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Intramolecular and Intermolecular N−H···$C_5H_5^-$ Hydrogen Bonding in Magnesocene Adducts of Alkylamines. Implications for Chemical Vapor Deposition Using Cyclopentadienyl Source Compounds

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Blue and green LEDs and laser diodes fabricated from magnesium-doped group 13 nitride films have many current and expected technological applications.[1] Devices containing these materials are created by chemical vapor deposition (CVD) processes involving group 13 alkyls, magnesocene (Cp_2Mg), and ammonia.[2] Despite the growing importance of magnesium-doped group 13 nitride films, almost nothing is known about how Cp_2Mg is activated by ammonia to create intermediates that lead to film growth. Moreover, other metal cyclopentadienyl source compounds are widely used for the CVD growth of thin films containing main group, transition metal, and lanthanide elements.[3] Given our interest in the development of alternative magnesium CVD source compounds,[4] we sought to explore the interaction of Cp_2Mg with nitrogen compounds to model the chemical reactions that might be occurring in a CVD process. Herein we describe the synthesis and characterization of a series of adducts $Cp_2Mg(NHRR')$ that are formed upon treatment of Cp_2Mg with primary or secondary amines. X-ray crystal structures of the primary amine adducts reveal structures containing η^5-cyclopentadienyl, η^2-cyclopentadienyl, and amine ligands. The amine hydrogen atoms exhibit intramolecular and intermolecular hydrogen bonding with the π-system of the η^2-cyclopentadienyl ligands. This is the first recognition of hydrogen bonding to the π-system of a coordinated cyclopentadienyl ligand. The results imply that protonolysis of the cyclopentadienyl ligands in Cp_2Mg and other cyclopentadienyl compounds upon treatment with ammonia or other acidic element hydrides in CVD film growth processes is facilitated by hydrogen bond formation.

Treatment of Cp_2Mg with 1 equiv of the primary amines 3-amino-2,4-dimethylpentane, isopropylamine, *tert*-butylamine, and benzylamine, or the secondary amine *N*-isopropylbenzylamine, afforded $Cp_2Mg(NH_2CH(CH(CH_3)_2)_2)$ (**1**, 91%), $Cp_2Mg(NH_2{}^iPr)$ (**2**, 80%), $Cp_2Mg(NH_2{}^tBu)$ (**3**, 67%), $Cp_2Mg(NH_2CH_2Ph)$ (**4**, 80%), and $Cp_2Mg(NH(CH(CH_3)_2)(CH_2C_6H_5))$ (**5**, 91%), respectively, as colorless or off-white crystalline solids (eq 1). Similar treatment of Cp_2Mg with triethylamine only afforded Cp_2Mg upon workup. The structural assignments for **1**−**5** were based on spectral and analytical data[5] and X-ray crystal structure determinations for **1** and **3**. In the solid state, these complexes contain η^5-cyclopentadienyl, η^2-cyclopentadienyl, and amine ligands, as described below. Adducts **1**−**5** are stable at ambient temperature and pressure under inert atmosphere. Complex **1** can be sublimed at 60 °C/0.05 Torr to afford unchanged **1** in 95% sublimed yield. There was no evidence for elimination of cyclopentadiene upon sublimation. The ^1H NMR spectra of **1**−**5** contain cyclopentadienyl singlets that range from δ 6.03−6.19, which are close to the cyclopentadienyl resonance for Cp_2Mg (δ 5.97). The $^{13}C\{^1H\}$ NMR spectra exhibit cyclopentadienyl carbon resonances between 106.71 and 107.74 ppm. For comparison, the carbon atoms of Cp_2Mg resonate at 107.76 ppm. At ambient temperature in toluene-d_8, the cyclopentadienyl resonance for **1** appeared as a sharp singlet at δ 6.15. At −80 °C, this resonance shifted slightly to δ 6.29, but it remained a sharp singlet. There were no major shifts or changes with the other resonances upon cooling from room temperature to −80 °C. The infrared spectra of **1**−**5** contain nitrogen−hydrogen stretches from 3313 to 3164 cm^{-1}. The low values for the nitrogen−hydrogen stretches are due to N−H···$C_5H_5^-$ hydrogen bonding, because the cyclopentadienyl π-systems are the only hydrogen bond acceptors that are present.

$$Cp_2Mg \quad + \quad NHRR' \xrightarrow[23\ ^\circ C,\ 18\ h]{toluene} Cp_2Mg(NHRR') \qquad (1)$$

1, R = H, R' = $CH(CH(CH_3)_2)_2$, 91%
2, R = H, R' = $CH(CH_3)_2$, 80%
3, R = H, R' = $C(CH_3)_3$, 67%
4, R = H, R' = $CH_2C_6H_5$, 80%
5, R = $CH(CH_3)_2$, R' = $CH_2C_6H_5$, 91%

Figure 1 contains a perspective view of **1**, along with selected bond lengths and angles. The crystal structure of **3** was also determined and was similar to that of **1**.[6] Complex **1** contains η^5-cyclopentadienyl, η^2-cyclopentadienyl, and 3-amino-2,4-dimethylpentane ligands. The magnesium−carbon bond lengths for the η^5-cyclopentadienyl ligand are identical within experimental error (2.407(4)−2.414(4) Å). The magnesium−carbon bond lengths for the η^2-cyclopentadienyl ligand are 2.301(3) and 2.380(3) Å. The next nearest magnesium−carbon distances for the η^2-cyclopentadienyl ligand are 2.613(4) and 2.745(4) Å. Both cyclopentadienyl ligands are planar to within 0.008 Å. One of the nitrogen-bound hydrogen atoms exhibits an intramolecular close contact of 2.620 Å with the centroid of C(6), C(7), and C(8) of the η^2-cyclopentadienyl ligand. The other amine-bound hydrogen atom shows an intermolecular close contact of 2.786 Å (to the C(6), C(7), and C(8) centroid) with the exo-face of an adjacent η^2-cyclopentadienyl ligand. By contrast, the closest contacts of the η^5-cyclopentadienyl centroid with the amine hydrogen atoms are 3.746 and 4.289 Å. A view of **1** that emphasizes the hydrogen bonding interactions is contained in the Supporting Information.

The structural parameters of **1** can be compared with those of $Mg(\eta^5\text{-}Cp)(\eta^2\text{-}Cp)(NH_2{}^tBu)(THF)$ (**6**),[7] which is the only structurally characterized Cp_2Mg adduct reported to date.[8] Complex **6**, similar to **1**, exists with η^5-cyclopentadienyl, η^2-cyclopentadienyl, *tert*-butylamine ligands, but also contains a tetrahydrofuran ligand. Hydrogen bonding was not described in the report. Reanalysis of the structure data from the Cambridge Crystallographic Database indicates that one of the amine hydrogen atoms forms an intra-

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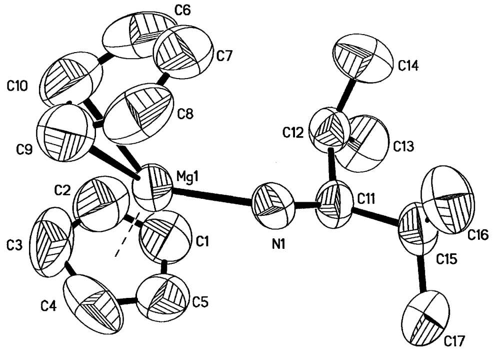

Figure 1. Perspective view of **1**. Selected bond lengths (Å) and angles (deg): Mg(1)−N(1) 2.112(3), Mg(1)−C(1) 2.410(4), Mg(1)−C(2) 2.414(4), Mg(1)−C(3) 2.407(4), Mg(1)−C(4) 2.409(4), Mg(1)−C(5) 2.407(4), Mg(1)−C(9) 2.380(4), Mg(1)−C(10) 2.301(3), Mg−centroid(η^5) 2.1101(23), Mg(1)−N(1)−C(11) 123.8(2).

molecular close contact of 2.274 Å with the centroid of the three uncoordinated carbon atoms of the η^2-cyclopentadienyl ligand. The other nitrogen-bound hydrogen atom has no intermolecular contacts within 3.7 Å. The X-ray crystal structures of several carbene and tetrahydrofuran adducts of ring-substituted magnesocenes have been reported,[9] although these ligands are not hydrogen bond donors.

We searched the Cambridge Crystallographic Database (version 5.22, October 2001) and were unable to find any complexes in which a ligand containing coordinated O−H or N−H fragments leads to a slipped cyclopentadienyl ligand, with the exception of **6** noted above.[10] However, hydrogen bonding between N−H bonds and the π-clouds of various neutral aromatic compounds is well precedented.[11,12] Such interactions usually entail a hydrogen−arene centroid distance of 2.75−3.11 Å.[12] Because the cyclopentadienyl ligand is aromatic and considerably more electron rich than a neutral aromatic compound due to the formal negative charge, its π-system should be a much better hydrogen bond acceptor than neutral aromatic π-systems. Consistent with this interpretation, the hydrogen−cyclopentadienyl centroid distances noted above range between 2.62 and 2.79 Å. It is likely that hydrogen bonding increases the thermal stability of **1**−**5**, relative to adducts with ligands that are not capable of hydrogen bonding. For example, $Cp_2Mg(THF)_{2.42}$ reverts completely to Cp_2Mg upon vacuum-drying at 20 °C/10^{-3} Torr for 6 h.[8b] By contrast, **1** can be sublimed quantitatively without any evidence of reversion to Cp_2Mg.

The final issue involves relating the results described herein to the activation of Cp_2Mg by ammonia under CVD conditions. It has been established that Cp_2Mg is about twice as efficient as 1,1′-dimethylmagnesocene in incorporating magnesium into GaN films grown using metal organic vapor phase epitaxy.[13] On the basis of the results described herein and previous adducts of ring-substituted magnesocenes,[9] it is likely that Cp_2Mg forms a more stable ammonia adduct than does 1,1′-dimethylmagnesocene, due to steric repulsion from the methyl groups and lower Lewis acidity in the latter compound. Formation of a more stable ammonia adduct with Cp_2Mg would give the complex a longer lifetime in the CVD reactor, which would allow more time for the presumably slow elimination of cyclopentadiene to occur. Cyclopentadiene elimination would lead to reactive magnesium amide complexes that can contribute to film growth. Cyclopentadiene elimination from other metal cyclopentadienyl complexes used in CVD may also proceed through hydrogen bonded intermediates similar to those documented herein.

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Supporting Information Available: Synthetic procedures, analytical and spectroscopic data for **1**−**5**; a perspective view of **1** showing the intramolecular and intermolecular hydrogen bonding (PDF). An X-ray crystallographic file for **1** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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