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Synthesis and Structures of Cyclic and Acyclic Metallasiloxanes of Groups 5−7

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Cyclic metallasiloxanes have been synthesized using t-Bu$_2$Si(OH)$_2$ (**1**), O(t-Bu$_2$SiOH)$_2$ (**2**), and O(Ph$_2$SiOH)$_2$ (**3**) as starting materials. The molecular structures of [t-Bu$_2$Si(O)$_2$W(N-t-Bu)$_2$]$_2$ (**4**), {t-Bu$_2$Si(O)$_2$[Cp*Ta(Cl)]$_3$(μ_2-Cl)(μ_2-O)$_2$(μ_3-O)}·2C$_7$H$_8$ (**5**) (Cp* = η^5-C$_5$(CH$_3$)$_5$), t-Bu$_2$Si(O)$_2$[(t-Bu$_2$Si(OH)O)$_2$Nb]$_2$[η^5-C$_5$Me$_4$EtNb(Cl)](μ_2-Cl)(μ_2-O)$_2$(μ_3-O)·$^3/_4$C$_7$H$_8$ (**6**), O(t-Bu$_2$SiOReO$_3$)$_2$ (**8**), and [O(Ph$_2$SiO)$_2$]$_2$Mn$_3$[N(SiMe$_3$)$_2$]$_2$(THF)$_2$·$^1/_2$THF (**11**) have been determined by X-ray crystallography. Additionally, the cyclic molybdasiloxane [O(t-Bu$_2$SiO)$_2$MoO$_2$]$_2$ (**10**) has been characterized.

Introduction

The synthesis of organosilicon heterocompounds containing the Si−O−metal group dates back to the end of the last century.[1] A competent review on this subject has been published by Voronkov et al.[2] Subsequently, low molecular weight poly(metallasiloxanes) containing group 7 and group 8 elements have been reported by Zhdanov et al.[3] Since the early 80s Feher et al. have worked with silesquioxanes structurally related to the natural SiO$_2$-modification β-cristobalite.[4] They succeeded in synthesizing a range of metal-containing silesquioxanes.[5] The surface investigation of such complexes is of high interest for the understanding of elementary steps occurring in catalytic systems, where silica-supported metal oxides are used. In our group we were able to characterize a model compound for a three-dimensional network by X-ray investigations of both *tert*-butylsilanetriol and the product of its reaction with Re$_2$O$_7$.[6] We extended our concept by developing small units containing Ti, Zr,[7] V, Mo,[8] and Re[9] as models using t-Bu$_2$Si(OH)$_2$ (**1**) as the SiO source.

Herein we report the synthesis of three new complexes containing W, Ta, and Nb based on t-Bu$_2$Si(OH)$_2$ (**1**). Furthermore we describe the reactions of O(t-Bu$_2$SiOH)$_2$ (**2**) and O(Ph$_2$SiOH)$_2$ (**3**) with Mn[N(SiMe$_3$)$_2$]$_2$(THF), MoO$_2$Cl$_2$, and Re$_2$O$_7$, respectively.

The synthesis of the silanediols have been previously described in the literature. t-Bu$_2$Si(OH)$_2$ (**1**) is synthesized by oxidation of t-Bu$_2$SiHCl using AgNO$_3$.[10] The best route for the synthesis of O(t-Bu$_2$SiOH)$_2$ (**2**), published by Klingebiel et al., is the reaction of t-Bu$_2$SiF$_2$ with monolithiated t-Bu$_2$Si(OH)$_2$ (**1**) followed by treatment with KOH.[11] The desired product can be obtained according to this route in satisfactory yields. O(Ph$_2$SiOH)$_2$ (**3**) is synthesized in good yields using simple pH-controlled hydrolysis of Ph$_2$SiCl$_2$[12] (Scheme 1).

Results and Discussion

The reaction of t-Bu$_2$Si(OH)$_2$ (**1**) with (t-BuN)$_2$W(t-BuNH)$_2$[13] in a molar ratio of 1:1 gives compound **4** (Scheme 2).

The X-ray diffraction study of **4** (Figure 1) reveals a planar centrosymmetric eight-membered ring (mean deviation 0.015 Å), similar to that previously found for Ti and Zr compounds in our group.[7] The tungsten atoms are distorted tetrahedrally and surrounded by two nitrogen and two oxygen atoms. The O(1)−W(1)−O(2) ring angle of 112.3° verifies this geometry. The mean values of the W−O single bond (1.889 Å) and the W=N double bond (1.743 Å) are similar to those reported in the literature (W−O, 1.888 Å; W=N, 1.742 Å).[14] The angle at the nitrogen atom is almost linear (average 165.5°).

In order to obtain smaller rings, sterically demanding Cp* (Cp* = η^5-C$_5$(CH$_3$)$_5$) and C$_5$Me$_4$Et groups in complexes such as Cp*TaCl$_4$[15] and η^5-C$_5$Me$_4$EtNbCl$_4$[16] are used as starting materials. After activation of t-Bu$_2$Si-

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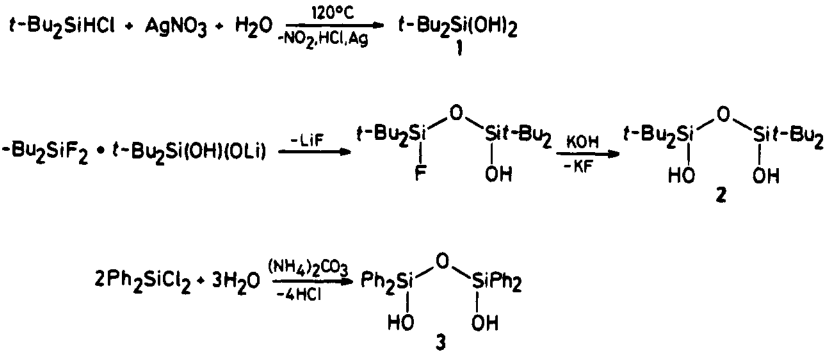
Scheme 1



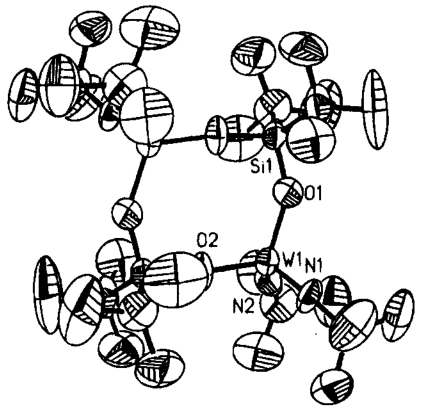
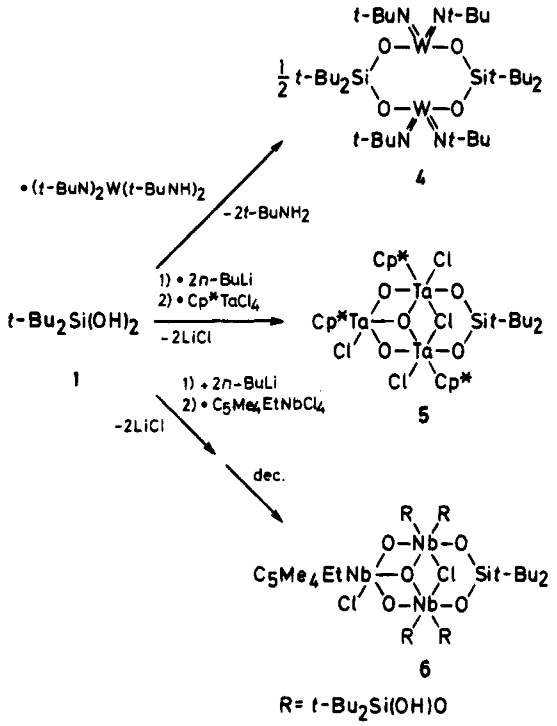


Figure 1. Structure of 4 in the crystal.

Scheme 2



(OH)$_2$ (**1**) with 2 equiv of n-butyllithium followed by reaction with 1 equiv of Cp*TaCl$_4$ and η^5-C$_5$Me$_4$-EtNbCl$_4$, compounds **5** and **6** are obtained, respectively (Scheme 2). The exact mechanism leading to **5** and **6** is not yet clear.

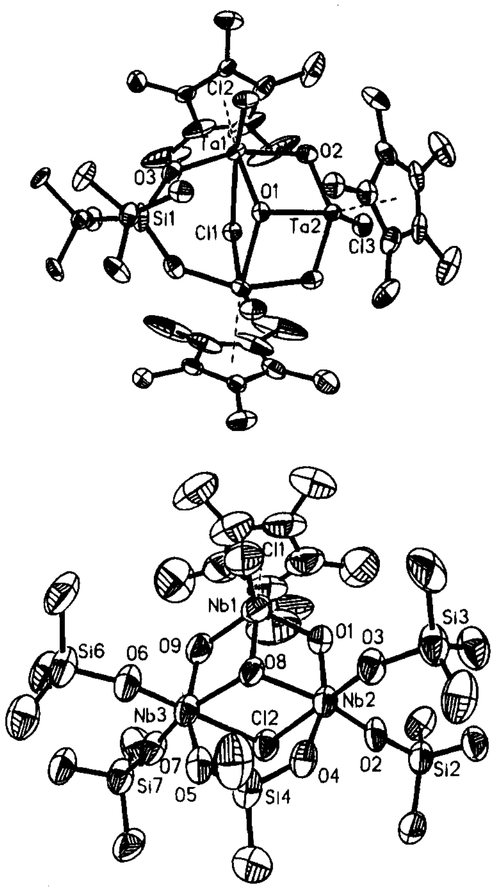


Figure 2. Structures of **5** (upper) and of one molecule of **6** (lower) in the crystal. For **6** the *tert*-butyl groups are represented as single carbon atoms.

Although not identical, the molecular structures of **5** and **6** (Figure 2) have common basic structural features. As shown in Figure 2, three Cp*TaCl or one η^5-C$_5$Me$_4$-EtNbCl unit and two Nb(O-t-Bu$_2$SiOH)$_2$ units form a triangle. Two sides are bridged by oxygen and one side by a t-Bu$_2$SiO$_2$ unit. Interestingly, in **5** two Cp* rings are located one above and one below the plane, whereas in both structures an additional oxygen (O(1) and O(8), respectively) covers the triangle within 0.78 (0.75) Å. Additionally, Ta(1) and Ta(1a) as well as Nb(2) and Nb(3) are bridged by a chlorine (Cl(1) and Cl(2), respectively), which is fixed 1.80 (1.87) Å below the triangle. The silicon atoms of the ring systems (**5**, Si(1); **6**, Si(4)) lie 1.20 and 1.40 Å, respectively, out of the plane. A similar type of structure is found in **7a**[17] and **7b**.[18]

5 possesses a crystallographic mirror plane containing Ta(2), O(1), Cl(1), Cl(3), and Si(1). In contrast to **5**,

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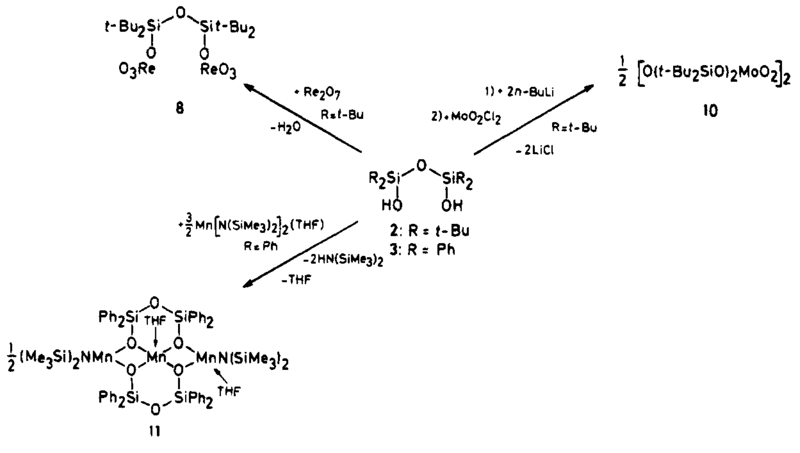
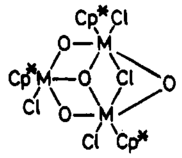
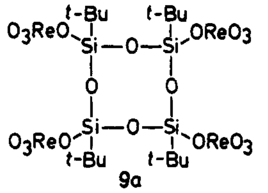
Scheme 3





7a: M = Ta

7b: M = Nb



9a

$t\text{-}Bu_2Si(OReO_3)_2$

9b

compound **6** crystallizes with two molecules in the asymmetric unit. Therefore, all values given for structure **6** are mean values. Remarkably, in **6** two Nb atoms have lost their C_5Me_4Et groups and chlorine atoms, being replaced by four terminal silanediol groups.

Ta(1), Nb(2), and Nb(3) have a distorted octahedral coordination sphere, whereas Ta(2) possesses a distorted tetragonal pyramidal and Nb(1) a distorted trigonal bipyramidal environment. As already found in **7a**, the μ_3-O atom in **5** is not symmetrically connected to all three tantalum atoms, although the differences in **5** are much smaller. The Ta(1)—O(1) distance is 2.152 Å (**7a**, 2.22 Å) and Ta(2)—O(1) is 2.067 Å (**7a**, 1.97 Å), whereas the Nb—(μ_3-O) bond lengths are almost equal (mean 2.083 Å; **7b**, 2.062 Å). In both, the μ_2-O atoms are asymmetrically connected. The observed values for Ta(1)—O(2) (1.967 Å) and Nb(2,3)—(μ_2-O) (mean 1.979 Å) are longer than for Ta(2)—O(2) (1.894 Å) and Nb(1)—(μ_2-O) (1.898 Å).

The reaction of $O(t\text{-}Bu_2SiOH)_2$ (**2**) with Re_2O_7 leads to compound **8** (Scheme 3), which fills the gap between **9a**[6] and **9b**[9] recently synthesized by our group.

The molecular structure of **8** (Figure 3) reveals two ReO_4 units, each attached to one silicon. In contrast to **9a** and **9b**, the ReO_4 groups have not a *cis* but a *gauche* conformation due to the sterically demanding *tert*-butyl and ReO_4 groups. The angle between the planes formed by Si(1), O(1), O(3) and Si(2), O(2), O(3), respectively, is 73.7°. Consequently, the angles between the *tert*-butyl groups are widened (122.1 and 119.5°). The environment of rhenium is tetrahedral. The angles at the bridging oxygen atoms Si(1)—O(1)—Re(1) (165.7°), Si(2)—O(2)—Re(2) (165.2°), and Si(1)—O(3)—Si(2) (163.5°) are almost linear. The Re—O bond length for terminal oxygen atoms is 1.68 Å (mean) and for the bridging ones 1.788 and 1.81 Å. These values are comparable to those found in **9b** (1.674 and 1.802 Å).

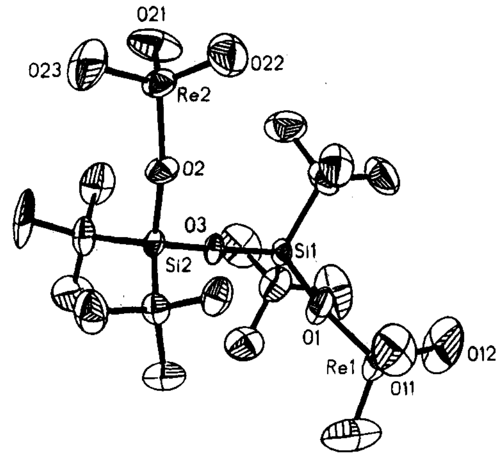


Figure 3. Structure of **8** in the crystal.

Previously published results reveal the formation of an eight-membered ring by reaction of dilithiated *t*-$Bu_2Si(OH)_2$ (**1**) with MoO_2Br_2.[8] Similarly, the reaction of dilithiated $O(t\text{-}Bu_2SiOH)_2$ (**2**) with 1 equiv of MoO_2Cl_2 leads to compound **10** (Scheme 3). EI-MS and preliminary results of X-ray investigations[19] prove a dimeric structure forming a twelve-membered ring similar to previous results.[8] However, the quality of the X-ray structure does not warrant publication of the details of the investigations at this time.

The reaction of 3 equiv of $Mn[N(SiMe_3)_2]_2(THF)$[20] with 2 equiv of $O(Ph_2SiOH)_2$ (**3**) gives compound **11** in good yield (Scheme 3). Due to the paramagnetism of Mn(II), ESR measurements were performed. In solution (hexane) an *isotropic signal* at $g = 2.003$ with the characteristic hyperfine structure (sext, $J = 80$ G) of Mn(II) is observed.

11 (Figure 4) can be described as a trinuclear Mn(II) complex with two $O(Ph_2SiO)_2$ units bridging the three metal atoms. Usually, the angle between the manganese atoms in comparable Mn(II) complexes is ap-

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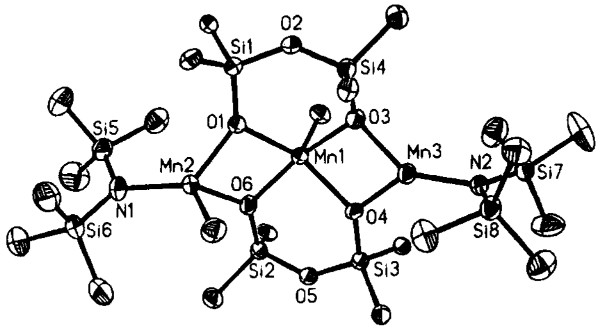

Figure 4. Structure of **11** in the crystal. The phenyl rings are repesented by single carbon atoms, and the carbon atoms of the THF groups are omitted for clarity.

proximately 180°.[21] In **11**, however, the angle is 139.5°. To the best of our knowledge, **11** is the first structurally characterized trinuclear Mn(II) complex with an angular structure. Noticeably, each Mn possesses a different coordination number: Mn(1) is five, Mn(2) is four, and Mn(3) is three-coordinate. Typically for coordination number 5 the coordination sphere of Mn(1) is between tetragonal pyramidal and trigonal bipyramidal. Regarding the Mn(1) environment as tetragonal pyramidal, the square plane is formed by O(1), O(3), O(4), and O(6) (mean deviation 0.172 Å). Mn(1) is located 0.448 Å above this plane. The top of the pyramid is formed by the oxygen atom of a coordinating THF molecule (O(7)). But the square plane is twisted: O(1) and O(4) are ca. 0.17 Å below and O(3) and O(6) are ca. 0.17 Å above the plane. Regarding the coordination sphere as trigonal bipyramidal, O(4), O(1), and O(7) are equatorial and O(3) and O(6) are axial. The corresponding angles O(3)—Mn(1)—O(7) (91.7°) and O(6)—Mn(1)—O(7) (103.0°) are close to 90°, whereas O(1)—Mn(1)—O(7) (108.2°) and O(4)—Mn(1)—O(7) (105.5°) tend toward 120°. In agreement with this geometry the O(6)—Mn(1)—O(3) angle (164.5°) is close to 180°, but the O(1)—Mn(1)—O(4) angle is at 146.0°, between 120° and 180°.

Mn(2) is distorted tetrahedrally and surrounded by three oxygens and one nitrogen. The N(1)—Mn(2)—O(1) (131.0°) and N(1)—Mn(2)—O(6) (128.6°) angles are widened. The angles O(1)—Mn(2)—O(8), O(6)—Mn(2)—O(1), and O(6)—Mn(2)—O(8) (93.0, 84.7, and 95.3°) are reduced, whereas N(1)—Mn(2)—O(8) (114.4°) is almost tetrahedral.

Mn(3) has a trigonal planar environment with $\Sigma^\circ = 359.6$. The O(3)—Mn(3)—O(4) (84.2°) angle is smaller, while N(2)—Mn(3)—O(3) (139.9°) and N(2)—Mn(3)—O(4) (135.5°) are larger than expected 120°. The bridging Mn(1)—O bond lengths are effectively longer than Mn(2)—O and Mn(3)—O, respectively. The μ_2-O bond distances for Mn(3) and Mn(2) vary from 2.017 Å (Mn(3)—O(3)) to 2.091 Å (Mn(2)—O(1)) and can be compared with the bond lengths found in $[\mathrm{Mn(O(2,4,6\text{-}}t\text{-}\mathrm{Bu_3C_6H_2))_2}]_2$ (approximately 2.05 Å).[22] The value for Mn(1)—O(1) is 2.105 Å and for Mn(1)—O(3) 2.155 Å. Remarkably, the Mn(1)—Mn(2) distance (3.083 Å) is little shorter than Mn(1)—Mn(3) (3.163 Å).

Conclusion

The introduction of sterically demanding groups at the metal center in reactions with **1** does not favor the formation of cyclic monomers, but leads either to the dimeric ring **4** or to rearrangement of the initial product, giving **5** and **6**. However, the use of $\mathrm{O(}t\text{-}\mathrm{Bu_2SiOH)_2}$ (**2**) allows an easy access to metalla-1,3-disiloxanes without competition from oligomerization reactions. Furthermore, the synthesis of **11**, via the utilization of bis[(trimethylsilyl)amino] compounds as the metal source, is a promising approach to the synthesis of other metalla-1,3-disiloxanes.

Although the synthesis of **10** and **11** confirms the low tendency for the formation of six-membered rings, the preparation of a monomeric metalla-1,3-disiloxane has been achieved in the acyclic compound **8**. Recently, Sullivan and co-workers[23,24] reported the synthesis of cyclic metallasiloxanes containing Co(II), Cu(II), and Cr(II). In the case of chromium the catalytic activity in olefin oligomerization has been studied. The interesting catalytic properties of compound **8** remain to be investigated.

Experimental Section

General Data. All reactions were carried out using standard Schlenk procedures. Solvents were dried and purified by known procedures and distilled from sodium/benzophenone prior to use. $t\text{-}\mathrm{Bu_2Si(OH)_2}$[10] (**1**), $\mathrm{O(}t\text{-}\mathrm{Bu_2SiOH)_2}$[11] (**2**), $\mathrm{O(Ph_2SiOH)_2}$[12] (**3**), $(t\text{-}\mathrm{BuN)_2W(}t\text{-}\mathrm{BuNH)_2}$,[13] $\mathrm{Cp^*TaCl_4}$,[15] $\mathrm{C_5Me_4EtNbCl_4}$,[16] and $\mathrm{Mn[N(SiMe_3)_2]_2{\cdot}THF}$[20] were prepared according to literature methods. NMR spectra were recorded on a Bruker WP 80 SY, a Bruker AM 250, or a Bruker AS 400 instrument. Infrared spectra were recorded on a BIO-RAD Digilab FTS 7 (Nujol mulls between KBr windows), and UV−vis spectra were recorded on a Perkin-Elmer 320 spectrometer. The ESR spectra were performed by a Varian Spectrometer E-line, Bruker ECS 106. Mass spectra were obtained on a Finnigan MAT System 8230 and a Varian MAT CH 5 mass spectrometer. Melting points (uncorrected) were obtained by using a Büchi 510 and a HWS-SG 3000 apparatus. Elementary analyses and molecular weight analyses were performed by the analytical laboratory of the Department of Inorganic Chemistry at Göttingen and by the microanalytical laboratory Beller at Göttingen.

$[t\text{-}\mathbf{Bu_2Si(O)_2W(N\text{-}}t\text{-}\mathbf{Bu)_2}]_2$ (4). Hexane (30 mL) is added to a mixture of 0.2 g (1.1 mmol) of $t\text{-}\mathrm{Bu_2Si(OH)_2}$ (**1**) and 0.5 g (1.1 mmol) of $(t\text{-}\mathrm{BuN)_2W(}t\text{-}\mathrm{BuNH)_2}$. After stirring for 18 h and removal of the solvent under reduced pressure, the crude product is recrystallized from 10 mL of toluene. A yield of 0.5 g (91%) of pale yellow crystals is obtained (mp 174 °C). IR (ν, cm^{-1}): 1385 (s, sh), 1357 (vs), 1299 (s), 1249 (vs, sh), 981 (vs, sh), 826 (vs, sh), 654 (s). EI-MS: *m/z* 1000 (M, 25%), 985 (M − Me, 100), 943 (M − Bu, 75). ^{1}H NMR (250 MHz, $\mathrm{C_6D_6}$): δ 1.32 (s, $\mathrm{Si(C(C}H_3)_3)_2$, 36H), 1.42 (s, $\mathrm{NC(C}H_3)_3$), 36H). ^{13}C NMR (63 MHz, $\mathrm{C_6D_6}$): δ 23.1 (s, ^1J(C,Si) = 75 Hz, ^3J(C,W) = 1 Hz, $\mathrm{Si(}C\mathrm{(CH_3)_3)_2}$), 27.9 (s, $\mathrm{Si(C(}C\mathrm{H_3)_3)_2}$), 33.7 (s, ^3J(C,W) = 2 Hz, $\mathrm{NC(}C\mathrm{H_3)_3}$), 66.5 (s, ^2J(C,W) = 27 Hz, $\mathrm{N}C\mathrm{(CH_3)_3}$). ^{29}Si NMR (50 MHz, $\mathrm{C_6D_6}$): δ −17.6 (s, ^2J(Si,W) = 13 Hz). Anal. Calcd

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for $C_{32}H_{72}N_4O_4Si_2W_2$ (1000.8): C, 38.4; H, 7.3; N, 5.6; W, 36.7. Found: 37.0; H, 7.4; N, 5.3; W, 36.3.

$\{t\text{-}Bu_2Si(O)_2[Cp^*Ta(Cl)]_3(\mu_2\text{-}Cl)(\mu_2\text{-}O)_2(\mu_3\text{-}O)\}\cdot 2C_7H_8$ (5). A solution of 0.8 mL (2.0 mmol) of 2.4 N *n*-BuLi/hexane is added to a solution of 0.2 g (1.0 mmol) of *t*-$Bu_2Si(OH)_2$ (**1**) in 10 mL of THF. After stirring for 0.5 h, this solution is added to a solution of 0.4 g (1.0 mmol) of Cp^*TaCl_4 in 20 mL of THF at −78 °C and stirred for 8 h. The solvent is removed under reduced pressure, 5 mL of toluene is added, LiCl is filtered, and the filtrate is kept at −20 °C. A yield of 150 mg (33%) of pale yellow crystals is obtained after 6 weeks (mp 291 °C). IR (ν, cm^{-1}): 1093 (s), 1020 (s), 923 (vs), 881 (vs), 823 (s), 723 (vs). EI-MS: *m/z* 1178 (M − Cp*, 25%), 1121 (M − Cp* − Bu, 25) 773 (M − 3Cp* − 3Cl − CHMe, 100). ^1H NMR (400 MHz, $CDCl_3$): δ 1.09 (s, $C(CH_3)_3$, 9H), 1.11 (s, $C(CH_3)_3$, 9H), 2.21 (s, $C_5(CH_3)_5$, 15H), 2.25 (s, $C_5(CH_3)_5$, 30H), 2.34 (s, $C_6H_5(CH_3)$, 6H), 7.17–7.24 (m, $C_6H_5CH_3$, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6 ($C_5(CH_3)_5$), 12.4 ($C_5(CH_3)_5$), 20.5 ($C(CH_3)_3$), 21.5 ($C_6H_5(CH_3)$), 24.8 ($C(CH_3)_3$), 29.5 ($C(CH_3)_3$), 29.7 ($C(CH_3)_3$), 124.5 ($C_5(CH_3)_5$), 125.3 (C(1) $C_6H_5CH_3$), 126.7 ($C_5(CH_3)_5$), 128.3 (C(2) $C_6H_5CH_3$), 129.1 (C(3) $C_6H_5CH_3$), 137.9 (C(4) $C_6H_5CH_3$). ^{29}Si NMR (80 MHz, $CDCl_3$): δ −24.1 (s). Anal. Calcd for $C_{38}H_{63}Cl_4O_5SiTa_3\cdot 2C_7H_8$ (1496.9): C, 41.7; H, 5.3; Cl, 9.5. Found: C, 41.9; H, 5.8; Cl, 9.4.

$t\text{-}Bu_2Si(O)_2[(t\text{-}Bu_2Si(OH)O)_2Nb]_2[C_5Me_4EtNb(Cl)](\mu_2\text{-}Cl)(\mu_2\text{-}O)_2(\mu_3\text{-}O)$ (6). Similar to the preceding route, 0.3 g (1.8 mmol) of *t*-$Bu_2Si(OH)_2$ (**1**) is treated with 1.5 mL (3.7 mmol) of 2.4 N *n*-BuLi/hexane in 10 mL of THF followed by reaction with 0.7 g (1.8 mmol) of $C_5Me_4EtNbCl_4$ in 20 mL of THF. After the filtrate is stored at −20 °C for 2 months, 0.1 g (yield 11%) of colorless crystals is obtained (mp 242 °C). IR (ν, cm^{-1}): 3400 (w, br), 1261 (s), 1093 (vs), 1019 (vs), 800 (vs). EI-MS: *m/z* 1273 (M − C_5Me_4Et, 5%), 1158 (M − C_5Me_4Et − 2Bu, 50), 532 ($C_4H_9Nb_3O_7Si_3$, 100). ^1H NMR (250 MHz, $CDCl_3$): δ 0.87–1.20 (m, $C(CH_3)_3$, 90H), 1.94–2.11 (m, $(CH_3)_4C_4CH_2CH_3$, 14H), 2.33 (s, *OH*, 4H). Anal. Calcd for $C_{51}H_{111}Cl_2Nb_3O_{13}Si_5$ (1422.5): C, 43.1; H, 7.9; Cl, 5.0. Found: C, 44.4; H, 7.8; Cl, 4.7. The analytical data were determined for the solvent-free compound.

$O(t\text{-}Bu_2SiOReO_3)_2$ (8). Toluene (40 mL) is added to a mixture of 1.0 g (2.1 mmol) of Re_2O_7 and 0.7 g (2.1 mmol) of $O(t\text{-}Bu_2SiOH)_2$ (**2**) and the solution is stirred for 16 h. After removal of the resulting water together with toluene under reduced pressure, the crude product is dissolved in 20 mL of toluene. Slow removal of the solvent leads to 1.3 g (yield 76%) of colorless crystals (mp 129 °C). IR (ν, cm^{-1}): 1084 (vs), 1011 (s), 962 (vs), 917 (vs), 827(s), 659 (s). EI-MS: *m/z* 744 (M − Bu, 40%), 57, (Bu, 100). ^1H NMR (250 MHz, C_6D_6): δ 0.86 (s, $C(CH_3)_3$). ^{13}C NMR (63 MHz, C_6D_6): δ 22.1 (s, $C(CH_3)_3$), 27.0 (s, $C(CH_3)_3$). ^{29}Si NMR (50 MHz, C_6D_6): δ −9.3 (s). Anal. Calcd for $C_{16}H_{36}O_9Re_2Si_2$ (801.0): C, 24.0; H, 4.5. Found: C, 24.5; H, 4.4.

$[O(t\text{-}Bu_2SiO)_2MoO_2]_2$ (10). The reaction is performed by using the same procedure described for the preparation of **5**. $O(t\text{-}Bu_2SiOH)_2$ (**2**) (0.5 g, 1.5 mmol) in 40 mL of toluene is treated with 1.3 mL (3.1 mmol) of 2.4 N *n*-BuLi/hexane followed by reaction with 0.3 g (1.5 mmol) of MoO_2Cl_2. After filtration the solvent is removed under reduced pressure and the remaining pale yellow solid washed with 2 × 3 mL of hexane. Yield: 0.5 g, 72% (mp 276 °C). IR (ν, cm^{-1}): 1262 (vs), 1097 (vs, sh), 1020 (vs), 945 (s), 913 (s, sh), 868 (s), 800 (vs). EI-MS: *m/z* 864 (M − Bu, 55%), 57 (Bu, 100). ^1H NMR (250 MHz, CD_3CN/C_6D_6): δ 1.07 (s, $C(CH_3)_3$). ^{13}C NMR (63 MHz, CD_3CN/C_6D_6): δ 20.5 (s, $C(CH_3)_3$), 27.9 (s, $C(CH_3)_3$). ^{29}Si NMR (80 MHz, CD_3CN/C_6D_6): δ −10.2 (s). Anal. Calcd for $C_{32}H_{72}Mo_2O_{10}Si_4$ (921.1): C, 41.7; H, 7.9; Mo, 20.8. Found: C, 41.8; H, 8.2; Mo, 21.3.

$[O(Ph_2SiO)_2]_2Mn_3[N(SiMe_3)_2]_2(THF)_2\cdot{}^1/_2THF$ (11). In a similar procedure, 15 mL of toluene is condensed into a mixture of 0.7 g (1.5 mmol) of $Mn[N(SiMe_3)_2]_2(THF)$ and 0.4 g (1.0 mmol) of $O(Ph_2SiOH)_2$ (**3**). Upon stirring at room temperature, the solid slowly dissolves. After slow concentration of the mixture 0.6 g (yield 80%) of colorless crystals are obtained (mp 152 °C dec). IR (ν, cm^{-1}): 1244 (s, sh), 1125 (vs, sh), 1020 (vs, sh), 917 (vs), 873 (s), 827 (s, sh), 718 (s), 700 (s), 524 (vs). ESR (hexane): *H* = 3210 G; *g* = 2.003 (sext, *J* = 80 G). Anal. Calcd for $C_{70}H_{96}Mn_3N_2O_{8.5}Si_8$ (1491.0): C, 56.1; H, 6.4; N, 1.9. Found: C, 56.0; H, 6.5; N, 1.9.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 4

W(1)−N(2)	1.740(11)	W(1)−N(1)	1.746(9)
W(1)−O(2)	1.875(8)	W(1)−O(1)	1.902(9)
Si(1)−O(1)	1.606(10)	Si(1)−O(2)^a	1.626(8)
N(2)−W(1)−N(1)	112.1(5)	N(2)−W(1)−O(2)	108.3(4)
N(1)−W(1)−O(2)	108.5(4)	N(2)−W(1)−O(1)	109.0(5)
N(1)−W(1)−O(1)	106.7(4)	O(2)−W(1)−O(1)	112.3(4)
O(1)−Si(1)−O(2)^a	106.8(5)	Si(1)−O(1)−W(1)	147.7(6)
Si(1)^a−O(2)−W(1)	173.1(7)	C(31)−N(1)−W(1)	165.0(10)
C(41)−N(2)−W(1)	166.0(11)		

[a] Symmetry transformations used to generate equivalent atoms: −*x* + 1, −*y*, −*z*.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 5

Ta(1)−O(3)	1.943(4)	Ta(1)−O(2)	1.967(4)
Ta(1)−O(1)	2.152(3)	Ta(1)−Cl(2)	2.3996(14)
Ta(1)−Cl(1)	2.6287(14)	Ta(2)−O(2)	1.894(4)
Ta(2)−O(1)	2.067(6)	Ta(2)−Cl(3)	2.403(2)
Si(1)−O(3)	1.631(5)		
O(3)−Ta(1)−O(2)	155.8(2)	O(3)−Ta(1)−O(1)	83.7(2)
O(2)−Ta(1)−O(1)	72.1(2)	O(3)−Ta(1)−Cl(2)	89.07(13)
O(2)−Ta(1)−Cl(2)	89.42(13)	O(1)−Ta(1)−Cl(2)	85.85(14)
O(3)−Ta(1)−Cl(1)	83.96(13)	O(2)−Ta(1)−Cl(1)	87.29(13)
O(1)−Ta(1)−Cl(1)	69.60(14)	Cl(2)−Ta(1)−Cl(1)	155.04(5)
O(2)^a−Ta(2)−O(2)	135.2(3)	O(2)−Ta(2)−O(1)	75.45(14)
O(2)−Ta(2)−Cl(3)	87.74(13)	O(1)−Ta(2)−Cl(3)	132.9(2)
O(3)^a−Si(1)−O(3)	105.4(3)	Ta(2)−O(1)−Ta(1)	98.6(2)
Ta(1)^a−O(1)−Ta(1)	123.1(3)	Ta(2)−O(2)−Ta(1)	111.9(2)
Si(1)−O(3)−Ta(1)	143.1(3)		

[a] Symmetry transformations used to generate equivalent atoms: *x*, −*y* + $^1/_2$, *z*.

X-ray Structure Determination of 4–6, 8, and 11. Data were collected on a Siemens-Stoe-AED2 for **4**, **6**, **8**, and **11** and on a Siemens-Stoe-AED for **5**. Monochromated Mo Kα radiation (λ = 0.710 73 Å) was used. The collection temperature was −120 °C for **4**, **5**, and **11** and room temperature for **6** and **8**. A semiempirical absorption correction was employed. The structures were solved by direct methods.[25] All non-hydrogen atoms were refined anisotropically except for the solvent in **6**.[26] For the hydrogen atoms, the riding model was used; the structures were refined against F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (g_1P)^2 + g_2P$ with $P = (F_o^2 + 2F_c^2)/3$. The *R* values are defined as $wR_2 = (\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4)^{1/2}$ and $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.

In **4** one and in **5** two *tert*-butyl groups are disordered. In **5** also the solvent toluene is disordered. In **6** the two ethyl groups and the solvent toluene and in **11** the THF groups are disordered. All these groups were refined with distant restraints and restraints for the displacement parameters.

Crystal data for **4**: $C_{32}H_{72}N_4O_4Si_2W_2$, M_r = 1000.8, monoclinic, space group $P2_1/n$, *a* = 11.477(1) Å, *b* = 12.345(1) Å, *c* = 17.480(2) Å, β = 107.3(1)°, *V* = 2364.2(4) Å^3, *Z* = 2, ϱ(calcd) = 1.406 Mg m^{-3}, μ = 4.94 mm^{-1}, *F*(000) = 1000, crystal size (mm) 0.7 × 0.6 × 0.4, 3632 measured reflections in the range 7° < 2Θ < 45°, 3086 unique reflections, 3077 reflections and 114 restraints used for the refinement of 236 parameters, goodness of fit 1.138, R_1 = 0.0665 for $F > 4\sigma(F)$, wR_2 = 0.1843 for all data, and maximum/minimum residual electron density +3.58/−2.30 e Å^{-3}.

Crystal data for **5**: $C_{52}H_{79}Cl_4O_5SiTa_3$, M_r = 1496.9, monoclinic, space group $P2_1/m$, *a* = 9.358(1) Å, *b* = 20.044(4) Å, *c* = 14.542(3) Å, β = 98.08(2)°, *V* = 2700.6(8) Å^3, *Z* = 2, ϱ(calcd) =

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(25) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
(26) Sheldrick, G. M. SHELXL-93. Göttingen, 1993.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 6

Nb(1)−O(1)	1.894(7)	Nb(1)−O(9)	1.902(7)
Nb(1)−O(8)	2.112(7)	Nb(1)−Cl(1)	2.360(4)
Nb(2)−O(3)	1.859(7)	Nb(2)−O(2)	1.880(7)
Nb(2)−O(4)	1.908(8)	Nb(2)−O(1)	1.982(7)
Nb(2)−O(8)	2.070(7)	Nb(2)−Cl(2)	2.648(3)
Nb(3)−O(6)	1.870(7)	Nb(3)−O(7)	1.871(7)
Nb(3)−O(5)	1.901(8)	Nb(3)−O(9)	1.979(8)
Nb(3)−O(8)	2.068(7)	Nb(3)−Cl(2)	2.660(3)
Si(2)−O(2)	1.654(8)	Si(3)−O(3)	1.677(8)
Si(4)−O(4)	1.654(8)	Si(4)−O(5)	1.664(8)
Si(6)−O(6)	1.667(8)	Si(7)−O(7)	1.661(8)
Nb(1′)−O(1′)	1.888(6)	Nb(1′)−O(9′)	1.908(7)
Nb(1′)−O(8′)	2.109(7)	Nb(1′)−Cl(1′)	2.357(3)
Nb(2′)−O(3′)	1.872(7)	Nb(2′)−O(2′)	1.874(7)
Nb(2′)−O(4′)	1.912(7)	Nb(2′)−O(1′)	1.975(7)
Nb(2′)−O(8′)	2.071(6)	Nb(2′)−Cl(2′)	2.666(3)
Nb(3′)−O(6′)	1.873(7)	Nb(3′)−O(7′)	1.883(7)
Nb(3′)−O(5′)	1.896(7)	Nb(3′)−O(9′)	1.980(7)
Nb(3′)−O(8′)	2.072(6)	Nb(3′)−Cl(2′)	2.659(3)
Si(2′)−O(2′)	1.658(7)	Si(3′)−O(3′)	1.655(7)
Si(4′)−O(4′)	1.641(8)	Si(4′)−O(5′)	1.662(7)
O(6′)−Si(6′)	1.664(7)	O(7′)−Si(7′)	1.648(7)

O(1)−Nb(1)−O(9)	117.2(3)	O(1)−Nb(1)−O(8)	74.6(3)
O(9)−Nb(1)−O(8)	74.3(3)	O(1)−Nb(1)−Cl(1)	113.3(2)
O(9)−Nb(1)−Cl(1)	114.1(3)	O(8)−Nb(1)−Cl(1)	81.5(2)
O(3)−Nb(2)−O(2)	97.2(3)	O(3)−Nb(2)−O(4)	95.2(3)
O(2)−Nb(2)−O(4)	100.9(3)	O(3)−Nb(2)−O(1)	93.5(3)
O(2)−Nb(2)−O(1)	97.4(3)	O(4)−Nb(2)−O(1)	158.5(3)
O(3)−Nb(2)−O(8)	106.2(3)	O(2)−Nb(2)−O(8)	155.3(3)
O(4)−Nb(2)−O(8)	84.9(3)	O(1)−Nb(2)−O(8)	73.8(3)
O(3)−Nb(2)−Cl(2)	178.3(3)	O(2)−Nb(2)−Cl(2)	82.3(2)
O(4)−Nb(2)−Cl(2)	86.5(2)	O(1)−Nb(2)−Cl(2)	85.0(2)
O(8)−Nb(2)−Cl(2)	74.1(2)	O(6)−Nb(3)−O(7)	97.1(3)
O(6)−Nb(3)−O(5)	95.9(3)	O(7)−Nb(3)−O(5)	99.6(3)
O(6)−Nb(3)−O(9)	94.5(3)	O(7)−Nb(3)−O(9)	97.6(3)
O(5)−Nb(3)−O(9)	158.6(3)	O(6)−Nb(3)−O(8)	106.8(3)
O(7)−Nb(3)−O(8)	155.0(3)	O(5)−Nb(3)−O(8)	85.4(3)
O(9)−Nb(3)−O(8)	73.7(3)	O(6)−Nb(3)−Cl(2)	178.4(3)
O(7)−Nb(3)−Cl(2)	82.1(2)	O(5)−Nb(3)−Cl(2)	85.6(2)
O(9)−Nb(3)−Cl(2)	84.2(2)	O(8)−Nb(3)−Cl(2)	73.8(2)
Nb(2)−Cl(2)−Nb(3)	85.91(9)	O(4)−Si(4)−O(5)	104.9(4)
Nb(1)−O(1)−Nb(2)	111.5(4)	Si(2)−O(2)−Nb(2)	174.9(5)
Si(3)−O(3)−Nb(2)	155.5(5)	Si(4)−O(4)−Nb(2)	141.2(5)
Si(4)−O(5)−Nb(3)	141.0(5)	Si(6)−O(6)−Nb(3)	155.1(5)
Si(7)−O(7)−Nb(3)	174.8(5)	Nb(3)−O(8)−Nb(2)	121.9(3)
Nb(3)−O(8)−Nb(1)	100.4(3)	Nb(2)−O(8)−Nb(1)	100.0(3)
Nb(1)−O(9)−Nb(3)	111.6(3)	O(1′)−Nb(1′)−O(9′)	117.4(3)
O(1′)−Nb(1′)−O(8′)	74.2(3)	O(9′)−Nb(1′)−O(8′)	74.6(3)
O(1′)−Nb(1′)−Cl(1′)	112.6(2)	O(9′)−Nb(1′)−Cl(1′)	114.1(2)
O(8′)−Nb(1′)−Cl(1′)	81.0(2)	O(3′)−Nb(2′)−O(2′)	96.0(3)
O(3′)−Nb(2′)−O(4′)	95.4(3)	O(2′)−Nb(2′)−O(4′)	100.9(3)
O(3′)−Nb(2′)−O(1′)	94.3(3)	O(2′)−Nb(2′)−O(1′)	97.9(3)
O(4′)−Nb(2′)−O(1′)	157.8(3)	O(3′)−Nb(2′)−O(8′)	107.7(3)
O(2′)−Nb(2′)−O(8′)	155.1(3)	O(4′)−Nb(2′)−O(8′)	84.7(3)
O(1′)−Nb(2′)−O(8′)	73.3(3)	O(3′)−Nb(2′)−Cl(2′)	177.9(2)
O(2′)−Nb(2′)−Cl(2′)	82.2(2)	O(4′)−Nb(2′)−Cl(2′)	86.2(2)
O(1′)−Nb(2′)−Cl(2′)	84.8(2)	O(8′)−Nb(2′)−Cl(2′)	73.9(2)
O(6′)−Nb(3′)−O(7′)	97.7(3)	O(6′)−Nb(3′)−O(5′)	96.0(3)
O(7′)−Nb(3′)−O(5′)	99.9(3)	O(6′)−Nb(3′)−O(9′)	93.6(3)
O(7′)−Nb(3′)−O(9′)	97.8(3)	O(5′)−Nb(3′)−O(9′)	158.5(3)
O(6′)−Nb(3′)−O(8′)	106.5(3)	O(7′)−Nb(3′)−O(8′)	154.8(3)
O(5′)−Nb(3′)−O(8′)	84.9(3)	O(9′)−Nb(3′)−O(8′)	74.0(3)
O(6′)−Nb(3′)−Cl(2′)	178.6(2)	O(7′)−Nb(3′)−Cl(2′)	81.7(2)
O(5′)−Nb(3′)−Cl(2′)	85.4(2)	O(9′)−Nb(3′)−Cl(2′)	85.3(2)
O(8′)−Nb(3′)−Cl(2′)	74.0(2)	Nb(3′)−Cl(2′)−Nb(2′)	85.84(9)
O(4′)−Si(4′)−O(5′)	105.5(4)	Nb(1′)−O(1′)−Nb(2′)	112.2(3)
Si(2′)−O(2′)−Nb(2′)	176.1(4)	Si(3′)−O(3′)−Nb(2′)	155.3(5)
Si(4′)−O(4′)−Nb(2′)	140.5(4)	Si(4′)−O(5′)−Nb(3′)	140.7(4)
Si(6′)−O(6′)−Nb(3′)	154.5(4)	Si(7′)−O(7′)−Nb(3′)	173.2(4)
Nb(2′)−O(8′)−Nb(3′)	122.1(3)	Nb(2′)−O(8′)−Nb(1′)	100.2(3)
Nb(3′)−O(8′)−Nb(1′)	100.2(3)	Nb(1′)−O(9′)−Nb(3′)	111.2(3)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 8

Si(1)−O(3)	1.614(7)	Si(1)−O(1)	1.685(9)
O(1)−Re(1)	1.787(8)	Re(1)−O(13)	1.661(12)
Re(1)−O(11)	1.673(11)	Re(1)−O(12)	1.676(11)
O(3)−Si(2)	1.624(7)	Si(2)−O(2)	1.680(8)
O(2)−Re(2)	1.810(7)	Re(2)−O(22)	1.668(11)
Re(2)−O(23)	1.700(10)	Re(2)−O(21)	1.704(12)

O(3)−Si(1)−O(1)	106.0(4)	Si(1)−O(1)−Re(1)	165.7(6)
O(13)−Re(1)−O(11)	106.8(7)	O(13)−Re(1)−O(12)	113.0(8)
O(11)−Re(1)−O(12)	108.4(8)	O(13)−Re(1)−O(1)	111.0(6)
O(11)−Re(1)−O(1)	108.7(6)	O(12)−Re(1)−O(1)	108.7(6)
Si(1)−O(3)−Si(2)	163.5(5)	O(3)−Si(2)−O(2)	106.2(4)
Si(2)−O(2)−Re(2)	165.2(6)	O(22)−Re(2)−O(23)	109.3(6)
O(22)−Re(2)−O(21)	109.9(6)	O(23)−Re(2)−O(21)	108.5(7)
O(22)−Re(2)−O(2)	111.2(5)	O(23)−Re(2)−O(2)	109.5(5)
O(21)−Re(2)−O(2)	108.3(5)		

Table 5. Selected Bond Distances (Å) and Angles (deg) for 11

Mn(1)−O(1)	2.105(3)	Mn(1)−O(6)	2.129(3)
Mn(1)−O(4)	2.140(3)	Mn(1)−O(3)	2.155(3)
Mn(1)−O(7)	2.178(4)	Mn(2)−N(1)	2.011(5)
Mn(2)−O(6)	2.084(4)	Mn(2)−O(1)	2.091(3)
Mn(2)−O(8)	2.189(4)	Mn(3)−N(2)	1.963(4)
Mn(3)−O(4)	2.017(3)	Mn(3)−O(3)	2.017(3)
Si(1)−O(1)	1.621(4)	Si(1)−O(2)	1.639(4)
Si(2)−O(6)	1.619(4)	Si(2)−O(5)	1.643(4)
Si(3)−O(4)	1.616(4)	Si(3)−O(5)	1.628(4)
Si(4)−O(3)	1.618(4)	Si(4)−O(2)	1.631(4)

O(1)−Mn(1)−O(6)	83.23(13)	O(1)−Mn(1)−O(4)	146.02(14)
O(6)−Mn(1)−O(4)	93.09(13)	O(1)−Mn(1)−O(3)	96.88(13)
O(6)−Mn(1)−O(3)	164.45(14)	O(4)−Mn(1)−O(3)	78.09(13)
O(1)−Mn(1)−O(7)	108.21(14)	O(6)−Mn(1)−O(7)	103.04(14)
O(4)−Mn(1)−O(7)	105.53(14)	O(3)−Mn(1)−O(7)	91.73(14)
N(1)−Mn(2)−O(6)	128.6(2)	N(1)−Mn(2)−O(1)	131.0(2)
O(6)−Mn(2)−O(1)	84.66(13)	N(1)−Mn(2)−O(8)	114.4(2)
O(6)−Mn(2)−O(8)	95.3(2)	O(1)−Mn(2)−O(8)	93.0(2)
N(2)−Mn(3)−O(4)	135.5(2)	N(2)−Mn(3)−O(3)	139.9(2)
O(4)−Mn(3)−O(3)	84.24(14)	O(1)−Si(1)−O(2)	108.6(2)
O(6)−Si(2)−O(5)	110.5(2)	O(4)−Si(3)−O(5)	108.6(2)
O(3)−Si(4)−O(2)	109.0(2)	Si(1)−O(1)−Mn(2)	139.5(2)
Si(1)−O(1)−Mn(1)	125.9(2)	Mn(2)−O(1)−Mn(1)	94.54(14)
Si(4)−O(2)−Si(1)	137.8(2)	Si(4)−O(3)−Mn(3)	132.7(2)
Si(4)−O(3)−Mn(1)	125.3(2)	Mn(3)−O(3)−Mn(1)	98.56(14)
Si(3)−O(4)−Mn(3)	128.1(2)	Si(3)−O(4)−Mn(1)	131.4(2)
Mn(3)−O(4)−Mn(1)	99.05(14)	Si(3)−O(5)−Si(2)	138.3(2)
Si(2)−O(6)−Mn(2)	135.7(2)	Si(2)−O(6)−Mn(1)	127.0(2)
Mn(2)−O(6)−Mn(1)	94.05(14)		

1.841 Mg m^{-3}, $\mu = 6.33$ mm^{-1}, $F(000) = 1464$, crystal size (mm) 0.4 × 0.3 × 0.2, 7191 measured reflections in the range 8° < 2Θ < 54°, 6022 unique reflections, 6017 reflections and 459 restraints used for the refinement of 419 parameters, goodness of fit 1.094, $R_1 = 0.0383$ for $F > 4\sigma(F)$, $wR_2 = 0.0948$ for all data, and maximum/minimum residual electron density 2.59/−1.70 e Å^{-3}, extinction correction.

Crystal data for **6**: $C_{56.25}H_{117}Cl_2Nb_3O_{13}Si_5$, $M_r = 1491.6$, monoclinic, space group $P2_1/c$, $a = 27.380(4)$ Å, $b = 23.753(7)$ Å, $c = 24.873(4)$ Å, $\beta = 96.93(2)$°, $V = 16058(6)$ Å^3, $Z = 8$, ϱ(calcd) = 1.234 Mg m^{-3}, $\mu = 0.610$ mm^{-1}, $F(000) = 6284$, crystal size (mm) 0.8 × 0.6 × 0.4, 15 227 measured reflections in the range 7° < 2Θ < 40°, 14 902 unique reflections, 14 863 reflections and 252 restrains used for the refinement of 1408 parameters, goodness of fit 1.110, $R_1 = 0.0653$ for $F > 4\sigma(F)$, $wR_2 = 0.1678$ for all data, and maximum/minimum residual electron density +0.63/−0.44 e Å^{-3}.

Crystal data for **8**: $C_{16}H_{36}O_9Re_2Si_2$, $M_r = 801.0$, triclinic, space group $P\bar{1}$, $a = 8.825(5)$ Å, $b = 8.946(3)$ Å, $c = 19.192(7)$ Å, $\alpha = 88.63(2)$°, $\beta = 83.18(3)$°, $\gamma = 61.51(2)$°, $V = 1321(1)$ Å^3, $Z = 2$, ϱ(calcd) = 2.013 Mg m^{-3}, $\mu = 9.281$ mm^{-1}, $F(000) = 764$, crystal size (mm) 1.0 × 0.7 ×0.5, 4805 measured reflections in the range 7° < 2Θ < 45°, 3425 unique reflections, 3424 reflections and 20 restraints used for the refinement of 275 parameters, goodness of fit 1.001, $R_1 = 0.0602$ for $F > 4\sigma(F)$, $wR_2 = 0.1588$ for all data, and maximum/minimum residual electron density +2.23/−2.47 e Å^{-3}.

Crystal data for **11**: $C_{70}H_{96}Mn_3N_2O_{8.5}Si_8$, $M_r = 1491.0$, monoclinic, space group $P2_1/c$, $a = 28.475(8)$ Å, $b = 12.938(1)$ Å, $c = 21.490(3)$ Å, $\beta = 93.19(1)$°, $V = 7905(3)$ Å^3, $Z = 4$, ϱ(calcd) = 1.253 Mg m^{-3}, $\mu = 0.644$ mm^{-1}, $F(000) = 3140$, crystal size (mm) 0.7 × 0.6 × 0.3, 10 190 measured reflections in the range 7° < 2Θ < 45°, 10 173 unique reflections, 10 113 reflections and 312 restraints used for the refinement of 931 parameters, goodness of fit 1.102, $R_1 = 0.0550$ for $F > 4\sigma(F)$, $wR_2 = 0.1891$ for all data, and maximum/minimum residual electron density +0.48/−0.71 e Å^{-3}.

Tables **1**−**5** contain selected bond lengths (Å) and angles (deg) for compounds **4**−**6**, **8**, and **11**.

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Supplementary Material Available: For **4**−**6**, **8**, and **11** ORTEP drawings and tables of crystal data, atomic coordinates, displacement parameters, and bond distances and angles (62 pages). Ordering information is given on any current masthead page.

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