Organometallic Compounds

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Binding of Molecular Magnesium Hydrides to a Zirconocene–Enyne Template**

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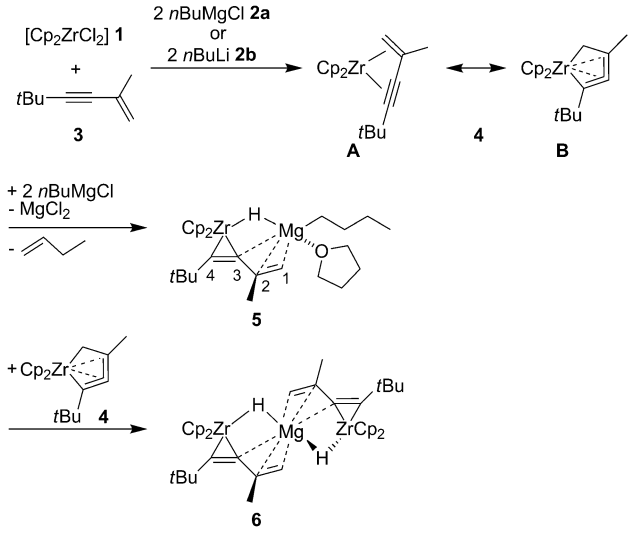
Magnesium hydride, $(MgH_2)_x$, is an inorganic solid-state material[1] that has become a candidate for hydrogen storage. For that purpose, it was prepared by reversible transition-metal-enhanced hydrogenation of magnesium, in some cases aided by activation of the Mg metal (Mg-anthracene; nano-sized Mg particles).[2] There is not much known about molecular forms of magnesium hydrides.[3] A few reports about nacnac-stabilized magnesium hydrides have been published,[4] and the titanocene unit was shown to have the ability to form heterobimetallic bridging hydride complexes with magnesium.[5] Even less is known about molecularly defined alkylmagnesium hydride systems. There are a few reports about hydridomagnesium halides and amidomagnesium hydride systems[6] and reports on a few alkylmagnesium hydride systems, for example "MeMgH" from the 1970s, but none of these materials was sufficiently structurally characterized.[7] We have now found that a readily prepared zirconocene–enyne complex may serve as a suitable template for stabilizing the elusive monomeric MgH_2 species and even an alkylmagnesium hydride by a well-defined interaction. First examples of this new development in magnesium hydride chemistry are described herein.

For this study, we have generated the zirconacycloallenoid complex **4** by a variant of the Negishi zirconocene formation,[8] similar to the method recently described by N. Suzuki et al.[9] In our case we treated $[Cp_2ZrCl_2]$ (**1**) with two molar equivalents of *n*-butylmagnesium chloride (**2a**) in a diethyl ether/THF mixture in the presence of the conjugated enyne **3** (60 °C, 1 h). Compound **4** was obtained as a red oil (95 %). Compound **4** could be obtained analogously by treatment of the Cp_2ZrCl_2/**3** mixture with 2 molar equivalents of *n*-butyllithium (**2b**). Compound **4** can formally be regarded as a resonance hybrid of the zirconocene–enyne π complex **4A** (Scheme 1) and the five-membered cyclic metallacycloalle-



Scheme 1. Formation of compound **5** from **4**, and compound **6** from **5** and **4**.

noid σ system, similar to the series of closely related zirconacycloallenoid compounds we[10] and others[11] had characterized previously. Consequently, compound **4** exhibits the NMR signals of a typical pair of diastereotopic Cp ligands on zirconium (^{1}H: $\delta = 5.37/5.04$ ppm; ^{13}C: $\delta = 104.0/102.3$ ppm) and a ^{1}H NMR AX pattern of the endocyclic $[Zr]CH_2$ group at $\delta = 3.10/0.94$ ppm ($^2J_{HH} = 6.7$ Hz).

The reaction of a $[Cp_2ZrCl_2]$/enyne **3** mixture with an excess of *n*-butylmagnesium chloride (4 equiv) gave a different product. Workup including crystallization from pentane gave the heterobimetallic Zr/Mg compound **5** as orange crystals in 66 % yield. The X-ray crystal structure analysis revealed that in this reaction, butylmagnesium hydride was formed and coordinated to the zirconocene–enyne unit. We find a hydride bridging between zirconium and magnesium.[12] The acetylene unit of the enyne ligand is η^2-bonded to zirconium and features the typical metallacyclopropene-type structure (see Figure 1 and Table 1). The magnesium atom features a strongly distorted pseudotetrahedral coordination geometry. It shows a reasonably short contact to the acetylene

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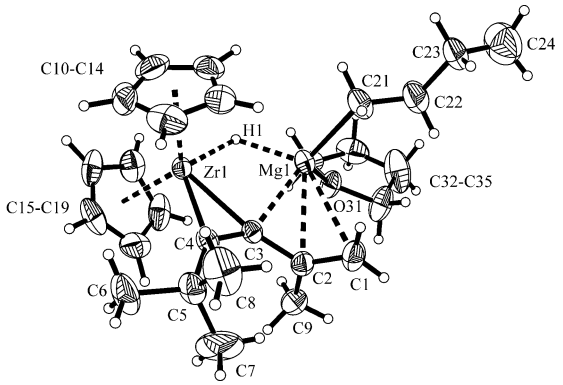

Figure 1. Molecular structure of the heterobimetallic Zr/Mg complex **5**.[17] Ellipsoids are set at 30% probability.

Table 1: Selected structural data of the Zr/Mg complexes **5** und **6**.[a]

	5	**6**
Zr-C4	2.198(4)	2.208(4)
Zr-C3	2.323(4)	2.338(4)
C4-C3	1.307(5)	1.308(6)
C3-C4-C5	132.0(4)	133.9(4)
C2-C3-C4	135.0(4)	132.5(4)
Mg-C3	2.356(4)	2.395(4)
Mg-C2	2.558(4)	2.546(4)
Mg-C1	2.809(5)	2.822(7)
C1-C2	1.339(6)	1.328(6)[b]
Mg-C21	2.135(5)	
Mg-O31	2.040(3)	
C21-Mg-C3	125.7(2)	130.8(2)[b]
C21-Mg-O31	111.4(2)	135.4(2)[c]
C1-C2-C3-C4	99.0(6)	104.4(6)

[a] Bond lengths are given in Å, angles in degrees. [b] C2-Mg-C2*. [c] C2-Mg-C3*.

carbon atom C3 and markedly longer contacts to the adjacent olefinic carbon atoms C1 and C2. The coordination sphere around magnesium is completed by the σ-*n*-butyl group and a single tetrahydrofuran donor ligand.

In compound **5**, the unsymmetrical coordination environment makes the magnesium atom a chiral center. Furthermore, the coordination of the magnesium atom to one face of the enyne π system resulted in the formation of an element of planar chirality inside the heterobimetallic molecule **5**. Consequently, we have observed a pair of diastereoisomers of **5** to be present in solution. At 213 K in [D_8]toluene solution, they were found in a circa 3:1 ratio. Most significantly, their ^{1}H NMR spectra show the bridging hydride signals at $\delta = -1.60$ ppm (major isomer) and $\delta = -1.89$ ppm (minor isomer), respectively. Both show the NMR signals of pairs of diastereotopic Cp ligands at zirconium, for example $\delta = 5.64$, 5.37 ppm (^{1}H, major isomer), and the pair of $=CH_2$ ^{1}H NMR signals of the bridging enyne ligands, for example, $\delta = 4.82$, 4.62 ppm for the major isomer (for details, see the Supporting Information).

We assume that compound **5** is formed by the addition of di(*n*-butyl)magnesium (from the Schlenk equilibrium) to the zirconacycloallenoid compound **4**. Transfer of an alkyl σ ligand to the transition metal followed by butene elimination would provide a straightforward way of describing the formation of **5**. This was in some way supported by an experiment that led to the formation of an equally interesting new heterobimetallic $(Zr)_2Mg$ product **6**. We generated the zirconacycloallenoid **4** in situ by treatment of [Cp_2ZrCl_2] with two molar equiv of *n*-butylmagnesium chloride in the presence of 1 equiv of the enyne **3**. A solution of **4** was then combined with a solution of the Zr/Mg complex **5** and kept at 80 °C for 5 h to give the doubly enyne-/doubly hydride-bridged $(Zr)_2Mg$ complex **6**, which was isolated as a yellow solid in 55% yield (see Scheme 1).

Compound **6** was characterized by X-ray diffraction (single crystals were obtained from pentane). In the crystal, compound **6** has a pair of zirconocene units C_2-symmetrically bridged by a magnesium dihydride (MgH_2) moiety. Each Zr/Mg connection occurs by a bridging hydride and a section of the enyne ligand (see Figure 2 and Table 1). Similar to compound **5**, the Mg–C3 interaction is short, with the

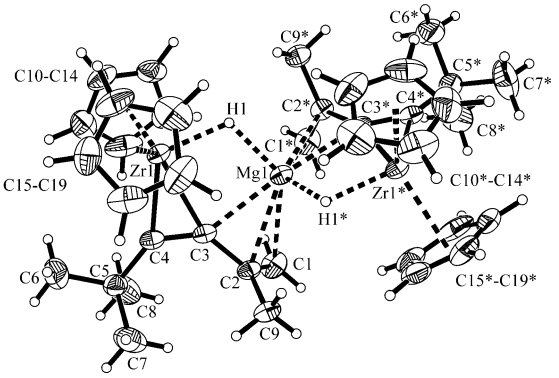

Figure 2. A view of the molecular structure of the $(Zr)_2Mg$ complex **6**.[17] Ellipsoids are set at 30% probability.

adjacent Mg–C2/C1 bonds becoming increasingly longer. The Mg···Zr separation in compound **6** is found at 3.08 Å.

We note that in the crystalline state, compound **6** has two enyne units bridging between the individual zirconium atoms and the single central magnesium atom. Owing to the planar chirality of each of the partial magnesium–enyne coordination modes, two diastereomers of **6** may be formed (with relative configurations pR*, pR* = *rac*-**6** and pR*, pS* = *meso*-**6**). Actually, a close inspection of the general structural features of the crystal structure analysis of C_2-symmetric *rac*-**6** (see Figure 2) reveals that there may be two conformers being formed, with orientations of the methyl groups at the enyne framework being both pseudoaxially or both pseudoequatorially oriented. There is only one C_1-symmetric conformation of *meso*-**6**. We have observed both the axial and equatorial conformers of *rac*-**6** and the single *meso*-**6** product as a mixture in solution (ratio 61:15:24%, ^{1}H NMR at 213 K; Figure 3). The separate *rac*-**6** conformers each show a ^{1}H NMR hydride signal ($\delta = -1.58$ ppm (major isomer), $\delta = -2.18$ ppm (minor *rac*-**6** isomer)), pairs of Cp signals and each a separate single set of enyne ligand signals. The *meso*-**6** diastereomer features a "frozen" conformation of lower symmetry (C_1) at 213 K and consequently features a total of four ^{1}H NMR Cp signals

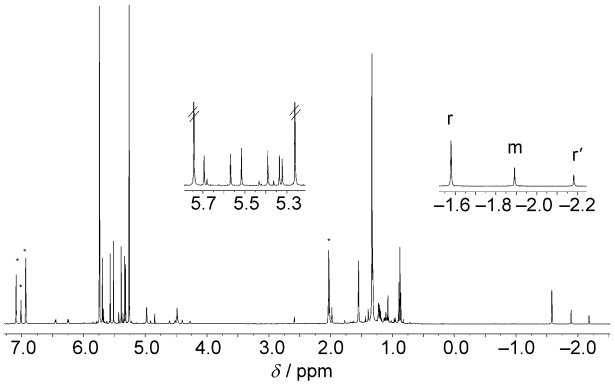

Figure 3. ^{1}H NMR spectrum of the mixture of isomers of **6** in [D$_8$]toluene (*) at 213 K. r,r′ = *rac*-**6** isomers, m = *meso*-**6**.

along with a hydride signal at $\delta = -1.89$ ppm (for further details, see the Supporting Information).

To obtain deeper insights into structural characteristics and bonding scenarios in the solid state, versatile ^{1}H and ^{13}C solid-state NMR techniques were applied to the precipitated products of **5** and **6**. Although the ^{13}C{^{1}H} CPMAS NMR spectrum of **5** indicates the presence of both diastereomers in the solid state as well, in the case of **6**, only one diastereomer is present. The bridging hydrides (H1) can unambiguously be identified in both cases owing to their characteristic chemical shift values at low frequencies ($\delta = -1.8$ ppm (**5**, major isomer) and $\delta = -2.2$ ppm (**6**); see Figure 4). Additionally, the absence of this resonance in the ^{13}C{^{1}H} heteronuclear correlated spectrum (CP-HETCOR) performed for **6** directly indicates that these protons experience no dipolar couplings to adjacent ^{13}C nuclei, as expected for the bridging ^{1}H nuclei (for additional data, see the Supporting Information).

The unusual bonding features of the zirconocene–enyne-stabilized magnesium hydrides as found in the complexes **5** and **6** were analyzed by DFT calculations[13] of the three isomers of **6** (TPSS-D3/def2-TZVP). Despite the good agreement between the DFT-optimized and the single crystal structure of *rac*-**6** (eq), it turned out that *rac*-**6** (ax) is the more stable isomer ($\Delta E = -0.9$ kcal mol^{-1}) of **6** in the gas phase and with a continuum solvation model. *Meso*-**6** is predicted to be 1 kcal mol^{-1} less stable than *rac*-**6** (eq). The order of the stabilities agrees with our NMR experiments.

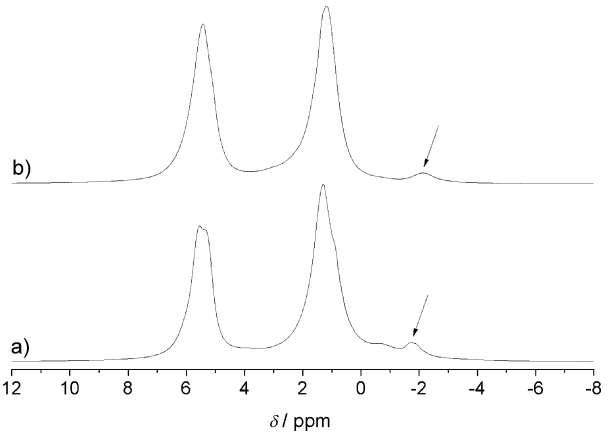

Figure 4. Solid-state ^{1}H MAS NMR spectra of a) **5** and b) **6** acquired at 11.7 T with spinning frequencies of 25 and 29 kHz, respectively. The characteristic resonance of the bridging Zr···H···Mg hydride (H1 in Figures 1 and 2) is marked by an arrow.

Further analysis of the interactions between the MgH_2 fragment and the zirconocene units reveals a stronger overlap (Wiberg bond order)[14] of hydride with Zr (0.695) than with Mg (0.267). The magnesium cation is stabilized by notable overlap (bond order up to 0.21) with the enyne units. This notion is also supported by an ETS-NOCV analysis[15] of the complex *rac*-**6** (eq), which reveals significant orbital interactions between MgH_2 and the two Zr/enyne fragments that is associated with electron density transfer from Mg to the Zr–H bonds and from the enyne fragment to Mg (for more details, see the Supporting Information).

In conclusion, we have shown that magnesium dihydride (MgH_2) and even an alkylmagnesium hydride (n-C_4H_9MgH) can be stabilized in their monomeric molecular forms in a straightforward manner by coordination to a single organometallic unit, namely a zirconocene–enyne framework. The coordination occurs through hydride bridging between magnesium and zirconium supplemented by an unusual distorted bonding of the magnesium to three carbon atoms of the Zr/Mg-bridging enyne ligand. In future studies, we will explore whether other related zirconocene complexes of conjugated dienes or diynes[16] might also be able to serve in that supporting role for magnesium hydride monomerization and if this unusual transition-metal/main-group-metal coordination chemistry might lead to facilitated or even new main-group metal hydride reactions.

Experimental Section

5: At −78 °C, *n*-butylmagnesium chloride solution (0.68 mL, 2 M diethyl ether solution, 1.36 mmol, 4 equiv) was added to a solution of [dichlorobis(η^5-cyclopentadienyl)zirconium] (100 mg, 0.34 mmol, 1 equiv) and 2,5,5-trimethyl-1-hexen-3-yne (37 mg, 0.30 mmol, 0.9 equiv) in THF (5 mL). After 1 h at 60 °C, the volatile components of the reaction mixture were removed under reduced pressure, the residue was extracted with *n*-pentane (3 × 5 mL), and was filtered. Finally the pentane filtrate was cooled to −30 °C to give complex **5** as orange crystals (99 mg, 66 %; two isomers were detected by NMR (^{1}H, 213 K) in a 3:1 ratio). Major isomer: ^{1}H NMR (500 MHz, 213 K, [D$_8$]toluene): $\delta = 5.64$, 5.37 (each s, each 5 H, Cp), 4.82/4.62 (each s, each 1 H, =CH$_2$), −1.60 ppm (s, 1 H, Mg–H). ^{13}C{^{1}H} NMR: $\delta = 202.7$ (ZrC=), 159.6 (MeC=)^{t}, 131.9 (−C=)^{t}, 105.1 (=CH$_2$), 101.8, 101.5 ppm (Cp). Minor isomer: ^{1}H NMR: $\delta = 5.56$, 5.41 (each s, each 5 H, Cp), 4.59/4.21 (each s, each 1 H, =CH$_2$), −1.89 ppm (s, 1 H, Mg–H). ^{13}C{^{1}H} NMR: $\delta = 204.0$ (ZrC=), 164.7 (MeC=)^{t}, 133.6 (−C=)^{t}, 103.2 (=CH$_2$), 101.7, 101.6 ppm (Cp), [t tentative assignment].

6: Complex **5** (77 mg, 0.15 mmol, 0.9 equiv) was added to a solution of complex **4** (1 equiv, generated in situ) in toluene (10 mL). The reaction mixure was then heated to 80 °C for 5 h. The obtained suspension was filtered and the brown filtrate was reduced in volume under reduced pressure. Subsequently, the residue was washed with *n*-pentane (3 × 5 mL) to give compound **6** as a yellow powder (59 mg, 55 %; three isomers were detected by NMR (^{1}H, 213 K): 61 % (rac):24 % (meso):15 % (rac)). Major isomer (rac): ^{1}H NMR (500 MHz, 213 K, [D$_8$]toluene): $\delta = 5.74$, 5.26 (each s, each 5 H, Cp), 4.98/4.49 (each m, each 1 H, 1-H), −1.58 ppm (s, 1 H, Mg–H). ^{13}C{^{1}H} NMR: $\delta = 205.0$ (ZrC=), 165.3 (MeC=)^{t}, 129.2 (−C=)^{t},

102.9, 102.0 (Cp), 105.4 ppm (br, $=CH_2$). Minor isomer (rac): ^{1}H NMR: $\delta = 5.52$, 5.39 (each s, each 5H, Cp), 4.51/4.40 (each m, each 1H, 1-H), −2.18 ppm (s, 1H, Mg–H). $^{13}C\{^1H\}$ NMR: $\delta = 205.3$ ($ZrC=$)^t, 167.3 (MeC=), 130.9 (−C=), 103.6 ($=CH_2$), 102.4, 101.8 ppm (Cp). Minor isomer (meso): ^{1}H NMR: $\delta = 5.69$, 5.57, 5.34, 5.32 (each s, each 5H, Cp), 4.91/4.61, 4.47/4.28 (each m, each 1H, $=CH_2$), −1.89 ppm (s, 2H, MgH). $^{13}C\{^1H\}$ NMR: $\delta = 205.6$, 204.1 ($ZrC=$)^t, 169.3, 164.7 (MeC=), 131.5, 129.9 (−C=), 106.3, 102.2 ($=CH_2$), 102.5, 102.31, 102.28, 102.0 ppm (Cp), [t tentative assignment].

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[17] CCDC 891966 (**5**) and CCDC 891967 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

