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Synthesis and Structural Characterization of the First Organosoluble Mononuclear Siloxane and Silylamide of Molybdenum and Tungsten†

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Reactions of Cp^*MCl_4 ($Cp^* = C_5Me_5$, M = Mo, W) with the silanetriol $(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)Si(OH)_3$ yield organosoluble metallasiloxanes of the type $Cp^*MoO[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)]_2Si_2O_3(OH)_2$ (**1**) and $Cp^*WO[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)]_2Si_2O_3(OH)_2$ (**2**) possessing the MSi_2O_3 core. The above-mentioned compounds can easily be oxidized to the corresponding acyclic products containing a chain of two condensed silanetriol moieties bound to the metal as $Cp^*MoO_2[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)]_2Si_2O_2(OH)_3$ (**3**) and $Cp^*WO_2[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)]_2Si_2O_2(OH)_3$ (**4**). However, the reactions of the isoelectronic organosilyltriamide $(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)Si(NH_2)_3$ with Cp^*MoCl_4 resulted in the formation of a mononuclear product $Cp^*MoCl_2N[Si(NH_2)_2N(SiMe_3)(2,6\text{-}i\text{-}Pr_2C_6H_3)]$ (**5**) containing a MoN triple bond.

Introduction

The synthesis of organosilicon compounds containing the Si−O−M unit (M = metal) dates back to the end of the last century using silanols with a single OH group.[1] A more extended and systematic approach in this field became viable with the synthesis of stable organosilanediols, disilanols, and, more recently, organosilanetriols and trisilanols.[2−4] Feher et al. reported the synthesis of incompletely condensed polyhedral oligosilasesquioxanes that retain reactive Si−OH functionality, which allows the use of these compounds as ligands for a wide variety of metals. These organometallasilasesquioxanes can be envisaged to be excellent model systems for heterogeneous silica-supported catalyst systems.[4] One restriction of the use of trisilanols is that there is little choice with regards to structural modification due to the fixed structure of the starting material, namely, $R_7Si_7O_9(OH)_3$. A more versatile building block strategy involves the use of stable silanetriols.[5]

As a matter of interest, the synthesis of the organosilyltriamide $RSi(NH_2)_3$ (R = $(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)$) was reported in 1995.[6] This precursor can be considered to be isoelectronic to the corresponding silanetriol $RSi(OH)_3$.[7] Since then, one of our main objectives has been to study closely related reactions for the silyltriamides with respect to the corresponding silanetriols. With regards to group 13 metal alkyls there seems to be a considerable difference in the reactivity and the composition of the final products.[8] However, with transition metals there has been only one report on the reactivity of $RSi(NH_2)_3$ with Cp^*TiMe_3.[9]

Our interest in this area is to obtain model compounds for transition metal complexes anchored on a silica surface, and we are currently trying to incorporate various transition metals in the silasesquioxane framework. If some of these systems show catalytic activity, they might be helpful to understand the mechanistic aspects of the reactions occurring on the surface of known catalysts. Here we report on the first synthetic results using the organometallic precursors Cp^*MoCl_4 and Cp^*WCl_4 for reactions with a stable silanetriol. This investigation also includes the reactivity studies on the isoelectronic organosilyltriamide $RSi(NH_2)_3$.

Results and Discussion

Reaction of Cp^*MoCl_4 and $RSi(OH)_3$ in the presence of triethylamine led to the isolation of a light-green product **1**. Starting from a molar ratio of 2:1 (silanetriol/Cp^*MoCl_4), **1** was the only product, while using a 1:1 ratio an additional product was isolated in 30% yield. The constitution of this brown product is not clear despite the fact that it contains one molybdenum and a

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† Dedicated to Professor Gerhard Fritz on the occasion of his 80th birthday.

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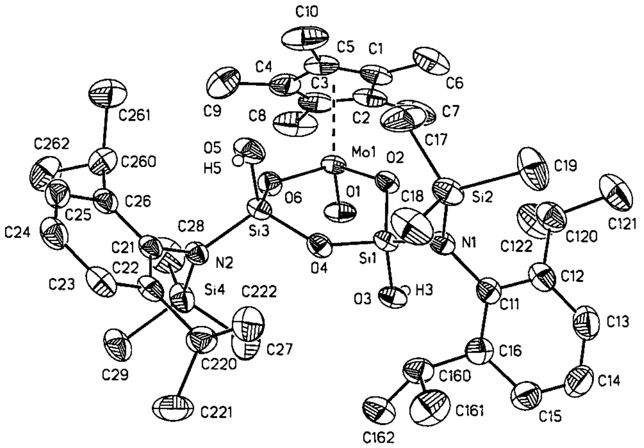


Figure 1. Molecular structure of Cp*MoO[(2,6-*i*-$Pr_2C_6H_3$)N-($SiMe_3$)]$_2Si_2O_3(OH)_2$ (**1**) showing 50% probability thermal ellipsoids and the atom-numbering scheme. Aryl and aliphatic hydrogen atoms have been omitted for clarity.

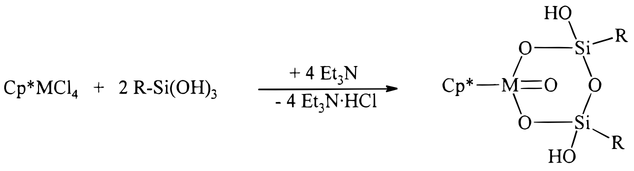
part of the silanetriol ligand. **1** has been fully characterized including a crystal structure. The IR spectrum of **1** still shows the presence of absorption bands corresponding to Si−OH groups in the molecule. The sharp band at 3660 cm^{-1} indicates the presence of free OH groups, while the broad band at 3520 cm^{-1} belongs to OH groups involved in hydrogen bonding as revealed from the X-ray structure. There is only one intense signal in the EI-MS spectrum at *m*/*e* 883 representing the molecular ion. The isotope pattern indicates that **1** contains a single molybdenum center with all chlorine atoms substituted by two ligands from the silanetriol. Examination of the ^1H NMR spectra over a wide range (δ −40 to 40 ppm) shows no resonances corresponding to the Cp* ligand. This was expected because even for the starting material (Cp*$MoCl_4$, paramagnetic) no signal in the proton spectra is detectable. Nevertheless the ^1H NMR spectra of **1** clearly reveals broad signals ($\Delta\nu_{1/2}$ 50−80 Hz) corresponding to the silanol moieties (δ 7.1, 3.8, 1.4, 0.1). Compound **1** crystallizes in the monoclinic space group *C*2/*c* with eight molecules in the unit cell (Figure 1).

The central element of the structure is a six-membered ring containing one molybdenum and two silicon atoms bridged by oxyen. Apart from the Cp* ligand, an oxygen atom is bonded to the metal. The significant shorter Mo−O bond length (1.69 Å) compared to the bond distances inside the ring (1.96 Å) clearly demonstrates a double-bond character. The six-membered ring reveals a boat conformation, the central plane formed by the molybdenum, the oxygen O(4) and O(6), and the silicon atom Si(1). As indicated by the IR spectrum, one of the residual Si−OH groups forms a weak intermolecular hydrogen bond.

The formation of **1** presumably starts from a penta-substituted molybdenum center that undergoes an intramolecular rearrangement. It is unlikely that the condensation of the silanetriol is the first step of the reaction, because under comparable conditions no condensation product was observed.

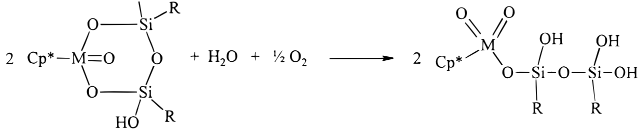
The reaction of the analogues tungsten compound Cp*WCl_4 with $RSi(OH)_3$ resulted in the formation of a blue-green-colored crystalline product **2** in high yield. All spectroscopic data indicate that **2** possesses an equivalent structure compared to **1**. The IR and NMR spectra of **1** and **2** are nearly identical. Again, the most prominent signal detected in the EI-MS spectrum (*m*/*e* 969) corresponds to the molecular ion, the isotope pattern matches exactly the theoretical values.

Scheme 1. Reaction of Cp*MCl_4 with $RSi(OH)_3$ (M = Mo, W)



M = Mo, W; R = (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)

Scheme 2. Reaction of Cp*MoO[(2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)]$_2Si_2O_3(OH)_2$ (1) with O_2/H_2O (M = Mo, W)



M = Mo, W; R = (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)

1 and **2** are very sensitive to air, forming diamagnetic oxidation products. The progress of the oxidation is documented in the ^1H NMR spectra by the appearance of new signals corresponding to the Cp* ligand (**3** δ 1.80; **4** δ 2.15). Moreover the signals belonging to the silanol moieties become less broad. The main products of these conversions could be isolated and have been fully characterized. **1** is oxidized on exposure to atmosphere to an amber-colored product **3** that can be crystallized from *n*-hexane. Compared to **1** the absorptions corresponding to OH vibrations are shifted to longer wavelengths, indicating that stronger hydrogen bonds are formed in the molecule, and no independent OH stretching frequencies were observed. The heaviest fragment observed in the EI-MS spectrum is exactly equivalent to the molecular ion peak of **1** but with significant decrease in intensity. The ^1H NMR spectrum clearly reveals three different signals for Si−OH groups. The molecule possesses four Si centers in different environment, as documented from the ^{29}Si NMR spectrum (δ 7.39, 7.27, −72.85, −74.13). This indicates that the formation of **3** includes the opening of the six-membered ring of **1**.

This is proved by the X-ray structure of **3**, crystallizing in the orthorhombic space group *Pccn*. The molybdenum center is in the +VI oxidation state and is bonded besides the Cp* ligand and two oxygen atoms to a chain of two condensed silanetriol molecules (Figure 2).

In the solid state **3** forms a dimeric arrangement through hydrogen bonds. All the residual Si−OH groups from the silanol moiety are involved in hydrogen-bonding interactions, forming four inter- and two intramolecular hydrogen bonds. The two Mo−O−Si−O−Si chains are distorted to 180° to minimize steric interactions in the solid state. It is likely that even in solution one hydrogen bond remains as indicated by three different Si−OH signals in the ^1H NMR spectrum (δ 2.90, 2.50, 2.37). Nearly similar spectral features are

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for $Cp^*MoO[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)]_2Si_2O_3(OH)_2$ (1), $Cp^*MoO_2[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)]_2Si_2O_2(OH)_3$ (3), and $Cp^*MoCl_2N[Si(NH_2)_2N(SiMe_3)(2,6\text{-}i\text{-}Pr_2C_6H_3)]$ (*5*)

			1		
Mo−O(1)	1.694(2)	Si(3)−O(6)	1.617(2)	O(2)−Mo−O(6)	89.42(9)
Mo−O(2)	1.964(2)	Si(3)−O(4)	1.632(2)	Mo−O(2)−Si(1)	125.32(12)
Mo−O(6)	1.951(2)	Si(3)−O(5)	1.631(2)	O(2)−Si(1)−O(4)	107.79(11)
Si(1)−O(2)	1.629(2)	Si(3)−N(2)	1.718(3)	Si(1)−O(4)−Si(3)	129.52(13)
Si(1)−O(4)	1.639(2)			O(4)−Si(3)−O(6)	108.07(11)
Si(1)−O(3)	1.626(2)	O(2)−Mo-O(1)	109.29(10)	Mo−O(6)−Si(3)	136.11(13)
Si(1)−N(1)	1.721(3)	O(1)−Mo-O(6)	110.31(10)		
			3		
Mo−O(1)	1.708(3)	Si(3)−O(6)	1.613(3)	O(2)−Mo−O(3)	105.78(11)
Mo−O(2)	1.711(3)	Si(3)−O(7)	1.631(3)	Mo−O(3)−Si(1)	126.71(14)
Mo−O(3)	1.915(2)	H(7)···O(2)	2.096(12)	O(3)−Si(1)−O(5)	108.04(12)
Si(1)−O(3)	1.644(2)	H(4)···O(7A)	2.010(2)	Si(1)−O(5)−Si(3)	131.71(14)
Si(1)−O(4)	1.602(3)	H(6)···O(1A)	1.936(12)	O(7)−H(7)···O(2)	171(3)
Si(1)−O(5)	1.633(2)	O(1)−Mo-O(2)	105.72(14)	O(4)−H(4)···O(7A)	148(4)
Si(3)−O(5)	1.636(2)	O(1)−Mo-O(3)	104.36(11)	O(6)−H(6)···O(1A)	170(3)
			5		
Mo−Cl(1)	2.356(17)	Si(1)−N(2)	1.700(3)	Cl(1)−Mo−N(1)	104.55(9)
Mo−Cl(2)	2.379(10)	Si(1)−N(3)	1.682(3)	Cl(2)−Mo−N(1)	108.51(9)
Mo−N(1)	1.723(3)	Si(1)−N(4)	1.723(3)	Mo−N(1)−Si(1)	174.50(15)
Si(1)−N(1)	1.790(3)	Cl(1)−Mo-Cl(2)	92.39(5)	N(1)−Si(1)−N(4)	103.75(13)

Table 2. Crystal Data and Structure Refinement Details for $Cp^*MoO[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)]_2Si_2O_3(OH)_2$ (1), $Cp^*MoO_2[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)]_2Si_2O_2(OH)_3$ (3), and $Cp^*MoCl_2N[Si(NH_2)_2N(SiMe_3)(2,6\text{-}i\text{-}Pr_2C_6H_3)]$ (5)

	1	3	5
empirical formula	$C_{40}H_{69}MoN_2O_6Si_4\cdot(^1/_2n\text{-hexane})$	$C_{40}H_{70}MoN_2O_7Si_4$	$C_{25}H_{45}Cl_2MoN_4Si_2$
fw	$882.28 + {}^1/_2 86.18$	899.28	624.67
cryst syst	monoclinic	orthorhombic	monoclinic
space group	*C*2/*c*	*Pccn*	$P2_1/n$
color of cryst	light-green	amber	brown
a (Å)	26.469(5)	17.873(12)	12.793(11)
b (Å)	29.214(6)	21.027(12)	15.032(12)
c (Å)	14.414(3)	24.798(14)	16.781(4)
α (deg)	90	90	90
β (deg)	114.38(3)	90	107.80(4)
γ (deg)	90	90	90
V (Å^3)	10150(1)	9320(1)	3070(1)
Z	8	8	4
D_{calcd} (g·cm^{-3})	1.211	1.282	1.350
μ (mm^{-1})	0.395	0.430	0.699
F(000)	3952	3824	1308
cryst size (mm)	0.47 × 0.30 × 0.23	0.50 × 0.45 × 0.37	0.43 × 0.22 × 0.15
θ range (deg)	2.09−25.00	2.22−25.00	2.15−25.00
index range	$-31 \le h \le 28$, $0 \le k \le 34$, $0 \le l \le 17$	$0 \le h \le 21$, $0 \le k \le 25$, $0 \le l \le 29$	$-15 \le h \le 14$, $0 \le k \le 17$, $0 \le l \le 19$
no. of reflns colld	59 552	109 651	35 207
no. of indep reflns	8948	8202	5407
R(int)	0.0539	0.1060	0.0702
no. of data	8948	8202	5407
no. of params	356	3	5
no. of restraints	639	517	332
goodness-of-fit on F^2	1.033	1.008	1.025
R_1, $[I > 2\sigma(I)]$	0.0402	0.0387	0.0324
wR_2 (all data)	0.1014	0.1116	0.0753
largest diff peak and hole (e·Å^{-3})	0.899, −0.437	0.399, −0.678	0.485, −0.325

observed in the ^{1}H NMR spectrum of **4** (δ 3.39, 2.83, 2.66) derived from aerobic oxidation of **2**. The colorless crystals of the diamagnetic product **4** possesses an exactly equivalent structure to **3** as corroborated by the spectroscopic details. All spectroscopic data are comparable to **3**; the EI-MS spectrum reveals the $M^+ - OH$ signal as the heaviest fragment (*m*/*e* 969). The IR spectrum reveals a single broad band for Si−OH at a wavenumber comparable to **3** (**4** 3416 cm^{-1}; **3** 3415 cm^{-1}), indicating strong hydrogen bonds as observed in **3**.

Reaction with Silyltriamide. The reaction of the isoelectronic organosilyltriamide $RSi(NH_2)_3$ with Cp^*MoCl_4 in a 1:1 molar ratio yielded the paramagnetic mononuclear product **5**. The isotope pattern of the molecular ion in the EI-MS spectrum reveals that two chlorine atoms remain in the mononuclear product (*m*/*e* 625). Even the use of 2 equiv of the silyltriamide and an excess of triethylamine leads to the same product formation, $Cp^*MoCl_2N[Si(NH_2)_2N(SiMe_3)(2,6\text{-}i\text{-}Pr_2C_6H_3)]$ (**5**). As previously observed, the ^{1}H NMR spectrum shows no signal according to the Cp* ligand bound to the non-diamagnetic metal center. The silylamide moiety is represented by broad signals with appropriate intensity. Compared to **1**, **5** is remarkably stable and can even be handled in air for a while without detectable decomposition. **5** crystallizes from toluene in the monoclinic space group $P2_1/c$ (Figure 3).

The molybdenum atom in the mononuclear complex is nearly tetrahedral, surrounded by the Cp* ligand, two

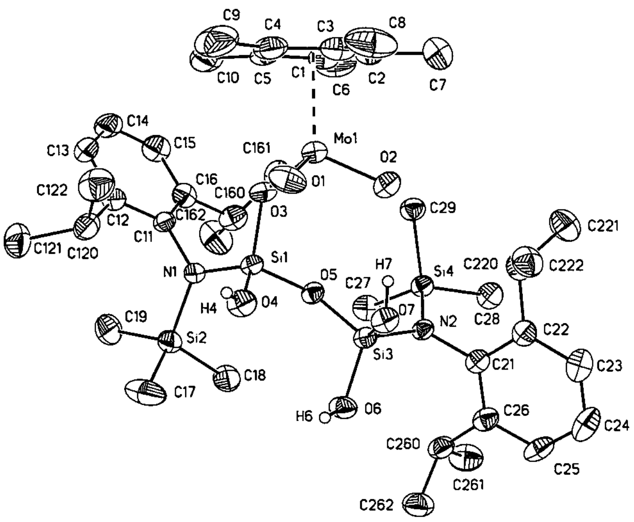


Figure 2. Crystal structure of $Cp^*MoO_2[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)]_2Si_2O_2(OH)_3$ (**3**). The drawing shows 50% probability thermal ellipsoids; aryl and aliphatic hydrogen atoms have been omitted for clarity.

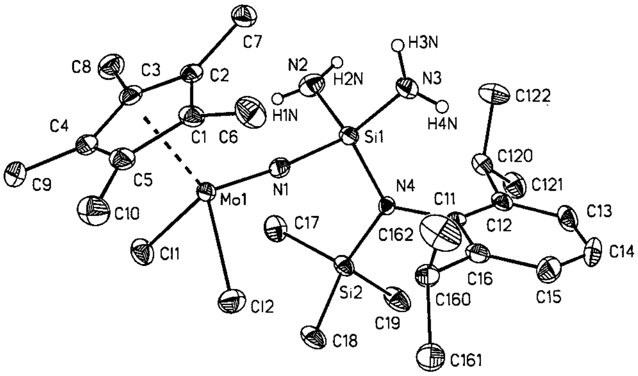


Figure 3. Crystal structure of $Cp^*MoCl_2N[Si(NH_2)_2N(SiMe_3)(2,6\text{-}i\text{-}Pr_2C_6H_3)]$ (**5**). Thermal ellipsoids are shown at the 50% level; aryl and aliphatic hydrogen atoms have been omitted for clarity.

chlorine atoms, and the amino ligand. The Mo−N bond length (1.72 Å) is comparable to the observed bond length in simple imine complexes of molybdenum, like $Cp^*Mo(t\text{-}BuN)Cl_2$ (1.72 Å).[10] This leads to the conclusion that the nitrogen atom undergoes an sp-hybridization where both the p-orbitals are involved in a MoN triple bond, as discussed in earlier reports.[10,11] Also, the nearly linear Mo−N−Si bond angle (174.5°) supports this statement.

We have shown that the reactions of Cp^*MoCl_4 and Cp^*WCl_4 with the silanetriol $RSi(OH)_3$ lead to the formation of mononuclear metal species of the constitution $Cp^*MO[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)]_2Si_2O_3(OH)_2$ (M = Mo **1**, W **2**). Even by changing the ratio of the starting materials and through the variations in the reaction conditions no dimetallic or higher nuclearity product was observed. Nevertheless the compounds **3** and **4** obtained from the oxidative ring-opening reactions might act as building blocks for products with a higher nuclearity. A new example of a heavy metal containing metallasilylamide is also reported. In addition the complementary features in reactivity of silanetriol and its isoelectronic analogue, the silyltriamide, with respect to the composition of the final product are also demonstrated.

Experimental Section

General Methods. All experimental manipulations were carried out either using Schlenk tube techniques or in a drybox under an inert nitrogen atmosphere.[12] Solvents were dried by standard methods and freshly distilled prior to use. Triethylamine was dried over CaH_2 and distilled under a nitrogen atmosphere. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AS 400 instrument. The chemical shifts are reported in ppm relative to external $SiMe_4$ for ^1H and ^{29}Si spectra. IR spectra were recorded on a Bio-Rad Digilab FTS 7 spectrometer. Mass spectra were obtained on a Finnigan MAT 8230 system and a Varian MAT CH5. Melting points were obtained on a HWS-SG 3000 instrument and are reported uncorrected. Elemental analyses were performed at the analytical laboratory of the Institute of Inorganic Chemistry, University of Göttingen.

Starting Materials. Cp^*MoCl_4 and Cp^*WCl_4 were prepared using literature procedures.[13] The silanetriol $(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)Si(OH)_3$ and the silyltriamide $(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)Si(NH_2)_3$ were prepared as reported previously and were dried under high vacuum prior to use.[6,7]

Preparation of $Cp^*MoO[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)]_2Si_2O_3(OH)_2$ (1). Triethylamine (3.66 mmol, 0.37 g) was added to a suspension of $RSi(OH)_3$ (1.37 mmol, 0.45 g) in *n*-hexane (40 mL). Cp^*MoCl_4 (0.67 mmol, 0.25 g) was added slowly as a solid in small portions, and the reaction mixture was stirred for an additional 12 h period. The progress of the reaction is marked by decrease in the violet Cp^*MoCl_4 color while a light-green solution containing a colorless solid formed. The solution was filtered, and all volatiles were removed in vacuo to yield the crude product as a green residue. This residue was dissolved in *n*-hexane (30 mL) and filtered again, and the filtrate was cooled to − 8 °C. After 24 h light-green crystals of analytically pure **1** were obtained; yield 90% (0.60 mmol, 0.53 g). Mp: 188 °C. Anal. Calcd for $C_{40}H_{69}MoN_2O_6Si_4$ (M = 882.3): C, 54.5; H, 7.9; N, 3.2; Si, 12.7. Found: C, 55.4; H, 7.7; N, 3.2; Si, 12.3. MS (EI, 70 eV): *m/e* 883 (100, M^+), 868 (4, $M^+ - CH_3$). IR (KBr, Nujol): 3660, 3520, 1260, 1249, 1183, 1053, 1043, 1011, 968, 959, 911, 900, 836, 802, 536 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, paramagnetic): δ 7.4−6.8 (m, 6H, aromatic CH), 4.1−3.4 (m, 4H, CH), 1.8−0.9 (m, 24H, $C(CH_3)_2$), 0.5−(−0.4) (m, 18H, $Si(CH_3)_3$). ^{29}Si NMR (80 MHz, $CDCl_3$, paramagnetic): δ 7.8, 7.4.

Preparation of $Cp^*WO[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)]_2Si_2O_3(OH)_2$ (2). Similar to the preparation of **1**, $RSi(OH)_3$ (1.53 mmol, 0.50 g) was reacted with Cp^*WCl_4 (0.76 mmol, 0.35 g) in the presence of triethylamine (3.66 mmol, 0.37 g). While stirring the reaction mixture changed from an orange suspension to a blue-green solution containing a colorless solid. After 12 h of stirring the colorless solid was filtered off and the solvent was removed in vacuo. Recrystallization of the residue from *n*-hexane (30 mL) at −8 °C yielded **2** as analytically pure blue-green crystals. Yield: 83% (0.64 mmol, 0.62 g). Mp: 193 °C. Anal. Calcd for $C_{40}H_{69}N_2O_6Si_4W$ (M = 969.4): C, 49.6; H, 7.2; N, 2.9; Si, 11.6. Found: C, 50.1; H, 7.2; N, 3.0; Si, 11.1.

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MS (EI, 70 eV): *m/e* 969 (100, M^+), 954 (5, $M^+ - CH_3$). IR (KBr, Nujol): 3659, 3450, 1261, 1249, 1183, 1043, 1014, 973, 960, 913, 902, 836, 803, 544 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$, paramagnetic): δ 7.2−6.7 (m, 6H, aromatic CH), 3.8−3.3 (m, 4H, CH), 1.5−0.9 (m, 24H, $C(CH_3)_2$), 0.3−(−0.3) (m, 18H, $Si(CH_3)_3$).

Preparation of Cp*MoO$_2$[(2,6-*i*-Pr$_2$C$_6$H$_3$)N(SiMe$_3$)]$_2$Si$_2$O$_2$(OH)$_3$ (3). **1** (0.45 mmol, 0.40 g) was dissolved in *n*-hexane (50 mL) at room temperature and stirred for 12 h. During this period the flask was opened for a few seconds from time to time, whereupon the color of the solution changed from green to amber. The solution was filtered, and the filtrate was reduced to half its volume in vacuo. Over a period of 10 days at room temperature amber crystals of analytically pure **3** were obtained. Yield: 71% (0.32 mmol, 0.29 g). Mp: 192 °C. Anal. Calcd for $C_{40}H_{70}MoN_2O_7Si_4$ (M = 899.3): C, 53.4; H, 7.9; N, 3.1; Si, 12.5. Found: C, 52.3; H, 8.2; N, 3.1; Si, 13.1. MS (EI, 70 eV): *m/e* 883 (22, $M^+ - OH$), 162 (100, $Pr_2C_6H_3^+$). IR (KBr, Nujol): 3415, 1259, 1248, 1179, 1014, 975, 936, 908, 882, 837, 802, 755 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 6.87 (m, 6H, aromatic CH), 3.32 (m, 4H, CH), 2.90 (s, 1H, Si−OH), 2.50 (s, 1H, Si−OH), 2.37 (s, 1H, Si−OH), 1.80 (s, 15H, $C_5(CH_3)_5$), 0.90 (m, 24H, $C(CH_3)_2$), −0.07 (s, 9H, $Si(CH_3)_3$), −0.11 (s, 9H, $Si(CH_3)_3$). ^{29}Si NMR (162 MHz, $CDCl_3$): δ 7.39 (s, $Si(CH_3)_3$), 7.27 (s, $Si(CH_3)_3$), −72.85 (s, $Si(O-)_3$), −74.13 (s, $Si(O-)_3$).

Preparation of Cp*WO$_2$[(2,6-*i*-Pr$_2$C$_6$H$_3$)N(SiMe$_3$)]$_2$Si$_2$O$_2$(OH)$_3$ (4). A solution of **2** (0.41 mmol, 0.40 g) in *n*-hexane (50 mL) was subjected to the same conditions as mentioned for the preparation of **3**. After stirring for 12 h the solution was filtered and the volume of the filtrate was reduced in vacuo to 20 mL. At − 30 °C colorless crystals of **4** were obtained; yield 55% (0.23 mmol, 0.22 g). Mp: 241 °C. Anal. Calcd for $C_{40}H_{70}N_2O_7Si_4W$ (M = 987.2): C, 48.7; H, 7.2; N, 2.8; Si, 11.4. Found: C, 48.9; H, 7.4; N, 2.6; Si, 11.5. MS (EI, 70 eV): *m/e* 969 (6, $M^+ - OH$), 738 (22, $M^+ - (Pr_2C_6H_3)NSi(CH_3)_3$), 162 (100, $Pr_2C_6H_3^+$). IR (KBr, Nujol): 3416, 1261, 1248, 1100, 1017, 978, 937, 891, 837, 802, 727 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.05 (m, 6H, aromatic CH), 3.51 (m, 4H, CH), 3.39 (s, 1H, Si−OH), 2.83 (s, 1H, Si−OH), 2.66 (s, 1H, Si−OH), 2.15 (s, 15H, $C_5(CH_3)_5$), 1.14 (m, 24H, $C(CH_3)_2$), 0.08 (s, 9H, $Si(CH_3)_3$), 0.06 (s, 9H, $Si(CH_3)_3$). ^{29}Si NMR (162 MHz, $CDCl_3$): δ 7.85 (s, $Si(CH_3)_3$), 7.30 (s, $Si(CH_3)_3$), −73.15 (s, $Si(O-)_3$), −74.00 (s, $Si(O-)_3$).

Preparation of Cp*MoCl$_2$N[Si(NH$_2$)$_2$N(SiMe$_3$)(2,6-*i*-Pr$_2$C$_6$H$_3$)] (5). Cp*MoCl$_4$ (0.54 mmol, 0.21 g) and $RSi(NH_2)_3$ (0.54 mmol, 0.18 g) were suspended in toluene (40 mL) at room temperature. To this mixture was added slowly triethylamine (2.20 mmol, 0.22 g), whereupon the color of the reaction mixture slowly changed from violet to dark brown. After 12 h of stirring the mixture was filtered and the filtrate was evaporated to dryness. The resulting brown solid was recrystallized from toluene over a period of 15 days at − 30 °C to obtain analytically pure **5**. Yield: 66% (0.36 mmol, 0.22 g). Mp: 195 °C. Anal. Calcd for $C_{25}H_{45}Cl_2MoN_4Si_2$ (M = 624.7): C, 48.1; H, 7.3; Cl, 11.4; N, 9.0; Si, 9.0. Found: C, 48.3; H, 7.1; Cl, 11.4; N, 8.9; Si, 8.7. MS (EI, 70 eV): *m/e* 625 (15, M^+), 249 (100, $(Pr_2C_6H_3)NSi(CH_3)_3^+$). IR (KBr, Nujol): 3475, 3389, 1534, 1316, 1261, 1251, 1179, 1109, 1074, 1027, 968, 959, 931, 842, 800, 750, 481, 461 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, paramagnetic): δ 7.1−6.9 (m, 3H, aromatic CH), 1.7−0.8 (m, 12H, $C(CH_3)_2$), 0.6-(−0.4) (m, 9H, $Si(CH_3)_3$).

Crystal Structure Determination. Data for **1**, **3**, and **5** were collected at 133 K on a Stoe-Siemens-Huber four-circle diffractometer coupled with a Siemens CCD area detector by the use of φ scans on a shock-cooled crystal in an oil drop;[14] monochromated Mo Kα (λ = 0.710 73 Å) radiation was used. Data integration was performed with the program SAINT. A semiempirical absorption correction was applied. The structures were solved by direct methods (SHELXS-97)[15] and refined against F^2 by least-squares.[16] All non-hydrogen atoms were refined anisotropically and the riding model was used for the hydrogen atoms. The hydrogen atoms attached to oxygen and nitrogen could be located in the difference Fourier synthesis and were refined freely with isotropic displacement parameters. OH and NH distances were restrained to a target value of 0.84 and 0.88 Å, respectively. One trimethylsilyl group in **1** shows two different rotameric conformations with occupancies of 0.58:0.42. The *n*-hexane solvent molecule in **1** is disordered around an inversion center. For the hydrogen atoms a riding model was employed. Ligand as well as solvent molecule disorder was successfully modeled by employing 1,2- and 1,3-distance- and ADP-similarity restraints.

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Supporting Information Available: Tables of crystal data and refinement parameters, bond lengths and angles, and positional and thermal parameters for **1**, **3**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org. They also have been deposited at the Cambridge Crystallographic Data Centre (CCDC). The deposition numbers are CCDC 113232 (**1**), 113233 (**3**), and 113234 (**5**).

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