Unusual Activation Pathways of Amines in the Reactions with Molybdenum Pentachloride

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The 1:1 molar reactions at room temperature of $MoCl_5$ with aliphatic amines were investigated in dichloromethane. Pyrrolidine, diethylamine and dibenzylamine underwent dehydrogenative oxidation when allowed to react with $MoCl_5$; the compounds $[MoCl_5\{NCH(CH_2)_3\}]$, **1**, and $[CH_3CH{=}NHEt][MoOCl_4]$, **2**, were isolated in moderate to low yields from $MoCl_5$/pyrrolidine and $MoCl_5/NHEt_2$, respectively. The chloride-amide complex $[MoCl_4(NEt_2)]$, **3**, was afforded in 65% yield from $MoCl_5$ and Et_2NSiMe_3. The interaction of $MoCl_5$ with Me_2NSiMe_3 was accompanied by activation of the solvent, and the complexes $[MoCl_3(NMe_2)(\kappa^2\text{-}Me_2NCH_2NMe_2)]$, **4a**, and $[MoCl_3(NMe)(\kappa^2\text{-}Me_2NCH_2NMe_2)]$, **4b**, co-crystallized from the reaction mixture. The reactions of $MoCl_5$ with a series of primary amines afforded mixtures of products, and the Mo(VI) chloride imido complexes $[MoCl_4(NR)]_2$ (R = Cy, **5a**; ^{t}Bu, **5b**) were isolated in *ca.* 40% yield from $MoCl_5/NH_2R$ (R = Cy, ^{t}Bu). C–H bond activation may be viable in the reactions of $MoCl_5$ with tertiary amines: the compounds $[(CH_2Ph)_2N{=}CHPh]_2[MoCl_6]\cdot CH_2Cl_2$, **6**, and $[NHEt_3]_2[Mo_2Cl_{10}]$, **7**, were obtained from $MoCl_5$/tribenzylamine and $MoCl_5$/triethylamine, respectively. Pyrrolidine and tribenzylamine underwent analogous activation pathways when allowed to react with $[MoCl_3\{OCH(CF_3)_2\}]_2$ in the place of $MoCl_5$. The isolated metal products were characterized by analytical and spectroscopic techniques, in addition the structures of **1**, **2**, **4**, **5a**, **6**$\cdot CH_2Cl_2$ and **7** were ascertained by single crystal X-ray diffraction studies. The organic products were identified by NMR and GC-MS after hydrolysis of the reaction mixtures. DFT calculations were carried out in order to assist the IR assignments, and clarify structural and mechanistic aspects.

Introduction

Homoleptic chlorides of high valent transition metals have been employed as effective catalytic precursors in a variety of organic reactions.[1] These compounds typically manifest their strong acidic nature towards primary and secondary amines, affording amido-derivatives via aminolysis reactions. This behaviour has been well established with reference to group 4 metal tetrahalides,[2] and Nb and Ta pentahalides.[3] Nevertheless alternative reaction pathways may be working, and this is probably the reason why mixed chloride amide complexes have been more frequently prepared by treatment of the parent metal chlorides with lithium amides.[4] More precisely, when the metal chloride is allowed to react with an excess of primary amine, the formation of metal-amido species (M–NHR) may be followed by proton abstraction affording imido ligands (M=NR). This usually takes place without a change in the oxidation state of the metal centre.[2e,3d,5] Alternatively, imido derivatives have been obtained by the addition of a suitable base to the metal chloride/amine system.[3c,6] In some cases, high valent transition metal chlorides act as single electron oxidant reagents towards amines, the amines possibly converting into the relevant iminium cations.[3a,7] This kind of reactivity usually regards tertiary amines, and, for instance, the redox interaction between $TiCl_4$ and trialkylamines constitutes an efficient catalytic system serving diverse organic transformations, such as the C–C coupling of esters,[8] the synthesis of 2,5-diarylpyrroles [9] and α,β-unsaturated carbonyl compounds.[10] Being involved with the coordination chemistry of group 6 chlorides, we have recently elucidated the reactions of WCl_6 with limited amounts of tribenzylamine and triphenylamine, respectively. Both the reactions proceed with single electron transfer from the organic reactant to the metal centre, followed by C–H bond activation and intermolecular hydrogen migration.[11]

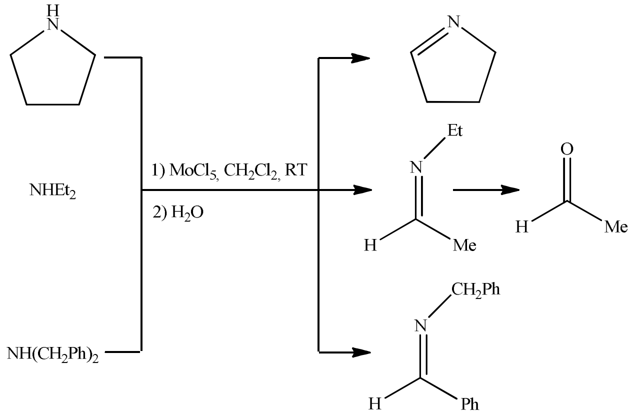
In this overall scenario, information on the direct interaction of molybdenum pentachloride, $MoCl_5$, with amines still remain rather sparse in the literature. Simple coordination adducts were claimed to be formed by combination of $MoCl_5$ with tertiary aliphatic amines.[12] On the other hand, based on elemental analyses, it was suggested that the reactions with an excess of primary and secondary aliphatic amines afforded mixed chloride amide complexes, as expected from aminolysis processes.[12] Later on, Nielson reported the Mo(V) compound $[Mo(NCMe_3)(NHCMe_3)Cl_2(NH_2CMe_3)]_2$, containing amino, amido and imido groups, as the prevalent product of the reaction of $MoCl_5$ with six equivalent of *tert*-butylamine in benzene.[5] Similarly, $[Mo(NCMe_3)Cl_3(NH_2CMe_3)]_2$ was obtained from $MoCl_5$ and $Me_3SiNHCMe_3$ (1:2 ratio).[5]

In the present paper, we describe the results of our investigation on the reactivity of $MoCl_5$ with a selection of primary, secondary and tertiary aliphatic amines, including *N*-(trimethylsilyl)dialkylamines, in a weakly coordinating solvent. A comparison with the analogous reactions of the Mo(V) chloride alkoxide compound $MoCl_3[OCH(CF_3)_2]_2$ [13] will be discussed.

Results and Discussion

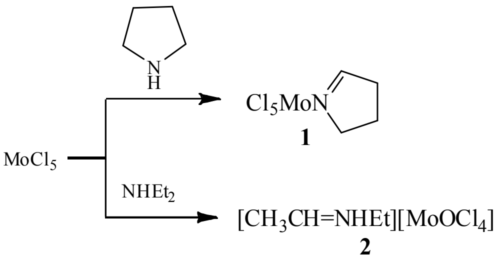
1. Reactions of $MoCl_5$ with secondary amines.

We were interested in the synthesis of Mo(V) mixed chloride amide compounds of the type $MoCl_x(NR_2)_{5-x}$. According to the information available in the literature,[12] we performed the reactions of $MoCl_5$ with a selection of secondary aliphatic amines. Surprisingly, these reactions did not furnish the expected products. When $MoCl_5$ was allowed to react with pyrrolidine, diethylamine and dibenzylamine, in 1:1 molar ratios in CH_2Cl_2, mixtures of metal products were obtained which could not be fully identified (vide infra). In order to understand the destiny of the organic material, we treated the respective solid residues with $CDCl_3$/water.[14,15] Subsequent NMR analyses pointed out the prevalent formation of dehydrogenative oxidation products (Scheme 1). More in detail, almost complete conversion of pyrrolidine to pyrroline was ascertained, while ca. 50% of dibenzylamine was found converted into the relevant imine. Pyrroline was detected in its monomeric form, and no evidence for oligomerization was found.[16] Acetaldehyde was the only product detected from $MoCl_5/NHEt_2$, the aldehyde presumably generating from *N*-ethylidene ethanamine in hydrolytic conditions (see below).



Scheme 1. $MoCl_5$-directed oxidation of dialkylamines.

Several attempts were conducted in order to isolate metal products from the highly moisture sensitive reaction systems. Hence, $[MoCl_5\{NCH(CH_2)_3\}]$, **1**, and minor amounts of $[CH_3CH{=}NHEt][MoOCl_4]$, **2**, were isolated as crystalline materials from $MoCl_5$/pyrrolidine and $MoCl_5/NHEt_2$, respectively, and X-ray characterized (scheme 2).



Scheme 2. Isolation of metal complexes from the reactions of $MoCl_5$ with pyrrolidine and diethylamine.

Compounds **1** and **2** contain a pyrroline ligand and a *N*-ethylidenium ethanamine cation, respectively, coherently with the NMR analyses on the corresponding hydrolyzed reaction mixtures. In particular, the detection of $[MeCH{=}NHEt]^+$ as found in **2** confirms the occurrence of dehydrogenative oxidation of diethylamine by means of $MoCl_5$ (Scheme 1); the presence of the oxido ligand within the counterion appears to be the result of fortuitous hydrolysis of Mo-Cl bonds in the course of the crystallization procedure.[17] Views of the X-ray structures of **1** and **2** are given in Figures 1 and 2, the relevant bonding parameters being reported in Tables 1 and 2.

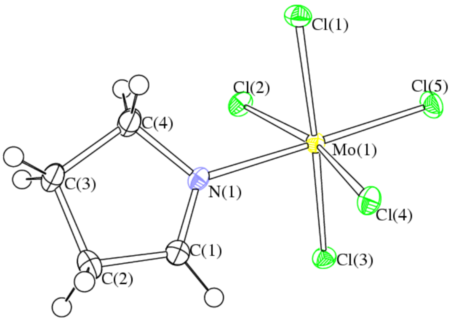


Figure 1. Molecular structure of **1**. Displacement ellipsoids are at the 50% probability level.

Table 1.Selected bond distances (Å) and angles (°) for **1**.

Mo(1)–N(1)	2.193(3)	Mo(1)–Cl(1)	2.3252(8)
Mo(1)–Cl(2)	2.2804(9)	Mo(1)–Cl(3)	2.3257(8)
Mo(1)–Cl(4)	2.2730(10)	Mo(1)–Cl(5)	2.2973(9)
N(1)–C(1)	1.281(4)	N(1)–C(4)	1.477(4)
C(1)–C(2)	1.481(5)	C(3)–C(4)	1.526(5)
C(2)–C(3)	1.541(5)		
Cl(1)–Mo(1)–Cl(3)	176.33(3)	Cl(2)–Mo(1)–Cl(4)	165.07(3)
Cl(5)–Mo(1)–N(1)	177.62(7)	Mo(1)–N(1)–C(1)	125.3(2)
Mo(1)–N(1)–C(4)	124.8(2)	C(1)–N(1)–C(4)	109.9(3)
N(1)–C(1)–C(2)	115.4(3)	C(1)–C(2)–C(3)	102.0(3)
C(2)–C(3)–C(4)	104.1(3)	C(3)–C(4)–N(1)	105.4(3)

Compound **1** represents a very rare example of crystallographically characterized $MoCl_5L$ (L = organic molecule) complex.[18] The Mo(V) centre is octahedrally coordinated to five chlorides and one pyrroline (3,4-dihydro-2H-pyrrole) ligand. Pyrroline is a valuable compound [19] which has been produced from pyrrolidine by means of various oxidants.[20]

A limited number of metal complexes containing pyrroline are known and in all of them the pyrroline ligand is bonded through the N-atom,[21] apart one case in which pyrroline is η^2 coordinated *via* the imine bond.[22] The Mo(1)–N(1) distance [2.193(3) Å] is typical of a $N(sp^2)$–Mo(V) dative bond,[23] while C(1)–N(1) [1.281(4) Å] is an imine double bond.[21,22,24]

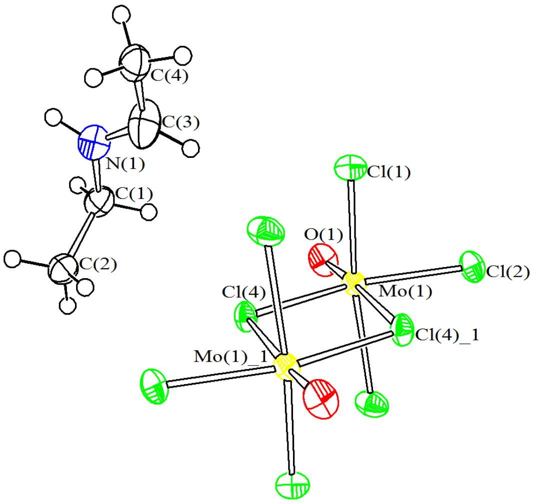


Figure 2. Molecular structure of **2**. Displacement ellipsoids are at the 50% probability level. Symmetry transformations used to generate equivalent atoms: –x,–y+1,-z+1.

Table 2. Selected bond distances (Å) and angles (°) for **2**.

Mo(1)-O(1)	1.648(2)	Mo(1)-Cl(1)	2.3718(10)
Mo(1)-Cl(2)	2.3380(10)	Mo(1)-Cl(3)	2.3650(10)
Mo(1)-Cl(4)	2.4055(9)	Mo(1)-Cl(4_1)	2.865(2)
N(1)-C(1)	1.472(5)	N(1)-C(3)	1.276(5)

C(1)-C(2)	1.501(5)	C(3)-C(4)	1.467(6)
Cl(1)-Mo(1)-Cl(3)	163.47(3)	Cl(2)-Mo(1)-Cl(4)	157.89(3)
O(1)-Mo(1)-Cl(4_1)	175.47(3)	Cl(4)-Mo(1)-Cl(4_1)	76.07(3)
O(1)-Mo(1)-Cl(2)	102.66(9)	Mo(1)-Cl(4)-Mo(1_1)	103.93
C(1)-C(1)-N(1)	109.8(3)	C(1)-N(1)-C(3)	125.1(4)
N(1)-C(3)-C(4)	122.3(4)		

Symmetry transformations used to generate equivalent atoms: –x,–y+1,-z+1

Compound **2** is an ionic one, composed of $[MeCH{=}NHEt]^+$ cations and $[Mo_2O_2Cl_8]^{2-}$ anions. The structure of $[MeCH{=}NHEt]^+$ is unprecedented, but closely related to the crystallographically characterized cation $[Me_2C{=}N(H)(Et)]^+$.[25] The iminium N(1)–C(3) interaction [1.276(5) Å] displays a typical double bond character. In addition, the NH iminium group is involved in inter-molecular H-bonds with the terminal Cl ligand of the anion [N(1)–H(1) 0.88 Å, H(1)···Cl(4)#1 2.92 Å, N(1)···Cl(4)#1 3.770(3) Å, <N(1)H(1)Cl(4)#1 163.7°; N(1)-H(1) 0.88 Å, H(1)···Cl(3)#1 2.99 Å, N(1)···Cl(3)#1 3.569(4) Å, <N(1)H(1)Cl(3)#1 125.1°; N(1)-H(1) 0.88 Å, H(1)···Cl(1)#2 2.92 Å, N(1)···Cl(1)#2 3.423(4) Å, <N(1)H(1)Cl(1)#2 117.7°; symmetry transformations used: #1 x+1/2, -y+1/2, z-1/2; #2 -x+1/2, y-1/2, -z+1/2]

The $[Mo_2O_2Cl_8]^{2-}$ anion is located on an inversion centre and displays a dimeric structure, approximately consisting of two edge-sharing octahedra, as previously found in related salts.[26] The Mo(1)–O(1) bond [1.648(2) Å] reveals a strong π-character, as expected for a Mo(V)=O unit.[33a-c,26] The chloride bridges are very asymmetric, being Mo(1)–Cl(4) [2.4055(9) Å], *trans* to Cl(2), considerably shorter than Mo(1)–Cl(4)_1 [2.865(2) Å], *trans* to the stronger oxido ligand.

The magnetic analyses of **1** and **2** were indicative of Mo(V) chloride derivatives.[33] In the IR spectrum of **1**, diagnostic absorption for the imine group has been detected at 1572 cm^{-1}. The IR spectrum of **2** displays the absorptions related to the [C=N] and [Mo=O] [33] moieties at ca. 1700 and at 989 cm^{-1}, respectively.

The oxidative dehydrogenation of secondary amines to imines is a known process [27] with implications in the hydrogen storage issue,[28] nevertheless this reaction is unusual in the landscape of the chemistry of metal chlorides.[29] In the present case, it is presumable that the Mo(V) centre exerts its oxidant power [30] towards the amine reactants, even though GC analyses on $MoCl_5$/diethylamine and $MoCl_5$/pyrrolidine mixtures evidenced the release of very low amounts of H_2 as possible reduction product. As a matter of fact, magnetic analysis on the pyrrolidine/$MoCl_5$ reaction residue suggested the presence of a mixture of Mo(V) and Mo(IV) species (μ = 1.91 BM). The formation of Mo(IV) by-products is in agreement with the computed thermodynamic variation for the reaction reported in Eqn. 1, $\Delta G = -72.3$ kcal mol^{-1}. Mo(IV) chloride was modelled on the basis of the hexameric structure reported in the literature.[31]

$$1.5Mo_2Cl_{10} + NH(CH_2)_4 \rightarrow [MoCl_5\{NCH(CH_2)_3\}] + 2\ HCl + 1/3\ Mo_6Cl_{24} \quad (1)$$

2. Reactions of $MoCl_5$ with *N*-(trimethylsilyl)dialkylamines.

With the idea in mind to access Mo(V) chloride amide compounds, we moved to study the reactions of $MoCl_5$ with variable amounts of *N*-(trimethylsilyl)dialkylamines, these being expected to act as clean Cl/NR_2 exchangers.[5,32] Indeed the 1:1 molar reaction of $MoCl_5$ with Et_2NSiMe_3 in dichloromethane afforded the chloride amide compound $[MoCl_4(NEt_2)]$, **3**, which was isolated in 65% yield after work up (Eqn. 2).

$$MoCl_5 + Et_2NSiMe_3 \rightarrow \underset{\mathbf{3}}{[MoCl_4(NEt_2)]} + Me_3SiCl \qquad (2)$$

The synthesis of **3** originates from the selective Cl/NEt_2 exchange between the reactants. The use of two/three equivalents of Et_2NSiMe_3 resulted in the formation of mixtures of products. Compound **3** was characterized by elemental analysis, magnetic analysis and IR spectroscopy. On account of the fact that crystallographic characterizations of Mo(V) chloride amide complexes are still absent in the literature, we made several attempts in order to obtain X-ray quality crystals of **3**. Unfortunately, these attempts were not successful. In the absence of X-ray data, we performed DFT calculations aimed to the prediction of the most stable structure. A range of possibilities were considered (see Figure S2, structures **3A-3C**); the mononuclear structure (**3-mono**) and the dinuclear one with the amido groups in relative *trans*-equatorial position (**3A**) resulted the most stable ones, exhibiting strictly comparable relative Gibbs energies (Figures 3a, 3b). It should be noted that the crystallographically characterized complex $[NbCl_4(NEt_2)]$ displays a dinuclear structure matching that of **3A**.[3a] DFT calculations ruled out the possibility of Mo–Mo covalent interaction in **3A**, being the triplet state more stable than the corresponding singlet one by about 11 kcal mol^{-1}. This is in agreement with the magnetic measurement performed on **3** (μ = 1.44 BM), indicating the presence of isolated Mo(V) centers.[33]

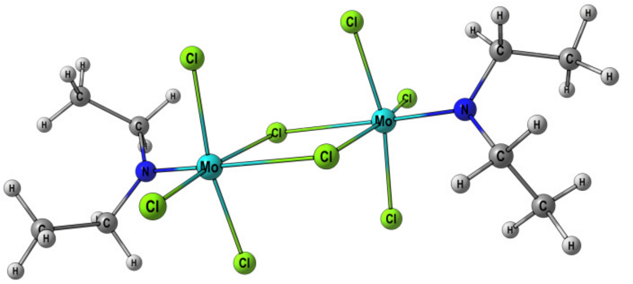


Figure 3a. DFT-optimized geometry of **3A**, C-PCM/–B97X calculations. Selected computed bond lengths (Å): Mo–N 1.878, 1.885; Mo–Cl (*terminal*) 2.295, 2.296, 2.316, 2.324, 2.325, 2.326; Mo–Cl (*bridging*) 2.504, 2.514, 2.713, 2.719; Mo···Mo 4.016. Selected computed angles (deg):N–Mo–Cl(*terminal*) 97.1, 100.5, 92.3, 92.8, 93.1, 94.6; Cl(*bridging*)–Mo–Cl(*bridging*) 79.5, 79.8; Mo–Cl(*bridging*)–Mo 100.3, 100.4.

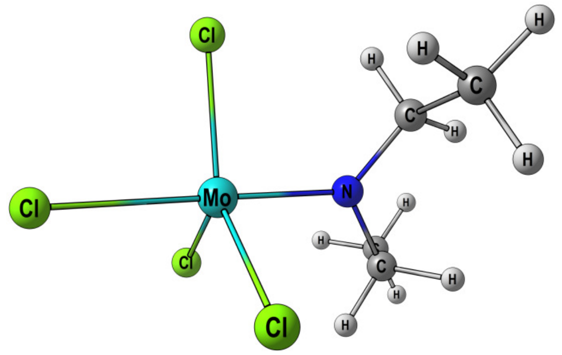


Figure 3b. DFT-optimized geometry of **3-mono**, C-PCM/–B97X calculations. Selected computed bond lengths (Å): Mo–N 2.022; Mo–Cl(*apical*) 2.389; Mo–Cl(*equatorial*) 2.263, 2.287, 2.308. Selected computed angles (deg): N–Mo–Cl(*apical*) 176.4; N–Mo–Cl(*equatorial*) 87.5, 90.1, 91.2.

The reaction of $MoCl_5$ with one equivalent of Me_2NSiMe_3 in dichloromethane led to a mixture of metal compounds presumably containing a prevalence of Mo(V) centres (μ = 1.33 BM).[33] A crystallization procedure furnished few X-ray quality crystals (**4**). These crystals consist of a 1:1 mixture of the Mo(IV) complex $[MoCl_3(NMe_2)(\kappa^2\text{-}Me_2NCH_2NMe_2)]$, **4a**, and the Mo(V) complex $[MoCl_3(NMe)(\kappa^2\text{-}Me_2NCH_2NMe_2)]$, **4b**. The two structures are shown in Figure 4, while relevant bonding parameters are reported in Table 3. In both **4a-b**, the Mo centres display a distorted octahedral geometry, being bonded to three chlorides in *mer* position, a chelating $\kappa^2\text{-}Me_2NCH_2NMe_2$ ligand and an imido [NMe] (**4a**) or [amido] NMe_2 (**4b**) ligand. As far as we are aware, **4a-b** represent the first cases of structurally characterized Mo-complexes with the $Me_2NCH_2NMe_2$ ligand, and only a few examples of Co, Ni, Fe and Re complexes with the same ligand have been found within the Cambridge Crystallographic Data Centre.[34] The Mo(1)–N(1) [2.332(5) Å] and Mo(1)–N(2) [2.255(3) Å] contacts of **2a** are considerably longer than Mo(1)–N(3) [1.911(5) Å], in view of the amido nature of the latter group.[35] A further decrease in the related Mo(2)–N(6) distance [1.746(5) Å] is observed in the imido complex **2b**, in keeping with previous findings.[36]

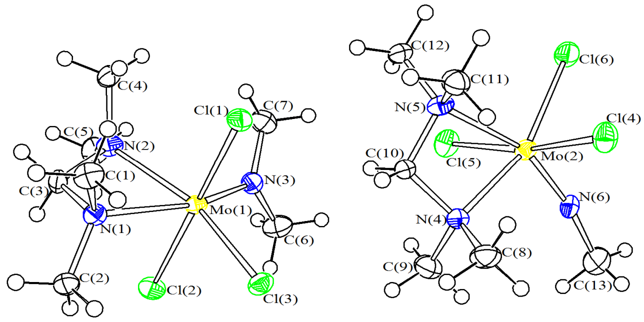


Figure 4. Molecular structure of **4**. Displacement ellipsoids are at the 50% probability level.

Table 3.Selected bond distances (Å) and angles (°) for **4**.

Mo(1)–Cl(1)	2.3954(15)	Mo(1)–Cl(2)	2.4289(15)
Mo(1)–Cl(3)	2.3817(14)	Mo(1)–N(1)	2.332(5)
Mo(1)–N(2)	2.255(5)	Mo(1)–N(3)	1.911(5)
N(1)–C(3)	1.487(7)	N(2)–C(3)	1.500(7)
C(6)–N(3)	1.484(8)	C(7)–N(3)	1.465(8)
Mo(2)–Cl(4)	2.3941(16)	Mo(2)–Cl(5)	2.4102(16)
Mo(2)–Cl(6)	2.3790(16)	Mo(2)–N(4)	2.235(5)
Mo(2)–N(5)	2.402(5)	Mo(2)–N(6)	1.746(5)
N(4)–C(10)	1.496(7)	N(5)–C(10)	1.481(7)
C(13)–N(6)	1.409(9)		
Cl(1)–Mo(1)–Cl(2)	175.26(5)	Cl(3)–Mo(1)–N(2)	158.21(13)
N(1)–Mo(1)–N(3)	160.62(18)	N(1)–Mo(1)-N(2)	62.85(16)
Mo(1)–N(3)–C(6)	124.9(4)	Mo(1)–N(3)–C(7)	124.5(4)
C(6)–N(3)–C(7)	109.9(5)	Cl(6)–Mo(2)–N(4)	159.51(13)
Cl(4)–Mo(2)–Cl(5)	169.13(6)	N(4)–Mo(2)–N(5)	61.62(17)
N(5)–Mo(2)–N(6)	156.9(2)	Mo(2)–N(6)–C(13)	166.3(5)

The presence of $Me_2NCH_2NMe_2$ in **4a,b** is the result of the involvement of the solvent (CH_2Cl_2) in the Cl/NMe_2 exchange.[37] Accordingly, significant amounts of $Me_2N(CH_2)_2NMe_2$ were recovered after hydrolysis of the $MoCl_5$/Me_2NSiMe_3 mixture in 1,2-dichloroethane.[37b] Neither $Me_2NCH_2NMe_2$ nor $Me_2N(CH_2)_2NMe_2$ were recognized from the reaction of $MoCl_5$ with Me_2NSiMe_3 in heptane, although even in this case unambiguous characterization of the metal products failed.

3. Reactions of $MoCl_5$ with primary amines.

The 1:1 reactions of $MoCl_5$ with NH_2R (R = Cy, ^{t}Bu, ^{i}Pr, 2,6-$C_6H_3Me_2$, CH_2Ph) were studied. These reactions afforded, after elimination of the volatile materials, paramagnetic solid mixtures. After hydrolytic treatment of the latter, the starting amines were identified (NMR) as largely prevalent components in the respective organic phases. Only traces of NH_2=CHPh were recognized from $MoCl_5$/NH_2CH_2Ph. These results indicate that primary amines are generally not prone to oxidation by molybdenum pentachloride, in contrast to what seen for secondary amines. Numerous attempts were performed with the aim of isolating clean metal products from $MoCl_5$/NH_2R. These attempts were successful in two cases, thus the Mo(VI) imido chloride complexes $[MoCl_4(NR)]_2$ (R = Cy, **5a**; R = ^{t}Bu, **5b**) were isolated in ca. 40% yields by crystallization procedures from $MoCl_5$/NH_2R (R = Cy, ^{t}Bu), Scheme 3.

$$MoCl_5 \xrightarrow{NH_2R} [MoCl_3(NR)(\mu\text{-}Cl)]_2$$

R = Cy, **5a**; ^{t}Bu, **5b**

Scheme 3. Formation of Mo(VI) imido chloride complexes from the reactions of $MoCl_5$ with primary amines.

Compound **5b** was previously obtained in modest yield by Cl_2 oxidation of a Mo(V) imido precursor.[38] Here, it was identified by elemental analysis and single crystal X-ray analysis. The novel **5a** was characterized by IR and NMR spectroscopy, and the structure was elucidated by a single crystal X-ray diffraction study. **5a** is diamagnetic, and displays an intense IR band at 1239 cm^{-1}, accounting for the [Mo=N] moiety. The ORTEP molecular structure of **5a** is shown in Figure 5, while relevant bonding parameters are reported in Table 4.

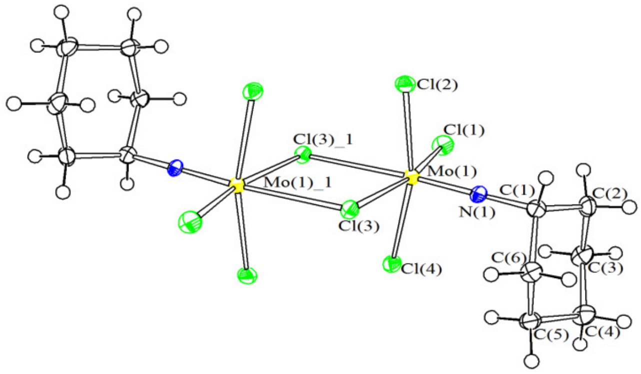


Figure 5. Molecular structure of **5a**. Displacement ellipsoids are at the 50% probability level. Symmetry transformations used to generate equivalent atoms: -x+1,-y+2,-z+2.

Table 4.Selected bond distances (Å) and angles (°) for **5a**.

Mo(1)–Cl(1)	2.2966(10)	Mo(1)–Cl(2)	2.2996(10)
Mo(1)–Cl(3))	2.4562(10)	Mo(1)–Cl(3_1)	2.6996(11)
Mo(1)–Cl(4)	2.3194(9)	Mo(1)–N(1)	1.689(3)
N(1)–C(1)	1.444(4)	C(1)–C(2)	1.543(5)
C(2)–C(3)	1.517(5)	C(3)–C(4)	1.540(5)
C(4)–C(5)	1.524(5)	C(5)–C(6)	1.522(5)
C(6)–C(1)	1.546(5)		
Cl(1)–Mo(1)–Cl(3)	166.62(3)	Cl(2)–Mo(1)–Cl(4)	165.62(3)
N(1)–Mo(1)–Cl(3_1)	172.23(9)	Cl(3)–Mo(1)–Cl(3_1)	79.03(3)
Mo(1)–N(1)–C(1)	175.3(2)	Mo(1)–Cl(3)–Mo(1_1)	100.97(3)

Symmetry transformations used to generate equivalent atoms: –x+1, –y+2, –z+2

The structure of **5a** is closely related to that previously reported for **5b**,[38] showing an almost identical geometry and bonding parameters. In **5a**, the Mo(VI) centres display a distorted octahedral geometry, being bonded to one imido, three terminal and two edge bridging Cl ligands. The Mo(1)–N(1) contact [1.689(3) Å] is rather short, as expected for a Mo(VI)–N multiple bond, and has a strong *trans* influence. Thus, Mo(1)–Cl(3)_1 [2.6996(11) Å] is considerably elongated compared to Mo(1)–Cl(3) [2.4562(10) Å], which is *trans* to a terminal chloride, and Mo(1)–N(1)–C(1) [175.3(2)°] is almost linear. The molecule is located on an inversion centre and, hence, only half of it is present within the asymmetric unit of the unit cell.

The synthesis of the Mo(VI) based imido complexes **5a,b** represents a very unusual result in the context of the chemistry of metal halides with aliphatic amines. Indeed imido ligands have been typically introduced in metal complexes via deprotonation of amines or amides (see Introduction).[39] This synthetic strategy does not imply any change in the oxidation state of the metal centre, unless specific oxidative co-reactants are involved.[40] Imido ligands have been generated also by metathesis of metal oxide chlorides with isocyanates [41] and by addition of azides, RN_3, to metal complexes.

The latter approach has been successfully employed for the synthesis of $[Mo^{(VI)}Cl_4(NR)(thf)]$ from $[Mo^{(IV)}Cl_4(thf)_2]$,[42] the oxidation of the metal centre being permitted by N_2 release.

DFT calculations were performed on the $MoCl_5/NH_2Cy$ system, in order to supply a plausible reaction pathway. The formation of $[MoCl_4(NCy)]_2$ is probably preceded by that of the intermediate Mo(V) dimeric complex $[MoCl_4(NHCy)]_2$ (Figure 6), from Mo_2Cl_{10} and NH_2Cy by HCl elimination ($\Delta G = -43.9$ kcal mol^{-1}).

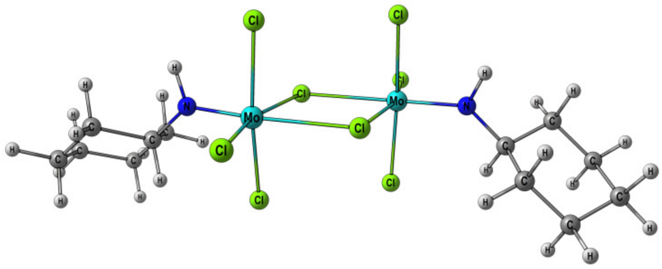


Figure 6. DFT-optimized geometry of $[MoCl_4(NHCy)]_2$, C-PCM/–B97X calculations. Selected computed bond lengths (Å): Mo-N 1.853, 1.853; Mo-Cl (*terminal*) 2.275, 2.275, 2.318, 2.318, 2.325, 2.325; Mo-Cl (*bridging*) 2.499, 2.499, 2.695, 2.695; Mo---Mo 4.030; N-H 1.029, 1.029. Selected computed angles (deg):N-Mo-Cl(*terminal*) 101.4, 101.4, 88.4, 88.4, 92.3, 92.3; Cl(*bridging*)-Mo-Cl(*bridging*) 78.3, 78.3; Mo-Cl(*bridging*)-Mo 101.7, 101.7.

A possible pathway going from $[MoCl_4(NHCy)]_2$ to $[MoCl_4(NCy)]_2$ could involve, in principle, the formation of H_2 as a by-product (Eqn. 3). This reaction should be slightly thermodynamically unfavourable (ΔG = ca. 0.9 kcal mol^{-1}) and, accordingly, GC analyses on $MoCl_5$/diethylamine and $MoCl_5$/pyrrolidine mixtures pointed out the formation of only minor amounts of H_2. It has to be observed that the H_2 dissociation from primary amines is not a common feature, being achieved only by powerful oxidative systems.[43]

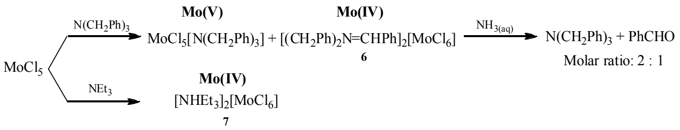
$$[MoCl_4(NHCy)]_2 \rightarrow [MoCl_4(NCy)]_2 + H_2 \qquad (3)$$

According to the calculations, a more plausible route from $[Mo^{(V)}Cl_4(NHCy)]_2$ to $[Mo^{(VI)}Cl_4(NCy)]_2$ involves the disproportion of the Mo(V) reactant to Mo(VI) and Mo(IV), Eqn. 4. This hypothesis is supported by the calculated $\Delta G = -8.7$ kcal mol^{-1}, and by the fact that magnetic analyses on the reaction residues were in alignment with the presence of mixtures of Mo(VI) and Mo(IV) species.

$$2\,[MoCl_4(NHCy)]_2 \rightarrow [MoCl_4(NCy)]_2 + 2\,NH_2Cy + ⅓\,Mo_6Cl_{24}{}^{31} \qquad (4)$$

4. Reactions of $MoCl_5$ with trialkylamines.

The 1:1 molar reaction of $MoCl_5$ with tribenzylamine afforded a precipitate whose Cl and magnetic analysis suggested the prevalent formation of a Mo(V) compound, presumably $[MoCl_5\{N(CH_2Ph)_3\}]$, in admixture with Mo(IV) containing side products (Scheme 4). A crystallization procedure allowed to isolate the iminium salt $[(CH_2Ph)_2N{=}CHPh]_2[MoCl_6]\cdot CH_2Cl_2$, **6**, containing Mo(IV) anions, that was X-ray characterized (Figure 7, Table 5).



Scheme 4. Reactions of $MoCl_5$ with trialkylamines.

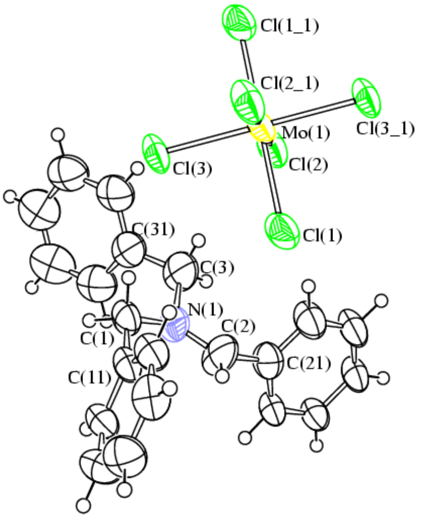


Figure 7. Molecular structure of $[(CH_2Ph)_2N{=}CHPh]_2[MoCl_6]$, **6**, with key atoms labeled. Displacement ellipsoids are at the 50% probability level. Symmetry transformation used to generate equivalent atoms: -x+2, -y+1, -z+1.

Table 5. Selected bond distances (Å) and angles (°) for **6**.

Mo(1)-Cl(1)	2.365(2)	Mo(1)-Cl(2)	2.362(2)
Mo(1)-Cl(3)	2.4169(17)	N(1)-C(1)	1.496(10)
N(1)-C(2)	1.306(11)	N(1)-C(3)	1.504(11)
C(1)-C(11)	1.487(11)	C(2)-C(21)	1.473(12)
C(3)-C(31)	1.486(13)		
C(1)-N(1)-C(2)	121.6(8)	C(1)-N(1)-C(3)	111.6(7)
C(2)-N(1)-C(3)	117.9(7)	N(1)-C(1)-C(11)	113.5(7)
N(1)-C(2)-C(21)	125.3(9)	N(1)-C(3)-C(31)	115.8(8)

The conversion of tribenzylamine into the relevant iminium cation was previously realized by WCl_6-directed C–H activation, initiated by amine to metal single electron transfer, and finally affording the salts $[(CH_2Ph)_2N{=}CHPh][WCl_6]$ and $[NH(CH_2Ph)_3][WCl_6]$.[11b] The formation of **6** probably follows a similar pathway, and evidence for the presence of the ammonium $[NH(CH_2Ph)_3]^+$ in the $MoCl_5/N(CH_2Ph)_3$ mixture was supplied by an IR absorption at 1595 cm^{-1}.[11b] According to NMR analysis on the hydrolyzed reaction mixture, *ca.* one third of the amine reactant was converted into the iminium upon interaction with $MoCl_5$, the iminium being detected as benzaldehyde PhCHO after hydrolysis.

The 1:1 molar reaction of $MoCl_5$ with NEt_3 proceeded with prevalent Mo(V) to Mo(IV) reduction (Scheme 4), and a crystallization procedure allowed to isolate some crystals of the Mo(IV) salt $[NHEt_3]_2[Mo_2Cl_{10}]$, **7** (Figure 8, Tables 6-7).[44] Actually, crystals of **7** contain a mixture of the Mo(IV) anion $[Mo_2Cl_{10}]^{2-}$ (80%) and the Mo(V) anion $[Mo_2(O)_2Cl_8]^{2-}$ (20%), in agreement with the proposed reaction scheme. Coherently with previous findings, the protonation source affording **7** might be a C–H activation process analogous to that suggested above for $MoCl_5/N(CH_2Ph)_3$.[12] Indeed the IR spectrum of the reaction residue contained two weak bands at 1680 and 1648 cm^{-1}, possibly ascribable to [C=N] containing species. Nevertheless, the possibility that fortuitous hydrolysis contributed to the generation of $[NHEt_3]^+$ must not be ruled out.

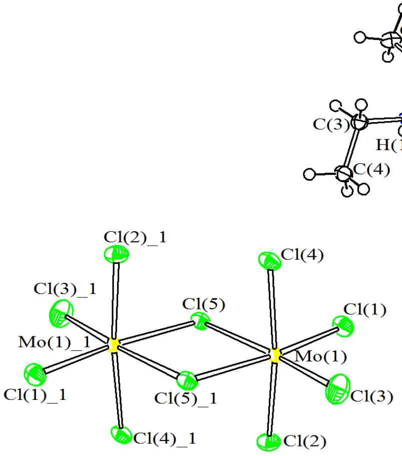


Figure 8. Molecular structure of $[NHEt_3]_2[Mo_2Cl_{10}]$, **7**, with key atoms labeled. Displacement ellipsoids are at the 50% probability level. Symmetry transformation used to generate equivalent atoms: –x+2, –y+2, –z.

Table 6. Selected bond distances (Å) and angles (°) for **7**.

Mo(1)-Cl(1)	2.312(3)	Mo(1)-Cl(2)	2.327(3)
Mo(1)-Cl(3)	2.229(3)	Mo(1)-Cl(4)	2.341(3)
Mo(1)-Cl(5)	2.584(3)	Mo(1)-Cl(5)_1	2.471(3)
N(1)-C(1)	1.503(12)	N(1)-C(3)	1.511(12)
N(1)-C(5)	1.527(12)	C(1)-C(2)	1.509(13)
C(3)-C(4)	1.518(13)	C(5)-C(6)	1.501(14)
Cl(1)-Mo(1)-Cl(5)_1	171.63(10)	Cl(3)-Mo(1)-Cl(5)	174.89(12)
Cl(2)-Mo(1)-Cl(4)	172.61(11)	Cl(5)-Mo(1)-Cl(5)_1	82.25(8)
Cl(1)-Mo(1)-Cl(3)	95.69(12)	Mo(1)-Cl(5)-Mo(1)_1	97.75(8)

Table 7. Hydrogen bonds for **7**.

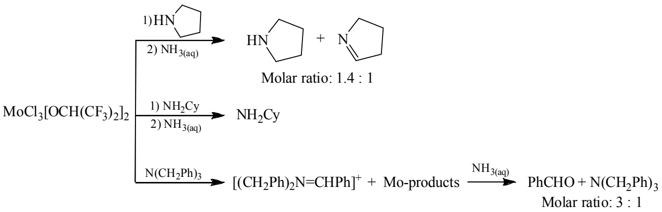
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...Cl(2)#1	0.91	2.78	3.520(9)	138.9
N(1)-H(1)...Cl(4)#2	0.91	2.58	3.283(8)	134.3

Symmetry transformations used to generate equivalent atoms:
#1 –x+1, –y+2, –z+1 #2 x, y, z+1.

5. Reactions of $MoCl_5$ with $[MoCl_3\{OCH(CF_3)_2\}_2]$.

Waldvogel and coworkers previously found that the substitution of chloride ligands in $MoCl_5$ with hexafluoropropoxide moieties supplied superior performances to the resulting metal species in promoting the coupling reactions of arenes.[13] We came interested to see whether the same strategy could enhance the activation capability of the molybdenum frame towards amines.

Thus the complex $[MoCl_3\{OCH(CF_3)_2\}_2]$, bearing a dinuclear structure analogous to that of $MoCl_5$, was synthesized following the literature procedure.[13] The reactions of $[MoCl_3\{OCH(CF_3)_2\}_2]$ with amines were carried out in the same conditions as those employed for $MoCl_5$. A better conversion of tribenzylamine into the iminium was realized with $[MoCl_3\{OCH(CF_3)_2\}_2]$ (Scheme 5). Otherwise, $[MoCl_3\{OCH(CF_3)_2\}_2]$ manifested a lower activation power than $MoCl_5$ towards pyrrolidine, in fact only limited conversion to pyrroline was ascertained (Scheme 5). A highly air sensitive solid was isolated from the reaction with NH_2Cy, bearing a magnetic susceptibility value typical for Mo(V) species. The IR spectrum did not show any intense band around 1240 cm^{-1} (compare IR spectrum of **5a**). These data suggest that the replacement of chloride ligands with hexafluoropropoxide moieties somehow inhibits the generation of the group $[Mo^{VI}{=}NCy]$.



Scheme 5. Reactions of a Mo(V) chloride alkoxide with amines.

Conclusions

$MoCl_5$ is a commonly known transition metal chloride, that has been increasingly employed in synthetic organic chemistry. We have elucidated the reactions of $MoCl_5$ with a variety of aliphatic amines, some of the reactions showing unusual features. Thus, while high valent metal chlorides generally react with primary and secondary amines via classical aminolysis, electron interchange processes dominate with $MoCl_5$. More in detail, the Mo(V) centre undergoes single electron reduction by converting a series of secondary amines into the relevant imines. A similar pathway works in the reactions of $MoCl_5$ with trialkylamines, in contrast with previous literature reports. Conversely Mo(V) to Mo(VI) oxidation may take place during the interaction of $MoCl_5$ with primary amines, in view of the specific nature of the latter possibly acting as sequential source of one H^+ cation and one H atom. Furthermore, although Et_2NSiMe_3 has been proved to act as a clean amido group transferor towards $MoCl_5$, such behaviour seems to be strictly dependent on electronic and steric features. Thus, the reaction of $MoCl_5$ with Me_2NSiMe_3 proceeds in a non selective way, possibly involving the solvent in the Cl/NMe_2 exchange process. The partial substitution of chloride ligands with hexafluoroisopropoxide groups did not substantially alter the activation capability towards amines of the Mo(V) centre.

Experimental

Warning! The metal compounds reported in this paper are highly moisture-sensitive, thus rigorously anhydrous conditions were required for the reaction, crystallization and separation procedures. The reaction vessels were oven dried at 140 °C prior to use, evacuated (10^{-2} mmHg) and then filled with argon. $MoCl_5$ (99.9%) was purchased from Strem and stored under argon atmosphere as received. $[MoCl_3\{OCH(CF_3)_2\}_2]$ was prepared according to the literature procedure.[13] The organic reactants were commercial products (Apollo Sci., Sigma Aldrich or TCI Europe) of the highest purity available, dried over P_4O_{10} and stored under argon atmosphere. Solvents were distilled from P_4O_{10} under argon atmosphere before use. Infrared spectra were recorded at 298 K on a FT IR-Perkin Elmer Spectrometer, equipped with UATR sampling accessory. Magnetic susceptibilities (reported per Mo atom) were measured at 298 K on solid samples with a Magway MSB Mk1 magnetic susceptibility balance (Sherwood Scientific Ltd.). Diamagnetic corrections were introduced according to König.[45] Carbon, hydrogen and nitrogen analyses were performed on a Carlo Erba mod. 1106 instrument. The chloride content was determined by the Mohr method [46] on solutions prepared by dissolution of the solid in aqueous KOH at boiling temperature, followed by cooling to room temperature and addition of HNO_3 up to neutralization. NMR spectra were recorded at 298 K on a Bruker Avance II DRX400 instrument equipped with a BBFO broadband probe. The chemical shifts for ^1H and ^{13}C were referenced to the non-deuterated aliquot of the solvent, while the chemical shifts for ^{29}Si were referenced to external tetramethylsilane. NMR assignments were assisted by DEPT experiments and $^1H,^{13}C$ correlation measured using gs-HSQC and gs-HMBC experiments. Gas chromatographic analyses were performed at 50 °C with a Dani 3200 gas chromatograph, equipped with a molecular sieves packed capillary column (2 m; 0.25 in ID), and using argon as the gas carrier (p = 1.5 atm). GC-MS analyses were performed on a HP6890 instrument, interfaced with MSD-HP5973 detector and equipped with Phenonex Zebron column.

1. Reactions of $MoCl_5$ with secondary amines.

A) NMR studies.

A suspension of $MoCl_5$ (120 mg, 0.439 mmol) in CH_2Cl_2 was treated with pyrrolidine (0.037 mL, 0.443 mmol). The mixture was allowed to stir at room temperature for 48 h, then the volatile materials were removed in vacuo. An aliquot of the resulting powdery solid underwent magnetic analysis: $\chi_M^{corr} = 1.53\times10^{-3}$ cgsu, $\mu_{eff} = 1.92$ BM. The residue was dissolved in $CDCl_3$ (1 mL), and $NH_{3(aq)}$ (40% *w/w*, 3 mmol) was added. The mixture was left stirring for 18 h. Then the organic phase was analyzed by NMR spectroscopy. ^1H NMR ($CDCl_3$): $\delta = 7.63$ (m, CH, pyrroline [47]), 3.87 (m, CH_2, pyrroline), 2.88 (m, NCH_2, pyrrolidine), 2.56 (m, CH_2, pyrroline), 1.82 (m, CH_2, pyrroline), 1.71 ppm (m, CH_2, pyrrolidine). Approximate pyrroline/pyrrolidine ratio = 5. The reactions of $MoCl_5$ (0.50 mmol) with one molar equivalent of diethylamine and dibenzylamine, respectively, were carried out by the same procedure described for $MoCl_5$/pyrrolidine. NMR analyses were as follows. From $MoCl_5/NHEt_2$: ^1H NMR ($CDCl_3$): $\delta = 9.83$ (q, $^3J_{HH} = 2.93$ Hz, MeC*H*=O); 2.24 ppm (d, $^3J_{HH} = 2.93$ Hz, *Me*CH=O). From $MoCl_5/NH(CH_2Ph)_2$: ^1H NMR ($CDCl_3$): $\delta = 9.83$ (q, $^3J_{HH} = 2.93$ Hz, MeC*H*=O); 2.24 ppm (d, $^3J_{HH} = 2.93$ Hz, *Me*CH=O). $NH(CH_2Ph)_2/PhCH_2N{=}CHPh$ ratio = ca. 1.

B) Isolation of $[MoCl_5\{NCH(CH_2)_3\}]$, 1, and $[CH_3CH{=}NHEt][MoOCl_4]$, 2.

The reaction of $MoCl_5$ (250 mg, 0.915 mmol) with pyrrolidine (0.078 mL, 0.934 mmol) was carried out in dichloromethane (10 mL) for 48 h. The final solution was filtrated in order to remove some solid, then the solution was concentrated to 3 mL, layered with hexane and stored at −30 °C. Green crystals of **3** suitable for X-ray analysis were recovered after one week. Yield 113 mg (36%). Anal. Calcd for $C_4H_7Cl_5MoN$: C, 14.03; H, 2.06; N, 4.09; Cl, 51.78. Found: C, 14.20; H, 1.98; N, 4.03; Cl, 51.60. IR (solid state): 1572m (C=N) cm^{-1}. Magnetic measurement: $\chi_M^{corr} = 9.70\times10^{-4}$ cgsu, $\mu_{eff} = 1.53$ BM.

Crystals of **2** were obtained by a procedure analogous to that described for **1**.

2 (dark yellow crystals). Yield 35 mg (10%), from $MoCl_5$ (293 mg, 1.07 mmol) and $NHEt_2$ (0.111 mL, 1.07 mmol). Anal. Calcd for $C_4H_{10}Cl_4MoNO$: C, 14.74; H, 3.09; N, 4.30; Cl, 43.52. Found: C, 14.57; H, 3.11; N, 4.35; Cl, 43.12. IR (solid state): 1700br ($\nu_{C=N} + \delta_{N-H}$), 989s (Mo=O) cm^{-1}. Magnetic measurement: $\chi_M^{corr} = 9.70\times10^{-4}$ cgsu, $\mu_{eff} = 1.53$ BM.

2. Reactions of $MoCl_5$ with *N,N*-dialkyltrimethylsilylamines.

A) Synthesis and characterization of $[MoCl_4(NEt_2)]$, 3.

A suspension of $MoCl_5$ (455 mg, 1.67 mmol) in CH_2Cl_2 (15 mL) was treated with Et_2NSiMe_3 (0.32 mL, 1.69 mmol), then the mixture was stirred at room temperature for 18 h. The resulting dark solution was filtered in order to remove some solid, then it was eliminated of the volatiles. The residue was washed with pentane (2 x 20 mL) and dried in vacuo. Yield 337 mg (65%). Anal. Calcd for $C_4H_{10}Cl_4MoN$: C, 15.50; H, 3.25; N, 4.52; Cl, 45.76. Found: C, 15.33; H, 3.12; N, 4.66; Cl, 45.53. IR (solid state): 3068m, 2983m, 1574m, 1452m-s, 1424m, 1389m-s, 1254m-s, 1193w, 1158w, 1038m-s, 842vs, 766s cm^{-1}. Magnetic measurement: $\chi_M^{corr} = 8.60\times10^{-4}$ cgsu, $\mu_{eff} = 1.44$ BM. In a different experiment, the reaction solution obtained from $MoCl_5$ (ca. 0.5 mmol) and one equivalent of Et_2NSiMe_3 was dried in vacuo. $CDCl_3$ (1 mL) was added to the residue in air, and the obtained mixture was treated with $NH_{3(aq)}$ (40% *w/w*, 0.20 mL). The mixture were left stirring at room temperature for 18 h. NMR analysis on the resulting organic phase evidenced the presence of $NHEt_2$ only [^1H NMR ($CDCl_3$): $\delta = 2.65$ (m, 2 H, CH_2); 1.10 ppm (t, 3 H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 44.1$ (CH_2); 15.5 ppm (CH_3)].

B) Isolation of $[MoCl_3(NMe_2)(\kappa^2\text{-}Me_2NCH_2NMe_2)]$, 4a, and $[MoCl_3(NMe)(\kappa^2\text{-}Me_2NCH_2NMe_2)]$, 4b.

A suspension of $MoCl_5$ (370 mg, 1.35 mmol) in CH_2Cl_2 (15 mL) was treated with Me_2NSiMe_3 (0.22 mL, 1.35 mmol), then the mixture was stirred at room temperature for 18 h. The resulting dark red solution was eliminated of the volatiles, thus the residue was washed with hexane (2 x 20 mL) and dried in vacuo. IR (solid state): 3154m, 3103m, 2984m, 2932m, 2965s, 2458m, 1596m, 1574m, 1463vs, 1410m, 1258m, 1116w, 1027m, 1011s, 949m, 923w, 886s, 800vs, 768w cm^{-1}. Magnetic measurement: $\chi_M^{corr} = 7.35\times10^{-4}$ cgsu, $\mu_{eff} = 1.33$ BM. Few crystals of **4a-b** suitable for X-ray analysis were obtained directly from a dichloromethane reaction solution, layered with hexane and settled at −30 °C.

C) NMR studies. The reaction of $MoCl_5$ (0.70 mmol) with Me_2NSiMe_3 (0.70 mmol) was performed also in 1,2-dichloroethane at reflux temperature and in heptane at room temperature. The distinct reaction residues were treated with $CDCl_3$ (1 mL) and then with $NH_{3(aq)}$ (40% *w/w*, 0.20 mL). Dimethylamine was clearly NMR identified in the organic phases after 18 h (^1H: $\delta = 2.38$ ppm; ^{13}C: $\delta = 45.9$ ppm);[48] moreover, a significant amount of $Me_2NCH_2CH_2NMe_2$ (ca. 1:1 ratio respect to Me_2NH) was found in the mixture obtained from the 1,2-dichloroethane reaction.

3. Reactions of $MoCl_5$ with primary amines.

A. Isolation of $[MoCl_4(NR)]_2$ (R = Cy, 5a; Bu^t, 5b). *General procedure*: The appropriate amine was added to $MoCl_5$ in CH_2Cl_2 (*ca.* 20 mL) in a Schlenk tube, and the mixture was allowed to stir at room temperature for 48 h. The resulting solution was filtered in order to remove some solid, concentrated to ca. 5 mL, layered with hexane and settled at −30 °C. Crystals of **5a** and **5b** suitable for X-ray analyses were recovered after ca. 1 week.

5a (red solid). Yield 139 mg (38%), from $MoCl_5$ (300 mg, 1.10 mmol) and NH_2Cy (0.126 mL, 1.10 mmol). Anal. Calcd for $C_6H_{11}Cl_4MoN$: C, 21.52; H, 3.31; N, 4.18; Cl, 42.34. Found: C, 21.37; H, 3.39; N, 4.11; Cl, 42.16. IR (solid state): 2932s, 2856m, 1448s, 1426sh, 1338s, 1291s, 1266m, 1239s (Mo=N), 1166m, 1139w, 1099w-m, 1005s, 921w-m, 860w-m, 851m-s, 793w, 736w, 709w-m cm^{-1}. Magnetic measurement: diamagnetic. ^1H NMR (CD_2Cl_2): $\delta = 5.47$ (br, 1 H, CH); 2.52-2.04 (m, 8 H, CH_2); 1.60 ppm (m, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 86.0$ (CH); 32.0, 24.8, 23.7 ppm (CH_2).

5b (dark red solid). Yield 129 mg (43%), from $MoCl_5$ (265 mg, 0.970 mmol) and NH_2Bu^t (0.103 mL, 0.975 mmol). Anal. Calcd for $C_4H_9Cl_4MoN$: C, 15.55; H, 2.94; N, 4.53; Cl, 45.91. Found: C, 15.29; H, 3.02; N, 4.38; Cl, 45.70. Magnetic measurement: diamagnetic.

B. Magnetic analyses and NMR studies. *General procedure*: $MoCl_5$ (0.50 mmol) and the appropriate amine (0.50 mmol) were allowed to react in CH_2Cl_2 (*ca.* 20 mL) for 72 h. Thus the volatile materials were removed in vacuo, and the residue was washed with pentane (2 x 20 mL). An aliquot of the solid underwent magnetic analysis: from $MoCl_5/NH_2Cy$, $\chi_M = 7.5\times10^{-4}$ cgsu; from $MoCl_5/NH_2Bu^t$, $\chi_M = 6.7\times10^{-4}$ cgsu; from $MoCl_5/NH_2{}^iPr$, $\chi_M = 5.5\times10^{-4}$ cgsu; from $MoCl_5/NH_2(2,6\text{-}C_6H_3Me_2)$, $\chi_M = 4.2\times10^{-4}$ cgsu; from $MoCl_5/NH_2CH_2Ph$, $\chi_M = 1.0\times10^{-3}$ cgsu. Another aliquot (ca. 50 mg) was treated with $CDCl_3$ (1 mL) and then with a large excess of $NH_{3(aq)}$ (40% *w/w*). The mixture was left stirring for 18 h, hence the organic phase was analyzed by NMR, showing the presence of the starting amine. A minor amount of [NH=CH(Ph)] (about 15% respect to NH_2Bz) was detected from $MoCl_5/NH_2CH_2Ph$ [$\delta(^1H) = 8.35$ ppm (s, 1 H, CH)].

4. Reactions of $MoCl_5$ with trialkylamines.

A) Reaction of $MoCl_5$ with $N(CH_2Ph)_3$: isolation of $[(CH_2Ph)_2N{=}CHPh]_2[MoCl_6]$, 6. $MoCl_5$ (250 mg, 0.915 mmol) was added to a solution of $N(CH_2Ph)_3$ (263 mg, 0.915 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred at room temperature for 18 h.

Hexane (80 mL) was added, and the resulting precipitate was separated from the colourless solution, washed with pentane (2 x 10 mL) and dried in vacuo. Yield 420 mg. IR (solid state): ν = 3034m-br, 2763w, 1640w-m (C=N, **6**), 1595w-m, 1497w-m, 1451s, 1415m, 1340w, 1266w, 1214w-m, 1087w, 1002m, 990m, 924m, 750vs, 736s-sh, 697vs cm^{-1}. Magnetic measurement: χ_M^{corr} = 1.29×10^{-3} cgsu, μ_{eff} = 1.76 BM. Anal. Calc. for $C_{21}H_{21}Cl_5MoN$: Cl, 31.62. Found: Cl, 29.40. Crystallization from CH_2Cl_2/hexane at −30°C afforded few crystals of **3** suitable for X-ray analysis. Anal. Calcd for Anal. Calc. for $C_{42}H_{40}Cl_6MoN_2$: C, 57.23; H, 4.57; N, 3.18; Cl, 24.13. Found: C, 57.11; H, 4.70; N, 3.22; Cl, 23.90. IR (solid state): ν = 1640s (C=N) cm^{-1}.

B) Reaction of $MoCl_5$ with NEt_3: isolation of $[NHEt_3]_2[Mo_2Cl_{10}]$, 7. This reaction was performed by using a procedure analogous to that described for $MoCl_5/N(CH_2Ph)_3$, from $MoCl_5$ (280 mg, 1.02 mmol) and NEt_3 (0.145 mL, 1.04 mmol). Yield 298 mg (light-red precipitate). Anal. Calcd for $C_6H_{15}Cl_5MoN$: Cl, 47.35. Found: Cl, 37.05. IR (solid state): ν = 3150m (N−H, **7**), 3051w, 2984w-m, 2943w, 1680m, 1648m, 1452s, 1395s, 1352m, 1287w, 1265m, 1170w, 1153w, 1103w, 1081w, 1029, 1006m-w, 832w, 804w, 786, 732vw, 700m-s cm^{-1}. Magnetic measurement: χ_M^{corr} = 1.93×10^{-3} cgsu, μ_{eff} = 2.16 BM. Crystallization from CH_2Cl_2/hexane at −30°C afforded **7** as dark-red crystals suitable for X-ray analysis. Yield 96 mg, 25%. Anal. Calcd for $C_{12}H_{32}Cl_{10}Mo_2N_2$: C, 19.20; H, 4.30; N, 3.73; Cl, 47.22. Found: C, 19.31; H, 4.15; N, 3.52; Cl, 46.98.

C) NMR studies. According to the procedure described above for $MoCl_5$/pyrrolidine, organic solutions were obtained by allowing the solid residues isolated from $MoCl_5/N(CH_2Ph)_3$ and $MoCl_5/NEt_3$, respectively, to react with $CDCl_3/NH_{3aq}$ in contact with air. NMR analyses were as follows.

From $MoCl_5/N(CH_2Ph)_3$. ^1H NMR ($CDCl_3$): δ = 10.02 (s, PhC*H*=O); 7.90, 7.67-7.36 (Ph); 3.90 ppm [s, N(C*H*$_2$Ph)$_3$]. ^{13}C NMR{^1H} ($CDCl_3$): δ = 192.4 (Ph*C*H=O); 139.9, 136.7, 134.4, 129.7, 129.1, 128.5, 128.3, 127.1 (Ph); 53.9 ppm [N(*C*H$_2$Ph)$_3$]. Ratio $N(CH_2Ph)_3$/PhCH=O 2:1.

From $MoCl_5/NEt_3$. ^1H NMR ($CDCl_3$): δ = 2.43 [m, N(C*H*$_2$CH$_3$)$_3$]; 0.97 ppm [t, $^3J_{HH}$ = 7.13 Hz, N(CH$_2$C*H*$_3$)$_3$]. ^3C NMR{^1H} ($CDCl_3$): δ = 44.5 [N(*C*H$_2$CH$_3$)$_3$]; 11.8 ppm [N(CH$_2$*C*H$_3$)$_3$].

5. Reactions of $[MoCl_3\{OCH(CF_3)_2\}_2]$ with amines.

The reactions of $MoCl_3[OCH(CF_3)_2]_2$ (ca. 0.80 mmol) with amines (1 molar equivalent) were carried out by using the same conditions described for the corresponding $MoCl_5$/amine reactions.

A) From $[MoCl_3\{OCH(CF_3)_2\}_2]$ and pyrrolidine. Brown solid. IR (solid state): 3185m, 3111m, 2909w, 1579w, 1461m, 1366m-s, 1272m-s, 1228s, 1214s, 1175vs, 1123m, 1102vs, 1019w, 972vs, 895w, 885w, 851s, 803w, 749s, 735m-sh, 686vs cm^{-1}. Magnetic measurement: χ_M^{corr} = 9.77×10^{-4} cgsu, μ_{eff} = 1.53 BM. After treatment with $NH_{3(aq)}$: pyrroline and pyrrolidine (molar ratio 1.4 : 1).

B) From $[MoCl_3\{OCH(CF_3)_2\}_2]$ and cyclohexylamine. Brown solid. IR (solid state): 3145m-br, 2939w-m, 2860w, 1582w-m, 1477m, 1451w-m, 1374w, 1352w, 1282s, 1228w-m, 1184s, 1104vs, 1015m, 991m, 919w, 892m, 857m, 802w, 761m-s, 687vs cm^{-1}. Magnetic measurement: χ_M^{corr} = 8.53×10^{-4} cgsu, μ_{eff} = 1.43 BM. After treatment with $NH_{3(aq)}$: cyclohexylamine.

C) From $[MoCl_3\{OCH(CF_3)_2\}_2]$ and tribenzylamine. Dark red solid. IR (solid state): 3066w, 3036w, 2962w, 1639m, 1597m, 1497w-m, 1457m, 1379w, 1287m, 1260w-m, 1225m, 1216m, 1175s, 1124w-m, 1100s, 989s, 894w, 837w, 803w, 750vs, 734m-s, 698vs, 685s cm^{-1}. Magnetic measurement: χ_M^{corr} = 1.47×10^{-3} cgsu, μ_{eff} = 1.88 BM. After treatment with $NH_{3(aq)}$: $N(CH_2Ph)_3$ and PhCHO (molar ratio 1:3).

6. GC analyses. Samples for gas chromatographic analyses were prepared as follows: a mixture of $MoCl_5$ (ca. 1 mmol) and the appropriate amine (1 molar equivalent) in CH_2Cl_2 (10 mL) was stirred at room temperature for 48 h in a Schlenk tube tapped with a silicon stopper. Then an aliquot of the reaction atmosphere was withdrawn by a 1 mL syringe through the stopper, and injected into the GC instrument. The yield of H_2 formation was estimated based on analyses of gaseous standard mixtures containing known amounts of H_2. From $MoCl_5$/pyrrolidine: 1% yield; $MoCl_5/NHEt_2$: 1% yield; from $MoCl_5/NH_2Cy$: 2% yield; from $MoCl_5/NH_2Bu^t$: 1% yield.

7. X-ray Crystallographic Studies. Crystal data and collection details for **1**, **2**, **4**·0.5CH_2Cl_2, **5a**, **6**·CH_2Cl_2 and **7** are listed in Table 8. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector and using Mo-Kα radiation (λ = 0.71073 Å). Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).[49] The structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[50] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were fixed at calculated positions and refined by a riding model. The crystals of **4**·0.5CH_2Cl_2 are twinned with twin matrix 1 0 0 0 -1 0 0 0 -1 and refined batch factor 0.1434(12). The asymmetric unit of the unit cell of **6**·CH_2Cl_2 contains one half of a $[MoCl_6]^{2-}$ anion (located on an inversion centre), one $[(CH_2Ph)_2N{=}CHPh]^+$ cation (on a general position) and one CH_2Cl_2 molecule disordered over two equally populated and symmetry related (by an inversion centre) positions. The C-atoms of the disordered solvent molecule was refined isotropically. The C–Cl distances of the CH_2Cl_2 molecule were restrained to be 1.75 Å (DFIX command in SHELXL, s.u. 0.02). The asymmetric unit of the unit cell of **7** contains one $[NHEt_3]^+$ cation (on a general position) and one half of a $[Mo_2Cl_{10}]^{2-}$ anion (on an inversion centre). The crystals are contaminated by the oxide derivative $[Mo_2(O)_2Cl_8]^{2-}$ (20%) and this has been included in the final refinement.

Insert Table 8 about here

Supplementary Material. Figures S1-S2 show DFT-calculated structures, while Table S1 contains the computed relevant bonding parameters for **1**. Cartesian coordinates of the DFT-optimized compounds are reported in a separated .xyz file. CCDC reference numbers 1491992 (**1**), 1491993 (**2**), 1491991 (**4**·½CH_2Cl_2), 1491994 (**5a**), 1511406 (**6**·CH_2Cl_2) and 1511407 (**7**) contain the supplementary crystallographic data for the X-ray studies reported in this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).

8. Computational studies. The computational geometry optimizations were carried out without symmetry constrains, using the hybrid-GGA EDF2 functional [51] in combination with the 6-31G** basis set (ECP-based LANL2DZ basis set for elements beyond Kr).[52] The "unrestricted" formalism was applied for compounds with unpaired electrons, and the lack of spin contamination was verified by comparing the computed $\langle S^2\rangle$ values with the theoretical ones. The stationary points were characterized by IR simulations (harmonic approximation), from which zero-point vibrational energies and thermal corrections (T = 298.15 K) were obtained. [53] Further optimization of selected geometries was carried out using the range-separated DFT functional ωB97X,[54] in combination with the split-valence polarized basis set of Ahlrichs and Weigend. [55] The C-PCM implicit solvation model (ε = 9.08) was added to ωB97X calculations.[56] The software used for C-PCM/ωB97X calculations was Gaussian '09, [57] while EDF2 calculations were performed with Spartan '08.[58].

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Table 8. Crystal data and measurement details for **1**, **2**, **4**·½CH_2Cl_2, **5a, 6**·CH_2Cl_2 and **7**.

	1	**2**	**4**·½CH_2Cl_2	**5a**	**6**·CH_2Cl_2	**7**
Formula	$C_4H_7Cl_5MoN$	$C_8H_{20}Cl_8Mo_2N_2O_2$	$C_{14}H_{39}Cl_8Mo_2N_6$	$C_{12}H_{22}Cl_8Mo_2N_2$	$C_{43}H_{42}Cl_8MoN_2$	$C_{12}H_{32}Cl_{9.6}Mo_2N_2O_{0.4}$
FW	342.30	651.74	766.99	669.80	966.33	742.99
T, K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$Pna2_1$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$Pbca$
a, Å	11.8263(17)	8.449(3)	7.9913(5)	6.6315(17)	10.0833(9)	13.8611(7)
b, Å	8.2825(12)	13.113(4)	27.2271(8)	7.648(2)	13.2029(10)	13.6266(7)
c, Å	10.2388(15)	9.937(3)	13.7004(8)	11.839(3)	16.6033(12)	14.1240(6)
α,°	90	90	90	106.915(2)	90	90
β,°	90	102.064(3)	90.321(4)	96.903(3)	103.818(6)	90
γ,°	90	90	90	102.798(3)	90	90
Cell Volume, Å^3	1002.9(3)	1076.6(6)	2980.9(3)	549.1(2)	2146.4(3)	2667.7(2)
Z	4	2	4	1	2	4
D_c, g·cm^{-3}	2.267	2.011	1.079	2.026	1.495	1.850
μ, mm^{-1}	2.577	2.161	1.574	2.115	0.837	1.907
F(000)	660	636	1540	328	948	1474
Crystal size, mm	0.19 x 0.16 x 0.12	0.19 x 0.12 x 0.10	0.19 x 0.15 x 0.10	0.19 x 0.16 x 0.12	0.14 x 0.12 x 0.10	0.18 x 0.16 x 0.13
θ (limits)°	3.00 - 26.99	2.61 - 27.00	0.75 - 26.00	1.83 - 27.00	1.99-25.02	2.54-27.00
Reflections collected	10237	11565	34636	6004	30144	30112
Independent reflections	2180 [R_{int} = 0.0392]	2351 [R_{int} = 0.0489]	5833 [R_{int} = 0.0613]	2382 [R_{int} = 0.0385]	3791 [R_{int} = 0.2415]	2888 [R_{int} = 0.0282]
Data / restraints /parameters	2180 / 1 / 100	2351 / 0 / 100	5833 / 0 / 272	2382 / 0 / 109	3791 / 2 / 253	2888 / 0 / 124
Goodness on fit on F^2	1.083	1.041	1.063	1.093	0.970	1.212
R_1 ($I > 2\sigma(I)$)	0.0227	0.0278	0.0461	0.0317	0.0627	0.0803
wR_2 (all data)	0.0398	0.0682	0.1092	0.0760	0.1378	0.1913
Largest diff. peak and hole, e Å^{-3}	0.416 / –0.480	0.756 / –0.615	1.293 / –0.724	0.882 / –0.765	0.530 / –1.061	2.147 / –2.430