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Structure Elucidation

Magnesiacyclopentadienes as Alkaline-Earth Metallacyclopentadienes: Facile Synthesis, Structural Characterization, and Synthetic Application**

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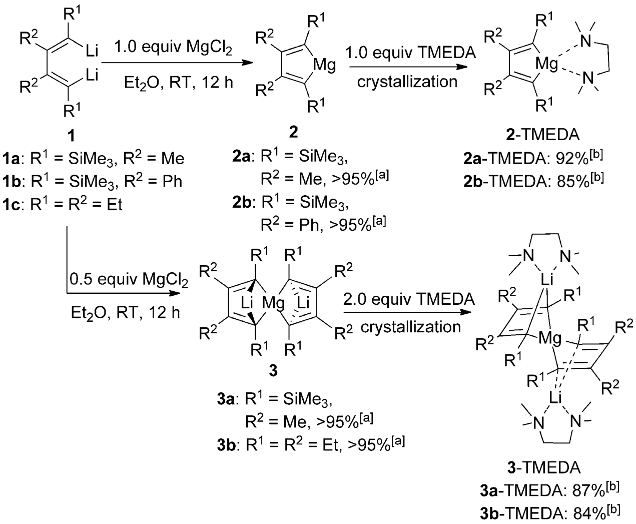
Abstract: *Metallacyclopentadienes have attracted much attention as building blocks for synthetic chemistry as well as key intermediates in many metal-mediated or metal-catalyzed reactions. However, metallacyclopentadienes of the alkaline-earth metals have not been reported, to say nothing of their structures, reaction chemistry, and synthetic applications. In this work, the first series of magnesiacyclopentadienes, spiro-dilithio magnesiacyclopentadienes, and dimagnesiabutadiene were synthesized from 1,4-dilithio 1,3-butadienes. Single-crystal X-ray structural analysis of these magnesiacycles revealed unique structural characteristics and bonding modes. Their reaction chemistry and synthetic application were preliminarily studied and efficient access to amino cyclopentadienes was established through their reaction with thioformamides. Experimental and DFT calculations demonstrated that these magnesiacyclopentadienes could be regarded as bis(Grignard) reagents wherein the two Mg–C(sp^2) bonds have a synergetic effect when reacting with substrates.*

Metallacyclopentadienes are a class of important organometallic compounds which are very useful as building blocks for synthetic chemistry, and often proposed as key intermediates in metal-mediated or metal-catalyzed reactions.[1] However, in many cases their synthesis, isolation, and structural characterization are challenging. For example, metallacyclopentadienes of the alkaline-earth metals (group 2 elements in the Periodic Table) have not been reported, although alkaline-earth metallacyclopentenes $M(RCHRC{=}CRCHR)$ are known and magnesiacyclopentadienes are proposed in some reactions as elusive intermediates.[2,3]

Organomagnesium compounds (Grignard reagents or diorganomagnesium reagents) are among the most useful organometallic reagents for synthetic chemistry and related science.[4,5b] Magnesiacyclopentadienes are expected to have unique molecular structures and be useful, but display different reaction chemistry from normal Grignard reagents. Recently, Mulvey and co-workers reported the formation and crystal structure of 1,4-dimagnesiated 1,3-butadiene through bimetallic-induced fragmentation of tetrahydrofuran. This represents an exciting cleave and capture chemistry realized by the cooperative effect of bimetallic bases.[5] Nevertheless, this 1,4-dimagnesiated 1,3-butadiene could not form its corresponding magnesiacycle because of the *trans* configuration of the two C–C double bonds. Therefore, study on the synthesis, structural characterization, and reaction chemistry of magnesiacyclopentadienes still remain a great challenge.

We have been working on the synthesis and synthetic applications of multiply substituted 1,4-dimetal 1,3-butadienes, especially 1,4-dilithio 1,3-butadienes (**1**; Scheme 1).[6]



Scheme 1. Synthesis of the magnesiacyclopentadienes **2** and **3**, and their TMEDA complexes **2**-TMEDA and **3**-TMEDA. [a] Yield determined by NMR spectroscopy. [b] Yield of isolated product.

Because of their *s-cis* configuration, these dilithio reagents **1** demonstrate remarkable cooperative effects. We envisioned that **1** could undergo transmetalation with magnesium salts to generate the unknown magnesiacyclopentadienes. Herein we report the first synthesis and crystal structures of the magnesiacyclopentadienes **2** and spiro-dilithio magnesiacyclopentadienes **3** (Scheme 1). An unprecedented dimagnesiabutadiene compound (**5a**; for structure see Scheme 3) having two magnesia bridges was also obtained and determined by single-crystal X-ray structural analysis. Structural

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transformations between the compounds **1**, **2**, and **3** were observed in this system. Furthermore, preliminary reaction chemistry and synthetic application of **2** were investigated. An efficient synthetic method for amino cyclopentadienes (**6**) was thus developed.

When the dilithio reagent **1a** was treated with one equivalent of $MgCl_2$ in Et_2O at room temperature for 12 hours, the expected magnesiacyclopentadiene **2a** was formed cleanly in greater than 95% yield (NMR; Scheme 1). However, when 0.5 equivalents of $MgCl_2$ was used, the spiro-dilithio magnesiacyclopentadiene **3a** was generated almost quantitatively as determined by NMR spectroscopy. Similarly, **2b** and **3b** could be also synthesized highly efficiently. When tetramethylethylenediamine (TMEDA) was added to the above solution of **2** and **3**, their corresponding TMEDA-coordinated crystals **2a**-TMEDA, **2b**-TMEDA, **3a**-TMEDA, and **3b**-TMEDA were obtained in 92, 85, 87, and 84% yields, respectively, upon isolation.

For **2a**, the two carbon atoms (C1 and C4) bonded with the magnesium atom show a singlet at $\delta = 161.7$ ppm in the ^{13}C NMR spectrum in [D_8]tetrahydrofuran, while the other two carbon atoms of the butadiene skeleton (C2 and C3) display a singlet at $\delta = 168.8$ ppm. These NMR data are close to those in 1,4-dimagnesiated 1,3-butadiene reported by Mulvey and co-workers ($\delta = 155.0$ and 163.3 ppm, respectively).[5a] For **2a**-TMEDA, the single-crystal X-ray structure analysis reveals a nearly coplanar MgC1C2C3C4 ring skeleton (Figure 1). The lengths of the two Mg–C(sp^2) bonds are 2.131(5) and 2.127(5) Å, respectively, and are comparable with the classic Mg–C(sp^2) bonds [e.g., Mg-C distances in $\{2,4,6\text{-}(t\mathrm{Bu})_3C_6H_2\}_2Mg$ (2.12 Å)].[7] The bite angle of C1-Mg-C4 is 91.54(19)°, which is much smaller than the classic C-Mg-C angles in usual tetracoordinate magnesium compounds (115–130°).[4b]

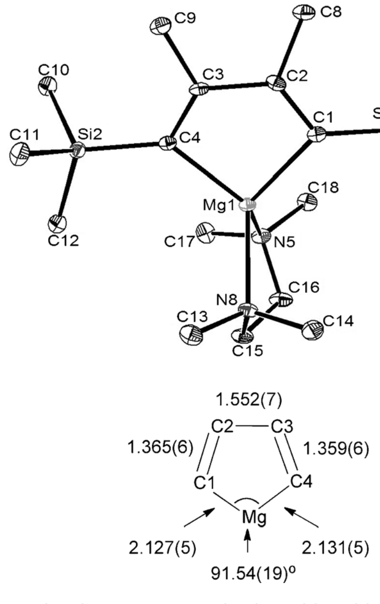

Figure 1. Molecular structure and selected bond lengths [Å] of magnesiacyclopentadiene-TMEDA complex **2a**-TMEDA. Thermal ellipsoids are shown at 30% probability. H atoms are omitted for clarity.

The spiro-dilithio magnesiacyclopentadiene **3a** might also be regarded as a novel ate complex.[4d] The two carbon atoms (C1 and C4) bonded with the magnesium atom have a singlet at $\delta = 181.3$ ppm in the ^{13}C NMR spectrum in [D_8]tetrahydrofuran, and is quite different from that of **2a**, but closer to that in the corresponding 1,4-dilithio 1,3-butadiene **1a** ($\delta = 192.3$ ppm).[8b] The two carbon atoms (C2 and C3) of the butadiene skeleton also display a singlet at $\delta = 161.8$ ppm, and it is smaller than that of **2a**. For **3a**-TMEDA, the single-crystal X-ray structure analysis reveals a Mg/Li double bridge (Figure 2). The Mg center is tetracoordinated with Mg–C(sp^2) bond lengths of 2.238(2) and 2.262(2) Å, respectively, which are a little longer than those in **2a**-TMEDA. The lithium bridge leads to a significantly smaller C-Mg-C bite angle [81.17(6)°]. The lengths of the bridged Li–C(sp^2) bonds are 2.226(3) and 2.281(3) Å, respectively, and longer than those in **1a**-TMEDA [2.180(7) Å and 2.129(7) Å].[8a] The magnesium atom is out of the plane of the C1C2C3C4 ring (Mg-C1-C2-C3, 31.78°), thus forming the magnesium bridge.

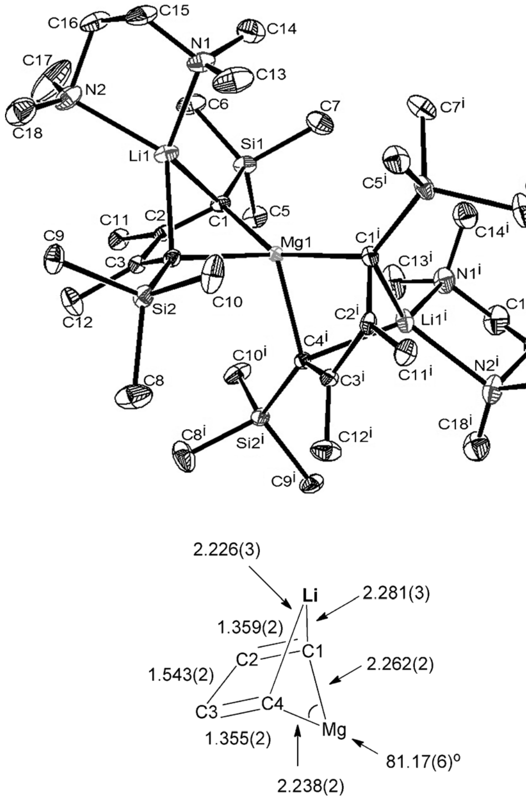

Figure 2. Molecular structure and selected bond lengths [Å] of the spiro-dilithio magnesiacyclopentadiene-TMEDA complex **3a**-TMEDA. Thermal ellipsoids are shown at 30% probability. H atoms are omitted for clarity.

Structural transformations between compounds **1a**, **2a**, **3a**, and **4a** were investigated (Scheme 2). When an excess amount of $MgCl_2$ (3.0 equiv) was used with **1a**, the reaction afforded **2a** as the sole product, just as in the treatment of **1a** with 1.0 equivalent of $MgCl_2$. No formation of the expected 1,4-bis(magnesium) **4a** was detected. Similarly, **2a** could not

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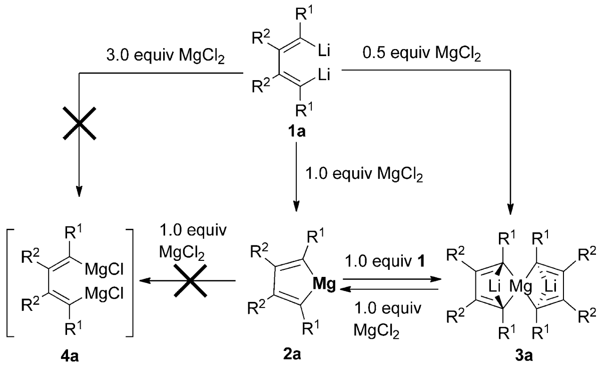
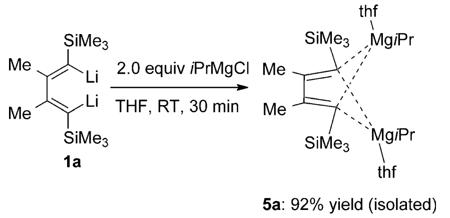


Scheme 2. Structural transformations between **1a**, **2a**, **3a**, and **4a** as detected by NMR spectroscopy.

be transformed into **4a** when 1.0 equivalent of $MgCl_2$ was added to **2a**. When **3a** was treated with 1.0 equivalent of $MgCl_2$, **3a** was completely transformed into **2a**. When **2a** was reacted with 1.0 equivalent of **1a**, **3a** was obtained quantitatively.

Since **4a** could not be obtained by using $MgCl_2$ (Scheme 2), Grignard reagents (RMgCl) were tested, instead of $MgCl_2$, in reactions with the dilithio reagents **1**,[9] with the aim of forming 1,4-$(RMg)_2$-1,3-butadienes. Thus, as shown in Scheme 3, when **1a** was treated with 2 equivalents of isopropylmagnesium chloride in THF at room temperature, the expected 1,4-$(i\text{PrMg})_2$-1,3-butadiene **5a** was obtained in 92% yield upon isolation.



Scheme 3. Synthesis of the dimagnesiabutadiene **5a** from **1a** and isopropylmagnesium chloride. THF = tetrahydrofuran, thf = tetrahydrofuran.

The X-ray single-crystal structural analysis of the dimagnesiabutadiene compound **5a** reveals a magnesium double bridge (Figure 3). The Mg center could be regarded as tetracoordinated, with Mg–C(sp^2) bond lengths of 2.344(3) and 2.223(3) Å, respectively. The magnesium bridge leads to a rather small C-Mg-C bite angle (79.54(11)°). The short distance between the two Mg atoms [2.860(1) Å] indicates a weak Mg–Mg interaction.

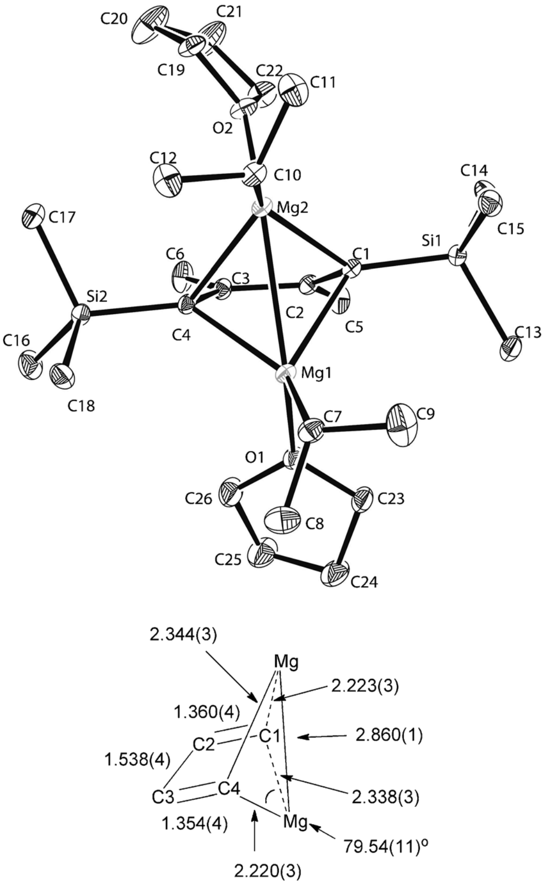
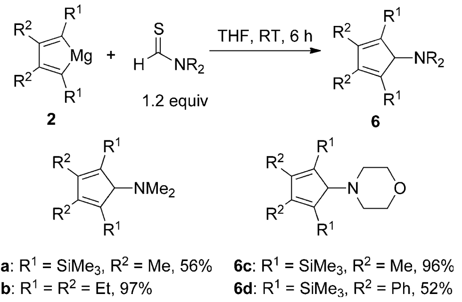


Figure 3. Molecular structure and selected bond lengths [Å] of the dimagnesiabutadiene-THF complex **5a**-THF. TThermal ellipsoids are shown at 30% probability. H atoms are omitted for clarity.



Scheme 4. Synthesis of amino cyclopentadienes from the isolated magnesiacyclopentadienes **2**.

We then investigated the reaction chemistry and synthetic application of these unprecedented magnesiacyclopentadienes **2**. We envisioned **2** might be regarded as bis(Grignard) compounds and the two Mg–C(sp^2) bonds might show a synergetic effect when reacting with substrates. Inspired by the work of Murai et al. on the formation of tertiary amines from coupling reactions of thioformamides with organolithium and Grignard reagents,[10] we studied the reaction between **2** and thioformamides, with the expectation of forming the amino cyclopentadienes **6** (Scheme 4). Although substituted cyclopentadiene derivatives are very useful in many aspects,[11] synthetic methods for **6** are limited.[12] Firstly, the isolated pure magnesiacyclopentadienes **2** were reacted with thioformamides. As shown in Scheme 4, **6a–d** were obtained in good to excellent yields upon isolation. When diethyl ether was used as the solvent, similar results were observed. The structure of **6b** was determined from the salt **6b**-HCl (Figure 4). It should be

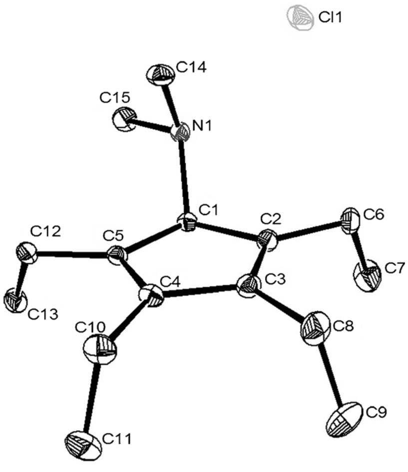
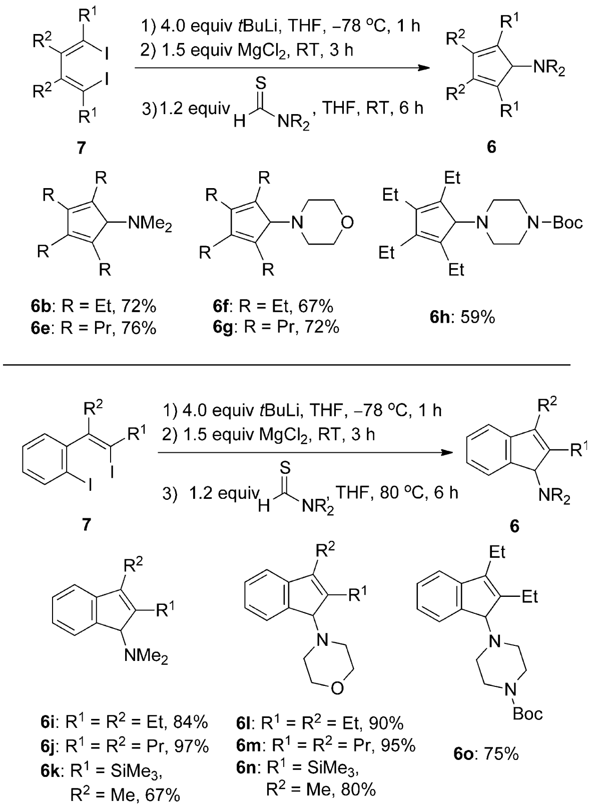


Figure 4. Molecular structure of the amino cyclopentadiene **6b**-HCl. Thermal ellipsoids are shown at 30% probability. H atoms are omitted for clarity.

noted that, when the pure dilithio reagents **1** were treated with thioformamides, a mixture of unidentified products were observed and the yields of the corresponding cyclopentadienamines were generally lower than 20%. This observation demonstrated the unique reactivity of **2**.

A one-pot approach for the synthesis of **6** was then carried out starting from the diiodo compounds **7** (Scheme 5). In this process, the magnesiacyclopentadienes **2** were generated in situ and used without isolation. A variety of the amino cyclopentadienes **6** could be prepared in good to excellent yields upon isolation.



Scheme 5. One-pot synthesis of amino cyclopentadienes **6**. Boc = *tert*-butoxycarbonyl.

The tertiary amines reported by Murai et al. were generated by double nucleophilic attack to thioformamides.[10c,d] However in our work, a synergetic mechanism might be more reasonable. We investigated the mechanism by DFT calculations (Figure 5).[13] The B3LYP density functional level of theory was used in the geometry optimizations and frequency calculations. The 6-31G* basis set was used for all atoms. Solvent effects were calculated by single-point calculations on the gas-phase optimized geometries with the polarizable continuum model (PCM). The solvent THF was used in the PCM calculations. All energies discussed below are Gibbs free energies (ΔG_{sol}) in solution. The relative enthalpies (ΔH_{gas}) and Gibbs free energies (ΔG_{gas}) in gas phase are also given. The first step was a ligand replacement. The sulfur atom coordinated to Mg to liberate a thf to form the intermediate **8**. The insertion step involved a four-membered ring transition state (**TS1**) with an activation barrier of 12.4 kcamol^{-1}. When the seven-membered ring intermediate **9** was formed, it would easily accept another thf to form **10**. Then through a four-membered ring transition state (**TS2**), the expected product **6b** was obtained with an activation barrier of only 3.1 kcalmol^{-1}. The whole process was feasible and exothermic by 55.6 kcalmol^{-1}. The calculation results were in good agreement with the experimental results.

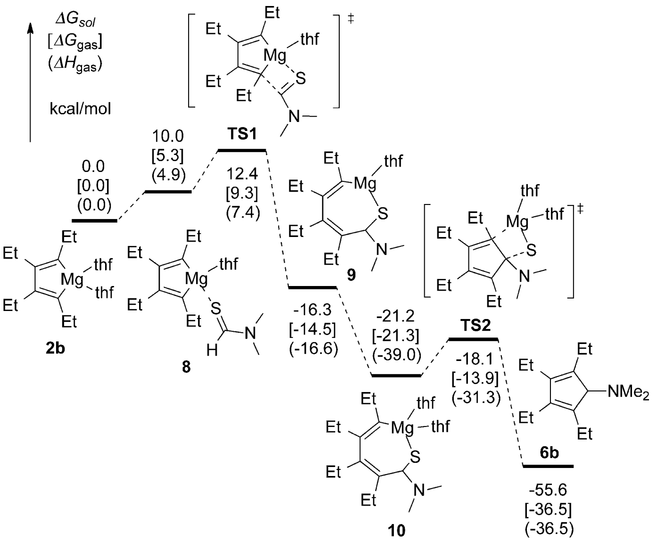


Figure 5. DFT computed energy surface for the reaction of **2b**.

In summary, we have synthesized and structurally characterized the first series of magnesiacyclopentadienes, spirodilithio magnesiacyclopentadienes and dimagnesiabutadiene. Unique structural characteristics and bonding were revealed. The reaction chemistry and synthetic application of these unprecedented magnesiacyclopentadienes were preliminarily studied through their reaction with thioformamides, thus demonstrating their unique reactivity and providing an efficient synthetic method for amino cyclopentadienes.

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