Structure Elucidation

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Fixation of CO_2 by Magnesium Cations: A Reinterpretation**

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Identifying the factors which determine the remarkable variety of bonding modes in the coordination of CO_2 to metal centers[1] is central to controlling electron transfer and ultimately the reactivity.[2–4] In this respect, it seems legitimate to state that d electrons are of critical importance since CO_2 coordination was never observed in d^0- or main-group-metal systems.[1] Furthermore, the CO_2 oxygen atoms do not possess sufficient basicity to form stable adducts with Lewis acids. The sole case of a genuine end-on-bound CO_2 complex[5] involves a very strongly reducing trivalent uranium center, for which it seems likely that partial electron transfer plays a role. Nevertheless, CO_2 is only weakly bound in this complex. As a rule with no exception until very recently, only low- and medium-valent metals have been used for CO_2 coordination. For these reasons, the recent findings[6] describing the robust end-on coordination of CO_2 to magnesium cations with formation of the unprecedented Mg/Al-containing cluster $[\{R_2Al(\mu\text{-}NSiMe_3)(\mu\text{-}OSiMe_3)Mg(thf)_2(\mu\text{-}O_2C)\}_3]\cdot 2\,thf$ (R = Me (**1a**), Et (**1b**)), certainly appear to be a major breakthrough. Not only do compounds **1** represent the first case of CO_2 coordination to a non-transition-metal center in an unprecedented bridging end-on fashion, but also the *irreversible* fixation occurs in THF, the oxygen atom of which is normally regarded as a far better donor than the oxygen atoms of CO_2.

We have revisited the experimental data and, on the basis of additional observations, propose herein that the triatomic units that bridge the magnesium atoms end-on, believed to be CO_2, are in reality isoelectronic NCO anions.

The formation of complexes **1a**,**b** was originally rationalized by assuming the attack of CO_2 at only one silazanate group.[6] It was not explanined why the second silazanate group did not follow the same fate in the presence of excess CO_2. Also, no conclusive evidence was provided for the identification of the bridging imido group generated by the attack of Me_3Al on the intermediate $[Mg(OSiMe_3)\{N(SiMe_3)_2\}]$. The presence of disorder between the imido and silanolate group with equal occupancy was claimed to account for the crystallographic equivalency of the two donor atoms bridging the Al and Mg centers. This interpretation was the only possibility to have the charges balanced within the complex if the triatomic unit bridging the three Mg atoms has to be CO_2. The NMR spectra unexplainably showed *only one resonance* for the silanolate and silylimido groups together.

To our surprise, geometry optimization[7] of the full complex **1a** as well as several simplified model compounds invariably led to fragmentation of the complex and release of CO_2, which thus appears *not* to be strongly bound at all (Figure 1a). This finding in turn made us question the assumptions behind the assignment of the structure of the complex.

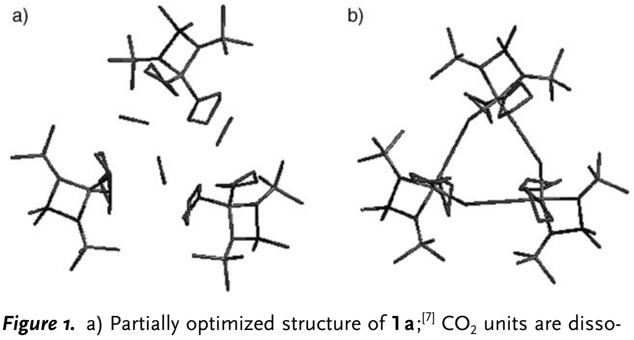

Figure 1. a) Partially optimized structure of **1a**;[7] CO_2 units are dissociating. b) Optimized structure of **1a** with N and O atoms exchanged.

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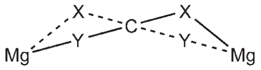
By strictly following the preparation of Chang et al.,[6] we therefore reprepared complex **1a** as air-sensitive, colorless crystals. The crystal structure confirmed the formula $[\{Me_2Al(\mu\text{-}ESiMe_3)_2Mg(thf)_2(\mu\text{-}E_2C)\}_3]\cdot 1.5\,thf$ (E = O, N, or a combination of both; see the Supporting Information). The lattice molecule of thf gave better refinement when refined with partial occupancy. We found no indication whatsoever for the presence of any sort of disorder involving the two atoms bridging the Mg and Al centers. These two bridging atoms could be best refined as only oxygen atoms of silanolate groups (arbitrarily attributing a 50% nitrogen character to these bridging atoms, in accordance with the silanolate/imido formulation proposed by Chang et al., increased the final convergence factor by 0.7%). Instead, the X-ray structure showed a 50:50 disorder in the three-atom XCY units bridging the Mg atoms (Scheme 1).[8] Each arrangement of the XCY unit has a bent Mg-X-C geometry and a nearly linear Mg-Y-C geometry; the carbon atoms of the two arrangements coincide. The distinctly different angles around X and Y suggest that they are, in fact, different atoms, as the symmetrical CO_2 molecule would not be expected to prefer very different bond angles at its two oxygen atoms. Assuming that the atoms bridging the Mg and Al centers are all oxygen atoms, electroneutrality requires the XCY units to be NCO. The X-ray data do not allow us to distinguish between N and O assignments for the X and Y atoms; these atoms refine equally well as either N or O, or as a mixture of both. In line with the calculations described below, we refined the X atoms as oxygen and the Y atoms as nitrogen. The negative charge of the bridging unit could well explain the robust coordination to the Mg centers in the presence of a Lewis base such as thf. Indeed, DFT geometry optimization[7] of the N/O-switched molecule and simplified model compounds resulted in geometries very close to the observed one (Figure 1b). In particular, the peculiar bent coordination *at one end only* of "CO_2" is now nicely reproduced.



Scheme 1. Disorder in bridging XCY units.

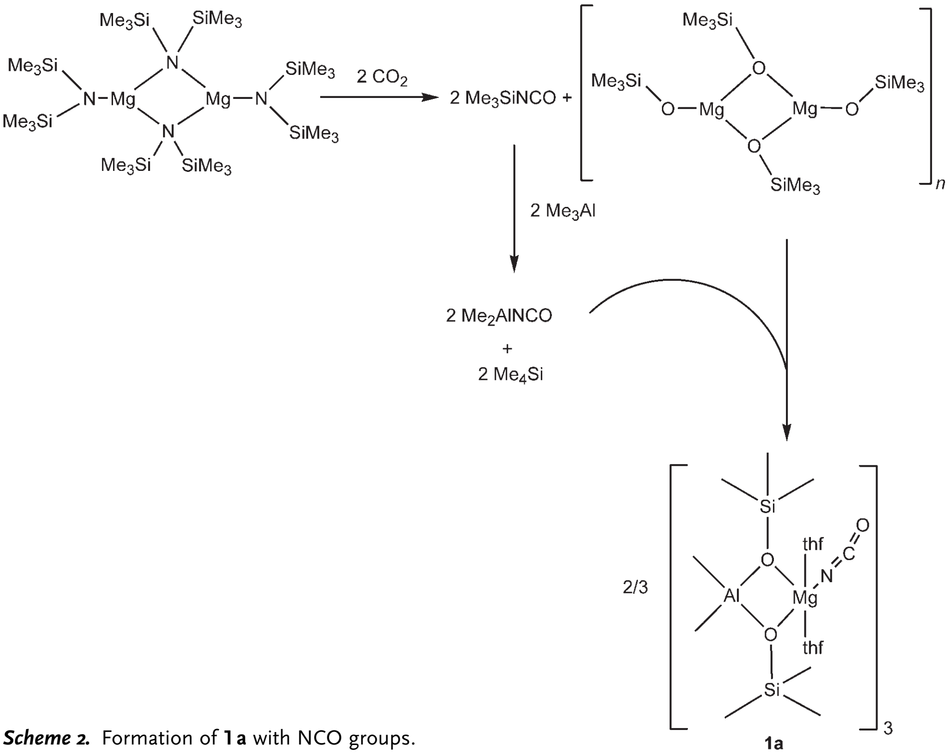
Calculations were also helpful in explaining the preferential formation of a trimeric structure. The NCO unit prefers a nearly linear geometry at the N atom and a bent geometry at the O atom already in the hypothetical monomeric compound $[Me_2Al(OSiMe_3)_2Mg(thf)_2(NCO)]$ (Mg-N-C 163°; $[Me_2Al(OSiMe_3)_2Mg(thf)_2(OCN)]$: Mg-O-C 128°). In a hypothetical dimeric structure, bending at the N atom cannot be avoided, although it remains less than the bending at the O atom ($[\{Me_2Al(OSiMe_3)_2Mg(thf)_2(\mu\text{-}NCO)\}_2]$: Mg-N-C 150°, Mg-O-C 123°). Trimer formation, however, fully relieves angle strain by allowing linear coordination at the N atom, as seen in both the X-ray structure and the calculated geometry (Mg-N-C 168°, Mg-O-C 142°).

^{1}H NMR spectra of **1a** in [D$_8$]THF showed only one sharp proton resonance for the silanolate group and one for the Al–CH_3 groups at $\delta = 0.06$ and -0.97 ppm, respectively. Although Me_3Si groups that are bound at either N or O could in principle produce identical chemical shifts in the ^{1}H NMR spectra, this coincidence is much less likely in the ^{13}C NMR spectra, which *also* showed only one resonance each for the Me_3Si and Al–CH_3 groups (at $\delta = 3.21$ and -5.22 ppm, respectively). The ^{29}Si NMR spectrum (in [D$_8$]toluene) showed only one resonance at $\delta = 14.13$ ppm in the temperature range 355–223 K rather than the two resonances which would be expected if both silanolate and silylimido groups were to be present in the complex. On the other hand, two nonequivalent Me_3Si groups could be expected in principle for a bis(silanolate)-bridged complex (*cis* and *trans* to N of the NCO bridge; see Figure 1b). Indeed, cooling of the solution resulted in splitting of the silanolate resonances in the ^{1}H NMR spectrum, thus giving rise to two singlets at 203 K. The variable-temperature ^{29}Si NMR spectrum showed a far more complex solvent-dependent fluxional behavior for which no straightforward interpretation is possible at this stage. Evidently, a dynamic process, possibly involving opening of the 12-membered $\{Mg(NCO)\}_3$ ring, exchanges the silanolate groups at higher temperature. Furthermore, there is some indication of further broadening of the signal of the Me groups attached to the Al centers, which might take place at even lower temperatures. Considering that the structure is formed by three different anions ($OSiMe_3$, NCO, Me) which may scramble with different ratios over the two cations and further form mono- and polynuclear structures, a very complex fluxional behavior can be anticipated.

Finally, the ^{14}N NMR spectrum gave a rather broad resonance at $\delta = -304.67$ ppm (the resonance of silazanate groups occurs in the region around $\delta = -338$ ppm) which is in the expected region for the NCO group. In addition, chemical degradation of **1a** with a diluted solution of aqueous KOH at pH 8 and subsequent centrifugation of $Al(OH)_3$ and $Mg(OH)_2$, neutralization with HNO_3, and treatment with $AgNO_3$, afforded a colorless precipitate of Ag(NCO), which showed the characteristic intense resonance at 2176 cm^{-1} in the IR spectrum.

A possible rationalization for the formation of $[\{Me_2Al(\mu\text{-}OSiMe_3)_2Mg(thf)_2(\mu\text{-}OCN)\}_3]\cdot 1.5\,thf$ may consist of the reaction of $[\{[(Me_3Si)_2N]Mg[\mu\text{-}N(SiMe_3)_2]\}_2]$[9] with CO_2 to afford Me_3SiNCO (Scheme 2). In turn, Me_3SiNCO reacts with Me_3Al to form the NCO anions which are incorporated into the final trinuclear cluster. In partial support of this speculation, the formation of Me_3SiNCO was clearly observed in the GC–MS of the solution that was obtained from exposure of a solution of $[\{[(Me_3Si)_2N]Mg[\mu\text{-}N(SiMe_3)_2]\}_2]$[9] to CO_2. Reaction of Me_3Al with Me_3SiNCO in the stoichiometric ratio 1:1 completely consumed the two starting materials to afford a complex mixture from which, besides Me_4Si (confirmed by GC), no component could be conclusively identified. Nonetheless, the crude reaction mixture that was obtained upon solvent evaporation produced a broad resonance in the ^{14}N NMR spectrum at $\delta = -248$ ppm and a series of four IR absorptions (2255, 2202, 2143, 2065 cm^{-1}), which can only be attributed to Al-coordinated NCO anions.

In conclusion, our observations suggest that, rather than a sensational case of irreversible fixation of CO_2 at magnesium cations, complex **1a** is more reasonably formulated as



Scheme 2. Formation of **1a** with NCO groups.

the isocyanate derivative $[\{Me_2Al(\mu\text{-}OSiMe_3)_2Mg(thf)_2(\mu\text{-}OCN)\}_3]\cdot 1.5\,thf$.

Experimental Section

All experiments were conducted inside a drybox equipped with a vacuum-line manifold to supply CO_2. Chemical-degradation experiments were carried out in air on samples weighed inside a drybox. All the NMR spectra were recorded on a Varian spectrometer (500 MHz) by using NMR tubes that were prepared inside a drybox and flame sealed.

1a: A solution of $AlMe_3$ (2.0 M in toluene, 2.2 mL, 4.4 mmol) was added dropwise to a solution of $[\{[(Me_3Si)_2N]Mg[\mu\text{-}N(SiMe_3)_2]\}_2]$ (1.5 g, 2.17 mmol) in THF (20 mL). The resulting solution was cooled in an ice bath and stirred for 2 h in an atmosphere of carbon dioxide. The resultant solution was concentrated to a smaller volume (10 mL) and cooled in a freezer. Colorless crystals of **1a** separated upon standing five days (yield: 21%). ^1H NMR (500 MHz, $[D_8]$THF, 23°C): $\delta = -0.97$ (s, 18H, Al-CH_3), 0.06 (s, 54H, $OSiMe_3$), 1.78 (m, 30H, thf), 3.59 ppm (m, 30H, thf); ^{13}C NMR (125.72 MHz, $[D_8]$THF, 23°C): $\delta = -5.22$ (Al-CH_3), 3.21 ($OSiMe_3$), 67.65 (thf), 25.21 (thf), 120.98 ppm (NCO); ^{29}Si NMR (99.32 MHz, $[D_8]$THF, 263 K): $\delta = 6.96$ ppm; ^{29}Si NMR (99.32 MHz, $[D_8]$toluene, 23°C): $\delta = 14.13$ ppm; ^{14}N NMR (36.12 MHz, $[D_8]$THF, 23°C): $\delta = -304.67$ ppm.

Crystal Data for **1a**: $C_{57}H_{132}Al_3Mg_3N_3O_{16.5}Si_6$, $M_r = 1446.07$, orthorhombic, space group *Pbcn*, $a = 12.526(4)$, $b = 25.615(6)$, $c = 28.167(6)$ Å, $V = 9037(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.063$ Mg m^{-3}, $T = 213$ K, absorption coefficient 0.194 mm^{-1}, $F(000) = 3144$, 39407 reflections collected, 4010 independent reflections, GoF = 1.099, $R = 0.0671$ ($I > 2\sigma(I)$), $wR2 = 0.1581$ ($I > 2\sigma(I)$). CCDC-606505 contains 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.

Coordinates for optimized structure of N/O-switched **1a** and simplified model compounds, including a partially dissociated structure for the originally proposed complex **1a**, in *xyz* format and an ORTEP drawing for **1a** with selected bond distances and angles can be found in the Supporting Information.

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119; A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3089; J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822) and b3-lyp levels (C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785; A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372; A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; note that the Turbomole functional "b3-lyp" is not identical to the Gaussian "B3LYP" functional) by employing the standard SV(P) basis sets (A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571).

[8] There was also disorder in some of the thf ligands bound to the Mg centers, which could be refined satisfactorily through partial splitting of the carbon atom positions.

[9] $C_{34}H_{72}Mg_2N_4Si_8$, $M_r = 690.20$, orthorhombic, space group *Pbcn*, $a = 18.040(8)$, $b = 14.888(7)$, $c = 18.038(8)$ Å, $V = 4270(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.074$ Mg m^{-3}, $T = 198$ K, absorption coefficient 0.301 mm^{-1}, $F(000) = 1520$, 14726 reflections collected, 3599 independent reflections, GoF = 1.039, $R = 0.0439$ ($I > 2\sigma(I)$), $wR2 = 0.1129$ ($I > 2\sigma(I)$).