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# **Unsupported Metal Silyl Ether Coordination**

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Simple silyl ethers like  $O(SiMe_3)_2$  are in contrast to normal ethers inert to metal bonding, however, a "naked", highly Lewis-acidic, cationic Mg species enforces complexation. DFT calculations indicate that agostic interactions and van-der-Waals attraction significantly contribute to the stability of this first example of unsupported silyl ether metal coordination.

Whereas carbon based ethers (Et<sub>2</sub>O or THF) are outstanding ligands for metal coordination, simple silyl ethers are essentially inert to bonding.1 Hexamethyldisiloxane, O(SiMe<sub>3</sub>)<sub>2</sub>, metal advantageously used as a lipophilic solvent in crystallizations.<sup>2</sup> Organometallic complexes crystallized from this "alkane-like" solvent often incorporate  $O(SiMe_3)_2$  in the crystal lattice, however, metal coordination to this simple silyl ether has never been observed (ESI). Additionally the silyl ether does not complexate with strong Lewis acids like BF<sub>3</sub> or BCl<sub>3</sub>.<sup>3</sup> Although O(SiMe<sub>3</sub>)<sub>2</sub> can bind to the highly electrophilic cation Me<sub>3</sub>Si<sup>+</sup>, the oxonium cation  $O(SiMe_3)_3^+$  has never been isolated.<sup>4</sup> Also the cation HO(SiMe\_3)\_2^+ is unknown, demonstrating the very weak hydrogen-bond acceptor properties of O(SiMe<sub>3</sub>)<sub>2</sub>.<sup>5</sup>

The unusually weak Lewis basicity of silyl ethers has been the subject of numerous theoretical<sup>6,7</sup> and experimental<sup>8-11</sup> investigations. Solely considering differences in element size (covalent radii: C 0.76 Å, Si 1.11 Å)<sup>12</sup> and electronegativity (Allred-Rochow: C 2.5, Si 1.8),<sup>13</sup> silyl ethers would be expected to be stronger, less sterically hindered, Lewis bases than normal ethers. Although the degree of Si-O bond ionicity is controversial,<sup>6c,d,f,h</sup> it is clear that the highly polar Si<sup>δ+</sup>-O<sup>δ-</sup> bond is substantially more ionic than the C<sup>δ+</sup>-O<sup>δ-</sup> bond. However, despite this polarization the electron lone-pairs at O are not readily available for metal bonding. The poor donor ability of silyl ethers was initially attributed to electron donation from O lone pairs into empty *d*-orbitals on Si ( $n_0 \rightarrow d_{si}$ ) (Fig. 1a).<sup>14</sup> The recognition that *d*-orbitals on Si are too high

in energy is in favor of negative hyperconjugation ( $n_0 \rightarrow \sigma^*_{Si-C}$ ) as an explanation (Fig. 1b).<sup>6d,6f,7</sup> Most recently metal<sup>δ+</sup>...Si<sup>δ+</sup> electrostatic repulsion (Fig. 1c) has been forwarded as an argument to justify poor metal coordination.<sup>6c,11d</sup> These explanations are in line with the exceptionally large Me<sub>3</sub>Si-O-SiMe<sub>3</sub> angle (148-152°).<sup>15</sup> As the H<sub>3</sub>Si-O-SiH<sub>3</sub> angle is only slightly smaller (142-144°),<sup>16</sup> these unusually large Si-O-Si angles are not related to steric crowding but correlated to their poor donor properties: constraining the Si-O-Si angle in silyl ethers to a near tetrahedral value increases the covalency in the Si-O bonds and enforces its Lewis base character.<sup>5a,6c</sup>



**Figure 1.** Decreased basicity of silyl ethers by: (a) Delocalization of O lone pairs in empty *d*-orbitals on Si  $(n_0 \rightarrow d_{si})$ . (b) Negative hyperconjugation  $(n_0 \rightarrow \sigma^*_{si-c})$ . (c) Metal<sup>§+</sup>...Si<sup>§+</sup> electrostatic repulsion.

The first evidence of metal silyl ether bonding was serendipitously obtained by  $K^{\dagger}$  promoted degradation of silicon grease to a  $K^{\dagger}$  silacrown ether complex (1).<sup>10</sup> This was followed by the systematic syntheses of metal sila-crown ether complexes.<sup>11</sup> Whereas normal metal crown ether complexes are stable in highly polar solvents,<sup>17</sup> sila-crown ethers are readily displaced, explaining the necessity of polar but weakly coordinating solvents like CH<sub>2</sub>Cl<sub>2</sub> or SO<sub>2</sub>.<sup>11d</sup> Weak coordination of the sila-crown ether in 1 partially originates from its different architecture: sila-crown ether complexes with metal-O-Si-Si-O five-membered rings (2) display enhanced stability<sup>11h</sup> but given a choice the metal avoids silvl ether bonding (e.g. 3).<sup>11i</sup> Apart from sila-crown ether complexes, there are some examples of metal bonding by silyl ether containing anions.9,18 Metal complexes with simple, monodentate, neutral silyl ethers O(SiR<sub>3</sub>)<sub>2</sub> are unknown. Herein we introduce synthesis and structure of the first metal complex with unsupported coordination of a simple silvl ether.

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Electronic Supplementary Information (ESI) available: Experimental procedures, selected <sup>1</sup>H and <sup>13</sup>C NMR spectra, crystallographic details, DFT calculations.

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Although calculational studies often model the silyl ether with  $O(SiH_3)_2^{6a-d,h}$  or  $O(SiH_2Me)_2$ ,<sup>6e</sup> silyl ethers containing Si-H moieties may pose problems. Whereas  $O(SiH_3)_2$  is cleaved BX<sub>3</sub> (X = F, Cl) at low temperature,  $O(SiMe_3)_2$  is much more stable.<sup>8</sup> Recent DFT calculations on the  $O(SiHMe_2)_2/B(C_6F_5)_3$  interaction show that Si-H…B bonding (4) is favored over formation of the classical Lewis pair adduct (Me<sub>2</sub>HSi)<sub>2</sub>O…B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> by more than 10 kcal/mol.<sup>6g</sup> Therefore, from a practical point of view, we investigate complexation of the bulkier  $O(SiMe_3)_2$ .

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Mg-O bonding range in three-coordinate Mg-OEt<sub>2</sub> and Mg-THF complexes: 1.969(6)-2.044(2) Å.<sup>22</sup> The strong bond to the weakly coordinating silyl ether originates from the cationic, highly Lewis acidic, nature of this complex. The Mg silyl ether bond is augmented by a distinct Mg···MeSi agostic interaction indicated by a very short Mg···C distance of 2.637(2) Å and strongly deviating Mg-O-Si1 and Mg-O-Si2 angles of 125.22(6)° and 107.31(6)°, respectively.



<sup>1</sup>H NMR investigations on  $C_6D_6$  solutions containing  $O(SiMe_3)_2$  and AlMe<sub>3</sub>, BH<sub>3</sub> or  $B(C_6F_5)_3$  essentially showed no silyl ether coordination and attempts to crystallize Lewis pairs failed (ESI). Using the stronger Lewis acids AlCl<sub>3</sub> and All<sub>3</sub> led to Si-O bond cleavage (ESI) that, in contrast to earlier observations,<sup>8</sup> already starts at room temperature instead of at 100 °C.

With few exceptions,<sup>11g,j</sup> most of the sila-crown ether metal complexes have been isolated using weakly coordinating anions (WCA's). These prevent metal-anion interactions that would perturb silyl ether coordination. 6e,11a-e It was suggested e that Krossing's WCA, Al[OC(CF<sub>3</sub>)<sub>3</sub>]<sub>4</sub><sup>-, 19</sup> could stabilize Li+ or Ag<sup>+</sup> complexes of simple disiloxanes. All our attempts to isolate  $Li^{+} \cdot [O(SiMe_{3})_{2}]_{n}$  complexes containing  $AI[OC(CF_{3})_{3}]_{4}^{-}$ , or the frequently used WCA  $B(C_6F_5)_4^-$ , failed on account of the poor solubility of these salts (ESI). We recently reported on soluble "naked", highly Lewis-acidic, ß-diketiminate (BDI) Mg and Ca cations (5) that strongly bind neutral  $C_6H_6$  or EtC=CEt.<sup>20</sup> The (BDI)Mg<sup>+</sup> cation was found to be a stronger Lewis acid than Jordan's (BDI)AIMe<sup>+</sup> (6);<sup>21</sup> BDI = CH[C(CH<sub>3</sub>)N-Dipp]<sub>2</sub>, Dipp =2,6-diisopropylphenyl. This is likely due to its more open coordination site. Whereas complexation of O(SiMe<sub>3</sub>)<sub>2</sub> by (BDI)AIMe<sup>+</sup> failed (ESI), carefully layering a solution of (BDI)MgnPr and  $[Ph_3C^{\dagger}][B(C_6F_5)_4^{-}]$  in chlorobenzene with  $O(SiMe_3)_2$  gave colorless crystals of  $[(BDI)Mg^+ O(SiMe_3)_2][B(C_6F_5)_4^-]$  in 76% yield. Its crystal structure revealed Mg silyl ether bonding (Fig. 2). The bulky silyl ether blocks the Mg metal for additional Mg···B( $C_6F_5$ )<sub>4</sub><sup>-</sup> interaction, resulting in a rare formally three-coordinate Mg. The Mg-O(SiMe<sub>3</sub>)<sub>2</sub> bond of 1.993(1) Å is unexpectedly short and falls at the lower end of the



**Figure 2.** (a) Crystal structure of  $[(BDI)Mg^+ \cdot O(SiMe_3)_2][B(C_6F_5)_4^-]$ ; the anion (which shows no contacts to the metal) and the H atoms are not shown. (b) Comparison of bond lengths (Å) and angles (°) in cationic  $(BDI)Mg^+ \cdot O(SiMe_3)_2$  (in black) and neutral  $(BDI)Mg^- N(SiMe_3)_2$  (in red).

The cation (BDI)Mg<sup>+</sup>·O(SiMe<sub>3</sub>)<sub>2</sub> is isoelectronic to the neutral complex (BDI)MgN(SiMe<sub>3</sub>)<sub>2</sub><sup>23</sup> and shows a remarkably similar geometry (Fig. 2b). While the BDI-Mg bond distances are slightly shorter in the cationic complex, the Mg-O(SiMe<sub>3</sub>)<sub>2</sub> bond of 1.993(1) Å is only slightly longer than that between Mg and the anionic amide ligand, Mg-N(SiMe<sub>3</sub>)<sub>2</sub> 1.962(2) Å. Both complexes feature distinct Mg···MeSi agostic interactions that are significantly stronger in the cationic complex: Mg···C 2.637(2) vs. 2.887(2) Å.

Coordination of O(SiMe<sub>3</sub>)<sub>2</sub> to Mg results in a striking geometry change: the Si-O-Si angle is reduced from 148.3(1)° to 127.08(6)° and the Si-O distance increased from 1.631(1) to 1.718(1) Å. Complexation of Li<sup>+</sup> by the sila-crown ether (Me<sub>2</sub>SiO)<sub>6</sub> led to similar but much smaller distortions: Si-O-Si 149.6(1)  $\rightarrow$  141.7(1)° and Si-O 1.622(1)  $\rightarrow$  1.655(1) Å.<sup>11a</sup> The unusually acute Si-O-Si angle of 127.08(6)° in (BDI)Mg<sup>+</sup>·O(SiMe<sub>3</sub>)<sub>2</sub> lies outside the hitherto observed range (135°-180°) and indicates strong Lewis basicity.<sup>5a,6c</sup> Structural changes in the Mg bound silyl ether can be explained by the localization of electron density at O triggered by the Mg<sup>2+</sup>-O contact. The latter, clearly diminishes negative hyperconjugation

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which is normally expressed by wide Si-O-Si angles and short Si-O distances. However, negative hyperconjugation is partially still operative: the Mg···MeSi agostic interaction amplifies  $n_0 \rightarrow \sigma^*_{\text{Si-C}}$  charge transfer as can be recognized from a slightly shorter O1-Si2 bond of 1.711(1) Å (*cf.* O1-Si1 1.724(1) Å) and a slightly longer Si2-C35 bond of 1.873(1) Å (*cf.* other Si-C bonds: average: 1.849 Å).

In the solid state, the silyl ether is strongly bound to Mg: crystals of  $[(BDI)Mg^{+} O(SiMe_{3})_{2}][B(C_{6}F_{5})_{4}]$  do not lose  $O(SiMe_3)_2$  under high vacuum (10<sup>-5</sup> Torr). Also in solution evidence for Mg silvl ether coordination exists. Its <sup>1</sup>H NMR spectrum (298 K) in  $C_6D_5Br$  shows broad signals for the BDI ligand and two broad resonances for O(SiMe<sub>3</sub>)<sub>2</sub> that can be assigned to free and coordinated silyl ether. Two signals in the <sup>29</sup>Si NMR spectrum (253 K) confirm the presence of free and coordinated silyl ether. The proportion of bound O(SiMe<sub>3</sub>)<sub>2</sub> increases at higher sample concentration and decreases with a raise in temperature (Fig. S6-8), giving further support for the equilibrium (BDI)Mg<sup>+</sup>·O(SiMe<sub>3</sub>)<sub>2</sub>  $\rightleftharpoons$  (BDI)Mg<sup>+</sup> + O(SiMe<sub>3</sub>)<sub>2</sub>. A rough estimation of thermodynamic parameters gave the following:  $\Delta H^0 \approx -7 \text{ kcal} \cdot \text{mol}^{-1}$ ,  $\Delta S^0 \approx -22 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  (Figure S13). At 45 °C the <sup>1</sup>H NMR signals for bound and free O(SiMe<sub>3</sub>)<sub>2</sub> coalesce and at 60 °C irreversible decomposition is observed. The silvl ether in  $(BDI)Mg^+ O(SiMe_3)_2$  is partially replaced by addition of one equivalent of benzene and is fully substituted by addition of one equivalent of Et<sub>2</sub>O.

The interaction of the (BDI)Mg<sup>+</sup> cation with neutral ligands  $C_6H_6$ , Et<sub>2</sub>O, tBu<sub>2</sub>O and O(SiMe<sub>3</sub>)<sub>2</sub> has been studied by Density Functional Theory (DFT) calculations at the ωB97X/6-311+G\*\* and  $\omega$ B97XD/6-311+G\*\* (including dispersion correction) levels of theory. The calculated geometry of the  $(BDI)Mg^+ O(SiMe_3)_2$  cation (without  $B(C_6F_5)_4^-)$  compares well with its crystal structure (Fig. S14), except for the Mg···MeSi agostic interaction which is less pronounced (DFT: Mg---C 2.893 Å; X-ray: 2.637(2) Å). Analysis of the NPA charges in the free ethers (Table S5) demonstrates an increasing negative charge on O along the row  $Et_2O < tBu_2O < O(SiMe_3)_2$ . Coordination of these ether ligands to Mg induces additional polarization of negative charge towards O. This effect is strongest for the large tBu<sub>2</sub>O ligand but least pronounced for O(SiMe<sub>3</sub>)<sub>2</sub> in which the O-Si bonds are already extremely polarized. In all cases there is little electron transfer from ligand to Mg (0.05-0.07 e)indicating that ligand bonding is largely electrostatic.

As a measure for Mg-ligand bond strength, energies for exchange of Et<sub>2</sub>O in (BDI)Mg<sup>+</sup>·OEt<sub>2</sub> have been calculated (Table 1). Whereas exchange of OEt<sub>2</sub> for C<sub>6</sub>H<sub>6</sub> is expectedly endothermic ( $\Delta$ E = +14.24 kcal/mol), exchange for the bulkier ethers OtBu<sub>2</sub> and O(SiMe<sub>3</sub>)<sub>2</sub> is surprisingly exothermic by -5.53 and -3.59 kcal/mol, respectively. Including corrections for dispersion augments these exchange energies: -9.34 and -7.73 kcal/mol, respectively. The large dispersive correction for OEt<sub>2</sub>/O(SiMe<sub>3</sub>) exchange (4.14 kcal/mol) is due to secondary BDI···O(SiMe<sub>3</sub>)<sub>2</sub> interactions. The tight fit is evident from space-filling models (Fig. S15).

More realistic exchange energies were obtained by calculating  $\Delta G$  values. Entropic corrections hardly affect the energies for exchange of Et<sub>2</sub>O by C<sub>6</sub>H<sub>6</sub> or OtBu<sub>2</sub> ligands but the Et<sub>2</sub>O/O(SiMe<sub>3</sub>)<sub>2</sub> exchange energy is significantly reduced from  $\Delta E$  = -7.73 to  $\Delta G$  =

-2.19 kcal/mol. This is due to a large entropy loss of  $\Delta S = -15.06$  cal·mol<sup>-1</sup>·K<sup>-1</sup>. As illustrated by the low temperature flexibility of silicones, more ionically bound silyl ethers are extremely dynamic molecules. Bonding of O(SiMe<sub>3</sub>)<sub>2</sub> to (BDI)Mg<sup>+</sup> significantly restricts its dynamics, thus explaining entropy loss for Et<sub>2</sub>O/O(SiMe<sub>3</sub>)<sub>2</sub> exchange. Despite corrections for entropy, it is unexpected that Et<sub>2</sub>O/O(SiMe<sub>3</sub>)<sub>2</sub> exchange is slightly in favor of the silyl ether by -2.19 kcal/mol. This does not agree with the experimental observation that O(SiMe<sub>3</sub>)<sub>2</sub> can be easily replaced by Et<sub>2</sub>O. The origin of this mismatch stems from neglecting the weakly coordinating [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>] ion in the calculational model. Small ligands like C<sub>6</sub>H<sub>6</sub> or Et<sub>2</sub>O leave space at the metal for additional Mg···F interaction(s). Inclusion of the [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>] ion should therefore give much lower exchange energies for the larger tBu<sub>2</sub>O and O(SiMe<sub>3</sub>)<sub>2</sub> ligands that block such stabilizing cation-anion interactions.

**Table 1.** Energies for Et<sub>2</sub>O/ligand exchange at the  $\omega$ B97XD/6-311+G\*\* level; values for  $\omega$ B97X/6-311+G\*\* without dispersion correction are given between []. Calculations for the systems including the WCA's (lower Table) have been performed at the  $\omega$ B97XD/6-311+G\*\*//6-31G\* level of theory.  $\Delta$ E,  $\Delta$ H and  $\Delta$ G (298.15 K, 1 bar) in kcal·mol<sup>-1</sup>.  $\Delta$ S in cal·mol<sup>-1</sup>·K<sup>-1</sup>.

(BDI)Mg <sup>+</sup> ·OEt <sub>2</sub> + solvent → (BDI)Mg <sup>+</sup> ·solvent + OEt <sub>2</sub>						
solvent	ΔE	ΔH	ΔS	ΔG		
C <sub>6</sub> H <sub>6</sub>	+11.66	+10.97	+0.85	+10.72		
	[+14.24]	[+14.17]	[-1.67]	[+14.67]		
OtBu <sub>2</sub>	-9.34	-9.68	-3.55	-8.62		
	[-5.53]	[-4.95]	[-7.80]	[-2.62]		
O(SiMe <sub>3</sub> ) <sub>2</sub>	-7.73	-6.68	-15.06	-2.19		
	[-3.59]	[-2.80]	[-14.44]	[+1.50]		

 $[(BDI)Mg^{+} \cdot OEt_2][B(C_6F_5)_4^{-}] + solvent \rightarrow [(BDI)Mg^{+} \cdot solvent][B(C_6F_5)_4^{-}] + OEt_2$ 

solvent	ΔΕ	ΔH	ΔS	ΔG
C <sub>6</sub> H <sub>6</sub>	+10.77	+10.43	-5.10	+11.95
OtBu <sub>2</sub>	+8.54	+8.22	+0.07	+8.20
O(SiMe <sub>3</sub> ) <sub>2</sub>	+8.34	+8.43	-11.44	+11.84

Indeed, optimized structures including  $[B(C_6F_5)_4]$  show short Mg...F contacts for complexes with the smaller ligands  $C_6H_6$  (2.041 Å) or Et<sub>2</sub>O (2.097 Å) whereas the large ethers force the anion to be truly non-coordinating (Fig. S16): the shortest Mg···F distances for tBu<sub>2</sub>O (5.534 Å) and  $O(SiMe_3)_2$  (5.925 Å) are clearly non-bonding. Taking cation-anion interactions into account led to a dramatic lowering of the complexation energies for the larger ligands (Table 1) and predicts the expected ligand strength order:  $Et_2O >> tBu_2O > C_6H_6 \approx$ O(SiMe<sub>3</sub>)<sub>2</sub>. The computational results reflect the experimental observations: the silyl ether O(SiMe<sub>3</sub>)<sub>2</sub> is easily replaced by Et<sub>2</sub>O and has a coordination ability similar to that of benzene. The calculated thermodynamic parameters for the equilibrium (including the WCA):  $[(BDI)Mg^{+}][B(C_{6}F_{5})_{4}^{-}]$  $O(SiMe_3)_2$ ⊉  $[(BDI)Mg^{+} O(SiMe_{3})_{2}][B(C_{6}F_{5})_{4}^{-}]$  are:  $\Delta E = -8.48 \text{ kcal·mol}^{-1}$ ,  $\Delta H -6.24$ kcal·mol<sup>-1</sup>,  $\Delta$ S = -48.6 cal·mol<sup>-1</sup>·K<sup>-1</sup> and  $\Delta$ G (298.15 K, 1 bar) = +8.25

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kcal·mol<sup>-1</sup>. These values fit the experimentally determined values reasonably well ( $\Delta$ H -7 kcal·mol<sup>-1</sup>,  $\Delta$ S -22 cal·mol<sup>-1</sup>·K<sup>-1</sup>; *vide supra*) except for  $\Delta$ S, which in calculations is overestimated.<sup>25</sup>

Despite the very poor complexation energies of silvl ethers, the first metal complex of hexamethyldisiloxane has been isolated and was structurally characterized. The key to complexation is a "naked", highly Lewis acidic, cationic Mg complex with a large, highly accessible, coordination sphere. Mg...O(SiMe<sub>3</sub>)<sub>2</sub> coordination induces significant geometry changes in the silvl ether: substantial lengthening of the Si-O bond and squeezing of the Si-O-Si angle indicate strongly reduced negative hyperconjugation and increased Lewis basicity. The Mg···O(SiMe<sub>3</sub>)<sub>2</sub> bond is of similar strength as a Mg···C<sub>6</sub>H<sub>6</sub> interaction. Agostic Mg···MeSi interactions as well as attractive London dispersion forces<sup>26</sup> between the bulky BDI ligand and O(SiMe<sub>3</sub>)<sub>2</sub> are an important contribution to metal silyl ether bonding. Theoretical studies on metal silvl ether bonding should therefore preferably include ligands at the metal. For bonding to cationic species, inclusion of the weakly coordinating anion  $B(C_6F_5)_4^{-1}$  in the calculational model is essential and gave the following order of ligand strength:  $Et_2O >> tBu_2O > C_6H_6 \approx O(SiMe_3)_2$ . The isolation of a Mg complex with an unsupported silvl ether ligand demonstrates that weak metal···O(SiR<sub>3</sub>)<sub>2</sub> interactions should not be underestimated, a result that certainly may be of relevance in the larger fields of silicone and zeolite chemistry.

# **Conflicts of interest**

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There are no conflicts to declare.

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Silyl ethers surrender to magnesium: the very weak Lewis base hexamethyldisiloxane is forced to ligate a "naked" cationic Mg species. Agostic interactions and vanderWaals attraction contribute to stability.