17. Found: C, 31.01; H, 7.27; N, 8.79. ESR (CH_2Cl_2, 10 K): centered at 3470 G, $g = 1.94$.

Crystals of compounds **2**, **4**, and **5** were obtained by dissolving the residue insoluble in toluene in 15 mL of THF and layering the solution with hexanes.

(A2) Synthesis of $Mo_2Cl_4(NHEt_2)_4$ (1) Using $Co(C_5H_5)_2$. A 1 mL (9.62 mmol) portion of $NHEt_2$ was added to a mixture of 0.30 g (0.48 mmol) of $Mo_2Cl_6(THF)_3$ and 0.18 g (0.95 mmol) of $Co(C_5H_5)_2$ in 20 mL of toluene. The suspension was stirred overnight to form a dark red solution and brown solid. The mixture was filtered, the solid

discarded, and the solvent removed under vacuum. Compound **1** was extracted from the residue with 40 mL of benzene (60% yield).

(A3) Synthesis of $Mo_2Cl_4(NHEt_2)_4$ (1) Using Na/Hg Amalgam. A mixture of 0.15 g (0.24 mmol) of $Mo_2Cl_6(THF)_3$, 0.48 mmol of sodium amalgam (0.4 wt %), 1 mL (9.62 mmol) of $NHEt_2$, and 10 mL of THF in a dry ice/ethanol bath was allowed to reach room temperature and was stirred for 24 h. A 10 mL portion of benzene was added before filtration. The solution was evaporated to dryness to give **1** in 59% yield. Another portion of product (34%) could be obtained by an extraction from the residue with a mixture of 20 mL of benzene and 0.5 mL of $NHEt_2$. *Avoid handling solutions of 1 without the presence of free amine or pumping on the solid for a long time.*

(B) Reactions of $MoCl_3(THF)_3$ with $NHEt_2$. A 0.40 mL (3.85 mmol) portion of $NHEt_2$ was syringed into a suspension of 0.50 g (1.19 mmol) of $MoCl_3(THF)_3$ in 15 mL of THF. After 2 h of stirring, a mixture of 15 mL of THF and 15 mL of hexanes was layered over the reddish solution. In 10 days, yellow crystals of $[NH_2Et_2][MoCl_4(NHEt_2)_2]$ (**2**) were formed while the solution remained red. After removal of **2**, the red solution was evaporated to dryness, and an extraction with 10 mL of toluene gave again a red solution. Hexanes were layered to form red crystals of $[NH_2Et_2][Mo_2Cl_7(NHEt_2)_2]$ (**3**) after several days.

Crystals of $[NH_2Et_2][Mo_2Cl_7(NHEt_2)_2]$ (**3**) were also obtained from the reaction mixture under reflux for about 70 min, followed by an extraction with toluene and layering the resulting solution with isomeric hexanes.

The complex $Mo_2Cl_4(NHEt_2)_4$ (**1**) was present in this reaction mixture at very low concentration as indicated by ^1H NMR.

(C) Reactions of $Mo_2Cl_6(THF)_3$ with $NHEt_2/NHEt_2 \cdot HCl$. (C1) A 0.14 mL (1.35 mmol) portion of $NHEt_2$ was added to a suspension of 0.20 g (0.32 mmol) of $Mo_2Cl_6(THF)_3$ and 0.07 g (0.64 mmol) of $NHEt_2 \cdot HCl$ in 20 mL of THF. After 2 days of stirring at room temperature, the mixture was filtered and hexanes were added carefully. Crystals of $[NH_2Et_2][MoCl_4(NHEt_2)_2]$ (**2**) (70% yield) were obtained in 2 weeks.

(C2) A 0.10 mL (0.96 mmol) portion of $NHEt_2$ was added to a mixture of 0.21 g (0.34 mmol) of $Mo_2Cl_6(THF)_3$ and 0.10 g (0.91 mmol) of $NHEt_2 \cdot HCl$ in 20 mL of THF. After 3 days of stirring at room temperature, the solvent was removed under vacuum. The residue was dissolved in 15 mL of THF, and the solution was layered with isomeric hexanes. The first crystals obtained were found to be $[NH_2Et_2]_2[MoCl_5(NHEt_2)]$ (**4**).

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 16PC FTIR spectrometer using KBr pellets. ^1H NMR spectra were obtained on a UNITY-plus 300 multinuclear spectrometer. Resonances were referenced to TMS. X-band ESR spectra of dichloromethane glasses were recorded at 10 K with a frequency of 9.4 GHz on a Bruker ESP 300 spectrometer. Electronic spectral data were obtained in CH_2Cl_2 (with a drop of $NHEt_2$ to avoid decomposition), using a Cary 17D UV−vis spectrophotometer. Thermal analysis was performed by a TA 4000 thermogravimetric unit (under nitrogen; heating rate 2.5 °C/min). The positive FAB/DIP (DIP = direct insertion probe) mass spectra were acquired using a VG Analytical 70S high-resolution, double-focusing, sectored (EB) mass spectrometer. Samples

(10) $MoCl_3(THF)_3$: (a) Dilworth, J. R.; Richards, R. L. *Inorg. Synth.* **1980**, *20*, 121. (b) Dilworth, J. R.; Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1983**, 397. $Mo_2Cl_6(THF)_3$: (c) Boyd, I. W.; Wedd, A. G. *Aust. J. Chem.* **1976**, *29*, 1829.

Table 1. Crystallographic Data for Mo$_2$Cl$_4$(NHEt$_2$)$_4$ (**1**), [NH$_2$Et$_2$][MoCl$_4$(NHEt$_2$)$_2$] (**2**), [NH$_2$Et$_2$][Mo$_2$Cl$_7$(NHEt$_2$)$_2$]·C$_7$H$_8$ (**3**·C$_7$H$_8$), [NH$_2$Et$_2$]$_2$[MoCl$_5$(NHEt$_2$)] (**4**), and [NH$_2$Et$_2$]$_3$[Mo$_2$Cl$_8$(NEt$_2$)] (**5**)

	1	**2**	**3·C$_7$H$_8$**	**4**	**5**
formula	Mo$_2$Cl$_4$N$_4$C$_{16}$H$_{44}$	MoCl$_4$N$_3$C$_{12}$H$_{34}$	Mo$_2$Cl$_7$N$_3$C$_{19}$H$_{42}$	MoCl$_5$N$_3$C$_{12}$H$_{35}$	Mo$_2$Cl$_8$N$_4$C$_{16}$H$_{46}$
fw	626.23	458.16	752.59	494.62	770.05
space group	C2/c (No. 15)	P$\bar{1}$ (No. 2)	P2$_1$/n (No. 14)	P2$_1$/c (No. 14)	P2$_1$/n (No. 14)
a, Å	20.846(1)	9.820(3)	13.847(5)	11.710(2)	10.335(1)
b, Å	7.044(1)	10.305(1)	10.448(4)	12.363(2)	18.061(1)
c, Å	19.868(3)	11.510(1)	22.091(4)	30.272(7)	16.775(1)
α, deg		95.779(8)			
β, deg	118.72(2)	97.80(2)	96.68(2)	95.87(2)	95.558(8)
γ, deg		111.17(1)			
V, Å^3	2558.5(5)	1061.9(4)	3174(2)	4360(1)	3116.5(4)
Z	4	2	4	8	4
ρ_{calcd}, g·cm^{-3}	1.626	1.433	1.575	1.507	1.641
μ, mm^{-1}	1.407	1.117	1.392	1.213	1.504
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp, °C	−60	−60	−100	−100	−60
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.030, 0.068	0.041, 0.094	0.029, 0.073	0.060, 0.137	0.052, 0.115
R1,[a] wR2[b] (all data)	0.032, 0.071	0.048, 0.101	0.043, 0.079	0.099, 0.149	0.070, 0.132

[a] R1 $= \sum[|F_o| - |F_c|]/\sum|F_o|$. [b] wR2 $= [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$.

for analysis were prepared by dissolving the solid compound in either dichloromethane or diethylamine with *m*-nitrobenzyl alcohol (NBA) matrix and sodium iodide on the direct insertion probe tip. Elemental analyses were performed by Canadian Microanalytical Services, Ltd.

X-ray Crystallographic Procedures. Single crystals of compounds **1**−**5** were obtained as described above. X-ray diffraction studies of **3** and **4** were performed with an Enraf-Nonius CAD-4S diffractometer and graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\ 73$ Å) by using methods described previously.[11a,b] In each case, a suitable single crystal was affixed to the end of a quartz fiber with grease in a cold nitrogen stream (−100 °C). No appreciable decay was observed, as judged by periodic monitoring of the intensities of three standard reflections. The intensity data were corrected for Lorentz and polarization effects. For **3**, an empirical absorption correction based on a series of ψ scans was also applied.

X-ray diffraction experiments for **1**, **2**, and **5** were carried out on an Enraf-Nonius FAST diffractometer with an area detector using Mo Kα radiation. Details for data collection have been fully described elsewhere.[11c] Each crystal was mounted on the tip of a quartz fiber with silicone grease, and the setup was quickly placed in the cold N$_2$ stream (−60 °C) of a Model FR 558-S low-temperature controller. Fifty reflections were used in cell indexing and about 240 reflections in cell refinement ($16 < 2\theta < 42°$). Axial images were used to confirm the Laue group and all dimensions. The data were corrected for Lorentz and polarization effects by the MADNES program.[12] Reflection profiles were fitted and values of F^2 and $\sigma(F^2)$ for each reflection were obtained by the program PROCOR.[13]
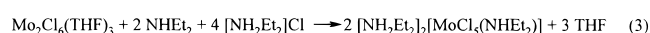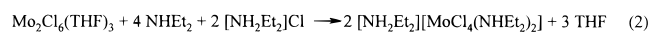
All calculations were done on a DEC Alpha running VMS. The coordinates of molybdenum and chlorine atoms for all of the structures were found in direct-method E maps using the structure solution program SHELXTL.[14] The positions of the remaining atoms were located by use a combination of least-squares refinements and difference Fourier maps in the SHELXL-93 program.[15] All hydrogen atoms for molecules **1**−**3** and those bonded to N atoms in molecules **4**

and **5** were refined independently. The rest of the H atoms for **4** and **5** were included in the structure factor calculations at idealized positions.

Relevant crystallographic data for complexes **1**−**5** are summarized in Table 1.
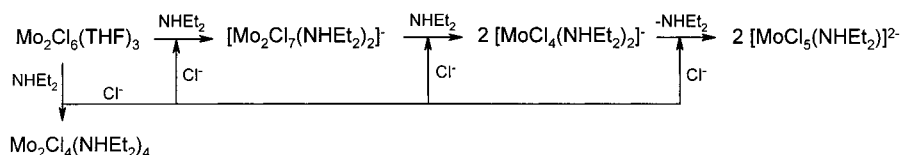
Results and Discussion

Synthetic Aspects. The complex Mo$_2$Cl$_4$(NHEt$_2$)$_4$ (**1**) can be isolated from the direct reaction of Mo$_2$Cl$_6$(THF)$_3$ with NHEt$_2$ in THF at room temperature. However, the yield by this method never exceeded 50%. The same observation was made[6,7] for the reactions between MoX$_3$ (X = Cl, Br) and NHMe$_2$ giving the complex Mo$_2$X$_4$(NHMe$_2$)$_4$. The authors of that work found that the reactions were very complex and the side products were heterogeneous. They suggested a disproportionation of the molybdenum(III) to molybdenum(II) and higher oxidation state compounds. In our case, we have managed to isolate those additional products and identified them all to be molybdenum-(III) complexes with Cl:Mo ratios higher than 3: [NH$_2$-Et$_2$][MoCl$_4$(NHEt$_2$)$_2$] (**2**), [NH$_2$Et$_2$]$_2$[MoCl$_5$(NHEt$_2$)] (**4**), and [NH$_2$Et$_2$]$_3$[Mo$_2$Cl$_8$(NEt$_2$)] (**5**). That led us to hypothesize that as the reaction proceeds, the starting material, Mo$_2$Cl$_6$(THF)$_3$, may react with amine in the presence of chloride liberated by the substitution process, thereby producing different molybdenum(III) complexes whose composition depends on the concentration of reactants. Variable-temperature monitoring of the interaction between Mo$_2$Cl$_6$(THF)$_3$ and NHEt$_2$ by ^{1}H NMR showed that the reaction to give **1** starts at about room temperature and is relatively slow. The presence of the starting molybdenum complex can be detected in solution for at least another 6 h. As a further test of our hypothesis, we carried out the reaction in the presence of NHEt$_2$·HCl, which is a source of both the diethylammonium ion and the chloride ion. As expected, the reduction to **1** was completely eliminated, and we were able to isolate the molybdenum(III) complexes [NH$_2$-Et$_2$][MoCl$_4$(NHEt$_2$)$_2$] (**2**) and [NH$_2$Et$_2$]$_2$[MoCl$_5$(NHEt$_2$)] (**4**) at different concentrations of the reactants (eqs 2 and 3).

$$\text{Mo}_2\text{Cl}_6(\text{THF})_3 + 4\ \text{NHEt}_2 + 2\ [\text{NH}_2\text{Et}_2]\text{Cl} \longrightarrow 2\ [\text{NH}_2\text{Et}_2][\text{MoCl}_4(\text{NHEt}_2)_2] + 3\ \text{THF} \quad (2)$$

$$\text{Mo}_2\text{Cl}_6(\text{THF})_3 + 2\ \text{NHEt}_2 + 4\ [\text{NH}_2\text{Et}_2]\text{Cl} \longrightarrow 2\ [\text{NH}_2\text{Et}_2]_2[\text{MoCl}_5(\text{NHEt}_2)] + 3\ \text{THF} \quad (3)$$
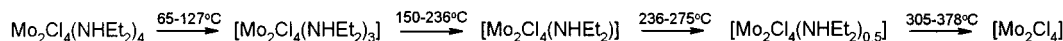
In view of all of this, an overall explanation of the reaction pathway seems clear. When the reduction to form complex **1**

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(12) Pflugrath, J.; Messerschmitt, A. MADNES, Munich Area Detector (New EEC) System, version EEC 11/9/89, with enhancements by Enraf-Nonius Corp., Delft, The Netherlands. A description of MADNES appears in: Messerschmitt, A.; Pflugrath, J. *J. Appl. Crystallogr.* **1987**, *20*, 306.

(13) (a) Kabsch, W. *J. Appl. Crystallogr.* **1988**, *21*, 67; (b) **1988**, *21*, 916.

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(15) Sheldrick, G. M. In *Crystallographic Computing 6*; Flack, H. D., Parkanyi, L., Simon, K., Eds.; Oxford University Press: Oxford, U.K., 1993; p 111.
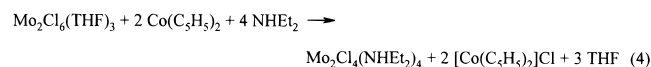
Scheme 1

$$\text{Mo}_2\text{Cl}_6(\text{THF})_3 \xrightarrow{\text{NHEt}_2} [\text{Mo}_2\text{Cl}_7(\text{NHEt}_2)_2]^- \xrightarrow{\text{NHEt}_2} 2\,[\text{MoCl}_4(\text{NHEt}_2)_2]^- \xrightarrow{-\text{NHEt}_2} 2\,[\text{MoCl}_5(\text{NHEt}_2)]^{2-}$$

(with Cl^- below each arrow, and a downward branch labeled NHEt_2, Cl^- to:)

$$\text{Mo}_2\text{Cl}_4(\text{NHEt}_2)_4$$

Scheme 2

$$\text{Mo}_2\text{Cl}_4(\text{NHEt}_2)_4 \xrightarrow{65\text{-}127\,^\circ\text{C}} [\text{Mo}_2\text{Cl}_4(\text{NHEt}_2)_3] \xrightarrow{150\text{-}236\,^\circ\text{C}} [\text{Mo}_2\text{Cl}_4(\text{NHEt}_2)] \xrightarrow{236\text{-}275\,^\circ\text{C}} [\text{Mo}_2\text{Cl}_4(\text{NHEt}_2)_{0.5}] \xrightarrow{305\text{-}378\,^\circ\text{C}} [\text{Mo}_2\text{Cl}_4]$$
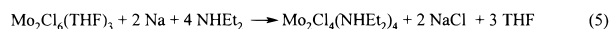
takes place, chloride ions are released and these react (together with amine) with more starting material thereby forming molybdenum(III) complexes that are inert toward reduction (Scheme 1). The only missing point here is the origin of the protons needed to form the ammonium cations. Their appearance is presumably connected with some oxidation process involving solvent, although this has not been proven yet.

Since we were considering complex **1** as a new starting material offering further access to Mo$^{\text{II}}$–Mo$^{\text{II}}$ chemistry, a better synthesis was required. To achieve this goal, we needed to accelerate the reduction process and to render the liberated chlorides unreactive. The use of tin was tried first but did not work well. The use of cobaltocene allowed us to increase the yield of the reaction (eq 4) up to 60%. In this case, a drawback

$$\text{Mo}_2\text{Cl}_6(\text{THF})_3 + 2\,\text{Co}(\text{C}_5\text{H}_5)_2 + 4\,\text{NHEt}_2 \longrightarrow$$
$$\text{Mo}_2\text{Cl}_4(\text{NHEt}_2)_4 + 2\,[\text{Co}(\text{C}_5\text{H}_5)_2]\text{Cl} + 3\,\text{THF} \quad (4)$$

is the low solubility of Co(C$_5$H$_5$)$_2$ in the solvents used, which slows down the reduction process.

The best results were obtained by employing 2 equiv of sodium amalgam in a reaction described by eq 5. Complex **1**

$$\text{Mo}_2\text{Cl}_6(\text{THF})_3 + 2\,\text{Na} + 4\,\text{NHEt}_2 \longrightarrow \text{Mo}_2\text{Cl}_4(\text{NHEt}_2)_4 + 2\,\text{NaCl} + 3\,\text{THF} \quad (5)$$

in nearly quantitative yield could easily be separated from sodium chloride and mercury in the reaction mixture and used directly for further syntheses. This, therefore, is the method of choice for preparing **1**.

The initial reaction between Mo$_2$Cl$_6$(THF)$_3$ and NHEt$_2$ is very unusual as it results in a two-electron reduction of the molybdenum(III) complex at room temperature. In general,[16a] the best way to obtain Mo$_2$X$_4$L$_4$ compounds is substitution on other molybdenum(II) complexes. The use of molybdenum(III) compounds, even under reflux conditions, is not commonly considered the preferred procedure for the purpose. We also found that to be true when we tried to employ the monomeric complex MoCl$_3$(THF)$_3$ instead of Mo$_2$Cl$_6$(THF)$_3$. The yield of complex **1** was very poor; indeed, it could just be detected in the reaction products by ^{1}H NMR at very low concentration. The main products in this process were the molybdenum(III) species: the already-mentioned **2** and the new complex [NH$_2$-Et$_2$][Mo$_2$Cl$_7$(NHEt$_2$)$_2$] (**3**). Moreover, compound **3** could be isolated as a major component of the reaction under reflux conditions when dimerization takes place.

$$2\,[\text{NH}_2\text{Et}_2][\text{MoCl}_4(\text{NHEt}_2)_2] \longrightarrow [\text{NH}_2\text{Et}_2][\text{Mo}_2\text{Cl}_7(\text{NHEt}_2)_2] + [\text{NH}_2\text{Et}_2]\text{Cl} + 2\,\text{NHEt}_2 \quad (6)$$

The presence of traces of the dimolybdenum(II) complex **1** in the reaction mixture becomes understandable if we take into

(16) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Oxford University Press: New York, 1993: (a) Table 3.1.2, p 181; (b) Table 3.1.1, p 143.

account the monomer–dimer equilibrium[10c] for the starting material in solution.

$$2\,\text{MoCl}_3(\text{THF})_3 \rightleftharpoons \text{Mo}_2\text{Cl}_6(\text{THF})_3 + 3\,\text{THF} \quad (7)$$
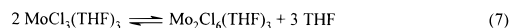
Even when amine was added rapidly, some of the Mo$_2$Cl$_6$-(THF)$_3$ material was present in solution at the very beginning of the interaction. However, the concentration of **1** is not enough to explain the amount of Cl$^-$ and H$^+$ sufficient to form the molybdenum(III) complexes **2** and **3**. In this case, there might be other products of molybdenum(III) with Cl:Mo ratios less than 3, such as [Mo$_2$Cl$_2$(NEt$_2$)$_4$] or [Mo$_2$Cl$_4$(NEt$_2$)$_2$(NHEt$_2$)$_2$], which were not isolated due to their high solubility.

Properties of Mo$_2$Cl$_4$(NHEt$_2$)$_4$ (1). The infrared spectrum of the complex exhibits the characteristic absorptions of the N–H stretch (3219 cm^{-1}) and N–H bend (1460 cm^{-1}). Corresponding bands appear at 3182 and 1438 cm^{-1} for W$_2$-Cl$_4$(NEt$_2$)$_2$(NHEt$_2$)$_2$, where there are strong hydrogen bonds.[3]

In the electronic spectrum of **1**, the maximum of the δ–δ^* transition absorption band appears at 534 nm, which is very close to the absorption at 555 nm found in the diffuse reflectance electronic absorption spectrum of Mo$_2$Cl$_4$(NHMe$_2$)$_4$.[7]

Complex **1** is air and moisture sensitive both in solution and in the solid state. However, the microcrystalline material can be kept for a long time under an atmosphere of nitrogen or argon. In benzene, toluene, or THF solution, **1** is relatively stable in the presence of free diethylamine, but the NHEt$_2$ groups are very labile, and compound **1** loses amine spontaneously even in benzene. A fresh solution of **1** in deuterated benzene shows the signals of the complex, but other signals corresponding to free amine start to grow rapidly, accompanied by the precipitation of a brown solid. All the peaks are broad, which indicates an exchange of amines. The brown insoluble compound from the decomposition is likely to be a product of polymerization of dimers after the loss of some amines. Indeed, the mass spectrum of **1** (FAB$^+$, NBA/NaI) exhibits a peak at *m/z* 804, which corresponds unequivocally to a high-nuclearity fragment from a polymerization process. In the ^{1}H NMR spectrum of complex **1** in deuterated dichloromethane, signals assigned to the cation [NH$_2$Et$_2$]$^+$ [7.13 (NH$_2$), 2.90 (CH$_2$), and 1.27 (CH$_3$) ppm] appear instead those for the free amine. Therefore the decomposition process is different in this solvent and probably involves an oxidation of **1**.

Compound **1** is also thermally unstable. The thermogravimetric weight loss curve for this compound under a nitrogen atmosphere shows that at 378 °C the weight loss is 47%. On the assumption that this decrease in weight is totally due to the loss of amine (which constitutes exactly this percentage of the molecular weight of **1**), the final product should have the composition [MoCl$_2$]. This process occurs in four steps. Complex **1** starts to lose weight very slowly at about 65 °C (the boiling point of the amine). The highest percentage of weight loss per degree is at 110 °C (0.7%/°C), and at 127 °C
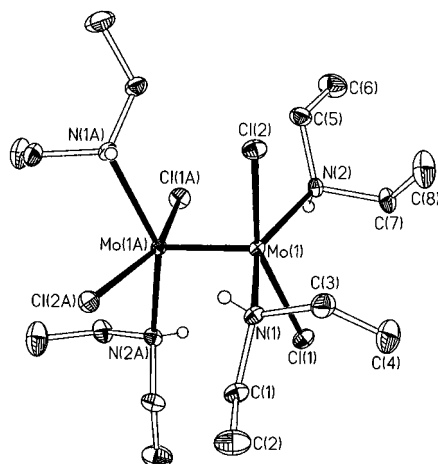
Figure 1. Perspective drawing of $Mo_2Cl_4(NHEt_2)_4$ (**1**). Atoms are represented by thermal ellipsoids at the 40% probability level. Hydrogen atoms of the ethyl groups are omitted.

the compound has lost exactly 1 mol of amine. Between approximately 127 and 150 °C, the loss is not significant. At 150 °C, the loss of amine increases again, and at 236 °C, another 2 moles of amine is released. At 275° C, another 0.5 mol of amine is gone. The last 0.5 mol of amine is liberated between 305 and 378 °C. According to the TGA data, the thermal decomposition route shown in Scheme 2 may be proposed for compound **1**.

Structural Details. $Mo_2Cl_4(NHEt_2)_4$ (1). This compound crystallizes in the monoclinic space group *C*2/*c* with four molecules in the unit cell. The molecule resides on a 2-fold axis and has a metal−metal distance of 2.1330(6) Å, which is consistent with the presence of a quadruple bond between the Mo atoms.[16b] Diethylamine ligands on each metal center are trans (Figure 1) with an N−Mo−N angle of 148.5(1)°. The disposition of the ligands corresponds to the well-known type of 1,3,6,8-isomers for compounds of $Mo_2X_4L_4$ stoichiometry (X = Cl, L = PMe_3,[17a] PEt_3,[17b] PMe_2Ph,[17c] $PMePh_2$,[17d] $PHPh_2$;[17c] SEt_2;[17e] L = $NHMe_2$, X = OCH_2CMe_3,[18a] OC_6F_5[18b]). As a matter of fact, **1** is isostructural with some of these complexes (L = PMe_3, PMe_2Ph, SEt_2, X = OC_6F_5). All of the above-mentioned species are characterized by $Mo_2X_4L_4$ cores with D_{2d} virtual symmetry. This is in contrast to the small group of compounds $Mo_2X_4L_4$ (X = Cl, Br, L = pic,[8] 4-Bu^{t}py[9]) which possess centrosymmetric cores with D_{2h} symmetry (Chart 1c). The latter complexes can be assigned as 1,3,5,7-isomers.

The complex $Mo_2Cl_4(NHEt_2)_4$ (**1**) is the first one structurally characterized for the composition of $M_2X_4(NR_3)_4$ (M = transition metal, X = halide, NR_3 = monodentate alkylamine). The same structure was earlier proposed[7] for $Mo_2Cl_4(NHMe_2)_4$, and now there is support for that. In the course of handling **1**, we did not observe any evidence of the presence of other isomers such as 1,3,5,7 or 1,2,7,8, recently discovered[19] for analogous phosphine complexes.

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Table 2. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for $Mo_2Cl_4(NHEt_2)_4$ (**1**)

Mo(1)−Mo(1A)	2.1330(6)	Mo(1)−Cl(1)	2.4436(9)
Mo(1)−N(1)	2.280(3)	Mo(1)−Cl(2)	2.4415(9)
Mo(1)−N(2)	2.289(3)		
N(1)−Mo(1)−N(2)	148.5(1)	Cl(1)−Mo(1)−Cl(2)	157.08(3)
N(1)−Mo(1)−Cl(1)	91.45(8)	Mo(1A)−Mo(1)−N(1)	106.07(7)
N(1)−Mo(1)−Cl(2)	82.13(8)	Mo(1A)−Mo(1)−N(2)	105.42(7)
N(2)−Mo(1)−Cl(1)	82.94(8)	Mo(1A)−Mo(1)−Cl(1)	101.27(3)
N(2)−Mo(1)−Cl(2)	91.09(8)	Mo(1A)−Mo(1)−Cl(2)	101.66(3)
N(1)−Mo(1)−Mo(1A)−Cl(2A)		8.47(8)	
N(2)−Mo(1)−Mo(1A)−Cl(1A)		8.88(8)	
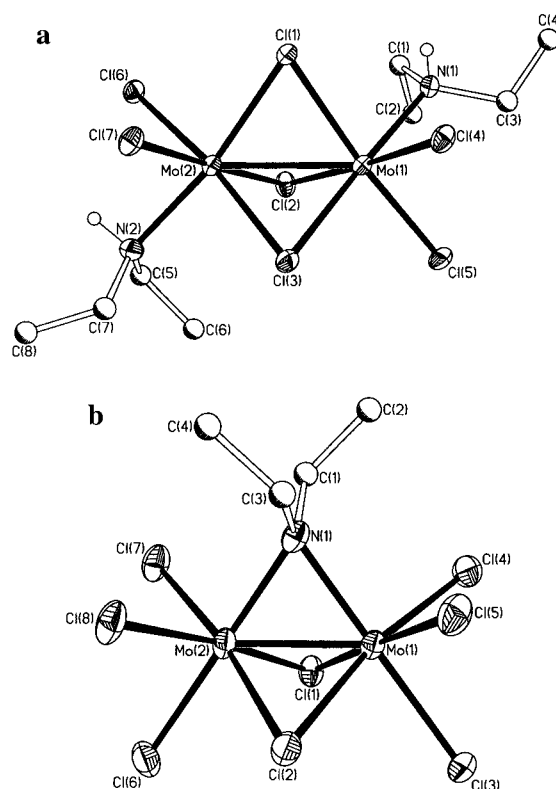
Figure 2. Perspective drawings of (a) $[Mo_2Cl_7(NHEt_2)_2]^-$ in **3**·C_7H_8 and (b) $[Mo_2Cl_8(NEt_2)]^{3-}$ in **5**. Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon and hydrogen atoms are shown as spheres of arbitrary radii. Hydrogen atoms of the ethyl groups are omitted.

Some key dimensions for complex **1** are displayed in Table 2. They are all about as expected. The average Mo−Cl distance 2.4426(9) Å falls within the range of 2.385−2.531 Å for those in the analogous $Mo_2Cl_4L_4$[17] (L = PR_3, SEt_2) species. The Mo−N distance of 2.285(3) Å corresponds well with the molybdenum−nitrogen single-bond lengths of 2.24−2.30 Å in dimethylamine complexes of the Mo_2^{4+} core, $Mo_2X_4(NHMe_2)_4$[18] (X = OCH_2CMe_3, OC_6F_5). The absence of strong intramolecular hydrogen bonding in the title compound is a little surprising since we have observed[3] strong N−H···Cl bonding (2.303 Å) in the ditungsten complex $W_2Cl_4(NEt_2)_2(NHEt_2)_2$. For compound **1**, this interaction is significantly weaker (all distances are about 2.88(4) Å), perhaps because it is distributed between two chlorine atoms, one on the same Mo center and another one across the metal−metal bond. On the other hand, the hydrogen bonding in **1** still affects the structure: for each nitrogen atom, one of the two N−Mo−Cl angles is about 10° smaller for the chlorine atom involved in this interaction (Table 2). Another secondary effect is the deviation from eclipsed geometry; the N−Mo−Mo−Cl torsion angles of 8.47(8) and

Table 3. Selected Bond Distances (Å) and Angles (deg) for
$[Mo_2Cl_7(NHEt_2)_2]^-$ in **3**

Mo(1)−Mo(2)	2.7348(9)	Mo(2)−Cl$_b$ (av)	2.451(1)
Mo(1)−N(1)	2.232(3)	Mo(1)−Cl$_t$ (av)	2.383(1)
Mo(2)−N(2)	2.226(3)	Mo(2)−Cl$_t$ (av)	2.394(1)
Mo(1)−Cl$_b$ (av)	2.465(1)		
Mo−Cl$_b$−Mo (av)	67.59(3)	Mo−Mo−Cl$_t$ (av)	125.20(3)
Mo−Mo−Cl$_b$ (av)	56.21(2)	N−Mo−Cl$_t$ (av)	86.46(8)
Cl$_b$−Mo−Cl$_b$ (av)	91.86(3)	Cl$_t$−Mo−Cl$_t$ (av)	90.31(3)
Mo−Mo−N (av)	129.91(7)		

Table 4. Selected Bond Distances (Å) and Angles (deg) for
$[Mo_2Cl_8(NEt_2)]^{3-}$ in **5**

Mo(1)−Mo(2)	2.431(1)	Mo(2)−Cl$_b$ (av)	2.465(2)
Mo(1)−N(1)	2.149(6)	Mo(1)−Cl$_t$ (av)	2.455(2)
Mo(2)−N(1)	2.154(7)	Mo(2)−Cl$_t$ (av)	2.458(2)
Mo(1)−Cl$_b$ (av)	2.466(2)		
Mo(1)−N(1)−Mo(2)	68.8(2)	N(1)−Mo−Cl$_b$ (av)	95.1(2)
Mo(1)−Cl$_b$−Mo(2) (av)	59.07(5)	Cl$_b$−Mo−Cl$_b$ (av)	96.67(7)
Mo−Mo−N(1) (av)	55.6(2)	Mo−Mo−Cl$_t$ (av)	125.65(6)
Mo−Mo−Cl$_b$ (av)	60.47(5)	Cl$_t$−Mo−Cl$_t$ (av)	89.41(8)

8.88(8)° are among the largest known for analogous Mo−Mo
quadruply-bonded molecules.

**$[NH_2Et_2][Mo_2Cl_7(NHEt_2)_2] \cdot C_7H_8$ ($3 \cdot C_7H_8$) and $[NH_2Et_2]_3$-
$[Mo_2Cl_8(NEt_2)]$ (5).** These two dimolybdenum(III) compounds
form crystals in the monoclinic space group $P2_1/n$ with four
formula units per unit cell. Complex **3** also contains four
molecules of toluene. Both dinuclear anions themselves have a
confacial bioctahedral geometry (Figure 2). In the crystal
structure of **3**, two molybdenum atoms are bridged by three
chlorine atoms while two amine groups occupy terminal
positions at each end of the molecule in a gauche configuration
(Figure 2a). The Mo−N distances are 2.232(3) and 2.226(3)
Å, clearly identifying both ligands as amine groups. These values
agree well with the Mo−NHMe$_2$ bond lengths in two edge-
sharing complexes,[20] $Mo_2(OAr-3,5-Me_2)_6(NMe_2)(NHMe_2)_2$ and
$[Mo_2(OAr-4-Me)_7(NHMe_2)_2]^-$, which range from 2.226 to 2.290
Å. A molybdenum to terminal amido group bond length would
be much shorter, are generally[21] in the range 1.90−1.95 Å. The
Mo−Cl bonds in **3** (Table 3) have normal values for that type
of complex, including the obvious difference between distances
from Mo to bridging (2.458(1) Å) and terminal (2.389(1) Å)
chlorides.

In the edge-sharing anion $[Mo_2Cl_8(NEt_2)]^{3-}$ of **5**, two metal
atoms are bridged by an amido group and two chlorine atoms,
with the other six chlorides being terminal (Figure 2b). The
Mo−N distances of 2.149(6) and 2.154(7) Å (Table 4) cor-
respond well with the molybdenum−bridging dimethylamido
bonds in the above-mentioned complexes[20,21] (2.107−2.168 Å).
There is little difference between the Mo−Cl$_b$ and Mo−Cl$_t$
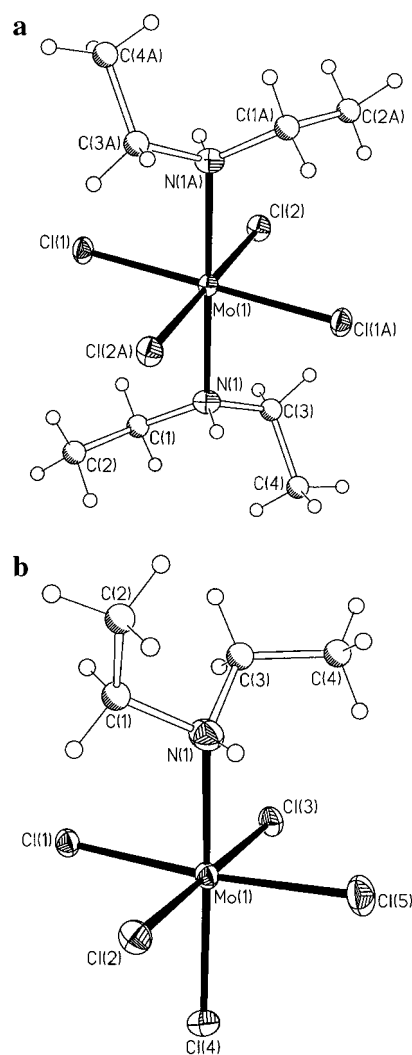
Figure 3. Perspective drawings of (a) $[MoCl_4(NHEt_2)_2]^-$ in **2** and (b)
$[MoCl_5(NHEt_2)]^{2-}$ in **4**. Atoms are represented by thermal ellipsoids
at the 40% probability level. Carbon and hydrogen atoms are shown
as spheres of arbitrary radii.

distances in this case, but there is an unambiguous trans effect,
the distances from Mo to terminal chlorides trans to N (2.518-
(2) Å) being considerably longer than those to terminal chlorides
trans to Cl (2.426(2) Å).

The main difference between the dimolybdenum anions in **3**
and **5** is the difference in the Mo−Mo distance, which is ∼0.3
Å shorter in the latter complex. These two complexes belong
to the large family of d^3−d^3 face sharing bioctahedral com-
pounds formed by molybdenum(III) (Table 5). The [Mo$_2$Cl$_7$-

Table 5. Face-Sharing Bioctahedral Dimolybdenum(III) Complexes

type	complex	Mo−Mo, Å	ref
$[Mo_2(\mu\text{-}Cl)_3Cl_6]^{3-}$	$[Mo_2Cl_9]^{3-}$	2.619(1)−2.815(1)	22
$[Mo_2(\mu\text{-}Cl)_3Cl_5L]^{2-}$	$[Mo_2Cl_8(PEt_3)]^{2-}$	2.767(2)	23
$[Mo_2(\mu\text{-}Cl)_3Cl_4L_2]^-$	$[syn\text{-}Mo_2Cl_7(PMe_3)_2]^-$	2.694(3), 2.713(2), 2.763(2)	24
	$[gauche\text{-}Mo_2Cl_7(PMe_3)_2]^-$	2.7171(3)	24
	$[gauche\text{-}Mo_2Cl_7(SMe_2)_2]^-$	2.746(9)	25
	$[gauche\text{-}Mo_2Cl_7(NEt_2H)_2]^-$	2.7348(9)	this work
$Mo_2(\mu\text{-}Cl)_3Cl_3L_3$	$anti\text{-}Mo_2Cl_6(THF)_3$	2.602(1), 2.620(1)	26
	$anti\text{-}Mo_2Cl_6(THT)_3$	2.6896(6)	27
	$anti\text{-}Mo_2Cl_6(PEt_3)_3$	2.815(4), 2.753(2)	28, 29
	$anti\text{-}Mo_2Cl_6(PMe_2Ph)_3$	2.6582(5)	29
$[Mo_2(\mu\text{-}Cl)_2(\mu\text{-}L)Cl_6]^{3-}$	$[Mo_2Cl_8H]^{3-}$	2.371(1)−2.384(1)	30
	$[Mo_2Cl_8(NEt_2)]^{3-}$	2.431(1)	this work
$Mo_2(\mu\text{-}Cl)_2(\mu\text{-}L)Cl_4L_2$	$Mo_2Cl_6(THT)_3$	2.470(1)	27
	$Mo_2Cl_6(SMe_2)_3$	2.462(2)	25

$(NHEt_2)_2]^-$ ion belongs with those complexes that have three bridging chlorides and a mixture of chloride ions and neutral ligands in the six terminal positions. All these species are characterized by Mo–Mo bond lengths from 2.602 to 2.815 Å, and they all show some paramagnetism. The other group of this family has only two bridging Cl atoms together with some neutral (THT, SMe_2) or anionic (H^-, NEt_2^- in the case of **5**) ligand. The metal–metal bond becomes much shorter (2.371–2.470 Å) for the latter species, which are now diamagnetic. Recently we found[31] that this same effect also occurs for d^3–d^3 edge-sharing dirhenium(IV) complexes when the Re–Re distance in $[Re_2(\mu\text{-Cl})_3Cl_6]^-$ (2.704 Å) is compared with that in $[Re_2(\mu\text{-PEt}_2)_3Cl_6]^-$ (2.402 Å).

$[NH_2Et_2][MoCl_4(NHEt_2)_2]$ (2) and $[NH_2Et_2]_2[MoCl_5(NHEt_2)]$ (4). Both of these compounds crystallize with two molecules per asymmetric unit. Their anionic parts are octahedrally coordinated molybdenum(III) monomers [*trans*-$MoCl_4(NHEt_2)_2]^-$ (**2**, Figure 3a) and $[MoCl_5(NHEt_2)]^{2-}$ (**4**, Figure 3b). The average Mo–N distances are 2.258(4) and 2.25(1) Å, Mo–Cl distances are 2.441(1) and 2.443(3) Å, and the bond angles are 85.1(1)–94.9(1) and 85.0(3)–94.15(8)° for **2** and **4**, respectively. These two anions are in no essential way different from a large group of other mononuclear molybdenum(III) species of types $[MoX_4L_2]^-$ and $[MoX_5L]^{2-}$ (L = H_2O, THF, py, PR_3).[32]

Concluding Remarks

We have now found that diethylamine can reduce dimolybdenum(III) species to dimolybdenum(II) complexes at room temperature. A parallel reaction takes place in this process when chloride ions, released upon substitution by amines, react with more starting material to produce different chloride/amine complexes of molybdenum(III) which are inert to reduction. Nevertheless, we present a method whereby the reduction product, $Mo_2Cl_4(NHEt_2)_4$ (**1**), can be isolated and purified in high yield. We believe that this complex will offer further access to the chemistry of Mo_2^{4+} core compounds with the possibility of the substitution of the amine groups by a variety of ligands at ambient (or even low) temperature. We shall demonstrate this point in forthcoming publications.

Supporting Information Available: Five X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

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