Dioxomolybdenum(VI) and dioxotungsten(VI) complexes supported by an amido ligand

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Stepwise addition of one equivalent of *n*-butyllithium and trimethylsilyl chloride to 2-*tert*-butylmercaptoaniline affords the new ligand 1-(Me_3SiNH)-2-(*t*-BuS)C_6H_4 (LH), that reacts with one equivalent of butyllithium to its lithium salt LLi. Dioxodichloromolybdenum [MoO_2Cl_2] and dioxodichlorotungsten dimethoxyethane [WO_2Cl_2(dme)] react in tetrahydrofuran solution at low temperature with two equivalents LLi to monomeric dioxomolybdenum(VI) [MoO_2L_2] (**1**) and dioxotungsten(VI) complex [WO_2L_2] (**2**) employing two bidentate amido thioether ligands. The crystallographic determination of the molecular structures of **1** and **2** show evidence for M ⋯ S contacts. The reaction of [MoO_2Cl_2] with LLi in tetrahydrofuran solution at room temperature leads next to **1** to two compounds where silyl group migration from nitrogen to oxygen atoms occurs forming [Mo(=NL′)$_2$($OSiMe_3$)$_2$] (**3**) and [Mo(=NL′)$_2$($OSiMe_3$)L] (**4**, L′ = N-2-*t*-$BuSC_6H_4$) as determined by NMR spectroscopy. Compound **4** was isolated in low yield and its molecular structure determined by X-ray crystallography. Higher yields of a bisimido complex can be obtained by the direct reaction of one equivalent of LLi with [Mo(NAr)$_2Cl_2$(dme)] (Ar = 2,6-$Me_2C_6H_4$) forming [Mo(NAr)$_2$LCl] (**5**).

Introduction

Molybdenum and tungsten oxo compounds are of great importance in catalytic reactions involving oxidation reactions, both in nature as well as in industrial processes.[1–5] A wide variety of dioxomolybdenum(VI) and -tungsten(VI) complexes have been prepared to develop new catalysts and to model active sites of molybdenum oxotransferase enzymes.[6–15] We have recently shown that the dioxomolybdenum complex that contains sterically demanding η^2-pyrazolate ligands ([$MoO_2(\eta^2$-Pz)$_2$]; Pz = 3,5-*t*-Bu_2Pz) is a catalyst for oxygen atom transfer (OAT) reactions from dimethyl sulfoxide to phosphines.[16,17] This is interesting in view of the abundance of nitrogen-based ligands in biological systems. However, in oxotransferase enzymes sulfur-based ligands (dithiolenes) are coordinated to the molybdenum oxo cores.[18] For this reason, MoO_2 and WO_2 complexes employing mainly thiolate ligands with chelating amino functionalities were prepared.[3,4,19] Our success with pyrazolate ligands prompted us to investigate the scope of amido molybdenum or tungsten dioxo complexes as possible functional models for molybdoenzymes. Beside tris(pyrazolyl)borate N-donor ligands that have rendered a significant impact in modelling such enzymes,[20–22] compounds of the type [MoO_2L_2] where L represents an anionic nitrogen ligand are extremely rare. To the best of our knowledge next to our pyrazolate system only one other report can be found in the literature.[23] Lee *et al.* synthesized a series of dioxomolybdenum and -tungsten compounds stabilized by pyridine-functionalised amido ligands.[23] Surprisingly, they employ silyl amido ligands despite the fact that silyl migration from the nitrogen to the oxygen atom forming imido complexes is a well documented phenomenon.[24–26] Thus, the vanadium(V) complex [VO{$N(SiMe_3)_2$}$_2$Br] rearranges into a imido siloxide species on heating for several hours.[24] For group 6 metals, Wilkinson and co-workers reported the formation of a low-melting compound [Mo($NSiMe_3$)$_2$($OSiMe_3$)$_2$] and [W($NSiMe_3$)($OSiMe_3$)$_3$Cl(py)] after reaction of [MO_2Cl_2] with $HN(SiMe_3)_2$, whereas with [CrO_2Cl_2] the amido complex [CrO_2{$N(SiMe_3)_2$}$_2$] was obtained.[25] Lee's molybdenum and tungsten complexes do not seem to rearrange. This encouraged us to start our investigation with silyl substituted anilido ligands. Due to the preference for sulfur ligands of these metals we introduced a chelating thioether functionality.

In this paper we report our attempts to generate molybdenum- and tungsten-dioxo complexes with 2-thioether functionalised anilido ligands (Fig. 1). Surprisingly, such ligands have not been previously employed in any metal compounds in contrast to similar ether functionalised molecules.[27–31]

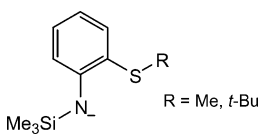

Fig. 1

Here we report the synthesis and molecular structure of several complexes containing the anilido ligand shown in Fig. 1 with R = *t*-Bu. In contrast to the work reported for pyridine-functionalised amido ligands,[23] we observe silyl group migration in the molybdenum but not in the tungsten compound.

Results and discussion

Synthesis of the ligand

The reaction of 2-*tert*-butylmercaptoaniline[32] with one equivalent of *n*-butyllithium and subsequent treatment with trimethylsilyl

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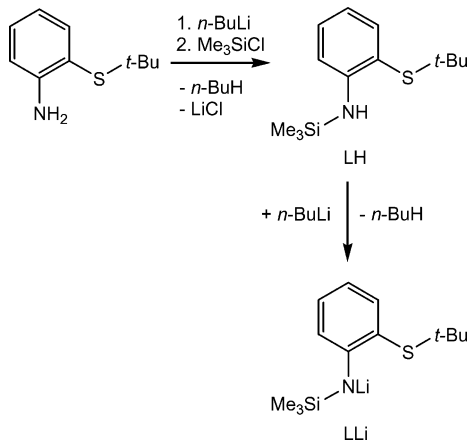
chloride gives the desired product LH as a colourless viscous liquid.

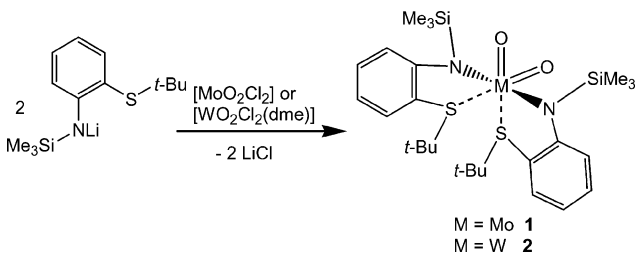
The amine can be conveniently purified by distillation at 73 °C under reduced pressure. ^{1}H and ^{13}C NMR spectra are consistent with the structure shown in Scheme 1. Deprotonation of the amine H-atom by one equivalent of *n*-BuLi in pentane leads to the formation of a white precipitate of the lithium salt that can be isolated and spectroscopically characterized. ^{1}H NMR spectroscopy showed two singlets at δ 0.30 and 1.07 ppm with equal intensity, shifted from those in the spectrum for LH (δ 0.16 and 1.20 ppm) indicating complete deprotonation. However, we generally synthesized the LLi *in situ* by addition of *n*-BuLi to the amine LH in tetrahydrofuran at −20 °C and subsequent stirring for an additional 30 min at room temperature (Scheme 1). Such solutions were directly used in the reactions described below.



Scheme 1

Synthesis of the complexes

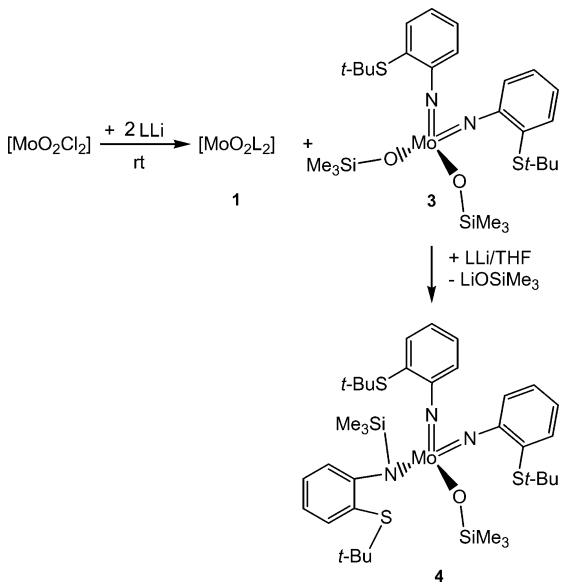
The reaction of $[MoO_2Cl_2]$[33] or $[WO_2Cl_2(dme)]$[34] (dme = dimethoxyethane) in tetrahydrofuran with two equivalents of LLi in ethereal solvents at low temperature leads after work up by extraction with pentane and crystallisation at −35 °C to yellow crystalline compounds $[MoO_2L_2]$ (**1**) and $[WO_2L_2]$ (**2**) as shown in Scheme 2.



Scheme 2 Synthesis of bisamido complexes.

For the synthesis of **1** it is critical that the temperature during the reaction, as well as during work-up, remains low (approx. −5 °C). Higher temperatures lead to mixtures of **1** and two other compounds described below. The isolated compounds **1** and **2** can be stored under a nitrogen atmosphere at room temperature for an unlimited amount of time, but by exposing the yellow crystals or solutions thereof to the laboratory atmosphere quick hydrolysis occurs. They are readily soluble in common organic solvents including pentane. The ^{1}H and ^{13}C NMR spectra in C_6D_6 of both compounds show signals for one type of ligand, which implies a symmetrical coordination of both ligands as shown in Scheme 2. This is consistent with their solid-state structures determined by single-crystal X-ray diffraction (see below). The IR spectrum of **2** exhibits moderate absorptions at 901 and 945 cm^{-1} attributable to the characteristic tungsten oxo stretching vibration.[23,35–37] Electron impact mass spectrometry revealed a peak at *m*/*z* 634 and 720 for **1** and **2**, respectively, for the molecular ions with correct isotopic contributions.

The reaction of $[MoO_2Cl_2]$ with 2 equiv. of LLi at room temperature was investigated by ^{1}H NMR spectroscopy. Thus, the two reagents were directly dissolved in a 5 : 1 mixture of deuterated benzene (C_6D_6) and deuterated tetrahydrofuran (THF-D_8) at room temperature. The immediate recording of the ^{1}H NMR spectrum of this mixture revealed resonances for two compounds with symmetrically coordinated ligands in the ratio 2 : 1. Resonances at 0.42 (s, 9H, $SiMe_3$), 1.15 (s, 9H, *t*-Bu), 6.5 (m, 1H, Ar) and 6.95 (m, 3H, Ar) ppm are assignable to compound **1** as an independently measured spectrum of isolated **1** in this solvent mixture shows identical shifts. This ^{1}H NMR experiment revealed signals for a second species **3** (Scheme 3) at 0.11 (s, 9H, $SiMe_3$), 1.24 (s, 9H, *t*-Bu), 6.74 (m, 1H, Ar), 7.02 (m, 1H, Ar), 7.31 (m, 1H, Ar) and 7.60 (m, 1H, Ar) that are different from those of LLi. The significant shift of the resonance for the $SiMe_3$ group form 0.48 for **1** to 0.11 ppm for the additional species points to the formation of a $OSiMe_3$ group, as this is the typical region for this type of silicon substituents.[25]



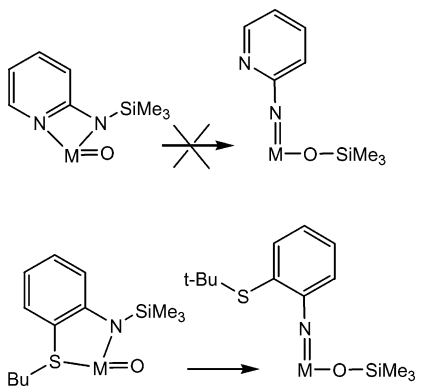
Scheme 3 Formation of compounds **3** and **4**.

The formation of **3** involves a $SiMe_3$ group migration from the nitrogen to the oxygen atom. This type of migration has previously been previously described by Wilkinson and co-workers in group 6 metal oxo chemistry.[25]

Further evidence for the silyl group migration gives the crystal structures analysis of a bisimido compound $[Mo(=NL')_2(OSiMe_3)L]$ (**4**, L′ = N-2-*t*-$BuSC_6H_4$) that is derived from compound **3**. Single crystals of **4** suitable for X-ray diffraction

were obtained from reactions of $[MoO_2Cl_2]$ and LLi in THF at room temperature, subsequent extraction with pentane and crystallisation at −35 °C. The thus obtained orange crystalline material contained **1**, **3** and **4** in various ratios depending on the crystallizing conditions, evidenced by ^{1}H NMR spectroscopy. Mass spectrometry shows peaks at *m*/*z* 634 and 797 with correct isotopic distribution for **1** (or **3**) and **4**, respectively. Changing the ratio of $[MoO_2Cl_2]$/LLi to 1 : 3 according to the stoichiometry of the reaction slightly increased the amount of **4** in comparison to **1** and **3**, however pure **4** could not be obtained. This points to equilibria of the involved reactions, so that slight changes of the reaction times and crystallizing conditions lead to varied distributions of **1**, **3** and **4**. The mechanism of formation of **3** and **4** is as yet unknown. However, a high-temperature ^{1}H NMR spectrum of isolated **1** in THF-D_8 shows only resonances for **1** and also the addition of 1 equiv. of LLi to a sample of **1** shows no evidence of **3** or **4**. Thus, silyl group migration must occur before the formation of **1**. We assume that **3** is formed stepwise after substitution of one chlorine atom of $[MoO_2Cl_2]$ by the nitrogen ligand followed by silyl group migration. The driving force for the substitution with a third equivalent of LLi in **4** is likely the high oxophilicity of lithium forming $LiOSiMe_3$[38] after the disappearance of the oxo groups by rearrangement to the bisimido form. It is somewhat surprising, that the second siloxide ligand is not substituted. However, this can be explained by steric considerations (see below).

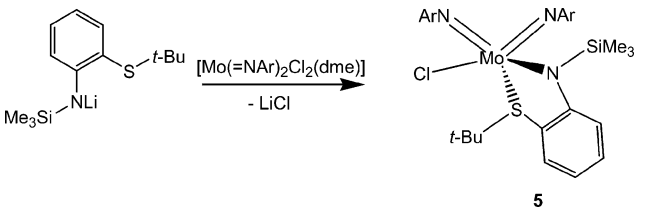
With pyridine-functionalised amido ligands no silyl group migration is reported.[23] The difference in reactivity is interesting. The conversion of the amido into the imido group involves a substantial movement of the aromatic ring as shown in Scheme 4. Imido groups in d^0 complexes show usually linear M–N–C units with sp hybridised N atoms.[25] Once **1** is formed this movement is less likely due to steric reasons. In the pyridine-functionalised amido complexes, the stronger bond to the pyridyl nitrogen atom in comparison to the crowded sulfur atom presumably prevents this movement. Whether silyl group migration occurs or not is apparently dependant on a delicate equilibrium between the bond strengths within the involved species. For this reason, tungsten compound **2** is formed in the absence of silyl group migration.



Scheme 4 Comparison to pyridine-functionalised amido ligands.

It is worth noting that with analogous ligands to L having 2-MeS or 2-MeO groups instead of 2-*t*-BuS, we were not able to isolate any pure compounds, although mass spectrometry pointed to the existence of $[MO_2L_2]$ species. At this point it is not clear whether the steric bulk of the *t*-Bu group is stabilizing compounds **1** and **2** and whether increased silyl group migration hampers the isolation with analogous anilido ligands.

We were interested why the remaining $OSiMe_3$ group in **4** is not substituted by a second amido ligand under elimination of a further equivalent of $LiOSiMe_3$. For this reason we investigated the reaction of a preformed imido complex with various amounts of LLi. Treatment of $[Mo(=NAr)_2Cl_2(dme)]$[39] (Ar = 2,6-$Me_2C_6H_3$) with one equivalent of LLi in diethyl ether at room temperature overnight and usual work-up by extraction with toluene gave **5** as bright orange crystals (eqn (1)).



(1)

The ^{1}H NMR spectrum of **5** shows one resonance for the protons of the $SiMe_3$ group (δ 0.36 ppm) and one for those of the *t*-Bu group (δ 1.35 ppm). The protons of the methyl groups at the aromatic ring systems appear as one broad singlet (δ 1.78 ppm) and multiplets for the 10 aromatic protons can be found between δ 6.60 and 7.48 ppm. The broad resonance for the four methyl groups, indicative of a dynamic process, splits into two broad resonances at 1.9 and 2.4 ppm upon cooling to −80 °C. This can be explained by a structural situation where the two imido groups are inequivalent but rotation along N–aryl bond still occurs. At room temperature the additional dynamic process most likely involves reversible S–Mo bond breaking and formation. Similar behaviour has been found in bisimido complexes with bidentate phenolate ligands $[Mo(=NAr)_2(ON)X]$, where the four *ortho*-substituents on the imido aryl groups are found to be equivalent at room temperature.[40] Electron impact mass spectrometry (peak at *m*/*z* 623 for the molecular ion) and elemental analysis support the formation of **5**. In addition, X-ray diffraction analysis of a suitable single crystal confirms the structure shown in eqn (1).

Interestingly, treatment of $[Mo(NAr)_2Cl_2(dme)]$ with two or more equivalents of LLi does not lead to the substitution of two chloride ligands but rather compound **5** is isolated in all attempts. Apparently, the steric bulk of the amido ligand prevents a second substitution. This provides an explanation for the question why the second siloxide ligand in the bisimido compound **4** is not substituted by L.

Crystallographic studies

The crystal structures of complexes **1**, **2**, **4** and **5** were determined by single-crystal X-ray techniques. The molecular structures are displayed in Fig. 2–5. Selected bond lengths and angles are presented in Table 1, while crystal data and refinement details are given in Table 2.

Complexes **1** and **2** are isostructural and exhibit distorted octahedral metal centres coordinated by two mutually *cis* terminal oxo and two bidentate amido ligands. The two nitrogen atoms are *transoid* to each other with N1–M–N2 angles of 146.1(1)° in **1** and 146.7(1)° in **2** thus rendering the sulfur atom approximately *trans*

Table 1 Selected bond distances (Å) and angles (°) for complexes $[MoO_2(L)_2]$ (**1**), $[WO_2(L)_2]$ (**2**), $[Mo(NL')_2(OSiMe_3)L]$ (**4**) and $[Mo(NAr)_2(L)Cl]$ (**5**)

1							
Mo1–S1	2.805(1)	Mo1–N1	2.044(2)	Mo1–O1	1.709(2)	Mo1–O2	1.704(2)
Mo1–S2	2.775(1)	Mo1–N2	2.059(2)				
O2–Mo1–N1	97.3(1)	O1–Mo1–O2	104.9(1)	O2–Mo1–S2	89.0(1)	O2–Mo1–S1	165.9(1)
O1–Mo1–N2	96.7(1)	O1–Mo1–N1	103.4(1)	N2–Mo1–S2	74.1(1)	N1–Mo1–S1	73.9(1)
O2–Mo1–N2	103.5(1)	N1–Mo1–N2	146.1(1)	N1–Mo1–S2	80.0(1)	N2–Mo1–S1	79.9(1)
S2–Mo1–S1	78.8(1)	O1–Mo1–S2	165.0(1)	O1–Mo1–S1	88.1(1)		
2							
W1–S1	2.787(1)	W1–N1	2.038(2)	W1–O1	1.720(2)	W1–O2	1.725(2)
W1–S2	2.766(1)	W1–N2	2.055(2)				
O2–W1–N1	103.1(8)	O1–W1–O2	104.3(1)	O2–W1–S2	165.1(1)	O2–W1–S1	88.6(6)
O1–W1–N2	103.4(8)	O1–W1–N1	97.3(1)	N2–W1–S2	74.2(1)	N1–W1–S1	74.2(6)
O2–W1–N2	96.8(8)	N1–W1–N2	146.7(1)	N1–W1–S2	80.1(6)	N2–W1–S1	79.9(6)
S2–W1–S1	78.2(3)	O1–W1–S2	89.6(1)	O1–W1–S1	166.0(5)		
4							
Mo1–N1	1.747(2)	Mo1–N3	2.009(2)	Mo1–S3	2.906(1)	Mo1–S2	4.487(1)
Mo1–N2	1.763(2)	Mo1–O1	1.920(1)	Mo1–S1	4.074(1)		
Mo1–N1–C4	168.0(1)	N1–Mo1–O1	116.5(1)	N1–Mo1–S3	76.9(1)	N2–Mo1–S3	172.0(1)
Mo1–N2–C14	152.3(1)	N2–Mo1–N3	98.3(1)	N2–Mo1–O1	104.7(1)	O1–Mo1–S3	80.1(1)
N1–Mo1–N2	106.1(1)	N1–Mo1–N3	104.7(1)	O1–Mo1–N3	123.8(1)	N3–Mo1–S3	73.7(1)
5							
Mo1–N1	2.020(2)	Mo1–N3	1.754(2)	Mo1–S1	2.737(1)	Mo1–Cl1	2.382(1)
Mo1–N2	1.753(2)						
Mo1–N2–C7	168.3(2)	N2–Mo1–N1	101.2(1)	N3–Mo1–S1	85.7(1)	N3–Mo1–Cl1	107.4(1)
Mo1–N3–C8	153.6(2)	N3–Mo1–N1	105.7(1)	N1–Mo1–S1	76.3(1)	N1–Mo1–Cl1	137.1(1)
N2–Mo1–S1	167.0(1)	N2–Mo1–N3	107.2(1)	N2–Mo1–Cl1	94.3(1)	Cl1–Mo1–S1	79.7(1)

Table 2 Crystal data and refinement details for complexes **1**, **2**, **4** and **5**

	1	**2**	**4**	**5**
Formula	$C_{26}H_{44}MoN_2O_2S_2Si_2$	$C_{26}H_{44}N_2O_2S_2Si_2W$	$C_{36}H_{57}MoN_3OS_3Si_2$	$C_{29}H_{40}ClMoN_3SSi$
M	632.87	720.78	796.15	622.18
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a/Å	9.622(3)	9.610(2)	11.834(2)	8.982(2)
b/Å	12.052(3)	12.010(2)	12.365(3)	20.696(3)
c/Å	13.693(4)	13.775(3)	15.082(3)	16.862(3)
α/°	85.06(1)	85.31(3)	78.65(3)	90
β/°	82.80(1)	82.58(3)	76.75(3)	101.65(2)
γ/°	88.44(3)	88.53(3)	76.53(3)	90
V/Å^3	1569(1)	1571(1)	2065(1)	3070(1)
Crystal size/mm	0.20 × 0.10 × 0.10	0.25 × 0.02 × 0.01	0.05 × 0.05 × 0.02	0.20 × 0.15 × 0.10
D_c/Mg m^{-3}	1.339	1.524	1.280	1.346
Z	2	2	2	4
μ/mm^{-1}	5.582	8.975	4.799	5.464
θ range/°	3.26 to 58.92	3.25 to 58.86	3.05 to 58.87	3.42 to 59.05
No. observed data	14417	14658	22428	27816
No. indep. reflns (R_{int})	4334 (0.0347)	4390 (0.0229)	5702 (0.0279)	4397 (0.0471)
$R1$,[a] $wR2$[b] ($I > 2\sigma(I)$)	0.0259, 0.0613	0.0160, 0.0396	0.0201, 0.0513	0.0276, 0.0729
$R1$,[a] $wR2$[b] (all data)	0.0351, 0.0651	0.0168, 0.0400	0.0220, 0.0525	0.0280, 0.0733

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

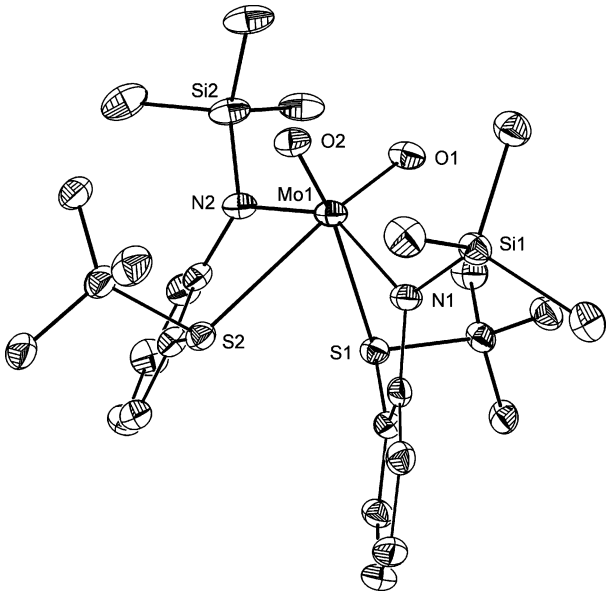


Fig. 2 Molecular structure of $[MoO_2L_2]$ (**1**). Hydrogen atoms have been omitted for clarity.

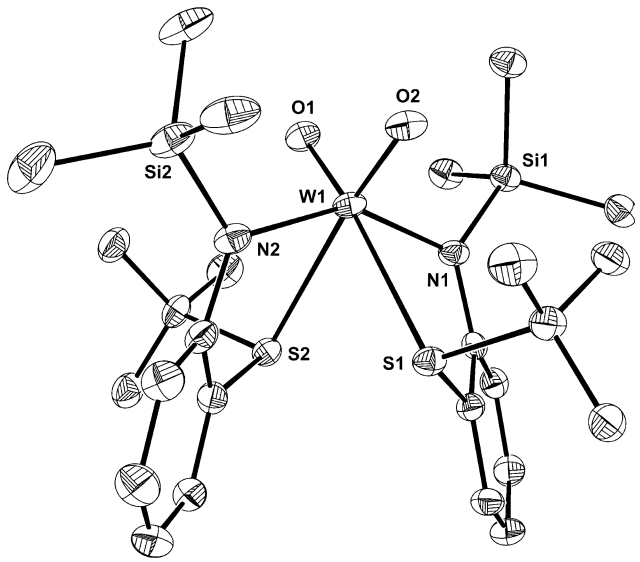


Fig. 3 Molecular structure of $[WO_2L_2]$ (**2**). Hydrogen atoms have been omitted for clarity.

to the oxo groups (*trans* S–M–O 165.0–166.0°). The M=O bond lengths are 1.709(2) Å (Mo1–O1), 1.701(2) Å (Mo1–O2), 1.704(2) Å (W1–O1) and 1.725(2) Å (W1–O2), which is in the typical region for group 6 oxo bonds.[23,25,41] The M–N bond distances in **1** and **2** (Mo1–N1 2.044(2) Å, Mo1–N2 2.059(2) Å, W1–N1 2.038(2) Å and W1–N2 2.055(2) Å are comparable to another report of amido complexes of this type (2.079(2)–2.081(2) Å).[23] Molybdenum–sulfur distances are Mo1–S1 2.805(1) Å and Mo1–S2 2.775(1) Å, which are significantly shorter than in **4** pointing to a stronger Mo–S interaction in the bisamido complex. Tungsten–sulfur distances are W1–S1 2.787(1) Å and W1–S2 2.766(1) Å, which are similar to those reported in literature.[42]

In complex **4**, the Mo(VI) centre is coordinated by two imido ligands, one siloxide and one amido ligand with an additional

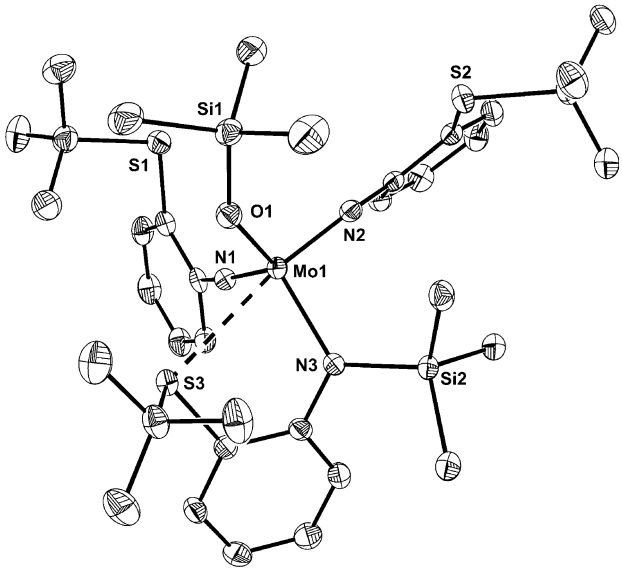


Fig. 4 Molecular structure of $[Mo(=NL')_2(OSiMe_3)L]$ (**4**) showing the weak interaction between sulfur and molybdenum.

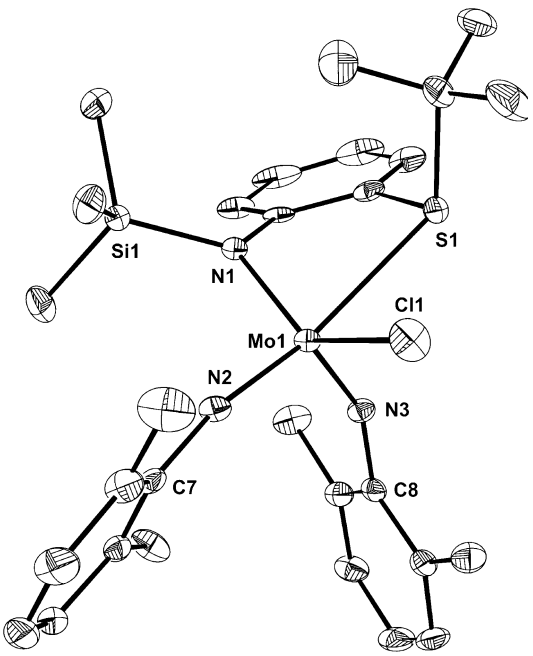


Fig. 5 Molecular view of $[Mo(=NAr)_2LCl]$ (**5**).

weak interaction to the thioether sulfur atom. The geometry of these five ligands about the metal centre is best described as distorted trigonal bipyramidal (largest angle: N2–Mo1–S3 172.0(1)°), second largest angle: N3–Mo1–O1 123.8(1)°),[43] where the imido nitrogen atom N2 and the sulfur atom S3 are in the apical positions (N2–Mo1–S3 172.0(1)°). The two sulfur atoms within the imido ligands are not close enough to the metal centre for a bonding interaction (Mo1–S1 4.074(1) Å and Mo1–S2 4.487(1) Å), whereas the Mo1–S3 is 2.906(1) Å, which is significantly longer than in **1** and **5** (see below) but can be considered as a weak interaction belonging to the longer bonds reported for this type of compounds.[44]

The Mo1–O1 in **4** is 1.920(1) Å, which corresponds to molybdenum–oxygen single bonds described in literature.[45–47] The bond length to the amido nitrogen atom (Mo1–N3) is 2.009(2) Å, that should be compared to the few other bisimido amido complexes reported in the literature. For example, $[Mo(NAr)_2\{N(SiMe_3)_2\}Cl]$ exhibits a metal–amido bond distance of 1.947(3) Å and $[Mo(NAr)_2\{N(SiMe_3)_2\}(NMe_2)]$ 2.012(1) and 1.953(2) Å, respectively.[48,49]

The imido N1 ligand exhibits a Mo1–N1 distance of 1.747(2) Å and a linear Mo1–N1–C4 angle of 168.0(1)° consistent with the expected sp hybridised nitrogen atom and a M≡N triple bond.[40] The other imido ligand shows a longer bond distance (Mo1–N2 1.763(2) Å) and a significantly less obtuse Mo1–N2–C14 angle of 152.3(1)°, which is at the low end of the linear coordination. Bent structures with angles <150° are consistent with M=N double bonds and a lone pair at the nitrogen atom.[40,48] In compound **4**, the lone pair at nitrogen is likely to be involved in bonding interactions to the d^0 metal due to the otherwise low electron count suggesting steric reasons for the low metal–nitrogen carbon angle.[26,40,50]

Comparison of compounds **4** and **5** reveals close overall geometries, with the latter showing a more pronounced distortion in the trigonal bipyramid (largest angle: N2–Mo1–S1 167.0(1)°), second largest angle: N1–Mo1–Cl2 137.1(1)°). Again, in **5** both imido groups exhibit different coordination modes (Mo1–N2 1.753(2) Å; Mo1–N2–C7 168.3(2)° and Mo1–N3 1.754(2) Å; Mo1–N3–C8 153.6(2)°.[46,47] However, in compound **4** the more bent N2 imido ligand is in axial position (*trans* to the thioether sulfur atom), whereas in compound **5** the more bent N3 imido group is found in equatorial position. Apparently, the energy difference between the linear and bent form is small, so that steric factors determine the structure.[40] This has also been found by molecular orbital calculations on $[Cp^*_2Ta(NR)H]$, where the two forms are found to be only slightly different in energy.[51]

Conclusion

The work reported here shows that the silyl amido ligand L with a chelating *tert*-butylthioether functionality allows the synthesis of d^0 tungsten dioxo complex. The analogous bisamido molybdenum compound can only be obtained by careful addition of two equiv of LLi at low temperature. Room-temperature conditions promote silyl group migration from the nitrogen to the oxygen atom and subsequent substitution of a siloxide by an amido ligand. This is in contrast to an earlier report of $[MoO_2]^{2+}$ complexes with silyl amido ligands where no migration is observed.[23] Keeping this in mind, our results allow the conclusion that a stable bidentate coordination of the ligand systems prevents migration, which is relevant for the design of new ligands for high oxidation state molybdenum and tungsten oxo complexes.

Experimental

General

All manipulations were carried out under dry nitrogen using standard Schlenk line or glove box techniques. All solvents were purified by standard methods and distilled under a nitrogen atmosphere immediately prior to use. 2-*tert*-mercaptoaniline,[32] $[WO_2Cl_2(dme)]$,[34] $[MoO_2Cl_2]$[33] and $[Mo(=NAr)_2Cl_2(dme)]$[39] were prepared according to literature procedures. All other chemicals mentioned were used as purchased from commercial sources (Aldrich, Merck).

Samples for mass spectrometry were measured on a BIO-RAD Digilab FTS-7 mass spectrometer with a Finnigan MAT 95 and all NMR spectra on a Bruker Avance 500 or 200 MHz. Elemental analyses were performed by the Analytisches-Chemisches Laboratorium des Instituts für Anorganische Chemie, Göttingen. IR spectra were recorded on Bio-Rad Digilab FTS-7 spectrometer as Nujol mulls between KBr plates.

X-Ray crystallographic determinations

Crystals of compounds **1**, **2**, **4** and **5** were taken from the solution, covered with oil, mounted on glass fibres and placed immediately in a protective stream of cold nitrogen (100 K). Data were collected on a Bruker three-circle diffractometer equipped with Smart 6000 CCD area detector using mirror-monochromated Cu-Kα radiation (λ = 1.54178 Å). The structures were solved by direct methods using SHELXS-97[52] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[53] All non-hydrogen were refined anisotropically, while all hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model with U_{ij} tied to the parent atom.

CCDC reference numbers 292971 (**1**), 286078 (**2**), 286079 (**4**) and 284752 (**5**).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b514873a

Syntheses

Synthesis of *N*-trimethylsilyl-2-*tert*-butylmercaptoaniline (LH). 10 g (0.055 mol) of 2-*tert*-butylsulfanylaniline[32] were dissolved in diethyl ether (30 ml), cooled to 0 °C and *n*-BuLi (22 ml of a 2.5 M solution, 0.055 mol) was added slowly. After 1 h stirring at room temperature the mixture was cooled to 0 °C and 6.9 ml (0.055 mol) of freshly distilled Me_3SiCl were added. The reaction mixture was allowed to come to room temperature and after 1 h the solvent volume was reduced *in vacuo* until a residual oil remained, which was distilled at high vacuum at 73 °C, giving 11.5 g (83%) of the product as a colourless oil.

^{1}H NMR (200 MHz, C_6D_6): δ 0.16 (s, 9H, $Si(CH_3)_3$), 1.20 (s, 9H, $SC(CH_3)_3$), 5.56 (br s, 1H, NH), 6.6 (m, 1H, H-Ar) 6.83 (m, 1H, H-Ar), 7.06 (m, 1H, H-Ar), 7.55 (m, 1H, H-Ar); ^{13}C NMR (500 MHz, C_6D_6): δ −0.2 ($Si(CH_3)_3$), 31.0 ($SC(CH_3)_3$), 47.5 ($SC(CH_3)_3$), 114.7, 117.4, 118.6, 130.9, 140.1, 151.7 (C-Ar).

Synthesis of LLi. To a −20 °C cold solution of LH (3.2 g, 0.013 mol) in pentane was added *n*-BuLi (5.0 ml of a 2.5 M solution, 0.013 mol) dropwise *via* syringe during which a white precipitate appeared. The mixture was allowed to come to room temperature and stirred for an additional hour. The white precipitate was collected on a frit and rinsed with pentane, dried *in vacuo* to yield 2.6 g (81%) of the product as a white solid.

^{1}H NMR (200 MHz, C_6D_6): δ 0.30 (s, 9H, $Si(CH_3)_3$), 1.07 (s, 9H, $SC(CH_3)_3$), 6.60–7.45 (m, 4H, H-Ar); ^{13}C NMR (500 MHz, C_6D_6–THF-d_8 5 : 1): δ 2.3 ($Si(CH_3)_3$), 30.9 ($SC(CH_3)_3$), 47.8 (quat. C), 109.3, 117.9, 121.7, 130.5, 139.7, 166.1 (C-Ar); IR (KBr, cm^{-1}): 1574m, 1458s, 1375s, 1283m, 1245m, 1158m, 1034m, 919m, 826m.

Synthesis of $[MoO_2L_2]$ (1). To a precooled solution of LH (0.504 g, 0.002 mol) in THF, *n*-BuLi (0.8 ml of a 2.5 M solution, 0.002 mol) was slowly added *via* syringe. The mixture was warmed to room temperature, stirred for 30 min, than cooled to −5 °C. This solution was added dropwise to a pale-yellow solution of $[MoO_2Cl_2]$[33] in THF (0.2 g, 0.001 mol) at −5 °C. The mixture was left to stir at −5 °C for 30 min. After removing the solvent *in vacuo*, the obtained solid was extracted with hexane. The orange solution was filtered over Celite, concentrated to approx. 5 ml and left in the freezer at −35 °C overnight, where yellow crystals appeared (0.24 g, 38%).

^{1}H NMR (200 MHz, C_6D_6): δ 0.71 (s, 9H, $NSi(CH_3)_3$) 1.23 (s, 9H, $SC(CH_3)_3$), 6.52 (m, 1H, H-Ar), 6.95–7.05 (m, 3H, H-Ar); ^{13}C NMR (500 MHz, C_6D_6): δ 2.6 ($NSi(CH_3)_3$), 28.5 ($SC(CH_3)_3$), 55.9 ($SC(CH_3)_3$), 119.9, 121.7, 122.5, 130.8, 136.4, 163.3 (C-Ar); MS (EI): *m*/*z* 634 (30%) $[MoO_2L_2]^+$; Anal. Calc. for $C_{26}H_{44}MoN_2O_2S_2Si_2$: C, 49.34; H, 7.01; N, 4.43. Found: C, 49.10; H, 6. 89; N, 4.21%.

Synthesis of $[WO_2L_2]$ (2). To a precooled solution of LH (0.504 g, 0.002 mol) in THF *n*-BuLi (0.8 ml of a 2.5 M solution, 0.002 mol) was slowly added *via* syringe. The mixture was warmed to room temperature, stirred for 30 min, than added dropwise to a colourless solution of $[WO_2Cl_2(dme)]$[34] in THF (0.377 g, 0.001 mol). The mixture became immediately orange and after 40 min the colour changed to brown–orange. After 2 h stirring at room temperature, the solvent was removed *in vacuo* and the product extracted with pentane. The pale-yellow solution was filtered over Celite, concentrated to approx. 5 ml and left in the freezer at −35 °C overnight. Pale-lemon microcrystals were collected on a frit, and dried *in vacuo* giving 0.35 g (55%) of the product.

^{1}H NMR (500 MHz, C_6D_6): δ 0.74 (s, 9H, $NSi(CH_3)_3$), 1.25 (s, 9H, $SC(CH_3)_3$), 6.49–7.12 (m, H-Ar); ^{13}C NMR (500 MHz, C_6D_6): δ 2.6 ($NSi(CH_3)_3$), 28.2 ($SC(CH_3)_3$), 55.2 ($SC(CH_3)_3$), 119.9, 121.1, 123.7, 130.9, 136.4, 163.3 (C-Ar); MS (EI): *m*/*z* 720 (100%) $[WO_2L_2]^+$; Anal. Calc. for $C_{26}H_{44}N_2O_2S_2Si_2W$: C, 43.32; H, 6.15; N, 3.89. Found: C, 43.27; H, 6.32; N, 3.82%; IR (KBr, cm^{-1}): 1580m, 1289m, 1251m, 1158m, 945s, 902s, 859m, 839m, 724m.

Synthesis of $[Mo(=NL')_2(OSiMe_3)L]$ (4). To a precooled solution of LH (0.504 g, 0.002 mol) in THF, *n*-BuLi (0.8 ml of a 2.5 M solution, 0.002 mol) was slowly added *via* syringe. The mixture was warmed to room temperature, stirred for 30 min, than added dropwise to a pale-yellow solution of $[MoO_2Cl_2]$ (0.2 g, 0.001 mol) in THF. The mixture was left to stir at room temperature for 4 h. After removing the solvent *in vacuo*, the obtained solid was extracted with toluene. The brown–orange solution was filtered over Celite. After removing the solvent, the residual solid was recrystallized from cold pentane (−35 °C). The obtained orange crystals proved to be a mixture of **1**, **3** and **4**.

^{1}H NMR (200 MHz, C_6D_6) of **4**: δ 0.53 (s, 9H, $Si(CH_3)_3$), 0.59 (s, 9H, $Si(CH_3)_3$), 1.30 (br s, 27H, $SC(CH_3)_3$), 6.58 (m, H-Ar), 6.7 (m, H-Ar), 6.8 (m, H-Ar), 7.36–7.36 (m, H-Ar); ^{13}C NMR (500 MHz, C_6D_6) of **4**: δ 2.6 ($NSi(CH_3)_3$), 28.5 ($SC(CH_3)_3$), 55.9 ($SC(CH_3)_3$), 119.9, 121.7, 122.5, 130.8, 136.4, 163.3 (C-Ar); MS (EI): *m*/*z* 634 (40%) $[MoO_2L_2]^+$, 797 (30%) $[Mo(=NL')_2(OSiMe_3)L]^+$.

Synthesis of $[Mo(=NAr)_2LCl]$ (5). To a precooled solution of LH (0.506 g, 0.002 mol) in THF, *n*-BuLi (0.8 ml of a 2.5 M solution, 0.002 mol) was slowly added *via* syringe. The mixture was warmed to room temperature, stirred for 30 min, than added dropwise *via* cannula to a cold (−20 °C) deep red solution of $[Mo(=NAr)_2Cl_2(dme)]$[39] in THF (0.988 g, 0.002 mol). The solution was allowed to come to room temperature and stirred for additional 4 h. The solvent was removed *in vacuo* giving a brown solid, which was extracted with toluene. The solution was filtered over Celite, concentrated to approx. 10 ml and left at −30 °C. Bright orange crystals appeared that were filtered from the solution, washed thoroughly with hexane and dried *in vacuo* giving 0.64 g (52%) of the product.

^{1}H NMR (500 MHz, toluene-d_8): δ 0.4 (s, 9H, $NSi(CH_3)_3$), 1.47 (s, 9H, $SC(CH_3)_3$), 1.90 (br s, 6H, CH_3–Ar), 2,40 (br s, 6H, CH_3–Ar) 6.55–6.81 (m, 7H, H-Ar), 6.85–6.95 (m, 2H, H-Ar), 7.35 (d, 1H, H-Ar); ^{13}C NMR (500 MHz, C_6D_6): δ 3.4 ($NSi(CH_3)_3$), 18.7 (CH_3–Ar), 29.8 ($SC(CH_3)_3$), 51.7 (quat. C), 121.3, 122.4, 126.1, 129.1, 138.0, 163.0 (C-Ar); MS (EI): *m*/*z* 623 (100%) $[Mo(NAr)_2ClL]^+$; Anal. Calc. for $C_{26}H_{44}N_2O_2S_2Si_2W$: C, 55.85; H, 6.42; N, 6.74. Found: C, 55.02; H, 6.32; N, 6.46%; IR (KBr, cm^{-1}): 1577m, 1308m, 1263s, 1246m, 1160m, 1027m, 897m, 871m, 840s, 814s, 764s, 728s.

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