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Classical versus Bridged Allyl Ligands in Magnesium Complexes: The Role of Solvent

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Whether in its "classically" σ-bound (η^1) form or in a more symmetrical, bridged π-bound (η^3) arrangement, the conformation of a coordinated allyl ligand is strongly metal-dependent.[1] Compounds of the alkali and heavy alkaline-earth (Ca−Ba) metals, for example, almost always possess π-bound allyls,[2] whereas allyls in magnesium complexes are uniformly found to be σ-bound in the solid state; it has been suggested that π coordination of allyl ligands to magnesium is intrinsically disfavored.[3] However, evidence that π-bonded structures may exist in solution for some organomagnesium reagents[4] and catalyst initiators[5] suggests that the balance between σ and π coordination may be influenced by solvent coordination and steric effects.[6] Here we report the first crystallographic evidence for a polyhapto allylmagnesium species and the results of density funtional theory (DFT) calculations that help define the influence of coordinated bases on Mg allyl hapticity.

The colorless complex $[Mg\{C_3(SiMe_3)_2H_3\}_2(thf)_2]$ (**1**) was synthesized by the salt metathesis reaction of 1 equiv of $MgBr_2$ and 2 equiv of KA′ [A′ = 1,3-$(SiMe_3)_2C_3H_3$] in THF. The molecule is fluxional in solution; at −45 °C, the ^{1}H NMR spectrum indicates that the compound possesses σ-bonded A′ ligands, as evidenced, for example, by the appearance of inequivalent $SiMe_3$ groups. At room temperature and above, the spectrum presents an increasingly "π-like" ligand pattern with a triplet, a doublet, and a singlet (for the $SiMe_3$ groups). Similar solution behavior is observed for the $[GaA'_3]$ complex[7] and reflects the presence of equilibrating allylic isomers.

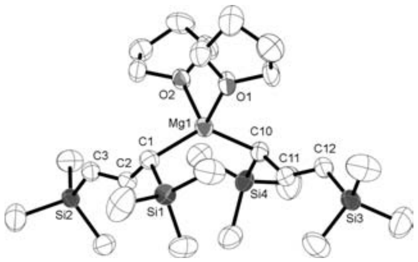

Figure 1. Diagram of the non-hydrogen atoms of **1**. Thermal ellipsoids are shown at the 50% probability level. Selected bond distances (Å): Mg−C1, 2.197(3); Mg−C10, 2.195(3); Mg−O1, 2.057(17); Mg−O2, 2.054(13); C1−C2, 1.467(4); C2−C3, 1.352(4); C10−C11, 1.469(4); C11−C12, 1.355(4).

In the solid state, molecules of **1** are nearly C_2-symmetric; each Mg center is surrounded by two σ-coordinated allyl moieties and two THF solvent molecules in a distorted tetrahedral environment [C−Mg−C, 130.7(1)°; O−Mg−O, 89.8(8)°; Figure 1]. The Mg−C distances of ∼2.20 Å are typical for terminal Mg allyl groups in neutral complexes.[8]

To determine the extent to which THF contributes to the σ-bound structure, $[Mg\{C_3(SiMe_3)_2H_3\}_2(Et_2O)]$ was synthesized analogously to **1**. The ether solvate also presents a "π-like" pattern in its ^{1}H NMR spectrum, but under vacuum the ether is readily lost, and the spectrum of the resulting pale-yellow, base-free **2** becomes more complex. The variable-temperature ^{1}H NMR spectra recorded from 210 to 350 K (see the Supporting Information) are not easily interpreted but suggest that the conformational changes in **2** are more elaborate than would be expected for a purely monomeric species.

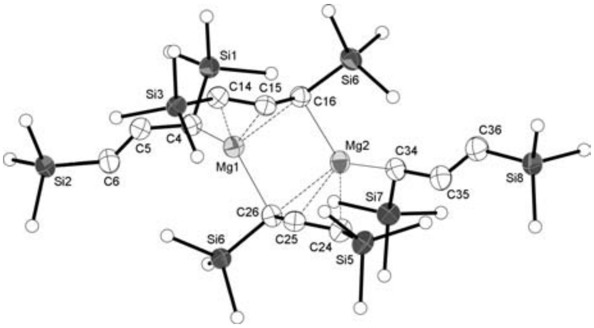

Figure 2. Diagram of the non-hydrogen atoms of **2**. Thermal ellipsoids are shown at the 50% probability level, and methyl groups have been rendered as circles of arbitrary size. Selected bond distances (Å): Mg1−C4, 2.139(2); Mg1−C14, 2.438(2); Mg1−C15, 2.444(2); Mg1−C16, 2.514(2); Mg2−C34, 2.138(2); Mg2−C24, 2.464(3); Mg2−C25, 2.435(2); Mg2−C26, 2.444(2); Mg1−C26, 2.234(3); Mg2−C16, 2.232(2).

Base-free **2** is found to be dinuclear in the solid state, with the Mg atoms coordinated in an irregular fashion (Figure 2). A σ-bound terminal allyl is present on each magnesium, and two allyl ligands bridge the metals. The $Mg-C_{terminal}$ distances are identical within error and are 0.06 Å shorter than the corresponding distance in solvated **1**; the ligands have strongly localized single and double bonds (Δ_{CC} = 0.15 Å). The bridging allyls (C14−C16 and C24−C26) are also of a localized type, with an average difference between the single and double bonds of 0.12 Å. Each metal contacts a bridging allyl through one relatively short distance of ∼2.23 Å (Mg1−C26, Mg2−C16).

The magnesium atoms are clearly not σ-bonded to the other carbon atoms in the bridging allyl ligands. The distances from Mg2 to C24−C26 are surprisingly uniform at 2.435(2)−2.464(3) Å, despite the difference in π-electron density on the ligands implied by the unequal C−C lengths. The distances from Mg1 to C14−C16 are more varied [in the range 2.438(2)−2.514(2) Å] and also span unequal C−C bond lengths. Except for the obvious difference of the additional terminal allyl ligands, the framework of **2** resembles that calculated for diallyllithium.[9]

A cation−π description fits the bonding of the magnesium centers to the C14−C16 and C24−C26 carbons. Allyl ligands can display

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cation$-\pi$ interactions with alkali metals,[10] but **2** is the first structurally authenticated compound to exhibit cation$-\pi$ interactions between Mg^{2+} and an allyl ligand. Mg$-$(π-donor) interactions have been studied by Vijay and Sastry,[11] who calculated a Mg$-$C distance of 2.41 Å and an interaction energy of 69 kcal mol^{-1} for $[Mg(C_2H_4)]^{2+}$. The distance and expected strength of the cation$-\pi$ bonding (sufficient to hold the dimer together in a hydrocarbon solvent) appear appropriate for **2**, although such secondary interactions must be weaker than the direct Mg$-$C(σ) bonds.

DFT investigations were carried out on a set of allyl complexes related to **1**.[12] Starting from a σ-bonded geometry, $[Mg(C_3H_5)_2]$ minimizes to a structure with C_2 symmetry (Figure 3a). The Mg$-$C1 and Mg$-$C2 distances of 2.226 and 2.231 Å, respectively, are clearly within bonding distance (note the average Mg$-$C distance of 2.30 Å in magnesocene[13]); Mg$-$C3 is slightly longer (2.326 Å). The C1$-$C2 and C2$-$C3 distances of 1.412 and 1.389 Å, respectively, indicate that considerable delocalization of the π electrons in the allyl ligand has occurred. In view of the spread in the Mg$-$C distances, it is probably appropriate to view the bonding as "slipped π".[14] Substitution of the allyl ligands with silyl moieties slightly refines the π-bound structure (Figure 3b), which has C1$-$C2 and C2$-$C3 distances that differ by only 0.007 Å, indicating virtually complete delocalization of the π electrons.

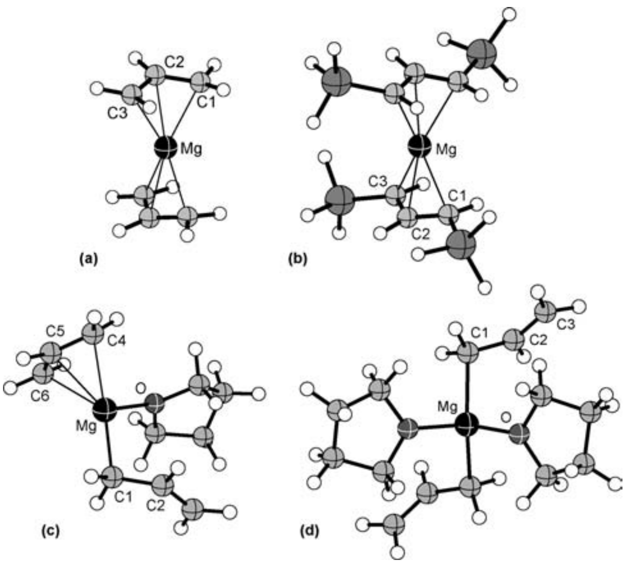

Figure 3. Calculated structures of diallylmagnesium complexes and selected bond distances (Å). (a) "Slipped-π" structure of unsubstituted $[Mg(C_3H_5)_2]$. (b) $[Mg\{C_3(SiH_3)_2H_3\}_2]$: Mg$-$C1, 2.261; Mg$-$C2, 2.222; Mg$-$C3, 2.289; C1$-$C2, 1.410; C2$-$C3, 1.403. (c) $[Mg(C_3H_5)_2(thf)]$: Mg$-$O, 2.070; Mg$-$C1, 2.141; Mg$\cdots$C2, 2.95; C1$-$C2, 1.463; C2$-$C3, 1.343; Mg$-$C4, 2.298; Mg$-$C5, 2.264; Mg$-$C6, 2.363; C4$-$C5, 1.404; C5$-$C6, 1.391. (d) $[Mg(C_3H_5)_2(thf)_2]$: Mg$-$O, 2.105; Mg$-$C1, 2.176; Mg$\cdots$C2, 3.02; C1$-$C2, 1.460; C2$-$C3, 1.344.

The calculations indicate that addition of a single THF ligand to $[Mg(\pi\text{-}C_3H_5)_2]$ results in slippage of one allyl ligand to the classical σ-bonding mode (Figure 3c). The Mg$-$C(σ) distance is 2.141 Å, and the C1$-$C2 and C2$-$C3 distances differ by 0.12 Å; they are substantially localized into single and double bonds. The other allyl adopts a "slipped-π" geometry, with a Mg$-$C range of 2.26$-$2.36 Å, but the C4$-$C5 and C5$-$C6 bonds differ by only 0.013 Å, indicating that the π electrons remain delocalized. The rearrangements here are reminiscent of those in $[Mg(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)(thf)_2]$, in which the change of one η^5-Cp in $[Mg(\pi\text{-}C_5H_5)_2]$ to η^1-Cp on coordination of the THF was ascribed to steric crowding.[15]

Addition of a second THF molecule to $[Mg(\eta^1\text{-}C_3H_5)(\eta^3\text{-}C_3H_5)(thf)]$ causes both allyl ligands to assume σ-bonding modes (Figure 3d). The calculated C_2-symmetric structure has Mg$-$C bond lengths of 2.176 Å, which are close to those observed in **1**.

In summary, it appears that π-type bonding in magnesium allyl compounds is energetically feasible, but only in the absence of perturbing forces.[16] Magnesium allyl complexes have typically been isolated as ether solvates, an experimental artifact that has undoubtedly contributed to the perception that σ-bonding is the preferred mode for Mg$-$allyl bonding. Both calculations and experimental data suggest that a shift to classic σ-bonding occurs upon coordination of solvent; a related shift is also expected in allyllithium chemistry.[8] The reactions of allyllithium reagents can change appreciably in the presence of coordinating solvents,[17] and the same may be true for their organomagnesium counterparts.

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Supporting Information Available: Synthetic details for **1** and **2**, crystallographic details, X-ray crystallographic files (CIF), additional views of **1** and **2**, details of the computations, and complete ref 12. This material is available free of charge via the Internet at http://pubs.acs.org.

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