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Novel Mono-alkyl Magnesium Complexes Stabilized by a Bulky β-Diketiminate Ligand: Structural Characterization of a Coordinatively Unsaturated Trigonal System

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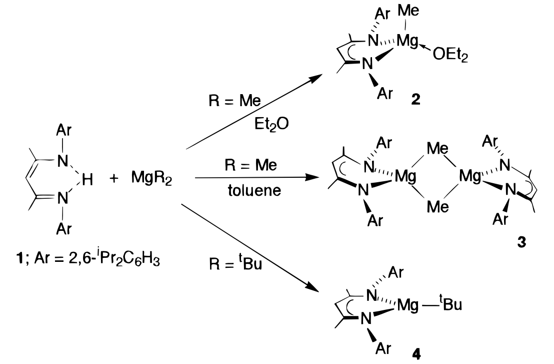
Despite the synthetic importance and widespread use of Grignard reagents, and the fact that magnesium alkyls have been known since the middle of the 19th century,[1] the chemistry of well characterized simple mono-alkyl magnesium systems is surprisingly undeveloped.[2] Indeed, it appears that only a handful of *halide-free*, uncharged mono-nuclear systems are known, these being based on pyrazolylborate,[3] carbazolyl[4] or triazinyl[5] ligands.[6] None of these systems is formally coordinatively unsaturated. Furthermore, alkyl-bridged dimeric systems are virtually unknown for simple mono-alkyl magnesium.[7,8] Our studies have been directed toward the formation of coordinatively unsaturated, and also alkyl bridged or solvent coordinated mono-alkyl magnesium complexes (i.e. systems that have a vacant coordination site or effectively a *protected* vacant site), these being designed as potential catalytic agents. In such systems a suitable ancilliary ligand could both stabilize the desired molecular arrangement and also influence the activity and selectivity of the reagent. A bulky β-diketiminate ligand[9] has been used to this effect in the present work. Here we report the first examples, for halide-free mono-alkyl magnesium systems, of: (i) a *coordinatively unsaturated* mononuclear complex and (ii) an alkyl-bridged dimer,[7] as well as a solvent coordinated derivative.

Scheme 1



The reaction of β-diketimine **1** ($Ar = 2,6\text{-}{}^iPr_2C_6H_3$)[9e] with dimethylmagnesium in 1:1 molar ratio in diethyl ether proceeds via the elimination of methane to form the mononuclear methylmagnesium complex **2** containing one coordinated ether molecule (Scheme 1). An X-ray analysis[10] shows (Figure 1) the molecule to have crystallographic C_s symmetry about a plane passing through Mg, O(1), C(1), and C(3), the ether ligand being disordered about the mirror plane. The geometry at magnesium is distorted tetrahedral with angles in the range 91.8(2) and 119.7(1)°, the most acute being associated with the bite of the chelating *N,N′* ligand. The Mg−N distances [2.076(3) Å] are unexceptional, and there is a typical pattern of bond delocalisation in the β-diketiminate ligand [N(1)−C(2) 1.326(4), C(2)−C(3) 1.412(4) Å]. The six-membered chelate ring adopts a sofa conformation with the C_3N_2 portion being coplanar (to within 0.06 Å), the magnesium center being displaced by 1.00 Å out of this plane.

The ^{1}H and ^{13}C NMR spectra of the compound are consistent with a C_s structure also being present in solution, and the ambient temperature proton spectrum shows line broadening of one of the iso-propyl methyls consistent with hindered rotation about the Ar−N bonds as observed previously in related aluminum[11a] and zirconium[11b] systems.

When the same reaction of the diketimine with $MgMe_2$ is carried out in the absence of the ether donor ligand (i.e., by using toluene as the solvent) then the methyl-bridged dimer **3** is formed in high yield. The X-ray structure[12] shows **3** to be centrosymmetric (Figure 2) with distortions from tetrahedral symmetry at each magnesium center similar to those in **2** (angles in the range 91.3(1) to 118.4(1)°, the most acute angle again being associated with the bite of the β-diketiminate ligand). The pattern of bond delocalisation in the β-diketiminate ligand is the same as in **2**. The folding of the chelate ring, however, is appreciably less than in **2** with the magnesium atom lying only 0.57 Å out of the C_3N_2 plane. The methyl bridges are distinctly asymmetric [Mg−C(1) 2.220(2), Mg−C(1A) 2.245(2) Å] and the nonbonded Mg···Mg distance is 2.878(1) Å, with an angle of 80.3(1)° subtended at the methyl groups. In common with **2**, the ^{1}H NMR spectrum of **3** again shows there to be fluxional behavior associated with the

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(1) Elschenbroich, Ch.; Salzer, A. *Organometallics*, 2nd ed.; VCH: Weinheim, 1992; p 2.

(2) For relevant reviews see Bickelhaupt, F. In *Grignard Reagents: New Developments*; Richey, H. G., Ed.; Wiley: Chichester, U.K., 2000; pp 299−328 and references therein.

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(7) The methyl-bridged cyclopentadienyl compound $[(C_5Me_4Et)MgMe(THF)]_2$, a *bis-hydrocarbyl* system, has been described, see Westerhausen, M.; Makropoulos, N.; Wieneke B.; Karaghiosoff, K.; Nöth, H.; Schwenk-Kircher, H.; Knizek, J.; Seifert, T. *Eur. J. Inorg Chem.* **1998**, 965−971.

(8) Some complex ionic or bimetallic (Mg/Al) systems are known. See ref 6a and (a) Vielbrock, H.; Behrens, U.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1257−1259. (b) Vielbrock, H.; Abeln, D.; Weiss, E. *Z. Naturforsch.* **1994**, *49b*, 89−99. (c) Her, T.-Y.; Chang, C.-C.; Lee, G.-H.; Peng, S.-M.; Wang, Y. *Inorg. Chem.* **1994**, *33*, 99−104. (d) Her, T.-Y.; Chang, C.-C.; Liu, L.-K. *Inorg. Chem.* **1992**, *31*, 2291−2294. (e) Chang, C.-C.; Srinivas, B.; Wu, M.-L.; Chiang, W.-H.; Chiang, M. Y.; Hsiung, C.-S. *Organometallics* **1995**, *14*, 5150−5159.

(9) For recent examples of the use of β-diketiminate complexes in catalytic applications see (a) Cheng, M.; Attygalle, A. B.; Lobkovsky, E. B.; Coates, G. W. J. *Amer Chem. Soc.* **1999**, *121*, 11583−11584. (b) Gibson, V. C.; Maddox, P. J.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 1651−1652. (c) Budzelar, P. H. M.; van Oort, A. B.; Orpen, A. G. *Eur. J. Inorg. Chem.* **1998**, 1485−1494. (d) Kim, W.-K.; Fevola, M. J.; Liable-Sands, L. M.; Reingold, A. L.; Theopold, K. H. *Organometallics* **1998**, *17*, 4541−4543. (e) Feldman, J.; McLain, S. J.; Parthasarathy, A.; Marshall, W. J.; Calabrese, J. C.; Arthur, S. D. *Organometallics* **1997**, *16*, 1514−1516.

(10) *Crystal data for* **2**: $C_{34}H_{54}N_2OMg$, $M = 531.1$, orthorhombic, space group *Pnma* (no. 62), $a = 16.144(4)$ Å, $b = 21.408(4)$ Å, $c = 9.600(2)$ Å, $V = 3318(1)$ Å^3, $Z = 4$, $D_c = 1.063$ g cm^{-3}, $\mu(\text{Mo K}\alpha) = 0.80$ cm^{-1}, $F(000) = 1168$, $T = 203$ K; 3004 independent reflections; $R_1 = 0.073$, $wR_2 = 0.172$. CCDC 146298.

(11) (a) Radzewich, C. E.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **1999**, *121*, 8673−8674. (b) Guerin, F.; Del Vecchio, O.; McConville, D. H. *Polyhedron* **1998**, *17*, 917−923.

(12) *Crystal data for* **3**: $C_{60}H_{88}N_4Mg_2$, $M = 914.0$, monoclinic, space group *C2/c* (no. 15), $a = 22.643(1)$ Å, $b = 14.901(1)$ Å, $c = 16.510(1)$ Å, $\beta = 90.11(1)°$, $V = 5570.3(3)$ Å^3, $Z = 4$, $D_c = 1.090$ g cm^{-3}, $\mu(\text{Cu K}\alpha) = 6.72$ cm^{-1}, $F(000) = 2000$, $T = 183$ K; 4625 independent reflections; $R_1 = 0.049$, $wR_2 = 0.125$. CCDC 146299.

10.1021/ja000359n CCC: $19.00

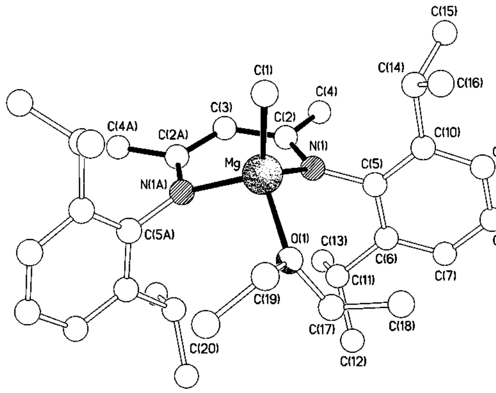

Figure 1. The molecular structure of **2**.

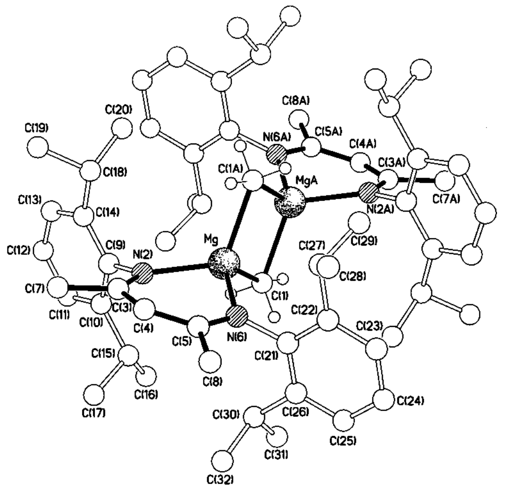

Figure 2. The molecular structure of the C_i-symmetric dimer **3**.

^{i}Pr methyl resonances which is consistent with hindered aryl group rotation.[13]

Reaction of **1** with Mg^tBu_2 etherate[14] in toluene followed by recrystallization from pentane resulted, depending upon the temperature and concentration, in the formation of two distinct crystalline forms: one orthorhombic,[15] the other monoclinic.[16] X-ray analysis showed (Figure 3) both of these crystalline forms to be the "trigonal" magnesium complex **4** (i.e., just different polymorphs). Both forms have virtually identical conformations, the orthorhombic polymorph **4a** having C_s symmetry about a plane that includes Mg, C(2) and C(4) with the tertiary butyl group being disordered about this mirror plane (the monoclinic polymorph **4b** does not have this symmetry constraint). The bonding in the six-membered chelate rings in both forms is the same as in **2** and **3** with a retention of the same bite angle at magnesium. The most striking feature of the complex is the adoption of a trigonal planar coordination geometry for the magnesium, and a planar geometry for the chelate ring (the magnesium atom lies only 0.03 Å out of the C_3N_2 plane in both polymorphs).

These three structures clearly demonstrate that quite large changes in the conformation of the six-membered C_3N_2Mg chelate ring can be accommodated without any significant perturbation of either the bond lengths or the bite angle. Furthermore, there is no correlation between the observed Mg−N bond lengths and the chelate fold angle and this implies that the observed folding is predominantly a sterically controlled phenomenon. The absence of a fourth coordinated ligand in **4** (cf. ether in **2**) is almost certainly a consequence of the increased bulk of the tertiary butyl unit (cf. the methyl in **2**). The reason for the adoption in **2** and **3** of conformations with different degrees of folding of the chelate ring as compared to the planar geometry observed in **4** was not immediately apparent. However, closer inspection of the structure of **2** reveals that, although a folded conformation for the chelate ring is clearly enforced by the steric bulk of the substituents, the observed fold favors a pair of C−H···π interactions between the ether methyl groups and their proximal 2,6-diisopropylphenyl rings. In **3** a planar chelate ring is sterically inhibited by intra-dimer interactions between the *syn* 2,6-diisopropylphenyl groups. The slightly folded geometry observed, however, relieves this congestion and again favors a pair of intra-dimer C−H···π interactions between the C(20) and C(29) methyl groups and their adjacent *syn* oriented 2,6-diisopropylphenyl ring systems. We thus consider that the planar geometry observed in **4** is the one most likely to be favored in the absence of any dominant steric or electronic interactions.

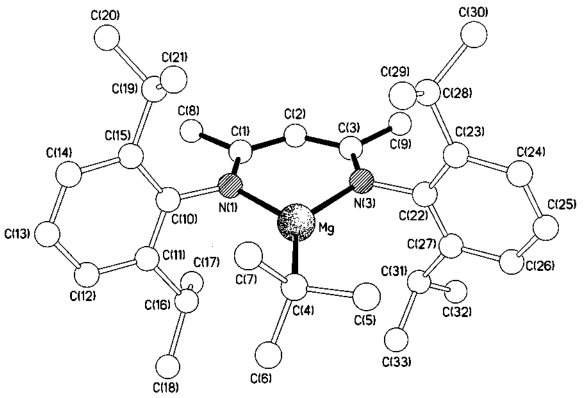

Figure 3. The molecular structure of **4**.

The ^{1}H NMR spectrum of **4** in C_6D_6 is consistent with the solid-state structure showing a pair of doublets of equal intensity for the diasteriotopically inequivalent ^{i}Pr methyl pairs and one septet for the four equivalent methine hydrogens.

This work shows that with a suitably bulky monoanionic ligand system it is possible to form simple mononuclear or alkyl-bridged dimeric compounds and that if the alkyl group employed is also bulky, as in **4**, then a coordinatively unsaturated complex can be isolated. These magnesium species are anticipated to be precursors for a wide range of new chemistry and, in particular, they have been designed for their catalytic behavior in initiating and controlling various polymerization processes.

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Supporting Information Available: Synthetic procedures, characterization data, and details of the X-ray structure determinations of **2**, **3**, **4a**, and **4b** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] The ^{1}H NMR spectrum of **3** in C_6D_6 at 318 K shows two well resolved resonances due to the ^{i}Pr methyls at δ 1.20 (d, $^3J_{HH} = 6.9$, CH*Me*$_2$) and 1.16 (d, $^3J_{HH} = 6.9$, CH*Me*$_2$). On cooling, only one of these broadens rapidly, the other remaining a sharp doublet over the narrow temperature range explored. At 298 K the resonances are at δ ~1.16 (br, CH*Me*$_2$) and 1.14 (d, $^3J_{HH} = 6.9$, CH*Me*$_2$), the downfield resonance being a broad hump.

[14] Kamienski, C. W.; Eastham, J. F. *J. Organomet. Chem*. **1967**, *8*, 542−546.

[15] *Crystal data for* **4a**: $C_{33}H_{50}N_2Mg$, $M = 499.1$, orthorhombic, space group *Pnam* (no. 62), $a = 17.851(2)$ Å, $b = 8.861(1)$ Å, $c = 21.238(3)$ Å, $V = 3359.2(8)$ Å^3, $Z = 4$, $D_c = 0.987$ g cm^{-3}, μ(Mo Kα) = 0.73 cm^{-1}, $F(000) = 1096$, $T = 293$ K; 3866 independent reflections; $R_1 = 0.070$, $wR_2 = 0.178$. CCDC 146300.

[16] *Crystal data for* **4b**: $C_{33}H_{50}N_2Mg$, $M = 499.1$, monoclinic, space group $P2_1/c$ (no. 14), $a = 20.795(1)$ Å, $b = 9.105(1)$ Å, $c = 17.178(1)$ Å, $\beta = 91.84(1)°$, $V = 3250.7(3)$ Å^3, $Z = 4$, $D_c = 1.020$ g cm^{-3}, μ(Cu Kα) = 6.10 cm^{-1}, $F(000) = 1096$, $T = 203$ K; 4803 independent reflections; $R_1 = 0.080$, $wR_2 = 0.207$. CCDC 146301.