Dimeric and Tetrameric Magnesium Acetylide Complexes. Unique Diorganomagnesium Aggregates and Structural Analogy with Organolithium Aggregates

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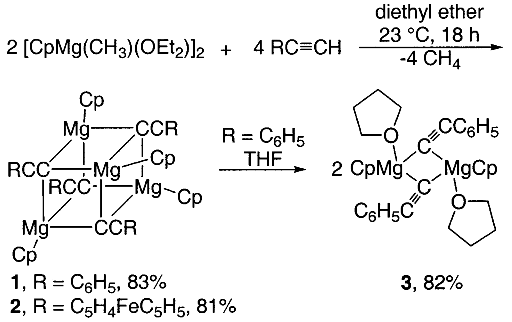
Summary: Treatment of $[CpMgMe(Et_2O)]_2$ *with phenylacetylene and ferrocenylacetylene at ambient temperature in diethyl ether afforded the tetrameric acetylide complexes* $[CpMg(\mu_3\text{-}C{\equiv}CPh)]_4$ *and* $[CpMg(\mu_3\text{-}C{\equiv}CC_5H_4FeC_5H_5)]_4$*, respectively. Treatment of* $[CpMg(\mu_3\text{-}C{\equiv}CPh)]_4$ *with tetrahydrofuran afforded the dimeric acetylide complex* $[CpMg(\mu_2\text{-}C{\equiv}CPh)(THF)]_2$*. These are the first diorganomagnesium compounds to have close structural analogies with organolithium compounds.*

There is a well-documented “diagonal relationship” between the chemical properties of lithium and magnesium.[1] Despite the numerous parallels, remarkable structural differences exist between organolithium[2] and diorganomagnesium compounds.[3] Organolithium compounds frequently form aggregated species, and the tetrameric structures with cubic Li_4C_4 cores found for methyllithium and ethyllithium are very common structural motifs.[4] However, similar structures are conspicuously absent in related diorganomagnesium compounds. Highly sterically hindered ligands lead to the formation of two-coordinate monomeric structures such as $Mg(2,4,6\text{-}tBu_3C_6H_2)_2$[5] and $Mg(C(SiMe_3)_3)_2$,[6] while less bulky ligands often afford polymeric chains in which magnesium adopts a pseudo-tetrahedral geometry through hydrocarbon bridges.[3,7] Aggregated diorganomagnesium compounds are rare and are restricted to the tetrahydrofuran-solvated tetramers (1,8-naphthalenediyl)magnesium, (*o*-phenylene)magnesium, and (*cis*-diphenylvinylene)magnesium.[8] In these compounds, tetrahedral magnesium centers are obtained through a combination of $\mu\text{-}\eta^2{:}\eta^1$ dicarbanionic ligands and capping with one tetrahydrofuran ligand per magnesium center. Herein, we report the synthesis, structural characterization, and properties of a series of magnesium acetylide complexes. These complexes adopt tetrameric or dimeric structures and have solid-state structures that are directly analogous to those of organolithium compounds. The results imply the existence of an extensive, unexplored structural analogy between organolithium and diorganomagnesium compounds and point to ligand steric bulk, group electronegativity, and blocking of solvent coordination as key structure determinants.

Treatment of $[CpMgMe(OEt_2)]_2$[9] with phenylacetylene and ferrocenylacetylene at ambient temperature in diethyl ether afforded the tetrameric acetylide complexes $[CpMg(C{\equiv}CPh)]_4$ (**1**; 83%) and $[CpMg(C{\equiv}CC_5H_4FeC_5H_5)]_4$ (**2**; 81%), respectively (eq 1). The structural assignments were based on the spectral and analytical data as well as X-ray single-crystal analyses.[10,11] In the solid state, compounds **1** and **2** are both tetrameric with cubic $Mg_4(\mu_3\text{-}C)_4$ cores. They are stable under argon, and no decomposition was observed after several days at ambient temperature in dichloromethane-d_2 solutions.



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(10) Preparation of **1**: Cp_2Mg (0.618 g, 4.00 mmol) and $MgMe_2$ (0.216 g, 4.00 mmol) were mixed together in diethyl ether (30 mL). The solution was stirred for 1 h at ambient temperature, at which time phenylacetylene (0.816 g, 8.00 mmol) was added. The mixture was stirred for a further 18 h at ambient temperature, and then the solvent was removed under reduced pressure to afford **1** as light yellow solid (1.260 g, 83%): mp 237−239 °C; IR (Nujol, cm^{-1}) 3070 (w), 2052 (s), 1606 (m), 1310 (m), 1008 (s), 922 (w), 777 (s), 758 (s), 727 (m), 689 (m), 551 (m); ^1H NMR (dichloromethane-d_2, δ) 7.80 (m, 8H, Ph), 7.66 (m, 12H, Ph), 6.11 (s, 20H, C_5H_5); $^{13}C\{^1H\}$ NMR (dichloromethane-d_2, ppm) 138.62 (C_{ipso} of Ph), 132.54 (C_p of Ph), 131.52 (C_o of Ph), 129.50 (C_m of Ph), 121.20 (C≡C), 109.04 (C≡C), 106.64 (C_5H_5). Anal. Calcd for $C_{52}H_{40}Mg_4$: C, 81.95; H, 5.29. Found: C, 81.79; H, 5.40. Crystals suitable for the X-ray diffraction experiment were grown by diffusion of hexane into a dichloromethane solution of **1**.

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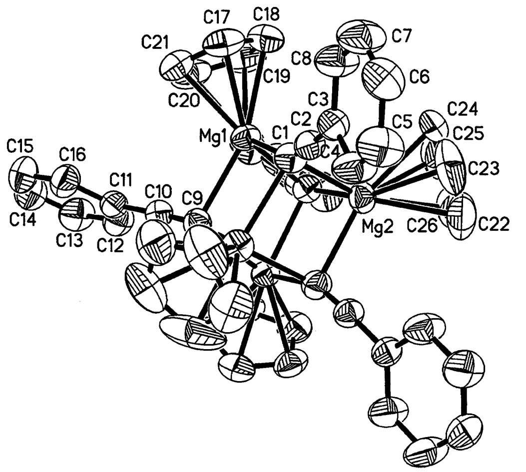

Figure 1. Perspective view of **1**. Selected bond lengths (Å) and angles (deg): Mg(1)−C(1) = 2.248(2), Mg(1)−C(9) = 2.348(2), Mg(1)−C(9)′ = 2.3056(19), Mg(2)−C(1) = 2.327(2), Mg(2)−C(9)′ = 2.249(2), Mg(2)−C(1)′ = 2.334(2), Mg(1)−C(17) = 2.387(2), Mg(1)−C(18) = 2.406(2), Mg(1)−C(19) = 2.398(2), Mg(1)−C(20) = 2.369(2), Mg(1)−C(21) = 2.362(2), Mg(2)−C(22) = 2.372(3), Mg(2)−C(23) = 2.369(3), Mg(2)−C(24) = 2.361(3), Mg(2)−C(25) = 2.355(3), Mg(2)−C(26) = 2.368(2), C(1)−C(2) = 1.214(4), C(9)−C(10) = 1.214(3); Mg(1)−C(1)−C(2) = 152.38(17), Mg(1)−C(9)−C(10) = 100.52(14), Mg(2)−C(1)−C(2) = 111.02(15).

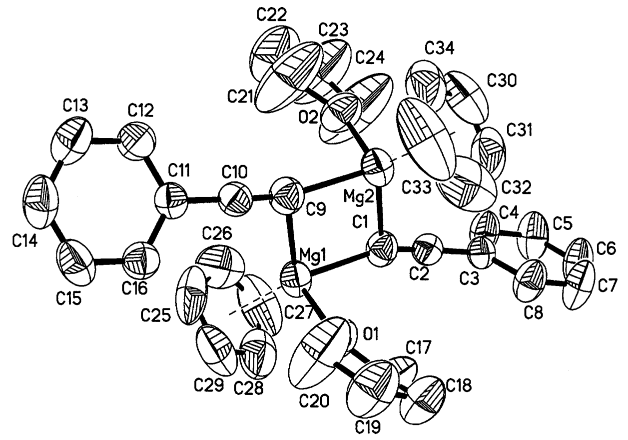

Figure 2. Perspective view of **3**. Selected bond lengths (Å) and angles (deg): Mg(1)−C(1) = 2.185(3), Mg(1)−C(9) = 2.277(3), Mg(2)−C(1) = 2.266(3), Mg(2)−C(9) = 2.197(3), Mg(1)−O(1) = 2.074(2), Mg(2)−O(2) = 2.048(2), Mg(1)−C(25) = 2.410(3), Mg(1)−C(26) = 2.415(4), Mg(1)−C(27) = 2.432(4), Mg(1)−C(28) = 2.400(4), Mg(1)−C(29) = 2.397(4), Mg(2)−C(30) = 2.410(4), Mg(2)−C(31) = 2.419(4), Mg(2)−C(32) = 2.424(5), Mg(2)−C(33) = 2.429(5), Mg(2)−C(34) = 2.394(4), C(1)−C(2) = 1.202(3), C(9)−C(10) = 1.200(3); Mg(1)−C(1)−C(2) = 161.2(2), Mg(2)−C(9)−C(10) = 166.0(2).

The ^{1}H NMR spectra of **1** and **2** contain cyclopentadienyl singlets at δ 6.11 and 6.18, respectively, while the ^{13}C{^{1}H} NMR spectra both reveal cyclopentadienyl resonances at 106.64 ppm. These chemical shifts are similar to those of Cp_2Mg (δ 6.19, 107.71 ppm, dichloromethane-d_2). In the infrared spectra, $\nu_{C\equiv C}$ absorptions appeared at 2052 and 2039 cm^{-1} for **1** and **2**, respectively. The values are similar to those previously reported for other magnesium acetylide complexes.[12] The low solubility of **1** in unreactive organic solvents has so far precluded a detailed analysis of solution structure.

Compound **1** crystallizes as a tetramer, with four cyclopentadienylmagnesium fragments that are connected by four μ_3-phenylacetylide ligands (Figure 1). The halves of the Mg_4C_4 cube are related by a C_2 axis. The cyclopentadienyl ligands are bonded to the magnesium centers in a η^5 fashion, with magnesium−carbon bond lengths ranging from 2.327(3) to 2.372(3) Å. The magnesium−cyclopentadienyl centroid distances are 2.062(2)−2.072(2) Å. The magnesium−carbon (acetylide) bond lengths are asymmetric and span 2.248(2)−2.348(2) Å. The carbon−carbon−carbon angles of the acetylide ligands (176−177°) and short carbon−carbon distance (1.214(3) Å) are typical of an acetylide carbon−carbon triple bond.[12] The angles about the Mg_4C_4 core range from 83.9 to 95.8°, with an average of 89.8°. The magnesium−magnesium distances range between 3.16 and 3.45 Å and are not consistent with bonding interactions. Complex **2** has a structure similar to that of **1**.[13]

Dissolution of **1** in tetrahydrofuran, followed by crystallization, afforded dimeric **3** as colorless crystals (eq 1). The structural assignment was based on the spectral and analytical data as well as X-ray single-crystal analysis.[14] A perspective view of **3** is shown in Figure 2. The compound exists as a dimer held together by μ_2-phenylacetylide ligands, with anti cyclopentadienyl ligands across the Mg_2C_2 core and a tetrahydrofuran ligand bonded to each magnesium ion. The cyclopentadienyl ligands are bonded to the magnesium centers in a η^5 fashion, with magnesium−carbon bond lengths ranging from 2.397(4) to 2.432(3) Å. The magnesium−cyclopentadienyl centroid distances are 2.120(3)−2.139(3) Å. The magnesium−carbon (acetylide) bond lengths are 2.185(2) and 2.277(3) Å for Mg(1) and 2.197(3) and 2.266(3) Å for Mg(2). The carbon−carbon−carbon angles of the acetylide ligands (177.3(3), 177.8(3)°) and short carbon−carbon distances (1.200(3) and 1.202(3) Å) are typical of a carbon−carbon triple bond and similar to the values in **1**. The Mg−C−C angles associated with the acetylide ligands (Mg(1)−C(1)−C(2)

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(11) Preparation of **2**: in a fashion similar to the preparation of **1**, treatment of Cp_2Mg (0.155 g, 1.00 mmol), $MgMe_2$ (0.054 g, 1.00 mmol), and ferrocenylacetylene (0.420 g, 2.00 mmol) in diethyl ether afforded **2** as an orange crystalline solid (0.483 g, 81%): mp 287−289 °C; IR (Nujol, cm^{-1}) 3070 (w), 2039 (m), 1605 (w), 1305 (m), 1004 (m), 913 (m), 823 (m), 767 (s), 745 (m), 728 (s), 597 (m); ^{1}H NMR (dichloromethane-d_2, δ) 6.18 (s, 20H, C_5H_5Mg), 4.75 (m, 8H, $C_5H_2H'_2$), 4.53 (m, 8H, $C_5H_2H'_2$), 4.51 (s, 20H, C_5H_5Fe); ^{13}C{^{1}H} NMR (dichloromethane-d_2, ppm) 140.55 (C≡C), 106.64 (MgC_5H_5), 104.49 (C≡C), 72.27 (FeC_5H_4), 70.88 (FeC_5H_5), 70.69 (FeC_5H_4), 62.88 (FeC_5H_4). Anal. Calcd for $C_{68}H_{56}Fe_4Mg_4$: C, 68.42; H, 4.73. Found: C, 68.02; H, 4.84.

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(13) The X-ray crystal structure of **2** will be described in a later full paper.

(14) Preparation of **3**: in a fashion similar to the preparation of **1**, treatment of Cp_2Mg (0.618 g, 4.00 mmol), $MgMe_2$ (0.216 g, 4.00 mmol), and phenylacetylene (0.816 g, 8.00 mmol) in tetrahydrofuran (20 mL) afforded **3** as a yellow crystalline solid (1.729 g, 82%): mp 210−215 °C dec; IR (Nujol, cm^{-1}) 3075 (w), 2066 (m), 1591 (m), 1570 (w), 1306 (m), 1197 (m), 1026 (m), 1006 (m), 917 (m), 880 (m), 760 (s), 725 (s), 690 (s); ^{1}H NMR (dichloromethane-d_2, δ) 7.49−7.36 (m, 10H, C_6H_5), 6.18 (s, 10H, C_5H_5), 4.05 (m, 8H, THF), 2.02 (m, 8H, THF); ^{13}C{^{1}H} NMR (dichloromethane-d_2, ppm) 131.80 (C_p), 128.68 (C_o), 128.21 (C_m), 124.82 (C_{ipso}), 119.90 (C≡C), 117.08 (C≡C), 105.49 (C_5H_5), 69.52 (THF), 25.69 (THF). Anal. Calcd for $C_{34}H_{36}Mg_2O_2$: C, 77.75; H, 6.91. Found: C, 77.68; H, 7.01. Crystals suitable for the X-ray diffraction experiment were grown by diffusion of hexane into a dichloromethane solution of **3**.

= 161.2(2), Mg(2)−C(9)−C(10) = 166.0(2), Mg(1)−C(9)−C(10) = 108.0(2), Mg(2)−C(1)−C(2) = 110.9(2)°) suggest a combination of σ-donation (Mg(1)−C(1), Mg(2)−C(9)) and π-donation (Mg(1)−C(9), Mg(2)−C(1)) from the bridging carbon atoms. The angles about the Mg_2C_2 core range from 85.9 to 93.8°, with an average of 90.0°. The magnesium−oxygen distances are 2.048(2) and 2.074(2) Å, which are typical values for magnesium complexes with tetrahydrofuran ligands.[8] Overall, the bond lengths and angles in **3** are similar to the related values in **1**, and **1** can be viewed as a dimer of dimeric **3** after tetrahydrofuran loss.[15]

Complexes **1**−**3** have structures that are unique among organomagnesium complexes. A few magnesium acetylide complexes have been structurally characterized, but most contain terminal acetylide linkages.[12] Chang and co-workers have reported a series of complexes of the formula $[Me_2Al(\mu\text{-}R_2N)_2Mg(\mu\text{-}C{\equiv}CR)]_2$, and these complexes contain central Mg_2C_2 cores with bridging acetylide ligands.[12a] $[Mg_2(Et)(C{\equiv}CPh)_3(tmeda)]_2{\cdot}C_6H_6$ crystallizes as a tetramer with bridging acetylide ligands;[12b] however, two of the magnesium atoms within the molecule are each stabilized by coordination to the π-systems of two adjacent phenylacetylide groups. Complexes **1**−**3** have many structural analogies with related organolithium compounds. For example, lithium *tert*-butylacetylide crystallizes as the cubic tetramer $[Li(C{\equiv}CtBu)(THF)]_4$ with a structure very similar to that of **1**,[16] is a solvated tetramer at −90 °C in a 1.5 M tetrahydrofuran solution,[17] and exists in a dimer−tetramer equilibrium in dilute tetrahydrofuran solutions at −108 °C.[18] Lithium phenylacetylide crystallizes as the dimer $[Li(C{\equiv}CPh)(\eta^2\text{-}Me_2NCH_2CH_2CH_2NMe_2)]_2$ and has a core structure very similar to that of **3**.[19] Several rationales have been proposed to account for the current limited structural analogy between organolithium and diorganomagnesium compounds.[3,8] Lithium is less electronegative than magnesium, and therefore, lithium−carbon bonds are more polar and more susceptible to aggregation. The higher positive charge of the magnesium ion makes it a stronger Lewis acid than lithium, and it therefore has a higher tendency to coordinate neutral Lewis bases such as tetrahydrofuran. Strong coordination of ether molecules to magnesium ions creates a steric barrier to aggregate formation. In **1** and **2**, several factors assist in stabilizing the tetrameric structure. The acetylide ligand has a much higher group electronegativity (χ = 3.3) than a methyl group (χ = 2.3),[20] and thus the magnesium−carbon (acetylide) bond is more polar than a magnesium−carbon (alkyl) bond. It is also possible that the group electronegativities of the $CpMg^+$ and $(R_2O)Li^+$ fragments are similar. In addition, the acetylide ligand has a low steric profile compared to that of many other hydrocarbon ligands, which can allow the formation of multiply bridging interactions. Finally, the cyclopentadienyl ligand has a relatively small steric profile but blocks coordination of diethyl ether due to the η^5 bonding. However, the better ligand tetrahydrofuran is sufficient to cleave the tetramer to afford **3**.

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Supporting Information Available: Text giving synthetic procedures and analytical and spectroscopic data for **1**−**3** and tables of crystal data, structure solution and refinement details, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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