Carbon Dioxide Complexes

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Aluminum–Magnesium Complexes with Linearly Bridging Carbon Dioxide**

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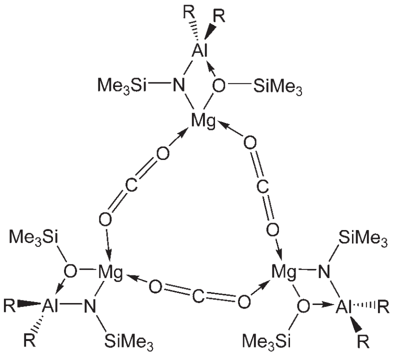
Earlier, we found that an oxygen atom of carbon dioxide bonds to a metal atom when carbon dioxide is fixed by the Al–Mg mixed-metal compounds $[Me_2Al(\mu\text{-}NR_2)_2Mg(\mu\text{-}Me)]_n$ ($R = i$Pr, $n = 4$; $R = $Et, $n = 2$). Subsequently, the amino leaving group migrates from the attacked metal 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 $\mu(O,O')$-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 $Mg[N(SiMe_3)_2]_2$ with carbon dioxide could also generate an oxo-transfer product, namely, $Mg(N(SiMe_3)_2)(OSiMe_3)$, and the expected $O{=}C{=}N(SiMe_3)$, instead of generating a carbamato complex.[5] In light of our previous experience with trialkylaluminum reagents and taking advantage of the oxo-transfer compound $Mg[N(SiMe_3)_2](OSiMe_3)$, we proposed a process for studying CO_2 fixation in a mixture of $Mg[N(SiMe_3)_2]_2$ and trialkylaluminum.

One equivalent of AlR_3 ($R = $Me, Et) was added to a solution of $Mg[N(SiMe_3)_2]_2$ in THF at room temperature, and an excess of carbon dioxide was bubbled through the stirred, ice-cooled mixture to yield compounds **1** ($R = $Me) and **2** ($R = $Et) [Eq. (1), Scheme 1].

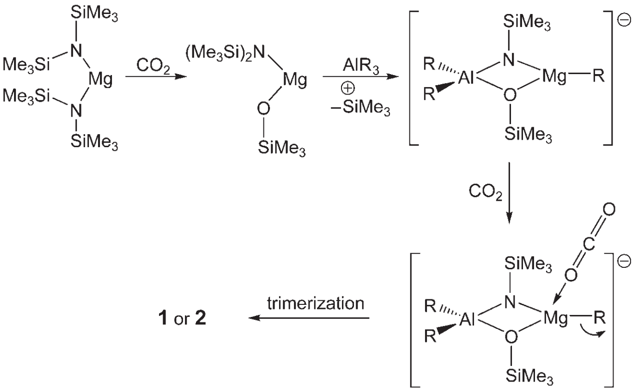
$$\mathrm{Mg[N(SiMe_3)_2]_2 + AlR_3 + CO_2 \xrightarrow[0^{\circ}C]{THF} [\{R_2Al(\mu\text{-}NSiMe_3)(\mu\text{-}OSiMe_3)Mg(thf)_2(\mu\text{-}O_2C)\}_3]}\ (\mathbf{1}, \mathbf{2}) \qquad (1)$$



1 R=Me
2 R=Et

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

Presumably, carbon dioxide reacted with $Mg[N(SiMe_3)_2]_2$ to give oxo-transfer product $Mg[N(SiMe_3)_2](OSiMe_3)$, which is assumed to form a bridged Al–Mg intermediate with AlR_3 ($R = $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 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



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

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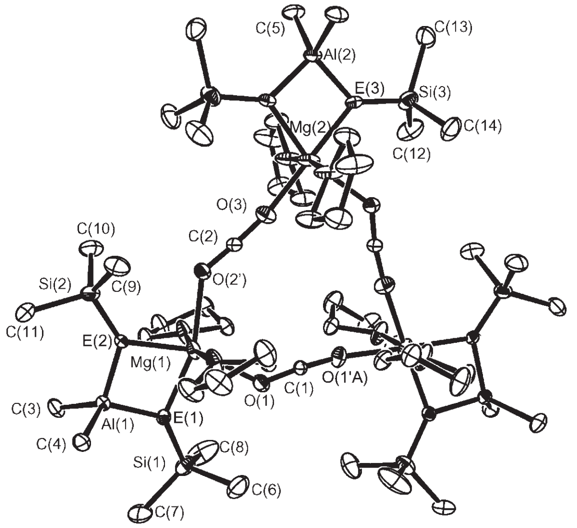

Figure 1. ORTEP view of **1** in the solid state. Thermal ellipsoids are drawn at the 20% probability level. Selected bond lengths [Å] and angles [°]: Mg(1)–O(1) 2.211(11), Mg(1)–O(2′) 2.232(12), Mg(2)–O(3) 1.944(10), O(1)–C(1) 1.208(10), O(2′)–C(2) 1.166(13), O(3)–C(2) 1.223(10); O(1′A)-C(1)-O(1) 173.6(10), 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).

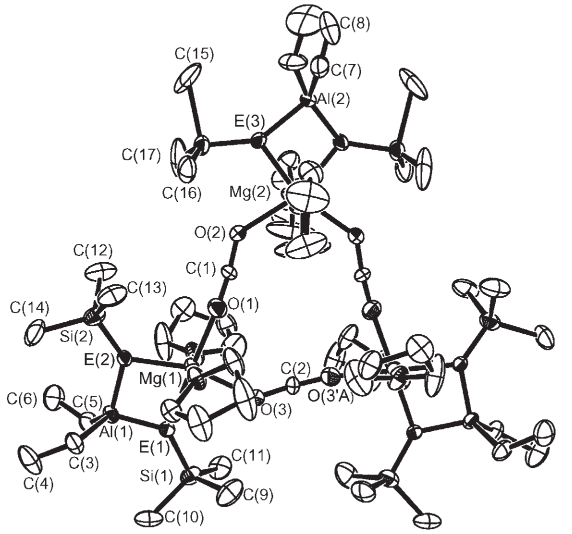

Figure 2. ORTEP view of **2** in the solid state. Thermal ellipsoids are drawn at the 20% probability level. Selected bond lengths [Å] and angles [°]: Mg(1)–O(1) 2.004(16), Mg(1)–O(3) 2.184(11), Mg(2)–O(2) 2.181(10), O(1)–C(1) 1.149(15), O(2)–C(1) 1.222(11), O(3)–C(2) 1.201(10); O(1)-C(1)-O(2) 173.3(9), 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 OSiMe$_3$ and NSiMe$_3$ 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 OSiMe$_3$ and NSiMe$_3$ 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 MgCO$_2$ moiety are within the range expected for such bonds (Mg$\leftarrow$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 $\mathrm{Mn(HCOO)_3\cdot{}^1\!/_2\,CO_2\cdot{}^1\!/_4\,HCOOH\cdot{}^2\!/_3\,H_2O}$,[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$\leftarrow$O=C=O$\rightarrow$Mg moieties show some disorder, with a shape like an hourglass.

The ^{1}H and ^{13}C NMR and IR spectroscopic data and the elemental analysis further characterized **1** and **2**.[10] The ^{13}C NMR spectra of **1** and **2** show peaks for the carbon atom of CO$_2$ 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 $\mathrm{Mn(HCOO)_3\cdot{}^1\!/_2\,CO_2\cdot{}^1\!/_4\,HCOOH\cdot{}^2\!/_3\,H_2O}$,[9] the values are only slightly red-shifted. Decreasing CO$_2$ stretching frequency is an accepted measure of increasing negative charge on the Mg atom. Hence, the coordinated CO$_2$ 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(SiMe$_3$)$_2$]$_2$ and AlR$_3$ (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(SiMe$_3$)$_2$]$_2$ and carbon dioxide under the same conditions are in progress.

Experimental Section

All experiments were carried out in an N$_2$-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 ^{1}H and ^{13}C NMR spectra were measured on a Varian-500 spectrometer. Chemical shifts are referenced to C_6D_6 (^{1}H, $\delta = 7.15$ ppm; ^{13}C{^{1}H}, δ=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). ^{1}H 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{^{1}H} 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). ^{1}H NMR (500 MHz, C_6D_6): $\delta = 0.24$ (q, 12H, $AlCH_2$), 0.35 (m, 54H, $NSi(CH_3)_3$, $OSi(CH_3)_3$), 1.43 ppm (t, 18H, $AlCH_2CH_3$). ^{13}C{^{1}H} 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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[1] a) D. Walther, M. Ruben, S. Rau, *Coord. Chem. Rev.* **1999**, *182*, 67; b) C. C. Chang, B. Srinivas, M. L. Wu, W. H. Chiang, M. Y. Chiang, C. S. Hsiung, *Organometallics* **1995**, *14*, 5150; c) C. C. Chang, M. S. Ameerunisha, *Coord. Chem. Rev.* **1999**, *189*, 199.

[2] a) K. C. Yang, C. C. Chang, C. S. Yeh, G. H. Lee, S. M. Peng, *Organometallics* **2001**, *20*, 126; b) K. C. Yang, C. C. Chang, C. S. Yeh, G. H. Lee, Y. Wang, *Organometallics* **2002**, *21*, 1296.

[3] a) A. Behr, *Angew. Chem.* **1988**, *100*, 681; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 661; b) D. H. Gibson, *Chem. Rev.* **1996**, *96*, 2063.

[4] L. R. Sita, J. R. Babcock, R. Xi, *J. Am. Chem. Soc.* **1996**, *118*, 10912.

[5] a) M. T. Caudle, J. W. Kampf, *Inorg. Chem.* **1999**, *38*, 5474; b) D. B. Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti, G. Pampaloni, *Chem. Rev.* **2003**, *103*, 3857; c) Y. Tang, L. N. Zakharov, A. L. Rheingold, R. A. Kemp, *Organometallics* **2004**, *23*, 4788; d) D. B. Dell'Amico, F. Calderazzo, U. Englert, L. Labella, F. Marchetti, M. Specos, *Eur. J. Inorg. Chem.* **2004**, 3938; e) E. García-España, P. Gaviña, J. Latorre, C. Soriano, B. Verdejo, *J. Am. Chem. Soc.* **2004**, *126*, 5082; f) Y. Tang, W. S. Kassel, L. N. Zakharov, A. L. Rheingold, R. A. Kemp, *Inorg. Chem.* **2005**, *44*, 359.

[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, $V = 8883.7(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.108$ g cm^{-3}, $\mu = 0.199$ mm^{-1}, $\lambda = 0.71073$ Å, transmission range 0.9520–0.9247, crystal size $0.40 \times 0.40 \times 0.25$ mm^3. A total of 29148 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 *C*2/*c*, $a = 30.5742(6)$, $b = 17.5555(3)$, $c = 21.1478(4)$ Å, $\beta = 127.6215(9)°$, $V = 8990.7(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.104$ g cm^{-3}, $\mu = 0.196$ mm^{-1}, $\lambda = 0.71073$ Å, transmission range 0.963–0.883, crystal size $0.25 \times 0.25 \times 0.22$ mm^3. A total of 52985 unique reflections were collected on a Nonius KappaCCD diffractometer at 150 K in the θ range 1.43–25.00°. Full-matrix 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.

[7] C. E. Holloway, M. Melnik, *J. Organomet. Chem.* **1994**, *465*, 1.

[8] a) K. K. Pandey, *Coord. Chem. Rev.* **1995**, *140*, 37; b) X. Yin, J. R. Moss, *Coord. Chem. Rev.* **1999**, *181*, 27.

[9] A. Cornia, A. Caneschi, P. Dapporto, A. C. Fabretti, D. Gatteschi, W. Malavasi, C. Sangregorio, R. Sessoli, *Angew. Chem.* **1999**, *111*, 1897; *Angew. Chem. Int. Ed.* **1999**, *38*, 1780.

[10] Elemental analysis (%) calcd for **1** ($C_{51}H_{120}Al_3Mg_3N_3O_{15}Si_6$): C 45.84, H 9.05, N 3.14, Mg 5.45; found: C 45.39, H 8.83, N 3.21, Mg, 5.31. Deviations from calculated values are attributed to the extremely air sensitive and hygroscopic nature of this compound.

[11] a) N. E. Schlörer, S. Berger, *Organometallics* **2001**, *20*, 1703; b) C. S. McCowan, T. L. Groy, M. T. Caudle, *Inorg. Chem.* **2002**, *41*, 1120.

[12] A. K. Brisdon, *Inorganic Spectroscopic Methods*, Oxford, New York, **1998**, chap. 2, p. 23.