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Soluble Molecular Compounds with the Mg−O−Al Structural Motif: A Model Approach for the Fixation of Organometallics on a MgO Surface

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Spinel is a very attractive and historically important gemstone and mineral. Spinel of composition $MgAl_2O_4$ is found in nature, and it is prepared by reacting aluminum oxide with MgO at high temperatures. The structure of $MgAl_2O_4$ consists of cubic closest packed oxide ions. A multitude of spinels using other elements has been reported.[1−3] These compounds have a variety of applications; for example, hot pressed $MgAl_2O_4$ is used as an optical window, and the ferrite spinels are an important family of magnetic materials. All spinels have in common that they are high melting inorganic solids and insoluble in organic solvents. Moreover, it was shown that SiO_2 and $MgCl_2$ function as supports for metallocene−methylaluminoxane (MAO) catalysts.[4] The magnesium-supported system exhibits activity 2-fold higher in ethylene polymerization than that with the silica analogues. An explanation of this phenomenon has not been given.[5,6] Previous quantum chemical calculations have shown that adsorbed rhenium subcarbonyls on MgO surfaces form strong Re−O adsorption bonds, justifying that the inert MgO surface is able to anchor organometallic fragments.[7] Recently, an alkoxy-bridged Mg−O(R)→Al compound has been reported.[8] However, the stability and bonding situation of this system is quite different from that of an oxide-bridged Mg−O−Al motif.

Herein, we report the molecular compounds containing the Mg−O−Al skeleton. The reaction of $Mg[N(SiMe_3)_2]_2$ (**1**)[9,10] with a stoichiometric amount of LAlOH(Me) [L = CH{(CMe)(2,6-$i$$Pr_2C_6H_3N$)}$_2$; **2**][11] in THF/*n*-hexane (1:1) at 0 °C results in the elimination of $HN(SiMe_3)_2$ and the formation of the heterobimetallic compound **3** in high yield (Scheme 1). Compound **3** is soluble in a wide range of common organic solvents. It was characterized by ^1H, ^{13}C, ^{29}Si NMR and IR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis. The ^1H NMR spectrum of **3** exhibits a resonance at −0.36 ppm for Al-*Me*, which by comparison with that of **2** (−0.88 ppm) clearly shows a downfield shift. The expected resonance for $SiMe_3$ is observed as a singlet (0.15 ppm). The ^{29}Si NMR shows a signal at −9.8 ppm which is shifted downfield compared to that of **1** (−12.6 ppm).[12] No molecular ion of **3** was detected in the EI mass spectrum; only small fragment ions are found.

Crystals of **3**[13] suitable for X-ray structural analysis were obtained from a THF/*n*-pentane solution at 0 °C. Compound **3** crystallizes in the monoclinic space group $P2_1/n$. The molecular structure is shown in Figure 1. The X-ray structural analysis of **3** revealed that the magnesium is bonded through a bridging oxygen atom to an aluminum atom. The geometry around the magnesium, as well as that of the aluminum, is tetrahedrally distorted. The Mg−O bond distances (1.850−2.095 Å) are consistent with the Mg−O bond lengths compiled by Holloway and Melnik for compounds of magnesium with the coordination number 4 at the magnesium (1.819−2.219 Å).[14] The Mg(1)−O(1)−Al(1) bond angle (157.1(1)°) is much wider compared to that in the alkoxy-bridged [$Al_3Mg_3(\mu_3\text{-}O)(THFFO)_4Cl_4(Me)_5(THF)$] (THFFO = 2-tetrahydrofurfuroxide) compound (Al−μ-$O_{(alkoxide)}$−Mg (128.2(2)°)).[8] The Al−C and Al−O bond distances are 1.975(2) and 1.682(2) Å, respectively, which are in good agreement with those observed in $[OCMeCHCMeNAr]_2AlMe$ (Ar = 2,6-$i$$Pr_2C_6H_3$) (Al−C = 1.975(2) Å) and $[HC(CMeNMe)_2AlCl]_2(\mu\text{-}O)$ (Al−O = 1.677(2) Å).[15,16]

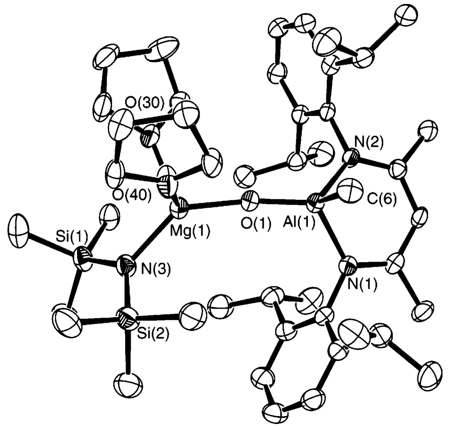
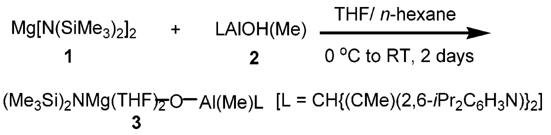
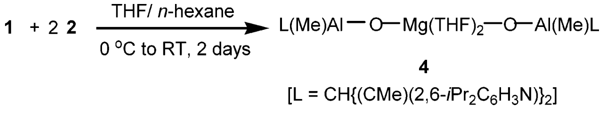


Figure 1. Molecular structure of **3**; thermal ellipsoids set at 50% probability. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Mg(1)−O(1) 1.850(2), Mg(1)−O(30) 2.094(2), Mg(1)−O(40) 2.070(2), Mg(1)−N(3) 2.019(2), O(1)−Al(1) 1.682(2), Al(1)−C(6) 1.975(2); Mg(1)−O(1)−Al(1) 157.1(1), O(40)−Mg(1)−O(30) 88.4(1), O(1)−Al(1)−C(6) 120.6(1), Si(1)−N(3)−Si(2) 125.1(1).

Scheme 1



Scheme 2



Compound **4** (shown in Scheme 2, also see Supporting Information) is soluble in hexane, benzene, toluene, and THF. It was characterized by ^1H, ^{13}C, ^{27}Al NMR and IR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis. The ^1H NMR spectrum of **4** shows a single resonance for the Al-*Me* (−0.66 ppm). The ^{27}Al NMR for **4** was silent, obviously due to the quadrupole moment of the aluminum atom.

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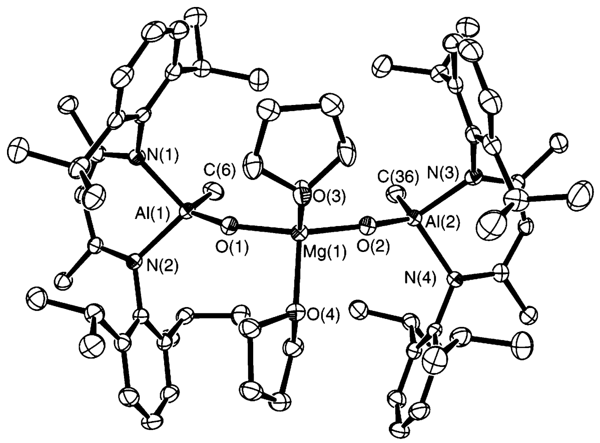

Figure 2. Molecular structure of **4**; thermal ellipsoids at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Al(1)−O(1) 1.671(2), O(1)−Mg(1) 1.873(2), Mg(1)−O(2) 1.858(2), O(3)−Mg(1) 2.043(2), O(4)−Mg(1) 2.089(2), O(2)−Al(2) 1.671(2), Al(1)−C(6) 1.971(3), Al(2)−C(36) 1.980(3); Al(1)−O(1)−Mg(1) 150.2(1), Al(2)−O(2)−Mg(1) 159.6(1), O(2)−Mg(1)−O(1) 142.4(1), O(3)−Mg(1)−O(4) 99.8(1).

Single crystals of **4**[13] suitable for X-ray structural analysis were obtained from a THF/*n*-hexane solution at 0 °C. Compound **4** crystallizes in the monoclinic space group $P2_1/c$. The molecular structure is shown in Figure 2. The magnesium atom in **4** is four coordinate and surrounded by two THF molecules and two μ-O-bonded oxygens, resulting in a distorted tetrahedral environment. The bond distances of Mg−O (1.858−2.089 Å) are in agreement with those found in **3** (1.850−2.094 Å).

Compounds **3** and **4** were investigated by theoretical methods to obtain further information of their spectroscopic properties. The molecules were first fully optimized with the DFT variant B3LYP[17,18] as implemented in the Gaussian 03[19] program suite, employing the 6-31G basis set.[20−23] Following this optimization, the harmonic vibrational frequencies were calculated by using analytical second derivatives. The character of the vibrations was then determined through a normal mode analysis available in Gaussian 03. The resulting equilibrium structures agree very well with the experimental data available by X-ray crystallography. For compound **3**, the calculated vibrations are clearly localized within the Mg−O−Al subunit. The calculated antisymmetric Mg−O−Al vibration (778.5 cm^{-1}) compares well with that found at 761 cm^{-1} in the IR spectrum. The deviation between the calculated and observed values might be due to the coordination of two THF molecules in **3**. From the calculation of **4**, three bands can be clearly assigned to isolated Mg−O−Al vibrations. The antisymmetric Mg−O−Al vibrations have calculated frequencies of 678.7 and 786.9 cm^{-1}. The symmetric Mg−O−Al vibration is calculated to be 747.9 cm^{-1}. From the three modes (1015, 1030, and 1060 cm^{-1}) belonging to Mg−O vibrations, the band at 1030 cm^{-1} is the most intensive one and compares to that found in the IR spectrum (1021 cm^{-1}). The difference in wavenumbers might be due to THF coordination. (Further data of calculation, including Figures S1 and S2, are given in the Supporting Information.)

In summary, we report a facile route to the molecular compounds with the Mg−O−Al structural motif. Compound **3** can be considered to function as a precursor for the preparation of heterotrimetallic systems. Furthermore, compounds **3** and **4** might be useful precursors for spin-coated spinel surfaces and function as a molecular model for surface fixation of the organometallic species. A tentative assignment of the Mg−O−Al vibrations has been made and was supported by calculations.

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Supporting Information Available: Crystallographic (CIF) and experimental details, complete ref 19, and details of the calculation. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Crystal data for compound **3**: $C_{44}H_{78}AlMgN_3O_3Si_2$, $M_r = 804.56$, monoclinic, space group $P2_1/n$, $a = 11.746(2)$ Å, $b = 21.439(3)$ Å, $c = 19.870(3)$ Å, $\beta = 101.66(2)°$, $V = 4900.5(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.091$ M gm^{-3}, $F(000) = 1760$, $T = 133(2)$ K, μ (Mo Kα) = 0.141 mm^{-1}. The final refinement converged to $R1 = 0.0394$ for $I > 2\sigma(I)$, $wR2 = 0.0855$ for all data. Crystal data for compound **4**: $C_{68}H_{104}Al_2MgN_4O_4$, $M_r = 1119.82$, monoclinic, space group $P2_1/c$, $a = 16.067(2)$ Å, $b = 23.113(2)$ Å, $c = 18.001(2)$ Å, $\beta = 102.06(2)°$, $V = 6537.3(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.138$ M gm^{-3}, $F(000) = 2440$, $T = 100(2)$ K, μ (Cu Kα) = 0.865 mm^{-1}. The final refinement converged to $R1 = 0.0422$ for $I > 2\sigma(I)$, $wR2 = 0.1057$ for all data.
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