

Carbon Dioxide Complexes

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Aluminum–Magnesium Complexes with Linearly Bridging Carbon Dioxide**

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Earlier, we found that an oxygen atom of carbon dioxide bonds to a metal atom when carbon dioxide is fixed by the Al–Mg mixed-metal compounds $[\text{Me}_2\text{Al}(\mu\text{-NR}_2)_2\text{Mg}(\mu\text{-Me})]_n$ ($\text{R} = i\text{Pr}$, $n = 4$; $\text{R} = \text{Et}$, $n = 2$). Subsequently, the amino leaving group migrates from the attacked metal atom to the carbon atom of the carbon dioxide to form Al–Mg carbamato complexes.^[1] The CO_2 -ligated Mg compounds show a variety of bonding modes.^[2] However, to date the linear $\mu(\text{O},\text{O}')$ - CO_2 coordination mode of carbon dioxide has not been observed, either in main group or in transition metal compounds.^[3]

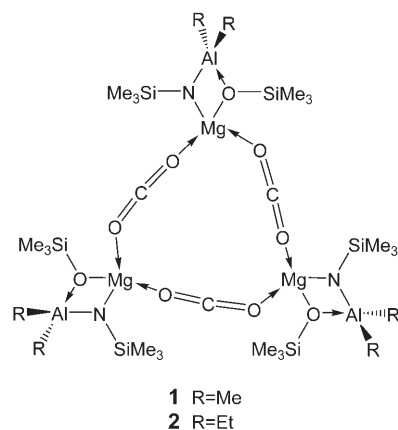
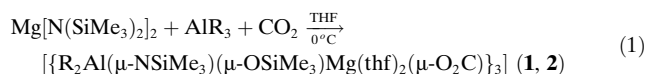
In accordance with earlier work by Sita et al.,^[4] we presume that the reaction of $\text{Mg}[\text{N}(\text{SiMe}_3)_2]_2$ with carbon dioxide could also generate an oxo-transfer product, namely, $\text{Mg}(\text{N}(\text{SiMe}_3)_2)(\text{OSiMe}_3)$, and the expected $\text{O}=\text{C}=\text{N}(\text{SiMe}_3)$, instead of generating a carbamato complex.^[5] In light of our previous experience with trialkylaluminum reagents and taking advantage of the oxo-transfer compound $\text{Mg}[\text{N}(\text{SiMe}_3)_2](\text{OSiMe}_3)$, we proposed a process for studying CO_2 fixation in a mixture of $\text{Mg}[\text{N}(\text{SiMe}_3)_2]_2$ and trialkylaluminum.

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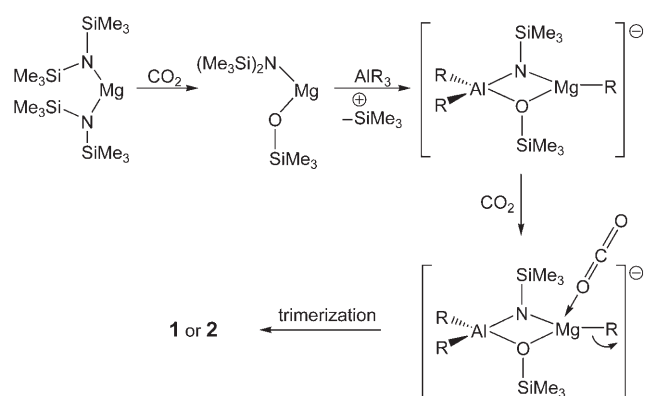
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One equivalent of AlR_3 ($\text{R} = \text{Me}$, Et) was added to a solution of $\text{Mg}[\text{N}(\text{SiMe}_3)_2]_2$ in THF at room temperature, and an excess of carbon dioxide was bubbled through the stirred, ice-cooled mixture to yield compounds **1** ($\text{R} = \text{Me}$) and **2** ($\text{R} = \text{Et}$) [Eq. (1), Scheme 1].



Scheme 1. Schematic representation of **1** and **2**. Coordinated THF omitted for clarity.

Presumably, carbon dioxide reacted with $\text{Mg}[\text{N}(\text{SiMe}_3)_2]_2$ to give oxo-transfer product $\text{Mg}[\text{N}(\text{SiMe}_3)_2](\text{OSiMe}_3)$, which is assumed to form a bridged Al–Mg intermediate with AlR_3 ($\text{R} = \text{Me}$, Et); this subsequently loses a ligand from the magnesium center and is attacked by a second molecule of carbon dioxide with the oxygen atom as a weak electron donor (Scheme 2). Finally, the carbon dioxide acts as a



Scheme 2. Proposed reaction path for the formation of **1** and **2**.

bridging ligand to form a trimer. The products were characterized by elemental analysis, FTIR spectroscopy, and X-ray analysis. The single-crystal X-ray diffraction data confirmed the molecular structures (Figures 1 and 2).^[6] The skeletons of **1** and **2** have a C_3 symmetry axis and can be viewed as composed of three equivalent motifs, each of which has a

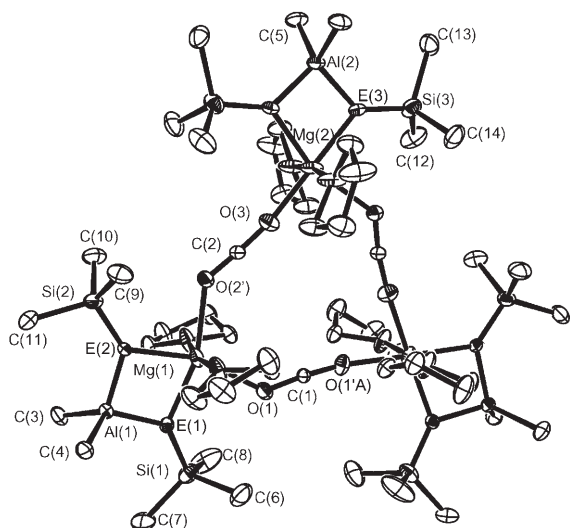


Figure 1. ORTEP view of **1** in the solid state. Thermal ellipsoids are drawn at the 20% probability level. Selected bond lengths [Å] and angles [°]: Mg(1)–O(1) 2.211(11), Mg(1)–O(2) 2.232(12), Mg(2)–O(3) 1.944(10), O(1)–C(1) 1.208(10), O(2)–C(2) 1.166(13), O(3)–C(2) 1.223(10); O(1′A)–C(1)–O(1) 173.6(10), O(2)–C(2)–O(3) 175.3(8), C(1)–O(1)–Mg(1) 133.2(6), C(2)–O(2)–Mg(1) 134.1(6), C(2)–O(3)–Mg(2) 171.1(8), E(1)–Mg(1)–E(2) 75.53(12), E(1)–Mg(1)–O(1) 85.9(2), E(2)–Mg(1)–O(2) 86.8(3), O(1)–Mg(1)–O(2) 111.8(3). Atoms E(1), E(2), and E(3) were refined as mixed atoms (50% O and 50% N).

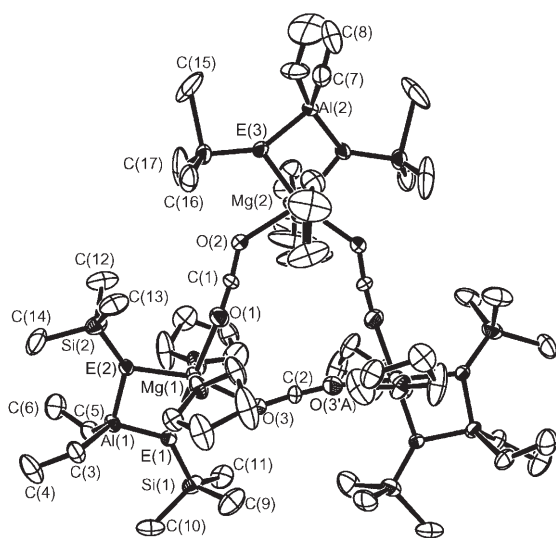


Figure 2. ORTEP view of **2** in the solid state. Thermal ellipsoids are drawn at the 20% probability level. Selected bond lengths [Å] and angles [°]: Mg(1)–O(1) 2.004(16), Mg(1)–O(3) 2.184(11), Mg(2)–O(2) 2.181(10), O(1)–C(1) 1.149(15), O(2)–C(1) 1.222(11), O(3)–C(2) 1.201(10); O(1)–C(1)–O(2) 173.3(9), O(3′A)–C(2)–O(3) 169.6(10), C(1)–O(1)–Mg(1) 171.3(11), C(1)–O(2)–Mg(2) 134.9(7), C(2)–O(3)–Mg(1) 136.9(7), O(1)–Mg(1)–E(2) 104.6(4), E(1)–Mg(1)–E(2) 76.03(13), O(1)–Mg(1)–O(3) 92.3(4), E(1)–Mg(1)–O(3) 86.9(3). Atoms E(1), E(2), and E(3) were refined as mixed atoms (50% O and 50% N).

bridged Al–Mg structure. The six-coordinate magnesium atom is linked to a four-coordinate aluminum atom by bridging OSiMe₃ and NSiMe₃ groups. Two alkyl groups are retained on each aluminum atom to attain a coordination

number of four. The magnesium atoms of the three motifs are joined through three approximately linear carbon dioxide bridges to form a twelve-membered ring.

Atoms O(4)–O(6) of **1** and N(1)–N(3) of **2** were refined as mixed atoms (50% O and 50% N) due to their disorder in the OSiMe₃ and NSiMe₃ groups. The requirement for charge balance in the molecule and elemental analysis supported the assignment of these atoms. Compounds **1** and **2** have very similar skeletons.

In **1** and **2**, the Mg–O bond lengths of 1.944(10)–2.232(12) and 2.004(16)–2.184(11) Å, respectively, in the MgCO₂ moiety are within the range expected for such bonds (Mg←O (monodentate O donor ligand): 2.012–2.236 Å).^[7] These bond lengths indicate that each oxygen atom donates a lone pair of electrons to the vacant p_z orbital of the electropositive magnesium atom in a dative bond. In other words, each carbon dioxide molecule links two magnesium atoms in a linear μ(O,O′) bonding mode. The C–O bond lengths of 1.166(13)–1.233(10) and 1.149(15)–1.222(11) Å, respectively, are very close to that of free carbon dioxide^[8] and Mn(HCOO)₃·¹/₂ CO₂·¹/₄ HCOOH·²/₃ H₂O,^[9] and thus suggest the presence of C=O bonds. The O–C–O bond angles of 173.6(10)–175.3(8) and 169.6(10)–173.3(9)°, respectively, are close to 180° and suggest sp-hybridized C atoms. The Mg←O=C=O→Mg moieties show some disorder, with a shape like an hourglass.

The ¹H and ¹³C NMR and IR spectroscopic data and the elemental analysis further characterized **1** and **2**.^[10] The ¹³C NMR spectra of **1** and **2** show peaks for the carbon atom of CO₂ at 120.87 and 120.76 ppm, respectively, shifted slightly upfield relative to free carbon dioxide.^[11]

The IR spectra provided further strong evidence for the introduction of carbon dioxide into **1** and **2**. Compounds **1** and **2** showed strong absorption at 2267 and 2275 cm^{−1}, respectively, originating from stretching vibration of the bridging carbon dioxide. In comparison to free linear carbon dioxide (ν_{asym} 2348 cm^{−1})^[12] and Mn(HCOO)₃·¹/₂ CO₂·¹/₄ HCOOH·²/₃ H₂O,^[9] the values are only slightly red-shifted. Decreasing CO₂ stretching frequency is an accepted measure of increasing negative charge on the Mg atom. Hence, the coordinated CO₂ molecules in **1** and **2** donate a small amount of electron density to the more electropositive Mg atoms.

In summary, we have reported a straightforward, one-pot synthetic pathway that leads to novel aluminum–magnesium complexes containing carbon dioxide in the heretofore-unknown linear μ(O,O′) bonding mode. The formation of **1** and **2** shows that interesting products can predictably be obtained when Mg[N(SiMe₃)₂]₂ and AlR₃ (R = Me, Et) are reacted with carbon dioxide. Investigations of the electronic and steric effects of substituents on the trialkylaluminum on the reaction with Mg[N(SiMe₃)₂]₂ and carbon dioxide under the same conditions are in progress.

Experimental Section

All experiments were carried out in an N₂-flushed glove bag, in a dry box, or under vacuum by using standard Schlenk techniques. All solvents were distilled and degassed prior to use. All ¹H and ¹³C NMR spectra were measured on a Varian-500 spectrometer. Chemical shifts

are referenced to C_6D_6 (1H , $\delta = 7.15$ ppm; $^{13}C\{^1H\}$, $\delta = 128.00$ ppm). FTIR spectra were obtained with a Bio-Rad model FTS-155 FTIR spectrometer.

1: $AlMe_3$ (2.0 M in toluene, 12 mL, 2.38 mmol) was added to a solution of $Mg[N(SiMe_3)_2]_2$ (8.21 g, 2.38 mmol) in THF (60 mL). The mixture was cooled in an ice bath, and an excess of carbon dioxide was bubbled through the stirred mixture for 2 h. An intermediate exothermic reaction ensued. The resultant solution was cooled in a freezer to give crystals of **1**. The preparation of complex **2** was similar to that of complex **1**.

1: Yield: 20%. M.p. > 112 °C (decomp). 1H NMR (500 MHz, C_6D_6): $\delta = -0.36$ (s, 18H, $AlCH_3$), 0.34 ppm (m, 54H, $NSi(CH_3)_3$, $OSi(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = -5.75$ ($AlCH_3$), 3.24 ($NSi(CH_3)_3$; $OSi(CH_3)_3$), 120.87 ppm (CO_2). IR (Nujol): $\tilde{\nu} = 2267$ (s), 1252(m), 1040(m), 890(s), 841(s) cm^{-1} .

2: Yield: 53%. M.p. > 116 °C (decomp). 1H NMR (500 MHz, C_6D_6): $\delta = 0.24$ (q, 12H, $AlCH_3$), 0.35 (m, 54H, $NSi(CH_3)_3$, $OSi(CH_3)_3$), 1.43 ppm (t, 18H, $AlCH_2CH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 3.12$ ($AlCH_2$, $NSi(CH_3)_3$, $OSi(CH_3)_3$), 10.42 ($AlCH_2CH_3$), 120.76 ppm (CO_2). IR (Nujol): $\tilde{\nu} = 2275$ (s), 1255(m), 1041(m), 889(s), 842(s) cm^{-1} .

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least-squares refinement on F^2 converged to $R1 = 0.1423$ (all data), 0.1006 ($I > 2\sigma(I)$); $wR2 = 0.3135$ (all data), 0.2731 ($I > 2\sigma(I)$). One molecule of THF was disordered. Atoms Al(2), Si(3), Si(3'), C(7), C(8), C(7'), C(8'), O(7), C(30), and C(32) all had half occupancies. All calculations were performed with the SHELXTL-97 package. CCDC-277386 (**1**) and -277385 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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 [6] Crystal data for **1**·2THF: $C_{59}H_{136}Al_3Mg_3N_3O_{17}Si_6$, $M_r = 1482.12$, orthorhombic, space group $Pbcn$, $a = 12.4718(6)$, $b = 25.4146(11)$, $c = 28.0272(12)$ Å, $V = 8883.7(7)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.108$ g cm⁻³, $\mu = 0.199$ mm⁻¹, $\lambda = 0.71073$ Å, transmission range 0.9520–0.9247, crystal size $0.40 \times 0.40 \times 0.25$ mm³. A total of 29 148 unique reflections were collected on a Nonius KappaCCD diffractometer at 150 K in the θ range 1.45–25.00°. Full-matrix least-squares refinement on F^2 converged to $R1 = 0.1225$ (all data), 0.0783 ($I > 2\sigma(I)$); $wR2 = 0.2401$ (all data), 0.2011 ($I > 2\sigma(I)$). Atoms O(1), O(2), O(3), C(18), C(22), C(23), O(1'), O(2'), O(3'), C(18'), C(22') and C(23') all had half occupancies. Crystal data for **2**·THF: $C_{61}H_{140}Al_3Mg_3N_3O_{16}Si_6$, $M_r = 1494.17$, monoclinic, space group $C2/c$, $a = 30.5742(6)$, $b = 17.5555(3)$, $c = 21.1478(4)$ Å, $\beta = 127.6215(9)^\circ$, $V = 8990.7(3)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.104$ g cm⁻³, $\mu = 0.196$ mm⁻¹, $\lambda = 0.71073$ Å, transmission range 0.963–0.883, crystal size $0.25 \times 0.25 \times 0.22$ mm³. A total of 52 985 unique reflections were collected on a Nonius KappaCCD diffractometer at 150 K in the θ range 1.43–25.00°. Full-matrix