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Steric and Solvent Effects on the CO_2 Fixation of Magnesium Compounds

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RMgBr (R=Ph,^{i}Pr) and MgY_2 (Y = ^{i}Pr, C≡CPh, NMe_2, NEt_2, NPh_2) react with carbon dioxide, yielding different bridging carboxylato and carbamato magnesium compounds: $[BrMg(\mu\text{-}O_2CPh)(THF)_2]_2$ (**1**) and $[Mg_n(O_2CY)_{2n}(Sol)_m]$ [$n = 3$, $m = 2$, Y = ^{i}Pr, Sol = THF (**2**), HMPA (HMPA = hexamethylphosphoramide) (**3**); $n = 3$, $m = 2$, Y = C≡CPh, Sol = THF (**4**); $n = 3$, $m = 2$, Y = NMe_2, Sol = THF (**5**), HMPA (**6**); $n = 6$, $m = 0$, Y = NEt_2 (**7**), and NPh_2 (**8**)]. The addition of HMPA/THF to hexamer **8** resulted in a deaggregation reaction, yielding the dimer $[Mg_2(O_2CNPh_2)_4(HMPA)_2]$ (**9**). Bubbling carbon dioxide into the THF solution of $Mg(N^iPr_2)_2$, we unexpectedly obtained two novel compounds: $[Mg_6(\mu_4\text{-}O)(O_2CN^iPr_2)_{10}]$ (**10**) and $[Mg_5(\mu_5,\eta_6\text{-}CO_3)(O_2CN^iPr_2)_8(HMPA)_2]$ (**11**), which were isolated from THF/hexane and HMPA/toluene solvents, respectively. X-ray crystallographic determinations were performed on compounds **1**, **3**, and **6**−**11**, which were found to be either linear or cage compounds, depending upon the steric size of Y and the bonding mode between magnesium atoms and the bridging carboxylato, carbamato, or carbonato. These compounds were characterized using ^1H, ^{13}C NMR, and IR spectroscopy, mass spectrometry, and elemental analyses.

Introduction

For several decades, in an attempt to use CO_2 as a one-carbon homologue, chemists have studied the fixation of CO_2 by organometallic compounds.[1−4] Recently, several observations regarding carbon dioxide fixation by magnesium compounds have been reported. In a previous study, we found that the reaction of $[Me_2Al(\mu\text{-}N^iPr_2)_2Mg(\mu\text{-}Me)]_4$ and $[Me_2Al(\mu\text{-}NEt_2)_2Mg(\mu\text{-}Me)]_2$ with CO_2 yields the carbamato dialuminum compounds $[(Me_2Al)_2(\mu\text{-}O_2CNR_2)_2]$ (R = ^{i}Pr, Et) and the aluminum−magnesium mixed metal compounds $[(Me_2Al)_2(\mu\text{-}O_2CNR_2)_4Mg]$ (R = ^{i}Pr, Et).[5] Parkin has reported that another acetato magnesium compound, $\{\eta^3\text{-HB(3-}^tBuPz)_3\}Mg(\eta^1\text{-}O_2CCH_3)$, can be produced by inserting CO_2 into $\{\eta^3\text{-HB(3-}^tBuPz)_3\}MgCH_3$.[6] Furthermore, Caudle et al. have described a carboxylate-shift-like dynamic equilibrium in bromomagnesium diethylcarbamate $[BrMg(\mu\text{-}Et_2NCO_2)(THF)_2]_2$.[7] In this area of research, because the organomagnesium compounds are extremely air-sensitive and hygroscopic, it is difficult to obtain single crystals. In our efforts to obtain suitable crystals for study by X-ray diffraction we found that the less bulky Y groups in MgY_2 (Y = ^{i}Pr, C≡CPh, NMe_2) react with CO_2, yielding linear magnesium carboxylato and carbamato trimers, but bulky Y groups in MgY_2 (Y = NEt_2, N ^{i}Pr_2, NPh_2) react with CO_2, yielding cage carbamato magnesium compounds (Scheme 1). A solvent effect was observed when the dimer $[Mg_2(O_2CNPh_2)_4(HMPA)_2]$ was obtained from the hexamer of cage compound $[Mg_6(O_2CNPh_2)_{12}]$ after adding HMPA/THF (HMPA = hexamethylphosphoramide).

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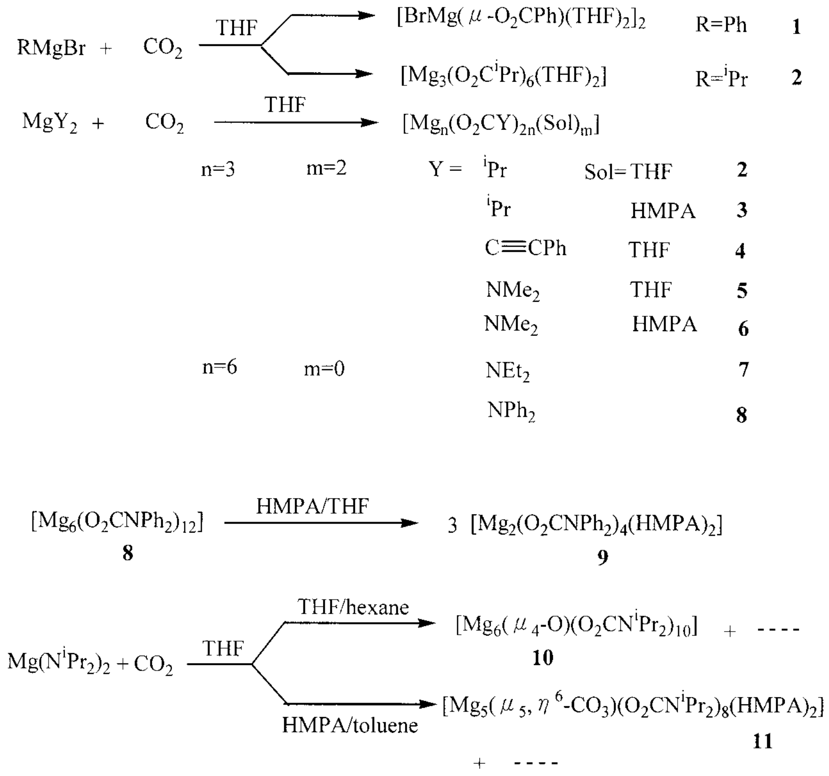
Scheme 1



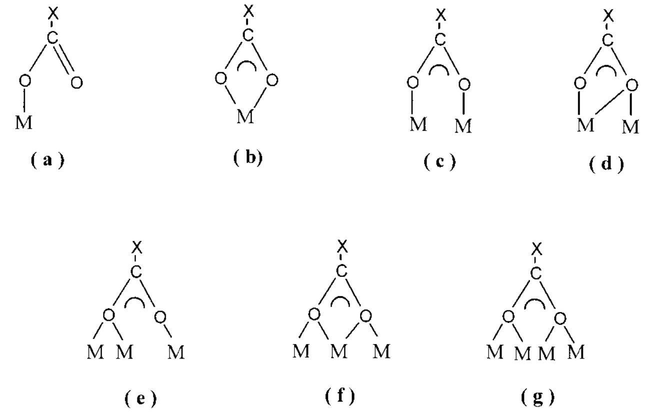


Figure 1. Possible bonding types of carboxylato (X: C), carbamato (X: N), and carbonato (X: O) ligands: (a) μ_1,η^1; (b) μ_1,η^2; (c) μ_2,η^2; (d) μ_2,η^3; (e) μ_3,η^3; (f) μ_3,η^4; (g) μ_4,η^4.

Results and Discussion

The products resulting from inserting carbon dioxide into Mg–C (alkyl) and Mg–N (amino) bonds are listed in Scheme 1 according to the steric size of alkyl and amino groups. The products can be divided into three categories: (1) linear, multinuclear carboxylato and carbamato magnesium compounds, such as **1**–**6** and **9**; (2) carbamato magnesium cage compounds, such as **7** and **8**; and (3) μ_4-O or μ_5-CO_3 carbamato magnesium cage compounds, such as **10** or **11**. Compounds **1**–**11** were fully characterized by ^1H, ^{13}C NMR, IR, and mass spectral data and elemental analyses. However, the elemental analyses for the authentic compound **10** caused some difficulty. Our analyses for the experimental stoichiometric ratio C(70):H(139.76):N(9.74) correspond closely with the theoretical ratio C(70):H(140):N(10). The X-ray structural analyses of compounds **1**, **3,** and **6**–**11** show various bonding types between the carboxylato and carbamato groups and magnesium, including types (c) (μ_2,η^2), (d) (μ_2,η^3), (e) (μ_3,η^3), and (g) (μ_4,η^4), shown in Figure 1.

Linear Multinuclear Carboxylato and Carbamato Magnesium Compounds. The binuclear compound **1** and trinuclear compounds **2**, **3**, **4**, **5**, and **6** were produced by bubbling gaseous carbon dioxide into a THF solution containing RMgBr (R = Ph, ^{i}Pr) or MgY_2 (Y = ^{i}Pr, C≡CPh, NMe_2) (Scheme 1). The compounds were then recrystallized using various solvents. Products **2**, **4**, and **5** were only soluble in HMPA or DMSO. In their ^1H NMR spectra, the aromatic protons of compounds **1** and **4** were observed in the regions δ 7.38–8.05 ppm and 7.36–7.46 ppm, respectively. For both compounds **2** and **3**, signals at δ 0.98, 2.26 and 1.39, 2.84 ppm were assigned to the isopropyl protons. Both the singlet at δ 2.75 ppm in compound **5** and the singlet at δ 2.95 ppm in compound **6** were assigned to the methyl protons. The ^{13}C NMR spectrum of compounds **1**–**6** showed signals at around δ 156–185 ppm and were thus assigned to the quaternary carbon of the CO_2 group.[8] The quaternary carbons of the acetylene group were observed at δ 76.21 and 89.46 ppm in compound **4**. In the mass spectrum of compound **2**, the ion peak at *m/e* 551 (relative intensity: 15%) was assigned as the fragment $[Mg_3(O_2C^iPr_2)_6]$-^{i}Pr. In all IR spectra of the compounds **1**, **2**, **3**, **4**, **5**, and **6**, the $\nu(CO_2)$ bands were always observed between 1599 and 1626 cm^{-1}, which is in the regions characteristic of metal carboxylate and carbamate compounds.[8a,9]

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Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for 1, 3, and 6

$[BrMg(\mu\text{-}O_2CPh)(THF)_2]_2$ (**1**)							
Mg−Br	2.4997(20)	Mg−O1	1.983(4)	Mg−O2	1.930(4)	Mg−O3	2.104(3)
O1−C1	1.255(7)	O2−C1	1.233(7)				
Br−Mg−O1	114.45(14)	Br−Mg−O2	118.02(17)	Br−Mg−O3	92.28(9)	O1−Mg−O2	127.52(21)
O1−Mg−O3	89.76(9)	O2−Mg−O3	88.24(9)	O3−Mg−O3	175.18(14)	O1−C1−O2	123.9(5)
$[Mg_3(O_2C^iPr)_6(HMPA)_2]$ (**3**)							
Mg(1)−O(1)	2.052(2)	Mg(1)−O(3)	2.068(2)	Mg(1)−O(5)	2.075(2)	Mg(2)−O(2)	1.964(2)
Mg(2)−O(4)	1.968(2)	Mg(2)−O(5)	2.181(2)	Mg(2)−O(6)	2.091(2)	Mg(2)−O(7)	1.948(2)
O(1)−C(1)	1.236(3)	O(2)−C(1)	1.263(3)	O(3)−C(5)	1.241(3)	O(4)−C(5)	1.264(3)
O(5)−C(9)	1.266(3)	O(6)−C(9)	1.257(3)				
O(1A)−Mg(1)−O(1)	180	O(1)−Mg(1)−O(3A)	87.92(9)	O(1)−Mg(1)−O(3)	92.07(9)	O(3A)−Mg(1)−O(3)	180
O(1)−Mg(1)−O(5)	89.24(7)	O(1)−Mg(1)−O(5A)	90.76(7)	O(3)−Mg(1)−O(5)	88.42(8)	O(3)−Mg(1)−O(5A)	91.58(8)
O(5A)−Mg(1)−O(5)	180	O(7)−Mg(2)−O(2)	98.43(9)	O(2)−Mg(2)−O(4)	117.75(10)	O(2)−Mg(2)−O(6)	114.14(10)
O(7)−Mg(2)−O(5)	157.18(9)	O(4)−Mg(2)−O(5)	94.13(8)	O(7)−Mg(2)−O(4)	96.86(9)	O(7)−Mg(2)O(6)	96.39(9)
O(4)−Mg(2)−O(6)	123.45(10)	O(2)−Mg(2)−O(5)	94.00(8)	O(6)−Mg(2)−O(5)	60.96(7)	O(1)−C(1)−O(2)	125.9(3)
O(3)−C(5)−O(4)	124.2(3)	O(6)−C(9)−O(5)	118.5(2)				
$[Mg_3(O_2NMe_2)_6(HMPA)_2]$ (**6**)							
Mg(1)−O(2)	2.094(2)	Mg(1)−O(4)	2.033(2)	Mg(1)−O(6)	2.045(2)	Mg(2)−O(1)	1.967(2)
Mg(2)−O(2)	2.179(2)	Mg(2)−O(3)	2.079(2)	Mg(2)−O(5)	1.972(2)	Mg(2)−O(7)	1.988(2)
O(2)−C(7)	1.271(3)	O(3)−C(7)	1.267(3)	O(4)−C(10)	1.255(3)	O(5)−C(10)	1.278(3)
O(6)−C(13)	1.260(3)	O(7)−C(13)	1.272(3)				
O(4A)−Mg(1)−O(4)	179.999(1)	O(4)−Mg(1)−O(6)	90.37(8)	O(4)−Mg(1)−O(6A)	89.63(8)	O(6)−Mg(1)−O(6A)	180
O(4)−Mg(1)−O(2A)	92.05(8)	O(6)−Mg(1)−O(2A)	92.10(7)	O(4)−Mg(1)−O(2)	87.95(8)	O(6)−Mg(1)−O(2)	87.90(7)
O(2A)−Mg(1)−O(2)	180.000(1)	O(1)−Mg(2)−O(5)	94.95(8)	O(1)−Mg(2)−O(7)	96.49(8)	O(5)−Mg(2)−O(7)	122.03(9)
O(1)−Mg(2)−O(3)	96.96(8)	O(5)−Mg(2)−O(3)	127.32(9)	O(7)−Mg(2)−O(3)	107.26(9)	O(1)−Mg(2)−O(2)	158.20(9)
O(5)−Mg(2)−O(2)	94.69(8)	O(7)−Mg(2)−O(2)	94.88(8)	O(3)−Mg(2)−O(2)	61.83(7)	O(3)−C(7)−O(2)	119.2(2)
O(4)−C(10)−O(5)	125.8(2)	O(6)−C(13)−O(7)	123.5(2)				

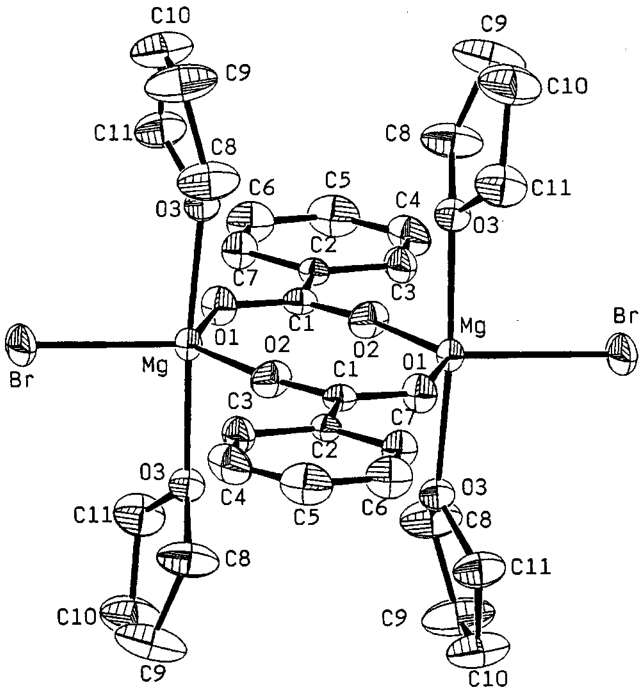

Figure 2. ORTEP view of the molecule $[BrMg(\mu\text{-}O_2CPh)(THF)]_2$ (**1**) using 50% probability ellipsoids. Hydrogen atoms have omitted for clarity.

The ORTEP representations of the compounds **1**, **3**, and **6** are shown in Figures 2−4. Selected bond lengths and bond angles are listed in Table 1. In compound **1**, two magnesium atoms are linked to the two $PhCO_2$ groups by type c bridging, giving them a coplanar eight-membered ring. A bromine atom and two THF oxygen atoms are coordinated to each magnesium atom, forming a distorted trigonal bipyramid. The mean Mg−O bond length in **1** (1.957 Å) was in good agreement with an Mg−O σ bond length, which has recently been found in the carboxylato dimer $[Mg_2(\mu\text{-}H_2O)(\mu\text{-}OAc)_2(imidazol)_4(OAc)_2]$ (Mg−μ-O: 2.083 Å)[10] and carbamato dimer $[BrMg(\mu\text{-}Et_2NCO_2)(THF)_2]_2$ (Mg−μ-O: 1.975 Å).[7] We found the lengths of the C−O bond (1.233(7) and 1.255(7) Å) to be shorter than the typical covalent single C−O bond (1.43 Å) and longer than the typical covalent double C═O bond (1.20 Å),[11] indicating of partial double-bond character. Similar values have been found for the closely related samarium compound (1.252(3) and 1.257(3) Å)[12] and another magnesium compound, (1.279(9) and 1.290(9) Å),[7] both having eight-membered ring structures.

As shown in Figures 3 and 4, compounds **3** and **6** display very similar skeletons. Each can be described as a centrosymmetric linear array of three magnesium atoms linked with isopropoxylato or dimethylcarbamato ligands, with type c and type d bonding between the magnesium atoms and their substituents. In compound **3**, the central magnesium Mg(1) has an almost regular octahedral configuration consisting of the bridging oxygen atoms of the isopropoxylato ligands. The outer magnesium atoms Mg(2) and Mg(2A) are additionally coordinated to an HMPA molecule to form distorted trigonal bipyramids. The Mg−O bond lengths of hexacoordinated Mg in type c are longer than those of pentacoordinated Mg. Comparing type c and type d bonding, it was found that the bridging ligands were linked in a similar manner across two magnesium atoms, the latter having another bond that interacts across the magnesium atom and oxygen atom to form a *terminal and bridging* structure.[13] This structure, found in compound **3**, contains two coplanar heterocyclic four-membered rings: Mg(2)O(5)C(9)O(6) and Mg(2A)O-

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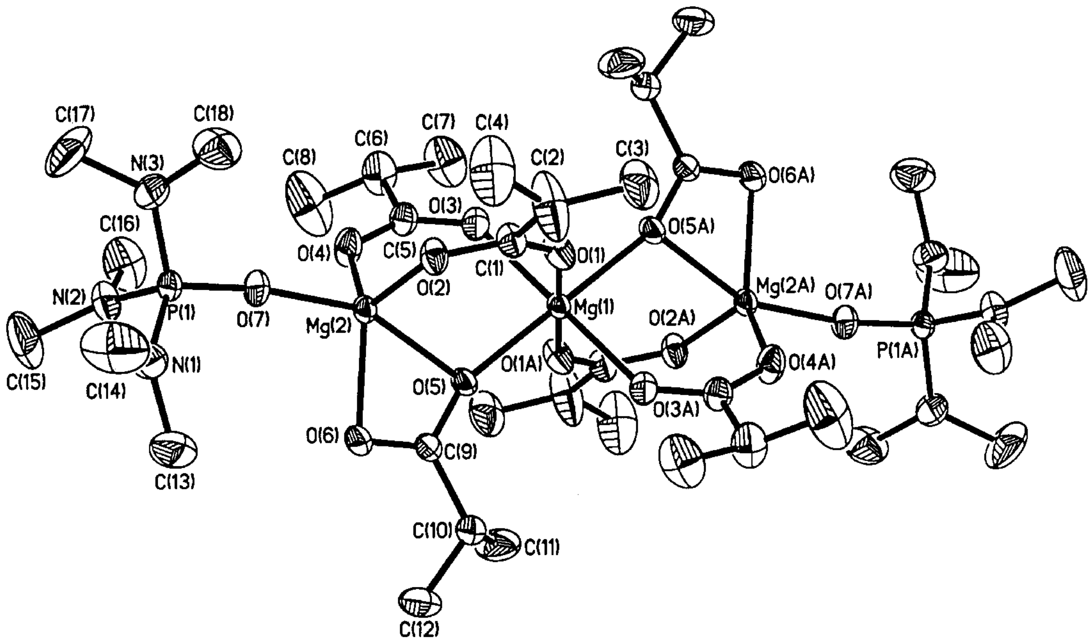

Figure 3. ORTEP view of the molecule $[Mg_3(O_2C^iPr)_6(HMPA)_2]$ (**3**) using 30% probability ellipsoids. Hydrogen atoms have omitted for clarity.

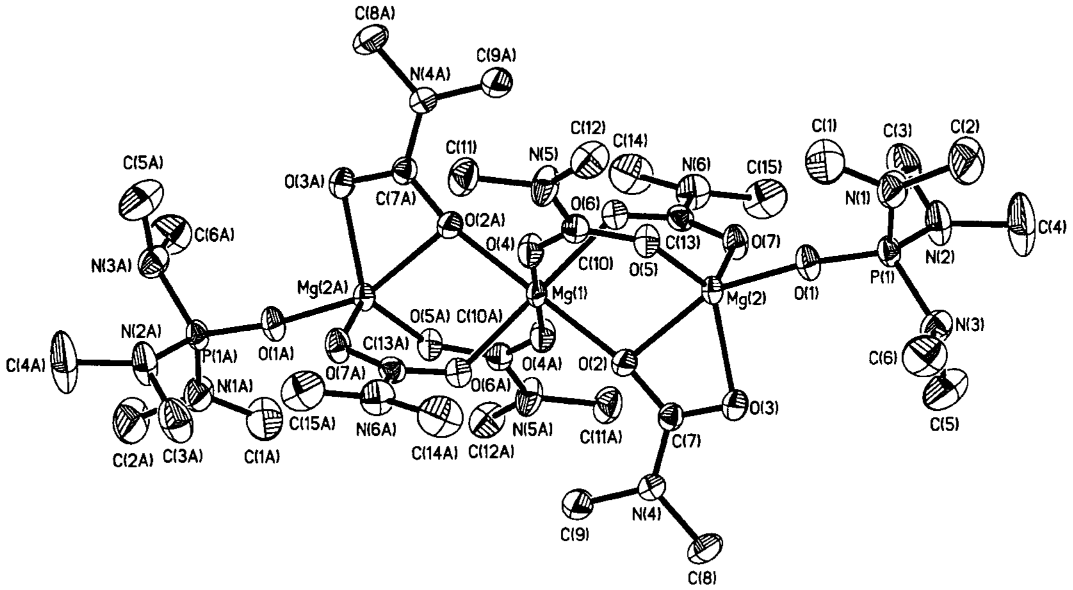

Figure 4. ORTEP view of the molecule $[Mg_3(O_2CNMe_2)_6(HMPA)_2]$ (**6**) using 50% probability ellipsoids. Hydrogen atoms have omitted for clarity.

(5A)C(9A)O(6A). There are three bond lengths found in the type d bonding: Mg(1)−O(5) (2.075(2) Å), Mg(2)−O(6) (2.091(2) Å), and Mg(2)−O(5) (2.181(2) Å), the latter being the longest. Moreover, the O−C−O angle in the four-member ring of type d was 118.5(2)°, which was compressed from the 125.9(3)° and 124.2(3)° angles in type c. Similar trends were observed in compound **6**, in which dimethylcarbamato ligands replaced the diisopropylcarboxylato ligands. The carbamate nitrogen atoms N(4), N(5), and N(6) found in compound **6** were nearly planar, the sum of bond angles being 360.0°, 359.2°, and 358.3°, respectively. Also, the C−N bond lengths (1.357−1.374 Å) are located between the typical C−N (1.47 Å) and C=N (1.27 Å) covalent distances.[14] These angles and bond lengths indicated that the nitrogen lone pair had been delocalized into the carboxyl group. Structures similar to those of compounds **3** and **6** have been found in other studies, including $[Co_3(PhCO_2)_6(quin)_2]$[15] and $[Zn_3(MeCH{=}CHCO_2)_6(C_9H_7N)_2]$.[16]

The CO_2 insertion reaction into phenylmagnesium bromide occurred selectively at the magnesium−carbon bond rather than the magnesium−bromide bond,[17] resulting in compound **1**, which had a bromine atom. To more fully understand the reactivity of CO_2 toward alkyl- and aryl-magnesium bromides, we inserted car-

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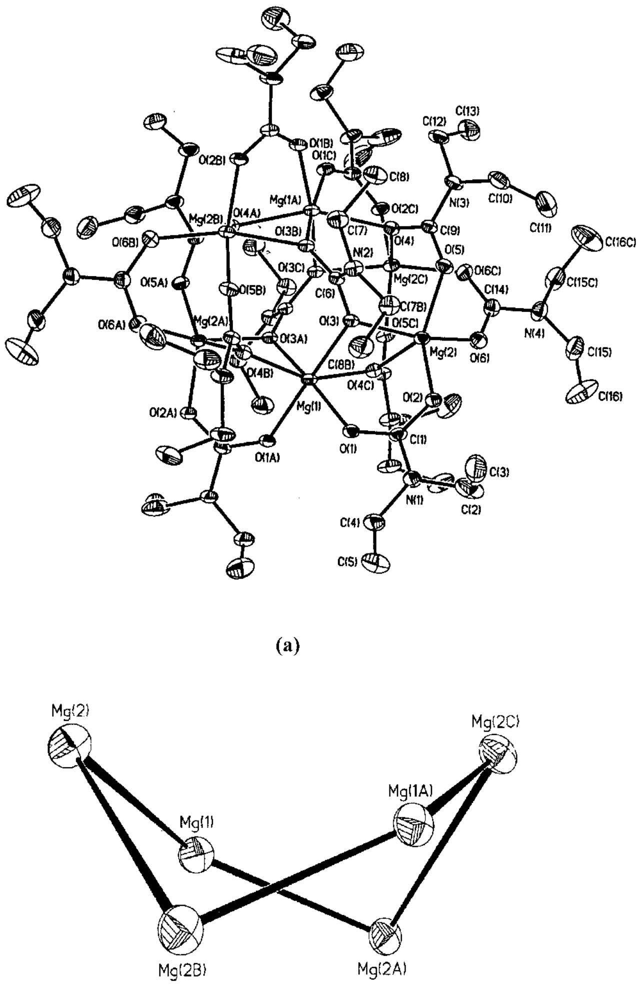
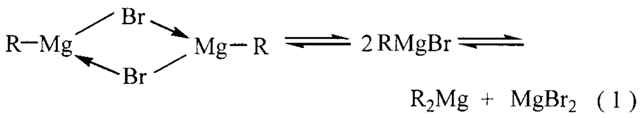


Figure 5. (a) ORTEP view of the molecule [$Mg_6(O_2CNEt_2)_{12}$] (**7**) using 30% probability ellipsoids. Hydrogen atoms have omitted for clarity. (b) Alternative view showing the Mg_6 core of **7**.

bon dioxide into isopropylmagnesium bromide. In doing so, we found that isopropylmagnesium bromide produced the trimeric compound **2**, which interestingly did not contain a bromine atom. This no doubt is due to the occurrence of the Schlenk equilibrium in solution (eq 1).[18] R_2Mg compounds are known to be more reactive than RMgBr,[19]and this provides a reasonable explanation for our observation.



$$R{-}Mg\langle Br_2\rangle Mg{-}R \rightleftharpoons 2\,RMgBr \rightleftharpoons R_2Mg + MgBr_2 \quad (1)$$

Cage Compounds of [$Mg_6(O_2CNEt_2)_{12}$] (7) and [$Mg_6(O_2CNPh_2)_{12}$] (8). Bis(diethylamido)magnesium and bis(diphenylamido)magnesium in the THF solution reacted with carbon dioxide. An immediate exothermic reaction took place that resulted in the crystallization of compound **7** from hexane and compound **8** from toluene. Figures 5a and 6a show the molecular structure of **7** and **8**, in which six magnesium atoms are linked together by diethylcarbamato or diphenylcarbamato ligands. Figures 5b and 6b show a Mg_6 core. The skeletons are described, respectively, as a twisted boat cyclohexane and a chair form cyclohexane. Compound **7** involves type c, type e, and type g bonding, while compound **8** involves type c and type e. Compound **7** possesses crystallographic C_{2v} symmetry and compound **8** C_i symmetry. In compound **7**, the magnesium in the molecule has two coordination geometries: (1) distorted octahedral configuration, including Mg(1) and Mg(1A), and (2) distorted square pyramidal configuration, including Mg(2), Mg(2A), Mg(2B), and Mg(2C). Around the magnesium atoms in compound **8**, only one kind of distorted trigonal bipyramidal configuration was observed. Selected bond lengths and bond angles of compounds **7** and **8** are listed in Table 2. In both compounds, the C−O bond lengths ranged between 1.234(5) and 1.289(4) Å, and the C−N bond lengths ranged between 1.331(5) and 1.411(5) Å, once again indicating delocalization over the O_2CN skeleton. It is interesting to note that the O−C−O angles in compounds **1**, **3**, **6**, **7**, and **8** are different and can be summarized as follows: type c > type e ≈ type g > type d (Tables 1 and 2).

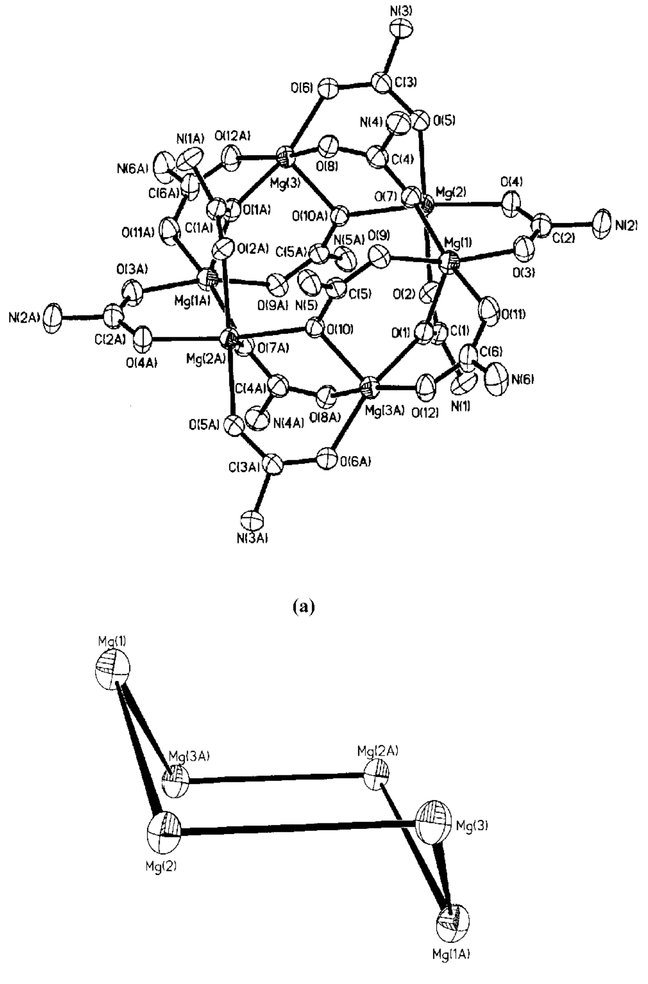


Figure 6. (a) ORTEP view of the molecule [$Mg_6(O_2CNPh_2)_{12}$] (**8**) using 30% probability ellipsoids. Carbon atoms of phenyl groups and hydrogen atoms have omitted for clarity. (b) Alternative view showing the Mg_6 core of **8**.

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 7, 8, and 9

$[Mg_6(O_2NEt_2)_{12}]$ (**7**)							
Mg(1)−O(1)	2.021(2)	Mg(1)−O(3)	2.084(2)	Mg(1)−O(4B)	2.165(2)	Mg(2)−O(2)	1.963(2)
Mg(2)−O(6)	1.987(3)	Mg(2)−O(5)	2.005(2)	Mg(2)−O(4C)	2.049(2)	Mg(2)−O(3)	2.100(2)
O(1)−C(1)	1.261(4)	O(2)−C(1)	1.275(4)	O(3)−C(6)	1.283(3)	O(4)−C(9)	1.289(4)
O(5)−C(9)	1.256(4)	O(6)−C(14)	1.271(3)	C(6)−O(3B)	1.283(3)	C(14)−O(6C)	1.27193)
O(1A)−Mg(1)−O(1)	87.15(13)	O(1)−Mg(1)−O(3)	86.65(8)	O(3)−Mg(1)−O(3A)	102.64(11)	O(1)−Mg(1)−O(4B)	109.76(9)
O(3)−Mg(1)−O(4B)	86.18(8)	O(1)−Mg(1)−O(4C)	88.38(8)	O(3)−Mg(1)−O(4C)	78.43(8)	O(4B)−Mg(1)−O(4C)	155.31(12)
O(2)−Mg(2)−O(6)	104.46(11)	O(2)−Mg(2)−O(5)	121.01(11)	O(6)−Mg(2)−O(5)	89.69(10)	O(2)−Mg(2)−O(4C)	99.19(10)
O(6)−Mg(2)−O(4C)	91.18(11)	O(5)−Mg(2)−O(4C)	138.14(10)	O(2)−Mg(2)−O(3)	92.27(9)	O(6)−Mg(2)−O(3)	162.43(10)
O(5)−Mg(2)−O(3)	86.16(9)	O(4C)−Mg(2)−O(3)	80.72(9)	O(1)−C(1)−O(2)	125.9(3)	O(3B)−C(6)−O(3)	121.3(4)
O(5)−C(9)−O(4)	122.5(3)	O(6)−C(14)−O(6C)	124.6(5)				
$[Mg_6(O_2CNPh_2)_{12}]$ (**8**)							
Mg(1)−O(1)	2.040(4)	Mg(1)−O(3)	1.998(4)	Mg(1)−O(9)	2.046(3)	Mg(1)−O(11)	1.993(3)
Mg(2)−O(2)	2.046(3)	Mg(2)−O(4)	2.008(3)	Mg(2)−O(5)	2.000(3)	Mg(2)−O(7)	2.042(3)
Mg(2)−O(10A)	2.074(3)	Mg(3)−O(1A)	2.054(3)	Mg(3)−O(6)	1.989(3)	Mg(3)−O(8)	2.053(4)
Mg(3)−O(10A)	2.032(3)	Mg(3)−O(12A)	2.008(3)	O(1)−C(1)	1.286(5)	O(2)−C(1)	1.235(5)
O(3)−C(2)	1.240(6)	O(4)−C(2)	1.262(6)	O(5)−C(3)	1.256(5)	O(6)−C(3)	1.253(5)
O(7)−C(4)	1.287(5)	O(8)−C(4)	1.234(5)	O(9)−C(5)	1.249(5)	O(10)−C(5)	1.282(5)
O(11)−C(6)	1.255(6)	O(12)−C(6)	1.248(6)				
O(11)−Mg(1)−O(3)	91.78(14)	O(11)−Mg(1)−O(1)	94.2(2)	O(3)−Mg(1)−O(1)	95.8(2)	O(11)−Mg(1)−O(9)	87.9(2)
O(3)−Mg(1)−O(9)	164.1(2)	O(1)−Mg(1)−O(9)	100.06(13)	O(11)−Mg(1)−O(7)	165.6(2)	O(3)−Mg(1)−O(7)	89.62(13)
O(1)−Mg(1)−O(7)	99.88(13)	O(9)−Mg(1)−O(7)	86.83(13)	O(5)−Mg(2)−O(4)	93.40(14)	O(5)−Mg(2)−O(7)	94.45(14)
O(4)−Mg(2)−O(7)	94.10(14)	O(5)−Mg(2)−O(2)	168.1(2)	O(4)−Mg(2)−O(2)	87.02(14)	O(7)−Mg(2)−O(2)	97.38(13)
O(5)−Mg(2)−O(10A)	91.06(12)	O(4)−Mg(2)−O(10A)	166.4(2)	O(7)−Mg(2)−O(10A)	98.38(12)	O(2)−Mg(2)−O(10A)	85.98(12)
O(6)−Mg(3)−O(12A)	93.7(2)	O(6)−Mg(3)−O(10A)	95.83(13)	O(12A)−Mg(3)−O(10A)	94.53(14)	O(6)−Mg(3)−O(8)	87.67(14)
O(12A)−Mg(3)−O(8)	168.1(2)	O(10A)−Mg(3)−O(8)	97.12(13)	O(6)−Mg(3)−O(1A)	163.5(2)	O(12A)−Mg(3)−O(1A)	90.30(13)
O(10A)−Mg(3)−O(1A)	99.87(13)	O(8)−Mg(3)−O(1A)	85.24(14)	O(2)−C(1)−O(1)	124.9(4)	O(3)−C(2)−O(4)	127.5(4)
O(6)−C(3)−O(5)	127.6(4)	O(8)−C(4)−O(7)	125.0(4)	O(9)−C(5)−O(10)	124.0(4)	O(12)−C(6)−O(11)	127.5(4)
$[Mg_2(O_2NPh_2)_4(HMPA)_2]$ (**9**)							
Mg(1)−O(1)	2.034(2)	Mg(1)−O(2A)	2.041(2)	Mg(1)−O(3)	2.022(2)	Mg(1)−O(4A)	2.060(2)
Mg(1)−O(5)	1.936(2)	O(1)−C(1)	1.255(3)	O(2)−C(1)	1.253(3)	O(3)−C(2)	1.250(3)
O(4)−C(2)	1.265(4)						
O(5)−Mg(1)−O(3)	106.36(9)	O(5)−Mg(1)−O(1)	102.46(8)	O(3)−Mg(1)−O(1)	85.34(8)	O(5)−Mg(1)−O(2A)	103.93(8)
O(3)−Mg(1)−O(2A)	87.55(8)	O(1)−Mg(1)−O(2A)	153.61(9)	O(5)−Mg(1)−O(4A)	100.95(9)	O(3)−Mg(1)−O(4A)	152.68(10)
O(1)−Mg(1)−O(4A)	89.26(8)	O(2A)−Mg(1)−O(4A)	85.51(8)	O(2)−C(1)−O(1)	127.4(2)	O(3)−C(2)−O(4)	126.0(3)

In the ^1H NMR spectrum of compound **7**, one set of multiplet signals at δ 2.89 (16H) could be assigned to the nonequivalent methylene protons of the O_2CNEt_2 ligands presently associated with N(1), N(1A), N(1B), and N(1C) in the crystal structure, two sets of multiplet signals at 3.21 (8H) and 3.54 (8H) with N(3), N(3A), N(3B), and N(3C), two sets of multiplet signals at 3.31 (4H) and 3.43 (4H) with N(4) and N(4A), and two sets of multiplet signals at 3.89 (4H) and 4.35 (4H) ppm with N(2) and N(2A). The resonance from the methylene protons of compound **7** proved useful in identifying the nature of the cage present in C_6D_6 solution. Also, by observing the methyl proton resonance of compound **7**, we found one set of many partial overlapping signals in the range δ 0.95−1.22 (60H) and a triplet at δ 1.38 (12H). In the ^{13}C NMR spectrum, four distinct signals at δ 163.26, 163.37, 163.68, and 163.97 ppm further indicated the quaternary carbon of the CO_2 groups arising from different bonding environments. Similarly, the ^1H NMR spectrum of compound **8** revealed complicated overlapping phenyl resonance in the region δ 6.83−7.63 ppm, and ^{13}C NMR revealed the quaternary carbon of the CO_2 group signals at around δ 144−147 ppm. For the compounds **7** and **8**, infrared spectra showed absorption bands at around 1622−1661 cm^{-1} assigned to the stretching frequencies of the NCO_2 moieties, which are characteristic frequencies in the IR spectra of metal carbamate compounds.[8a,9]

Why the cage compounds were generated from the bulky dialkylaminomagnesium compounds on CO_2 insertion was an interesting question that prompted us to investigate the structure of compounds **7** and **8**. In comparing the Mg−Mg−Mg angles in these two compounds, we found steric repulsion to be stronger in the Ph_2NCO_2 groups (for **8**), which had an angle of 103.28(5)°, than in the Et_2NCO_2 group (for **7**), which had an angle of 141.14(5)°. The Mg−Mg−Mg angles of compounds **3** and **6** were 180°. A comparison of this angle with the angles in compounds **7** and **8** revealed a stable linear trimer, which was probably formed because the Me_2NCO_2 was less bulky. Therefore, using a ligand with increased steric properties will bend a straight linear trimer, and by doing so we could generate a cage compound.

$[Mg_2(O_2CNPh_2)_4(HMPA)_2]$ (9) and the Solvent Effect on $Mg_6(O_2CNPh_2)_{12}$. Although the steric effect is very important for the formation of cage compounds, the effect of solvents on compound **8** also deserves mention. A new compound **9** was obtained in the attempted recrystallization of compound **8** from HMPA/THF solution. In the ^1H NMR spectrum of compound **9** a triplet at δ 6.38 ppm and one multiplet in the region δ 7.03−7.16 ppm were assigned to aromatic protons. The ^{13}C NMR spectrum showed a resonance at δ 164.37 ppm assignable to the quaternary carbon of the CO_2 unit. The infrared spectrum showed an absorption at 1596 cm^{-1} due to the stretching frequency of the NCO_2 moiety.[8a,9]

The structure of compound **9** was confirmed by single-crystal X-ray diffraction (Figure 7). A list of selected bond lengths and angles is provided in Table 2. The two magnesium atoms are bridged by four bidentate O_2CNPh_2 ligands in the form of a water-wheel-like structure, similar to those in $[Cu_2(CH_3COO)_4(Hbetain)_2]$[20] and $[Zn_2(MeCH{=}CO_2)_4(quinoline)_2]$.[21] The remaining coordination position for each magnesium atom was occupied by an HMPA oxygen atom, which resulted in

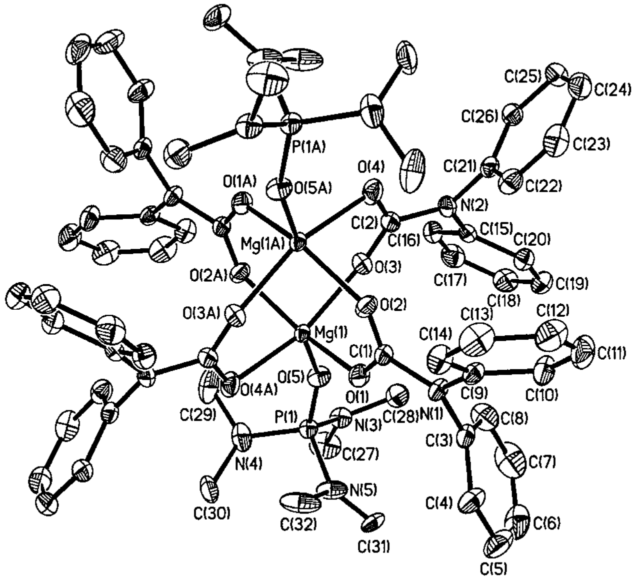

Figure 7. ORTEP view of the molecule $[Mg_2(O_2CNPh_2)_4(HMPA)_2]$ (**9**) using 30% probability ellipsoids. Hydrogen atoms have omitted for clarity.

the two magnesium centers having a distorted square pyramidal geometry. The magnesium centers of compound **8** were structurally the same as those of compound **9**. The carbamato groups were bonded to the magnesium atoms by means of type c bridging. The Mg−Mg distances of 3.150 Å in dimer **9** were shorter than those of 3.496 Å in trimer **3** and 3.459 Å in trimer **6**. The average Mg−O bond distance was 2.039 Å, which is also consistent with the single bond length of other molecules.[7,10] The observed C−O bond distances, which ranged from 1.250(3) to 1.265(4) Å, indicated that the C−O bond retained its partial double-bond character. The sum of the bond angles around N(1) and N(2) was nearly 360.0°, indicating an sp^2 structure. Compound **9** crystallized when the HMPA/THF solution was added to compound **8**. This happened almost spontaneously, so we could assume that compound **8** is highly sensitive to solvents. This effect has also been observed in the deaggregation of polymeric magnesium and zinc compounds with stronger donor solvents.[22,23]

Carboxylation Products of $Mg(N^iPr_2)_2$. $[Mg_6(\mu_4\text{-}O)(O_2CN^iPr_2)_{10}]$ (10) and $[Mg_5(\mu_5,\eta^6\text{-}CO_3)(O_2CN^iPr_2)_8(HMPA)_2]$ (11). On bubbling CO_2 into an $Mg(N^iPr_2)_2$ solution in THF for 5 min, the light yellow color of the solution instantaneously turned deep red. Small crystals of μ_4-oxo compound $[Mg_6(\mu_4\text{-}O)(O_2CN^iPr_2)_{10}]$ (**10**) were obtained upon addition of hexane. However, when CO_2 bubbled into the $Mg(N^iPr_2)_2$ solution in THF for 30 min, a color change from light yellow to red to orange occurred. Crystals of $[Mg_5(\mu_5\eta^6\text{-}CO_3)(O_2CN^iPr_2)_8(HMPA)_2]$ (**11**) were obtained by recrystallization with HMPA/toluene solution (Scheme 1). However, when the pure compound **10** was redissolved in THF and CO_2 was bubbled into the solution for 30 min, compound **11** was not isolated.

In compound **10**, the methyl proton resonance of its isopropyl group appeared as complicated overlapping multiplet signals in the region δ 0.85−1.53 ppm, and the methine proton appeared as four distinct sets of broad signals in the region δ 3.26, 3.61, 3.98, and 4.45. Such spectral complexity is consistent with a structure in solution, which contains three bonding types between the diisopropylcarbamato groups and magnesium atoms with different environments. However, the ^1H NMR spectrum of compound **11** showed only one doublet at δ 1.33 and a broad signal at δ 4.07, due to the isopropyl protons. The ^{13}C NMR spectra of compound **10** and **11** show signals at around 161−163 ppm, both assignable to the quaternary carbons of the CO_2 groups. The infrared spectra of **10** and **11** showed absorption at 1578 and 1590 cm^{-1}, respectively, which was caused by the stretching frequency of the NCO_2 moieties.[8,9a]

An ORTEP view of the compounds **10** is shown in Figure 8. A list of selected bond lengths and angles is provided in Table 3. X-ray diffraction established the structure of compound **10** consisted of a hexanuclear assembly of magnesium atoms joined together by μ_4-oxo ligands and diisopropylcarbamato bridges. The bonding between the diisopropylcarbamato groups with magnesium atoms in compound **10** involved type c, type e, and type g bridging. With respect to the oxygen atoms at each corner, the Mg(1) atom was centered within a distorted tetrahedral geometry, while Mg(2), Mg(3), Mg(4), Mg(5), and Mg(6) were centered within a distorted trigonal bipyramidal geometry. In compound **10** the Mg_6O system can also be considered to be one Mg_4O tetrahedron joined with $[Mg(O_2C^iPr_2)_2]_2$ on the edge. The coordination geometry of the oxygen atom to its four related magnesium atom was asymmetrical. This distorted structure resulted from linking the carbamato groups to Mg(5) and Mg(6). The distance from μ_4-oxo to the apical magnesium Mg(1)−O(1) (1.907(2) Å) is shorter than the distances from μ_4-oxo to the basal magnesium atoms (Mg(2)−O(1) 1.965(2), Mg(3)−O(1) 1.956(2), and Mg(4)−O(1) 1.972(2) Å). The Mg(1)−O(1) distance is shorter than the predicted ionic bond distance (2.05 Å)[11] or covalent bond distance (2.18 Å),[11] making Mg(1)−O(1) a strong bond. Furthermore, Mg(1)−O(1) is longer than that found in a tricoordinated magnesium compound $[\{(Me_3Si)_2N\}_4LiMg_2(O_2)_x(O)_y]$ (1.8575(4) Å),[24] but shorter than those found in pentacoordinated magnesium compounds Mg_4OBr_6 (1.952(8) Å)[25] and $[LiMg_4O(O\text{-}o\text{-}MeC_6H_4)_7\cdot 4THF]$ (2.041(2), 2.002(4) Å).[26]

X-ray crystallographic studies revealed the structure of compound **11**, shown in Figure 9. This compound consists of a pentanuclear assembly of magnesium atoms bridged by the oxygen atoms of the diisopropylcarbamato and carbanato groups. The diisopropylcarbamato bridging between magnesium atoms was type c and type d bridging, with each carbonato oxygen atom straddling the two magnesium atoms. Mg(1) was surrounded by oxygen atoms in a severely distorted octahedral manner at equatorial angles of 153.4° and 158.5°.

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Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for 10 and 11

$[Mg_6(\mu_4\text{-}O)(O_2CN^iPr_2)_{10}]$ (**10**)							
Mg(1)−O(1)	1.907(2)	Mg(1)−O(4)	1.936(3)	Mg(1)−O(6)	1.941(3)	Mg(1)−O(2)	1.944(2)
Mg(2)−O(1)	1.965(2)	Mg(2)−O(10)	1.978(2)	Mg(2)−O(3)	1.988(2)	Mg(2)−O(12)	2.149(2)
Mg(2)−O(8)	2.154(2)	Mg(3)−O(1)	1.956(2)	Mg(3)−O(14)	1.960(3)	Mg(3)−O(5)	1.993(2)
Mg(3)−O(16)	2.104(2)	Mg(3)−O(8)	2.266(2)	Mg(4)−O(1)	1.972(2)	Mg(4)−O(7)	1.974(3)
Mg(4)−O(18)	1.997(2)	Mg(4)−O(16)	2.078(2)	Mg(4)−O(12)	2.118(2)	Mg(5)−O(11)	1.979(2)
Mg(5)−O(20)	1.992(3)	Mg(5)−O(13)	2.062(3)	Mg(5)−O(19)	2.070(2)	Mg(5)−O(9)	2.095(2)
Mg(6)−O(21)	1.995(2)	Mg(6)−O(17)	2.002(2)	Mg(6)−O(15)	2.026(3)	Mg(6)−O(9)	2.036(2)
Mg(6)−O(19)	2.124(3)	O(2)−C(1)	1.278(4)	O(3)−C(1)	1.270(4)	O(4)−C(8)	1.279(4)
O(5)−C(8)	1.272(4)	O(6)−C(15)	1.270(4)	O(7)−C(15)	1.280(4)	O(8)−C(22)	1.289(4)
O(9)−C(22)	1.306(4)	O(10)−C(29)	1.266(4)	O(11)−C(29)	1.275(4)	O(12)−C(36)	1.308(4)
O(13)−C(36)	1.267(4)	O(14)−C(43)	1.269(4)	O(15)−C(43)	1.271(4)	O(16)−C(50)	1.303(4)
O(17)−C(50)	1.273(4)	O(18)−C(57)	1.264(4)	O(19)−C(57)	1.294(4)	O(20)−C(64)	1.277(4)
O(21)−C(64)	1.281(4)						
O(1)−Mg(1)−O(4)	108.90(11)	O(1)−Mg(1)−O(6)	112.57(11)	O(4)−Mg(1)−O(6)	104.53(12)	O(1)−Mg(1)−O(2)	111.95(11)
O(4)−Mg(1)−O(2)	113.28(11)	O(6)−Mg(1)−O(2)	105.39(12)	O(1)−Mg(2)−O(10)	168.79(11)	O(1)−Mg(2)−O(3)	100.81(10)
O(10)−Mg(2)−O(3)	88.80(10)	O(1)−Mg(2)−O(12)	79.56(9)	O(10)−Mg(2)−O(12)	89.99(10)	O(3)−Mg(2)−O(12)	128.06(11)
O(1)−Mg(2)−O(8)	84.62(9)	O(10)−Mg(2)−O(8)	96.03(11)	O(3)−Mg(2)−O(8)	118.06(11)	O(12)−Mg(2)−O(8)	113.70(9)
O(1)−Mg(3)−O(14)	163.21(10)	O(1)−Mg(3)−O(5)	103.22(10)	O(14)−Mg(3)−O(5)	93.57(10)	O(1)−Mg(3)−O(16)	81.71(9)
O(14)−Mg(3)−O(16)	90.42(10)	O(5)−Mg(3)−O(16)	116.93(10)	O(1)−Mg(3)−O(8)	81.89(9)	O(14)−Mg(3)−O(8)	89.89(10)
O(5)−Mg(3)−O(8)	120.95(10)	O(16)−Mg(3)−O(8)	121.98(9)	O(1)−Mg(4)−O(7)	105.64(10)	O(1)−Mg(4)−O(18)	164.93(11)
O(7)−Mg(4)−O(18)	89.38(11)	O(1)−Mg(4)−O(16)	81.96(9)	O(7)−Mg(4)−O(16)	114.43(11)	O(18)−Mg(4)−O(16)	93.11(10)
O(1)−Mg(4)−O(12)	80.16(9)	O(7)−Mg(4)−O(12)	118.74(11)	O(18)−Mg(4)−O(12)	91.64(10)	O(16)−Mg(4)−O(12)	126.64(11)
O(11)−Mg(5)−O(20)	98.08(11)	O(11)−Mg(5)−O(13)	91.06(10)	O(20)−Mg(5)−O(13)	117.82(10)	O(11)−Mg(5)−O(19)	168.78(11)
O(20)−Mg(5)−O(19)	88.15(10)	O(13)−Mg(5)−O(19)	94.27(10)	O(11)−Mg(5)−O(9)	91.57(10)	O(20)−Mg(5)−O(9)	97.21(10)
O(13)−Mg(5)−O(9)	144.10(10)	O(19)−Mg(5)−O(9)	78.35(9)	O(11)−Mg(5)−O(12)	91.35(9)	O(20)−Mg(5)−O(12)	169.31(10)
O(21)−Mg(6)−O(17)	56.65(8)	O(19)−Mg(5)−O(12)	83.39(9)	O(9)−Mg(5)−O(12)	87.49(8)	O(21)−Mg(6)−O(17)	127.57(10)
O(21)−Mg(6)−O(15)	99.79(10)	O(17)−Mg(6)−O(15)	91.37(10)	O(21)−Mg(6)−O(9)	99.52(10)	O(17)−Mg(6)−O(9)	131.13(10)
O(15)−Mg(6)−O(9)	92.83(10)	O(21)−Mg(6)−O(19)	88.49(10)	O(17)−Mg(6)−O(19)	89.37(10)	O(15)−Mg(6)−O(19)	168.90(10)
O(9)−Mg(6)−O(19)	78.42(9)	O(3)−C(1)−O(2)	124.2(3)	O(5)−C(8)−O(4)	124.0(3)	O(6)−C(15)−O(7)	123.5(3)
O(8)−C(22)−O(9)	118.4(3)	O(10)−C(29)−O(11)	123.6(3)	O(13)−C(36)−O(12)	119.2(3)	O(14)−C(43)−O(15)	124.1(3)
O(17)−C(50)−O(16)	121.7(3)	O(18)−C(57)−O(19)	122.4(3)	O(20)−C(64)−O(21)	123.6(3)		
$[Mg_5(\mu_5,\eta^6\text{-}CO_3)(O_2CN^iPr_2)_8(HMPA)_2]$ (**11**)							
Mg(1)−O(21)	1.980(3)	Mg(1)−O(6)	1.995(3)	Mg(1)−O(5)	2.047(3)	Mg(1)−O(4)	2.085(3)
Mg(1)−O(1)	2.143(3)	Mg(1)−O(3)	2.237(2)	Mg(2)−O(7)	1.940(3)	Mg(2)−O(8)	1.946(3)
Mg(2)−O(1)	1.960(2)	Mg(2)−O(10)	2.004(3)	Mg(2)−O(11)	2.284(3)	Mg(3)−O(14)	1.974(3)
Mg(3)−O(12)	1.995(3)	Mg(3)−O(9)	1.998(3)	Mg(3)−O(11)	2.056(3)	Mg(3)−O(2)	2.086(3)
Mg(4)−O(18)	1.975(3)	Mg(4)−O(15)	1.978(3)	Mg(4)−O(13)	2.034(3)	Mg(4)−O(2)	2.055(2)
Mg(4)−O(16)	2.077(3)	Mg(5)−O(19)	1.946(3)	Mg(5)−O(20)	1.952(3)	Mg(5)−O(3)	1.972(2)
Mg(5)−O(17)	1.989(3)	Mg(5)−O(16)	2.350(3)	O(1)−C(1)	1.282(4)	O(2)−C(1)	1.276(4)
O(3)−C(1)	1.282(4)	O(6)−C(14)	1.251(4)	O(7)−C(14)	1.278(4)	O(8)−C(21)	1.282(5)
O(9)−C(21)	1.260(5)	O(10)−C(28)	1.268(5)	O(11)−C(28)	1.281(4)	O(12)−C(35)	1.266(4)
O(13)−C(35)	1.262(4)	O(14)−C(42)	1.275(4)	O(15)−C(42)	1.266(4)	O(16)−C(49)	1.277(4)
O(17)−C(49)	1.277(4)	O(18)−C(56)	1.262(4)	O(19)−C(56)	1.268(4)	O(20)−C(63)	1.264(4)
O(21)−C(63)	1.264(4)						
O(21)−Mg(1)−O(6)	107.56(11)	O(21)−Mg(1)−O(5)	89.81(11)	O(6)−Mg(1)−O(5)	91.31(12)	O(21)−Mg(1)−O(4)	95.49(11)
O(6)−Mg(1)−O(4)	89.76(11)	O(5)−Mg(1)−O(4)	174.01(12)	O(21)−Mg(1)−O(1)	153.38(11)	O(6)−Mg(1)−O(1)	99.05(10)
O(5)−Mg(1)−O(1)	90.04(11)	O(4)−Mg(1)−O(1)	83.97(10)	O(21)−Mg(1)−O(3)	93.95(10)	O(6)−Mg(1)−O(3)	158.49(11)
O(5)−Mg(1)−O(3)	88.76(11)	O(4)−Mg(1)−O(3)	88.10(10)	O(1)−Mg(1)−O(3)	59.44(9)	O(7)−Mg(2)−O(8)	105.80(13)
O(7)−Mg(2)−O(1)	98.46(11)	O(8)−Mg(2)−O(1)	106.68(12)	O(7)−Mg(2)−O(10)	103.37(12)	O(8)−Mg(2)−O(10)	105.19(13)
O(1)−Mg(2)−O(10)	134.32(13)	O(7)−Mg(2)−O(11)	161.44(11)	O(8)−Mg(2)−O(11)	89.05(11)	O(1)−Mg(2)−O(11)	87.53(10)
O(10)−Mg(2)−O(11)	61.15(10)	O(14)−Mg(3)−O(12)	95.14(12)	O(14)−Mg(3)−O(9)	115.46(13)	O(12)−Mg(3)−O(9)	88.55(12)
O(14)−Mg(3)−O(11)	99.58(11)	O(12)−Mg(3)−O(11)	164.98(12)	O(9)−Mg(3)−O(11)	87.81(11)	O(14)−Mg(3)−O(2)	100.65(11)
O(12)−Mg(3)−O(2)	88.88(11)	O(9)−Mg(3)−O(2)	143.89(13)	O(11)−Mg(3)−O(2)	85.51(10)	O(18)−Mg(4)−O(15)	125.25(12)
O(18)−Mg(4)−O(13)	86.96(11)	O(15)−Mg(4)−O(13)	92.77(12)	O(18)−Mg(4)−O(2)	128.52(12)	O(15)−Mg(4)−O(2)	106.18(11)
O(13)−Mg(4)−O(2)	88.40(11)	O(18)−Mg(4)−O(16)	88.05(11)	O(15)−Mg(4)−O(16)	96.39(11)	O(13)−Mg(4)−O(16)	170.83(12)
O(2)−Mg(4)−O(16)	88.69(10)	O(19)−Mg(5)−O(20)	101.14(12)	O(19)−Mg(5)−O(3)	115.14(12)	O(20)−Mg(5)−O(3)	96.84(11)
O(19)−Mg(5)−O(17)	107.81(12)	O(20)−Mg(5)−O(17)	105.73(11)	O(3)−Mg(5)−O(17)	125.90(11)	O(19)−Mg(5)−O(16)	89.19(10)
O(20)−Mg(5)−O(16)	165.13(11)	O(3)−Mg(5)−O(16)	88.25(10)	O(17)−Mg(5)−O(16)	60.48(9)	O(2)−C(1)−O(3)	122.2(3)
O(2)−C(1)−O(1)	121.9(3)	O(3)−C(1)−O(1)	115.9(3)	O(6)−C(14)−O(7)	124.6(3)	O(9)−C(21)−O(8)	123.3(3)
O(10)−C(28)−O(11)	118.8(3)	O(13)−C(35)−O(12)	124.6(3)	O(15)−C(42)−O(14)	123.7(3)	O(16)−C(49)−O(17)	119.6(3)
O(18)−C(56)−O(19)	124.2(3)	O(20)−C(63)−O(21)	124.3(3)				

However, Mg(2), Mg(3), Mg(4), and Mg(5) were surrounded by a distorted trigonal bipyramidal configuration. The oxygen atoms of the C(1)O(1)O(3) moiety have a most unusual connection to the Mg(1), Mg(2), and Mg(5) atoms, insofar as this moiety is a bridging ligand that also acts as a chelating ligand, which is similar to type f. The Mg(1) atom bonded by the chelate appeared to form a coplanar four-membered ring with C(1), O(1), and O(3) atoms. The small 59.44° bond angle of O(1)-Mg(1)O(3) indicated a strong internal ring strain. Small OMO angles have also been observed in the μ-carbonatotrinickel compound $[Ni_3(N,N\text{-}Me_2en)_6(CO_3)(H_2O)_4](ClO_4)_4$ (61.4(5)°)[27] and μ-carbonatodirhodium compound $Rh_2(CO_3)(PPh_3)_5{\cdot}C_6H_6$ (62.6(6)°).[28] The Mg(1)−O(1) (2.143(3) Å) and Mg(1)−O(3) (2.237(3) Å) distances are longer than other Mg−O (1.960(2)−2.086(3) Å) distances. Because of its bridge and chelate interactions with the magnesium atoms, the carbonato moiety itself

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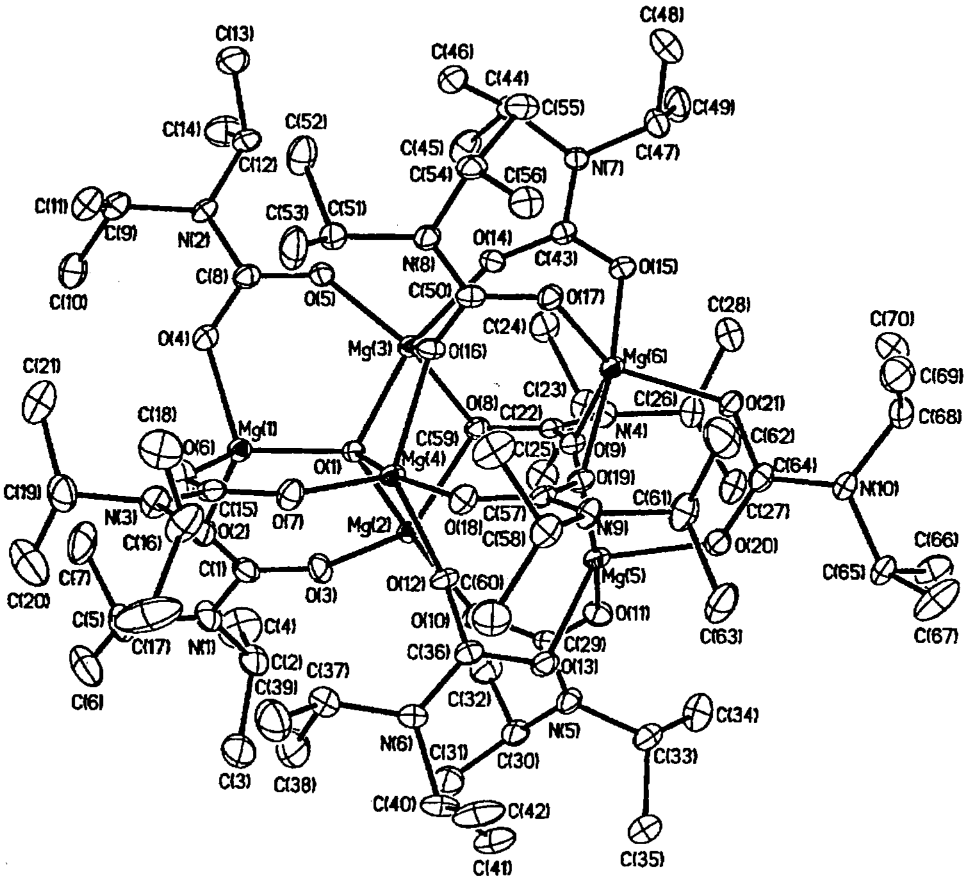

Figure 8. ORTEP view of the molecule $[Mg_6(\mu_4\text{-}O)(O_2CN^iPr_2)_{10}]$ (**10**) using 40% probability ellipsoids. Hydrogen atoms have omitted for clarity.

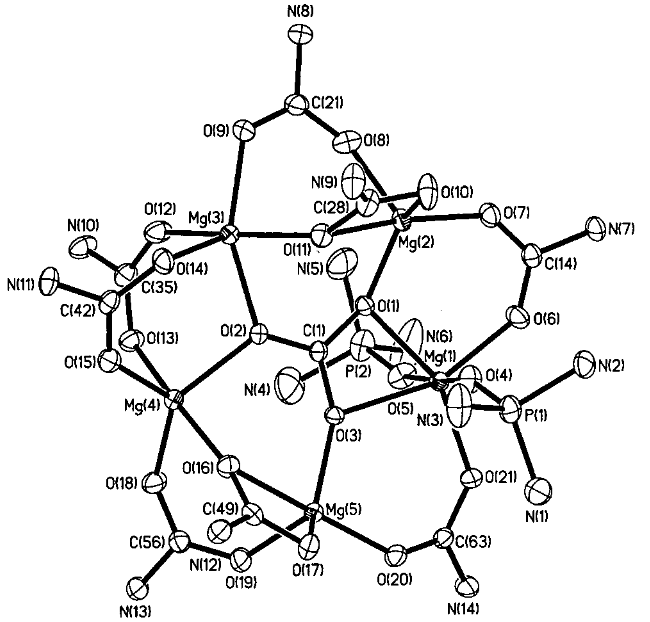

Figure 9. ORTEP view of the molecule $[Mg_5(\mu_5,\eta^6\text{-}CO_3)(O_2CN^iPr_2)_8(HMPA)_2]$ (**11**) using 30% probability ellipsoids. Carbon atoms of isopropyl groups and hydrogen atoms have omitted for clarity.

is distorted trigonal planar. Thus, the angles 121.9(3)° in O(1)C(1)O(2) and 122.2(3)° in O(2)C(1)O(3) are reduced to 115.9(3)° in O(1)C(1)O(3). Moreover, the mean C−O bond length of 1.28 Å in carbonate was in good agreement with those found in previously reported results, 1.277 Å in nesquehonite $MgCO_3{\cdot}3H_2O$[29] and 1.279 Å in hydromagnesite $Mg_5(CO_3)_4(OH)_2(H_2O)_4$.[30]

It was interesting to observe that compounds **3**, **6**, and **11** had the same bonding type (type d). The OMgO angles of type d in compound **3** (60.96°), **6** (61.83°), and **11** (61.15°, 60.48°) were very small. We noticed that are common feature of bonding type b, d, and f is the four-membered ring. The fact that we observed only types d and f, but, not type b, even in the literature, seems to indicate that the terminal bidentate can only exist when electron density on oxygen atoms is reduced by additional coordination to another metal center. The terminal bidentate bond angles of aluminum−magnesium[5,31,32] and magnesium[33] compounds with isothiocyanates, carbodimides, and carbon disulfide as ligands are shown in Scheme 2. Because the electron density at the oxygen atom is higher than at sulfur or nitrogen, it is hard to form CO_2 bonding with a magnesium atom in the highly internally strained four-membered ring structure (type b mode).

The source of the encapsulated-oxygen atom is still unknown. We recently reported that $[Me_2Al(\mu\text{-}N^iPr_2)_2\text{-}$

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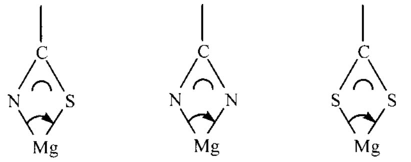
Scheme 2



$Me_2Al(\mu\text{-}{}^iPr_2N)_2Mg[({}^tBuN)C(Me)S]$	68.9(1)		
$Mg[(PhN)C(N^iPr_2)S]_2(THF)_2$	66.40(8)		
$Me_2Al(\mu\text{-}{}^iPr_2N)_2Mg[({}^iPrN)CMe(N^iPr)]$		65.6(3)	
$Me_2Al(\mu\text{-}{}^iPr_2N)_2Mg[({}^tBuN)CMe(N^tBu)]$		65.6(2)	
$Mg[{}^iPrNC(Ph)N^iPr]_2(THF)_2$		62.3(2)	
$Mg[({}^iPrN)_2CN^iPr_2]_2$ (THF)		63.0(2)	
$BrMg(S_2CPh)(THF)_3$			66.83(7)
$BrMg(S_2C^iPr)(THF)_3$			67.6(1)
$Mg(S_2CNEt_2)_2(THF)_2$			70.36(5), 69.91(5)
$Mg(S_2CN^iPr_2)_2(THF)$			72.34(6), 71.55(6)

$Mg(\mu\text{-}OMe)]_2$[34] could be obtained by the oxidation of $[Me_2Al(\mu\text{-}N^iPr_2)_2Mg(\mu\text{-}Me)]_4$. Mulvey et al. have also shown that the oxidized products of $[LiMg_4O(O\text{-}o\text{-}MeC_6H_4)_7]$[26] and $[\{(Me_3Si)_2N\}_4LiMg_2(O_2)_x(O)_y]$[24] were generated in situ by adventitious oxidation during reaction of a *n*-butyllithium/dibutylmagnesium mixture with bis(trimethylsily)amine and *o*-cresol, respectively. However, Calderazzo et al.[35,13] have reported that the hydrolysis of $[Al_2(O_2CN^iPr_2)_6]$ can generate $[Al_4(\mu\text{-}O)_2(O_2CN^iPr_2)_8]$ and that another hydrolysis product, $[U_4(\mu\text{-}O)_2(O_2CNEt_2)_{12}]$, was obtained from the reaction of a UCl_4 and $HNEt_2$ mixed solution when CO_2 was bubbled into it. Barron et al. have also demonstrated that hydrolysis of tri-*tert*-butylaluminum produces a series of alkylaluminoxanes $[({}^tBuAl)_2O]_n$ and $({}^tBuAlO)_n$.[36] In addition, Parkin et al. have isolated $\{[Tp^{Ar,Me}]Mg(\mu\text{-}OH)\}_2$[37] from the hydrolytic cleavage of magnesium−ligand bonds. In our own laboratory, we have isolated the intermediate product, $[Mg_3Br_4(OH)]^+[MgBr_3]^-$, obtained by reacting $[BrMg(S_2CPh)(THF)_3]$ with H_2O and $MgBr_2$ in a 1:1:3 molar ratio, and demonstrated the thermolysis of $[Mg_3Br_4(OH)]^+[MgBr_3]^-$, yielding the Mg_4Br_6O.[38] We prefer to believe that the contaminant is moisture rather than molecular oxygen.

Experimental Section

All experiments were carried out in an N_2 flushed glovebag, in a drybox, or in a vacuum using standard Schlenk techniques. Magnesium metal was purchased from Aldrich and used as received. PhMgBr, ${}^iPrMgBr$, $MgPr_2$, $Mg(C{\equiv}CPh)_2$, $Mg(NMe_2)_2$, $Mg(NEt_2)_2$, $Mg(N^iPr_2)_2$, and $Mg(NPh_2)_2$ were prepared by following the previous reports.[19,39] All solvents were distilled and degassed prior to use. All ${}^1H$, ${}^{13}C$, and ${}^{31}P$ spectra were measured on a Varian-300 spectrometer. Chemical shifts are referenced to either TMS(${}^1H$) or C_6D_6(${}^1H$, δ 7.15; ${}^{13}C\{{}^1H\}$, 128.00). ${}^{31}P$ NMR spectra were referenced to external 85% H_3PO_4. Mass spectra data were obtained on a VG-7025 GC/MS/MS spectrometer. IR spectra data were obtained on an FT-IR spectrometer. Elemental analyses (C, H, and N) were performed by the Analytsche Laboratorien of H. Malissa and G. Reuter GmbH, Germany. Deviations in the results from calculated values are attributed to the extremely air-sensitive and hygroscopic nature of these compounds.

Since all compounds were prepared in an analogous manner, a general synthetic route is described below, with any variation noted in the individual sections.

General Synthesis. Into a solution of the Grignard reagents RMgBr (R = Ph, ${}^iPr$) or MgY_2 (Y = ${}^iPr$, $C{\equiv}CPh$, NMe_2, NEt_2, N^iPr_2, NPh_2) in 100 mL of THF was bubbled an excess of gaseous carbon dioxide. An intermediate exothermic reaction ensued. The reaction mixture was divided into 12 8-mL bottles and was centrifuged, and the clear supernatant solution was evaporated to dryness in a vacuum. Colorless crystals were obtained by crystallization in various solvents or solvent mixtures.

$[BrMg(\mu\text{-}O_2CPh)(THF)_2]_2$ (1). PhMgBr (3.73 g, 20 mmol) was used, and small block crystals were obtained by recrystallization from benzene. Mp_{dec} > 88 °C. ${}^1H$ NMR $[(CD_3)_2SO]$: δ 1.73 (m, 8H, 3,4-thf *H*), 3.57 (m, 8H, 2,5-thf *H*), 7.38~7.41 (m, 3H, *m-H*/*p-H*), 8.05 (m, 2H, *o-H*). ${}^{13}C$ NMR $[(CD_3)_2SO]$: δ 135.67 (*ipso-C*), 172.25 (CO_2). IR (KBr, cm^{-1}): 1626 br (asm $-CO_2$). Anal. Calcd for $C_{36}H_{48}O_8Mg_2Br_2$: C, 49.95; H, 5.83; O, 17.76. Found: C, 48.62; H, 5.80; O, 17.20.

$[Mg_3(O_2C^iPr)_6(Sol)_2]$ [Sol = THF (2), HMPA (3)]. A solution of Mg^iPr_2 (5.71 g, 31.0 mmol) in 100 mL of THF was used. After carbon dioxide had been bubbled into the solution, 10 mL of hexane was added and the solution was cooled in a refrigerator, producing the white compound **2**. Subsequently, HMPA was added to dissolve **2**. After standing at room temperature for 24 h, small block crystals of **3** were deposited.

Compound **2**: ${}^1H$ NMR $[(CD_3)_2SO]$: δ 0.98 [d, 36H, $CH(CH_3)_2$], 1.76 (m, 8H, 3,4-thf *H*), 2.26 [m, 6H, $CH(CH_3)_2$], 3.60 (m, 8H, 2,5-thf *H*). ${}^{13}C$ NMR $[(CD_3)_2SO]$: δ 183.84 (CO_2). IR (KBr, cm^{-1}): 1582 m (asm $-CO_2$).

Compound **3**: Yield: 57%, mp_{dec} > 99 °C. ${}^1H$ NMR (C_6D_6): δ 1.39 [d, 36H, $CH(CH_3)_2$], 2.39 [d, 36H, $(Me_2N)_3PO$], 2.84 [br, 6H, $CH(CH_3)_2$]. ${}^{13}C$ NMR (C_6D_6): 185.42 (CO_2). ${}^{31}P$ NMR (C_6D_6): δ 24.09 [$(Me_2N)_3PO$]. IR (KBr, cm^{-1}): 1604 s (asm $-CO_2$). Anal. Calcd for $C_{36}H_{78}Mg_3N_6O_{14}P_2$: C, 45.32; H, 8.24; N, 8.81. Found: C, 45.46; H, 8.49; N, 9.09.

$[Mg_3(O_2CC{\equiv}CPh)_6(THF)_2]$ (4). $Mg(C{\equiv}CPh)_2$ (1.00 g, 4.4 mmol) was used. Small crystals were obtained by recrystallization from THF/hexane. Mp_{dec} > 160 °C. ${}^1H$ NMR $[(CD_3)_2SO]$: δ 1.74 (m, 8H, 3,4-thf *H*), 3.59 (m, 8H, 2,5-thf *H*), 7.36−

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Table 4. Crystal and Intensity Collection Data for Compounds 1, 3, 6, and 7

	1	**3**	**6**	**7**
formula	$C_{36}H_{48}O_8Mg_2Br_2$	$C_{36}H_{78}Mg_3N_6O_{14}P_2$	$C_{30}H_{72}Mg_3N_{12}O_{14}P_2$	$C_{60}H_{120}Mg_6N_{12}O_{24}$
fw	817.19	953.91	959.87	1539.54
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic
space group	*C*2/*m*	*C*2/*c*	$P2_{1/c}$	Ccca
a, Å	11.436(5)	24.5444(5)	9.4391(3)	20.9480(3)
b, Å	15.918(5)	11.51080(10)	11.0815(4)	25.1843
c, Å	12.217(3)	18.7256(4)	23.5656(8)	16.2816(1)
α, deg	90	90	90	90
β, deg	99.79(3)	91.1010(10)	91.777(1)	90
γ, deg	90	90	90	90
V, Å^3	2201.3	5289.5(2)	2463.8(2)	8589.53(14)
Z	2	4	2	4
D_{calc}, g/cm^3	1.233	1.198	1.294	1.191
μ, mm^{-1}	0.189	0.178	0.194	0.129
F(000)	844	2056	1028	3312
crystal size, mm	0.88 × 1.00 × 1.00	0.70 × 0.40 × 0.40	0.40 × 0.40 × 0.40	0.50 × 0.40 × 0.30
θ range, deg	8.88−15.50	1.66−26.83	1.73−26.38	1.62−25.02
no. of reflns collected	2055	12524	12356	17120
no. of ind reflns	2040	5379	5036	3806
transm factor (max, min)	1.000, 0.375	0.9280, 0.7230	0.9280, 0.8120	0.9281, 0.1053
T, K	298	200(2)	150(1)	295(2)
GOF	2.14	1.019	1.090	0.953
R1, wR2 ($>2\sigma$)	0.039, 0.038[a]	0.0594, 0.1536	0.0545, 0.1534	0.0566, 0.1593
R1, wR2 (all data)		0.0900, 0.1708	0.659, 0.1623	0.1054, 0.1850
largest diff peak and hole, e/Å^3	0.420, −0.400	0.596, −0.365	0.533, −0.394	0.320, −0.271

[a] $R_f = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$.

Table 5. Crystal and Intensity Collection Data for Compounds 8−11

	8·THF	**9**·THF	**10**·3THF	**11**·toluene
formula	$C_{160}H_{128}Mg_6N_{12}O_{25}$	$C_{68}H_{84}Mg_2N_{10}O_{11}P_2$	$C_{82}H_{164}Mg_6N_{10}O_{24}$	$C_{76}H_{156}Mg_5N_{14}O_{21}P_2$
fw	2764.60	1328.01	1820.09	1785.64
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a, Å	15.4528(6)	10.7465(2)	14.8404(3)	16.6733(3)
b, Å	15.5306(6)	18.7006(3)	22.4052(5)	23.0033(4)
c, Å	16.7324(6)	18.1833(2)	31.4608(6)	27.1890(2)
α, deg	103.826(1)	90	90	90
β, deg	103.406(1)	95.741(1)	96.481(1)	92.876(1)
γ, deg	109.074(1)	90	90	90
V, Å^3	3468.7(2)	3635.9(1)	10393.9(4)	10415.0(3)
Z	1	2	4	4
D_{calc}, g/cm^3	1.323	1.213	1.163	1.139
μ, mm^{-1}	0.114	0.140	0.116	0.137
F(000)	1444	1408	3960	3872
cryst size, mm	0.74 × 0.40 × 0.15	0.40 × 0.40 × 0.40	0.70 × 0.30 × 0.30	0.45 × 0.45×0.40
θ range, deg	1.33−25.00	1.57−26.37	1.12−25.00	1.16−25.00
no. of reflns collected	27391	17743	45636	43767
no. of ind reflns	11906	7297	18294	17897
transm factor (max, min)	0.9280, 0.7639	0.9280, 0.6872	0.9280, 0.6534	0.9280, 0.7593
T, K	150(2)	150(1)	100(2)	150(1)
GOF	1.062	1.050	1.059	1.045
R1, wR2 ($>2\sigma$)	0.0990, 0.2721	0.0599, 0.1570	0.0627, 0.1434	0.0791, 0.1864
R1, wR2 (all data)	0.1422, 0.3111	0.0793, 0.1689	0.1244, 0.1782	0.1080, 0.2045
largest diff peak and hole, e/Å^3	0.991, −0.531	0.574, −0.445	0.670, −0.428	1.472, −0.433

7.46 (m, 30H, C_6H_5). ^{13}C NMR [$(CD_3)_2SO$]: δ 122.13 (*ipso-C*), 156.54 (CO_2). IR (KBr, cm^{-1}): 1599 s (asm $-CO_2$). Anal. Calcd for $C_{62}H_{46}Mg_3O_{14}$: C, 68.45; H, 4.23. Found: C, 67.89; H, 4.42.

[$Mg_3(O_2CNMe_2)_6(Sol)_2$] [Sol = THF (5), HMPA (6)]. Mg(NMe)$_2$ (3.15 g, 46.0 mmol) was used. The procedures were similar to those used for compounds **2** and **3**.

Compound **5**: ^{1}H NMR [$(CD_3)_2SO$]: δ 1.74 (m, 8H, 3,4-thf *H*), 2.75 [br, 36H, N(C*H*$_3$)$_2$], 3.58 (m, 8H, 2,5-thf *H*). ^{13}C NMR [$(CD_3)_2SO$]: δ 162.51 (CO_2). IR (KBr, cm^{-1}): 1620 s (asm $-CO_2$).

Compound **6**: Mp$_{dec}$ > 95 °C. Yield: 68%. ^{1}H NMR (C_6D_6): δ 2.42 [br, 36H, (*Me*$_2$N)$_3$PO], 2.95 [d, 36H, N(C*H*$_3$)$_2$]. ^{13}C NMR (C_6D_6): δ 164.37 (CO_2). ^{31}P NMR (C_6D_6): δ 24.13 [(Me$_2$N)$_3$*P*O]. IR (KBr, cm^{-1}): 1601 s (asm $-CO_2$). Anal. Calcd for $C_{30}H_{72}Mg_3N_{12}O_{14}P_2$: C, 37.51; H, 7.56; N, 17.51. Found: C, 36.32; H, 7.42; N, 17.31.

[$Mg_6(O_2CY_2)_{12}$] [Y = NEt_2 (7), NPh_2 (8)]. For the preparation of **7**, Mg(NEt$_2$)$_2$ (0.62 g, 3.7 mmol) was used. The colorless crystals were obtained by recrystallization from hexane at room temperature. For the preparation of **8**, Mg(NPh$_2$)$_2$ (6.7 mmol) was used. Toluene was added for recrystallization, giving a deep violet solution. Small block crystals were obtained after the solution stood at room temperature for 2 days.

Compound **7**: Yield: 90%. Mp$_{dec}$ > 85 °C. ^{1}H NMR (C_6D_6): δ 1.14 (m, 60H, C*H*$_3$), 1.38 (t, 12H, C*H*$_3$), 2.89 (m, 16H, C*H*$_2$), 3.21 (m, 8H, C*H*$_2$), 3.31 (m, 4H, C*H*$_2$), 3.43 (m, 4H, C*H*$_2$), 3.54 (m, 8H, C*H*$_2$), 3.89 (m, 4H, C*H*$_2$), 4.35 (m, 4H, C*H*$_2$). ^{13}C NMR (C_6D_6): δ 163.26, 163.37, 163.68, and 163.97 (CO_2). IR (KBr, cm^{-1}): 1622 s (asm $-CO_2$). Anal. Calcd for $C_{60}H_{120}Mg_6N_{12}O_4$: C, 46.87; H, 7.86; N, 10.92. Found: C, 47.10; H, 7.87; N, 11.11.

Compound **8**: Yield: 83%. Mp$_{dec}$ > 49 °C. ^{1}H NMR (C_6D_6): δ 6.83−7.63 (m, 120H, C_6H_5). ^{1}H NMR (C_4D_8O): δ 6.91−7.25 (m, 120H, C_6H_5). ^{13}C NMR (C_4D_8O): δ 144.69, 144.78, and 146.57 (CO_2). IR (KBr, cm^{-1}): 1661 s (asm $-CO_2$). Anal. Calcd for $C_{156}H_{120}Mg_6N_{12}O_{24}$: C, 68.70; H, 4.49; N, 6.24. Found: C, 68.75; H, 4.62; N, 6.11.

$[Mg_2(O_2CNPh_2)_4(HMPA)_2]$ (9). Compound **8** was dissolved in HMPA/THF solvent. After the solution had stood at room temperature for 3 days, large block crystals were deposited. Yield: 67%. $Mp_{dec} > 142$ °C. ^{1}H NMR (C_6D_6): δ 2.35 [d, 36H, $N(CH_3)_2$]), 6.83 (t, 8H, *p-H*), 7.03~7.16 (m, 32H, *o/m-H*). ^{13}C NMR (C_6D_6): δ 144.39 (CO_2). ^{31}P NMR (C_6D_6): δ 24.75 [$(Me_2N)_3PO$]. IR (KBr, cm^{-1}): 1596 s (asm $-CO_2$). Anal. Calcd for $C_{64}H_{76}Mg_2N_{10}O_{10}P_2$: C, 61.21; H, 6.10; N, 11.15. Found: C, 61.38; H, 6.22; N, 11.40.

$[Mg_6(\mu_4\text{-}O)(O_2CN^iPr_2)_{10}]\cdot 3THF$, $[(10)\cdot 3THF]$. Into a solution of $Mg(N^iPr_2)_2$ (7.65 g, 34.1 mmol) in THF (100 mL) was bubbled an excess of carbon dioxide for 5 min. An exothermic reaction and a color change from light yellow to deep red were observed. After centrifugation, some solvent was removed in a vacuum, and then hexane (10 mL) was added. After the solution had stood at room temperature for 2 days, small colorless crystals were obtained. Yield: 38%. $Mp_{dec} > 63$ °C. ^{1}H NMR (C_6D_6): δ 0.85−1.53 (m, 132 H, $CH(CH_3)_2$ and 3,4-thf *H*), 3.26 [m, 6 H, $CH(CH_3)_2$], 3.61 (t, 12H, 2,5-thf *H*), 3.98 [br, 8H, $CH(CH_3)_2$], 4.45 [br, 2H, $CH(CH_3)_2$], 4.83 [br, 4H, $CH(CH_3)_2$]. ^{13}C NMR (C_6D_6): δ 161.32, 162.47, 162.72, 162.92, 163.08, 163.24, 165.36, 165.50, 165.63, and 165.81 (CO_2). IR (KBr, cm^{-1}): 1578 s (asm $-CO_2$). Anal. Calcd for $C_{70}H_{140}Mg_6N_{10}O_{21}$: C, 52.41; H, 8.72; N, 8.73. Found: C, 50.56; H, 7.81; N, 8.50.

$[Mg_5(\mu_5,\eta^6\text{-}CO_3)(O_2CN^iPr_2)_8(HMPA)_2]$ (11). A similar procedure was adopted. CO_2 bubbling time was 30 min. An exothermic reaction and a color change from light yellow to red to orange were observed. After centrifugation, the solvent was evaporated to dryness in a vacuum. Then, an HMPA/toluene mixture was added. The solution was kept room temperature. The solvent slowly evaporated until large block crystals formed. Yield: 21%. $Mp_{dec} > 54$ °C. ^{1}H NMR (C_6D_6): δ 1.33 [d, 48H, $CH(CH_3)_2$], 2.55 [d, 36H, $(Me_2N)_3PO$], 4.07 [br, 16H, $CH(CH_3)_2$]. ^{13}C NMR (C_6D_6): δ 162.49 (CO_2), 163.85 (CO_3). ^{31}P NMR (C_6D_6): δ 23.61 [$(Me_2N)_3PO$]. IR (KBr, cm^{-1}): 1590 s (asm $-CO_2$). Anal. Calcd for $C_{69}H_{148}Mg_5N_{14}O_{21}P_2$: C, 51.07; H, 8.81; N, 10.98. Found: C, 50.77; H, 9.08; N, 11.20.

Reaction of ^{i}PrMgBr with CO_2. Into a solution of ^{i}PMgBr (58 mmol) in THF (100 mL) was bubbled CO_2 gas for 20 min at room temperature. After centrifugation, the solution was evaporated to one-half volume. The solution was cooled in a refrigerator to obtain colorless crystals of $MgBr_2\cdot 4THF$. The crystals were filtered, and then some solvent was removed in a vacuum. Hexane (10 mL) was added to the filtrate solution. On cooling at 0 °C for 24 h, the white compound **2** was obtained, yielding 63%.

Structure Determination. Crystals for X-ray measurements were sealed in glass capillaries at room temperature and cooled to 200 K (**3**), 150 K (**6**, **8**, **9**, **11**), or 100 K (**10**) in a N_2 cold stream. Preliminary examinations and intensity data collections were carried out with a Enraf-Nonius CAD-4 automatic diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å). Intensity data were collected using the $\theta - 2\theta$ scan mode and corrected for absorption and decay. All structures were solved by MULTAN[40] and refined with full-matrix least-squares on *F*. In the final cycles all non-hydrogen atoms were refined anisotropically and all hydrogen atoms were fixed at idealized positions. All calculations were carried out with a Micro Vax 3600 computer using the NRC VAX program package.[41] In compound **8**, one of the coordinated THF's was disordered. All atoms O(13), O(13A), C(79), C(79A), C(80), C(80A), C(81), and C(81A) had half-occupancies. In compound **9**, one methyl group of each HMPA ligand was disordered. The carbons C(29), C(32), C(30), C(30′), C(31), and C(31′) had half-occupancies. Also, one of coordinated THF was disordered. All atoms O(6), O(6A), C(33), C(33A), C(34), C(34A), C(35), C(35A), C(36), and C(36A) had half-occupancies. A summary of the collected data and structure solution is given in Tables 4 and 5.

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Supporting Information Available: Tables of crystal data, atomic coordinates and temperature factors, and intramolecular bond distances and angles of **1**, **3**, and **6−11** and the complete spectroscopic and analytical data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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