Di-*tert*-butylmagnesium: Synthesis and Structure

Kazimierz B. Starowieyski,*,† Janusz Lewinski,† Robert Wozniak,†
Janusz Lipkowski,‡ and Andrzej Chrost†

*Faculty of Chemistry, Warsaw University of Technology, Koszykowa 75,
00-662 Warsaw, Poland, and Institute of Physical Chemistry,
Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland*

The synthesis and structure characterization of $^tBu_2Mg$ is reported. The X-ray structure and variable-temperature ^1H and ^{13}C NMR spectra and the molecular weight measurements show that the title compound occurs as a dimer with a folded $CMg(\mu$-C$)_2MgC$ skeleton in the solid state and solution. A detailed inspection of the crystal structures of $[^tBu_2Mg]_2$ reveals that intra- and intermolecular $CH_3\cdots Mg$ agostic interactions play a substantial role in the molecular assembly.

Introduction

Organomagnesium compounds are among the most common organometallic reagents used as alkylating agents in organic and organometallic synthesis, in industry as well as in research.[1−3] It is not surprising that much effort has been devoted to characterizing the structure of these compounds, both in solution and in the solid state.[4,5] For about 25 years the not very volatile Cp_2Mg and $(MeC_5H_4)_2Mg$ have been used as important doping reagents in the MOVPE technique, for III−V semiconductor materials.[6,7] These organometallics can be obtained directly at about 500 °C from magnesium turnings and corresponding cyclopentadienyl compounds.[1,8] But their low volatility, not very effective pyrolytical decomposition, and low electrical efficiency of magnesium atoms in the formed epitaxial layers motivated us to look for better magnesium sources. It is noteworthy that most of the dialkylmagnesium compounds are not volatile due to their polymeric structure.[4,9] The only relatively volatile compounds, which could be taken into account for the MOVPE technique, were those with strongly hindering substituents and rather low molecular weights, due to the dramatic decrease in the association ability.

Up until now only relatively few homoleptic organomagnesium compounds have been characterized by X-ray diffraction analysis. The lower homologues of dialkylmagnesium compounds are usually amorphous or microcrystalline solids with extremely low solubility in noncoordinating solvents. Powder diffraction studies revealed that the compounds occur as polymeric chains consisting of a four-coordinate metal center joined by bridging alkyl groups.[9] A similar polymeric structure was found for Ph_2Mg in the solid state.[4] The 1:1 mixture of Np_2Mg and $Np(Br)Mg$ forms the polymeric chain $[Mg(Np_2)Mg(Br)_2Mg(Np_2)Mg(Np_2)]_n$.[10] Dimeric $[(2,6-Et_2Ph)_2Mg]_2$ presents the only nonionic example of a structurally authenticated three-coordinate homoleptic, neutral organometallic compound.[11] Dimers with hindered amide group substituents $\{^sBuMg$-$[N(SiMe_3)_2]\}_2$,[12] monomeric monoalkylmagnesium derivatives stabilized by a bulky β-diketimine, (BDI)-MgR,[13] or ionic species, $[Mg(2,4,6-^iPr_3C_6H_2)_3]^-$,[14] are the other previously characterized three-coordinate structures. The two-coordinated monomeric, homoleptic compounds structurally characterized by X-ray crystallography, $Mg(2,4,6-^tBu_3C_6H_2)_2$,[15] $Mg[C(SiMe_3)_3]_2$,[16] $Mg[CH$-$(SiMe_3)_2]_2$,[17] and $Mg[N(2,6-^iPr_2C_6H_3)(SiMe_3)_2]_2$,[18] all consist of sterically strongly encumbered ligands. In strongly hindered dialkylmagnesium compounds there are rela-

* Corresponding author. Tel: 48 22 660 7371. Fax: 48 22 6255317. E-mail: kbs@ch.pw.edu.pl.
† Warsaw University of Technology.
‡ Institute of Physical Chemistry, Polish Academy of Sciences.
(1) *Methoden der Organischen Chemie*; Mueller, E., Ed.; Thieme: Stuttgart, 1970; Vol. XIII/2a, K. Nützel, Methoden zur Herstellung und Umwandlung Magnesium Organischer Verbindungen, pp 54−526.
(2) Coates, G. E.; Wade, K. *Organometallic Compounds*; Methuen: London, 1967; Vol. 1.
(3) Omae, I. *Application of Organometallic Compounds*; John Wiley & Sons: New York, 1999.
(4) Markies, P. R.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; van der Sluis, P.; Spek, A. L. *J. Organomet. Chem.* **1990**, *393*, 315.
(5) Markies, P. R.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Adv. Organomet. Chem.* **1991**, *37*, 47.
(6) Stringfellow, G. B. *Organometallic Vapour Phase Epitaxy, Theory and Practice*; Academic Press: Boston, MA 1989.
(7) Xia, A.; Heeg, M. J.; Winter, C. H. *J. Am. Chem. Soc.* **2002**, *124*, 11264.
(8) Haaland, A.; Lusztyk, J.; Brunvoll, J.; Starowieyski, K. B. *J. Organomet. Chem.* **1975**, *85*, 279.

(9) (a) Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501. (b) *J. Organomet. Chem.* **1964**, *2*, 314. (c) *J. Organomet. Chem.* **1965**, *4*, 101.
(10) Markies, P. R.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Duisenberg, A. J. M.; Spek, A. L. *J. Organomet. Chem.* **1989**, *375*, 11.
(11) Wehmschulte, R. J.; Twamley, B.; Khan, M. A. *Inorg. Chem.* **2001**, *40*, 6004.
(12) Engelhardt, L. M.; Jolly, B. S.; Junk, P. C.; Raston, C. L.; Skelton, B. L.; White, A. L. *Aust. J. Chem.* **1988**, *39*, 1337.
(13) Gibson, V. C.; Segal, J. A.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2000**, *122*, 7120.
(14) Waggoner, K. M.; Power, P. P. *Organometallics* **1992**, *11*, 3209.
(15) (a) Wehmschulte, R. J.; Power, P. P. *Organometallics* **1995**, *14*, 3264. (b) Sachdev, H. *Eur. J. Inorg. Chem.* **2002**, 2681.
(16) (a) Al-Juaid, S. S.; Eaborn, C.; Hitchcock, P. B.; McGeary, C. A.; Smith, J. D. *Chem. Commun.* **1989**, 273. (b) Al-Juaid, S. S.; Eaborn, C.; Hitchcock, P. B.; Kundu, K.; McGeary, C. A.; Smith, J. D. *J. Organomet. Chem.* **1994**, *480*, 199.
(17) Hitchcock, P. B.; Howard, J. A. K.; Lappert, M. F.; Leung, W. P.; Mason, S. A. *Chem. Commun.* **1990**, 847.
(18) Vargas, W.; Englich, U.; Ruhlands-Senge, K. *Inorg. Chem.* **2002**, *41*, 5602.

tively short, nonbonding distances between magnesium and some carbon and hydrogen atoms. For instance, in $[(Et_2Ph)_2Mg]_2$ the shortest $Mg \cdots H-C$ and $Mg \cdots C$ contacts are 2.79 and 2.36 Å, respectively (the latter value exceeds slightly the sum of Mg and C covalent radii, 2.13 Å[19]).[11] In the monomeric $(2,4,6\text{-tri-}^tBu_3C_6H_2)_2Mg$ the shortest $M \cdots H-C$ distance (involving the *tert*-butyl group hydrogens) is 2.28 Å,[15a] while in $Mg[N(Ph)-N(SiMe_2)_2]_2$ the corresponding distances are 2.42 and 2.63 Å.[15b] The crystal structure of monomeric $Mg[CH-(SiMe_3)_2]_2$[17] revealed a close approach of neighboring γ-methyl groups in an agostic fashion, and this was reported as the first example of this type of intermolecular interaction.[20]

When the hydrogen in close contact is bonded the carbon at β position, the agostic interaction of magnesium facilitates the cyclic synchronic reaction with the olefin elimination and the formation of a H—Mg bond. This rationalizes the low stability of R_2Mg. The formation of a six-membered ring through the $Mg \cdots H$ short contact in the monomeric $(2,4,6\text{-tri-}^tBu_3C_6H_2)_2Mg$ does not initiate the elimination reaction, resulting in a reasonably good stability up to 200 °C.[15a] The low-temperature cleavage of the Mg—C bond (with high activation energy) as a competitive decomposition reaction for β-elimination was eliminated by the investigations of the mechanisms of the reaction between ^nBuI and Mg.[21] We noted that monomeric Np_2Mg was the only structurally determined volatile, alkyl-substituted magnesium compound, which sublimed under vacuum at 130 °C. However the low volatility excluded its application as a magnesium source in MOCVD. The $^tBu_2Mg$, due to lower molecular weight and more compact structure, was expected to be a much better candidate for this aim. In the course of our recent investigations toward volatile main group organometallic compounds as precursors for MOCVD,[22] we report here on the synthesis, properties, and molecular structure of the dimeric three-coordinate $[^tBu_2Mg]_2$.[23]

Results and Discussion

To synthesize di-*tert*-butylmagnesium, solvent free and extremely pure, we did not apply the most commonly used dioxane method of synthesis;[1] dioxane forms a strong donor–acceptor complex, which is difficult to split completely into the components at the temperatures below visible β-elimination reaction. The ^tBuMgCl was alkylated with ^tBuLi in pentane solution, according to the method used by Kamienski and Eastman.[24] The evaporation at high vacuum of the solvents was perfect and reasonably easy. The very slow sublimation of the

(19) Emsley, J. *The Elements*; Clarendon Press: Oxford, 1991.

(20) For a comprehensive discussion on agostic interactions in organometallic compounds based on a Cambridge Structural Database study see: Braga, D.; Grepioni, F.; Biradha, K.; Desiraju, G. R. *J. Chem. Soc., Dalton Trans.* **1996**, 3925.

(21) Bryce-Smith, D.; Fox, G. F. *J. Chem. Soc.* **1958**, 1050.

(22) (a) Lewinski, J.; Zachara, J.; Starowieyski K. B. *J. Chem. Soc., Dalton Trans.* **1997**, 4217. (b) Lewinski, J.; Justyniak, I.; Ochal, Z.; Zachara, J. *J. Chem. Soc., Dalton Trans.* **1999**, 2909. (c) Starowieyski, K. B.; Chwojnowski, A.; Jankowski, K.; Lewinski, J.; Zachara, J. *Appl. Organomet. Chem.* **2000**, *14*, 616. (d) Lewinski, J.; Zachara, J.; Starowieyski, K. B.; Kopec, T.; Lipkowski, J.; Justyniak, I.; Kolodziejczyk, E. *Eur. J. Inorg. Chem.* **2001**, 5.

(23) Starowieyski, K. B.; Wozniak, R.; Chrost A.; Lewinski, J.; Lipkowski, J. *11 OMCOS, PO45*; Taipei, 2001.

(24) Kamienski, C. W.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *8*, 542.
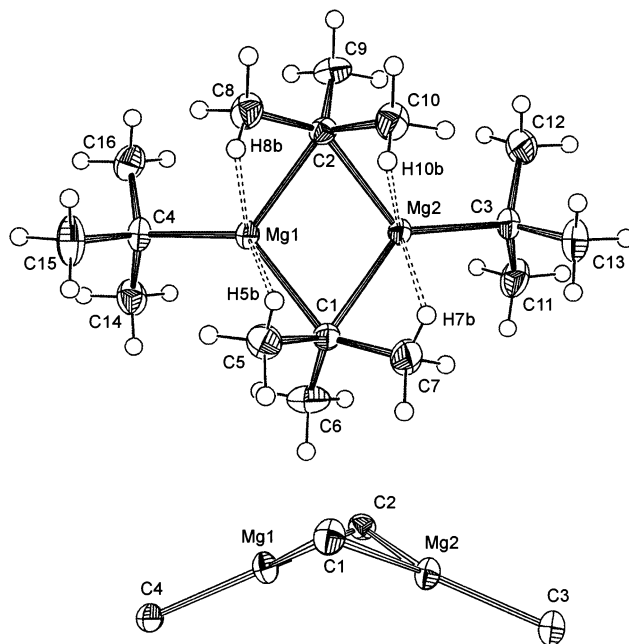

Figure 1. Molecular structure of $[^tBu_2Mg]_2$: (a) top view and (b) side view (skeletal atoms are only shown for clarity) with 50% probability thermal ellipsoids.

obtained solid, at temperatures not higher than 50 °C, results in the formation of nice crystals in low yield. The low volatility can be explained by the evaporation of $^tBu_2Mg$ predominantly, if not entirely, as a dimer. The proposal is supported by comparison with $[Np_2Mg]_3$ (high association energy = 142 kJ/mol), which exists as a monomer first at 130 °C[25] and $[Me_3Al]_2$ existing as a dimer in the vapor phase up to about 100 °C with lower association energy (84 kJ/mol).[26] During the sublimation, even at low temperature, elimination of $CH_2=C(CH_3)_2$ and $CH(CH_3)_3$ proceeds, indicating the very low stability of $^tBu_2Mg$. The presence of $(CH_3)_3$-$CC(CH_3)_3$ (mp 101 °C) as the first fraction in the sublimation of the title compound was observed. Di-*tert*-butylmagnesium is stable as a solid in the dark and under inert atmosphere; however, it slowly decomposes at ambient temperature, especially when exposed to sunlight. The resulting compound has been characterized in solution by ^1H and ^{13}C NMR spectroscopy and cryoscopic molecular weight measurements. In the solid state the molecular structure of $[^tBu_2Mg]_2$ has been determined by X-ray diffraction technique.

The molecular structure of $[^tBu_2Mg]_2$ with a complex system of bondings and interactions is given in Figure 1, and selected bond lengths and angles are given in Table 1. Four nearly equal Mg—C bonds connect the two monomers, forming a folded, four-membered ring [approximately C_{2v} symmetry of the skeleton $CMg(\mu\text{-}C)_2$-MgC]. This fold of the Mg_2C_2 ring can be best described by the $C(1)-Mg(2)-Mg(1)-C(2)$ torsion angle of 140.45-(4)°. Both MgC_3 wings of the bridge are flat, with magnesium atoms adopting a trigonal planar coordination geometry with the sum of C—Mg—C angles of both MgC_3 planes equal to 359.8°. The bridging bonds of this three coordinated magnesium are slightly longer (aver-

(25) (a) Andersen, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 809. (b) Ashby, E. C.; Fernholt, L.; Haaland, A.; Seip, R.; Smith, R. C. *Acta Chim. Scand. A* **1980**, *34*, 213.

(26) Henrickson, C. H.; Eyman, D. P. *Inorg. Chem.* **1967**, *6*, 1461.

Table 1. Selected Bond Lengths (Å) and Angles (deg) and Short Intramolecular C−H···Mg and C···Mg Distances (Å) for [$^tBu_2Mg]_2$

Bond Lengths

Mg(1)−C(1)	2.3044(9)	Mg(2)−C(1)	2.2978(8)
Mg(1)−C(2)	2.3057(8)	Mg(2)−C(2)	2.2987(8)
Mg(1)−C(4)	2.1424(9)	Mg(2)−C(3)	2.1483(8)
C(1)−C(6)	1.5265(15)	C(2)−C(8)	1.5457(13)
C(1)−C(5)	1.5468(13)	C(2)−C(10)	1.5473(13)
C(1)−C(7)	1.5467(15)	C(2)−C(9)	1.5266(13)
C(3)−C(11)	1.5268(14)	C(4)−C(14)	1.5243(14)
C(3)−C(12)	1.5283(14)	C(4)−C(15)	1.5298(15)
C(3)−C(13)	1.5275(15)	C(4)−C(16)	1.5285(14)

Intramolecular Contacts

Mg(1)···C(5)	2.4885(11)	Mg(2)···C(7)	2.4866(13)
Mg(1)···C(8)	2.5425(11)	Mg(2)···C(10)	2.5262(11)
Mg(1)···H(5a)	2.277(15)	Mg(2)···H(10a)	2.288(15)
Mg(1)···H(5b)	2.688(15)	Mg(2)···H(10b)	2.757(14)
Mg(1)···H(8c)	2.451(14)	Mg(2)···H(7b)	2.439(15)
Mg(1)···H(8b)	2.602(14)	Mg(2)···H(7c)	2.496(16)

Bond Angles

Mg(1)−C(1)−Mg(2)	70.91(2)	Mg(1)−C(2)−Mg(2)	70.87(2)
C(1)−Mg(1)−C(2)	99.90(3)	C(1)−Mg(2)−C(2)	100.30(3)
C(1)−Mg(1)−C(4)	130.59(3)	C(1)−Mg(2)−C(3)	131.84(3)
C(2)−Mg(1)−C(4)	129.51(3)	C(2)−Mg(2)−C(3)	127.66(3)
Mg(1)−C(1)−C(5)	77.77(5)	Mg(2)−C(1)−C(5)	125.62(6)
Mg(1)−C(1)−C(6)	107.57(6)	Mg(2)−C(1)−C(6)	123.14(7)
Mg(1)−C(1)−C(7)	141.76(7)	Mg(2)−C(1)−C(7)	77.91(5)
Mg(1)−C(2)−C(8)	79.97(5)	Mg(2)−C(2)−C(8)	142.26(6)
Mg(1)−C(2)−C(9)	116.10(6)	Mg(2)−C(2)−C(9)	106.49(6)
Mg(1)−C(2)−C(10)	131.92(6)	Mg(2)−C(2)−C(10)	79.50(5)
Mg(1)−C(4)−C(14)	112.94(6)	Mg(2)−C(3)−C(11)	112.65(6)
Mg(1)−C(4)−C(15)	110.06(7)	Mg(2)−C(3)−C(12)	111.66(6)
Mg(1)−C(4)−C(16)	110.72(6)	Mg(2)−C(3)−C(13)	110.28(6)

Torsion Angles

C(1)−Mg(2)−C(2)−Mg(1)	−31.87(3)	C(1)−Mg(1)−C(2)−Mg(2)	31.72(3)
C(1)−Mg(2)−Mg(1)−C(2)	140.45(4)	Mg(1)−C(2)−C(1)−Mg(2)	129.16(4)

Table 2. Degree of Association and Mg−C Bond Lengths Observed for R₂Mg Compounds.

organomagnesium compound	association (rt), [coordination]	terminal bonds Mg−C [Å]	bridging bonds Mg−C [Å]		literature
[($^tBu)_2Mg]_2$	dimer [III]	2.148	2.30 symmetric		this work
(Me$_2$Mg)$_n$	polymeric chain [IV]		2.24 symmetric		9b
(Et$_2$Mg)$_n$	polymeric chain [IV]		2.26 symmetric		9c
[Np$_3$Mg$_2$Br]$_n$	polymeric chain [IV]		2.23−2.29	2.41−2.42	10
(Np$_2$)Mg	(130 °C) monomer[a] (rt) solution, trimer [III] or [IV]	2.126			25
[(Et$_2$Ph)$_2$Mg]$_2$	dimer [III]	2.11	2.226−2.259	2.263−2.306	11
(Mez)$_2$Mg[b]	monomer [II]	2.12			15a

[a] Gas phase. [b] 2,4,6-tri-$^tBu_3C_6H_2$.

age value of 2.30 Å) than that of the terminals (2.14 Å), which are within a limit of error equal to the sum of Mg and C covalent radii (2.13 Å).[19] For comparison, the degree of association and bond lengths around magnesium in some other R₂Mg compounds are given in Table 2. The bridging *tert*-butyl groups of [$^tBu_2Mg]_2$ are oriented in such a way that two of their three methyl substituents are directed at the magnesium atoms. The methyl group is tilted toward magnesium atoms, forming strongly deformed angles of MgCC$_\beta$ (about 78−80°), as compared with 106.5° and 123.1° of the third MgCC$_\beta$ angles. For the terminal groups all corresponding values are about 110°. It is reasonable to assume that the observed tilting of the methyl groups toward the magnesium center results from the accommodation of additional intramolecular CH$_3$···Mg agostic interactions, which provide electron density to one face of the planar three-coordinate metal center. The Mg···C distances of the tilted methyl groups are short, 2.487−2.543 Å, as compared with the sum of their van der Waals (vdW) radii, 2.63 Å.[27] All four C−C$_\beta$ bonds involving the

interacting methyl groups are longer by about 0.02 Å than the other C−C$_\beta$ bonds in the molecule. Corresponding C−H···Mg contacts are also significantly shorter than the vdW limit for Mg and H (2.51 Å). Both magnesium atoms are slightly deshielded on one side, but the detailed analysis of the crystal structure revealed that a coordination unsaturation of the less hindered metal side is compensated by the intermolecular C−H···Mg (2.665 Å) interactions between one methyl group of the terminal *tert*-butyl group from one molecule and one metal center from the neighboring dimeric molecule (Figure 2). This secondary intermolecular interaction results in the formation of weakly bonded aggregates of [$^tBu_2Mg]_2$ in the solid state. There is no doubt that the secondary intra- and intermolecular C−H···Mg interactions in the three-coordinate dimer seem to be vital and play a substantial role in the molecular assembly. The intramolecular interactions cause an increase in the strength of the bridge due to
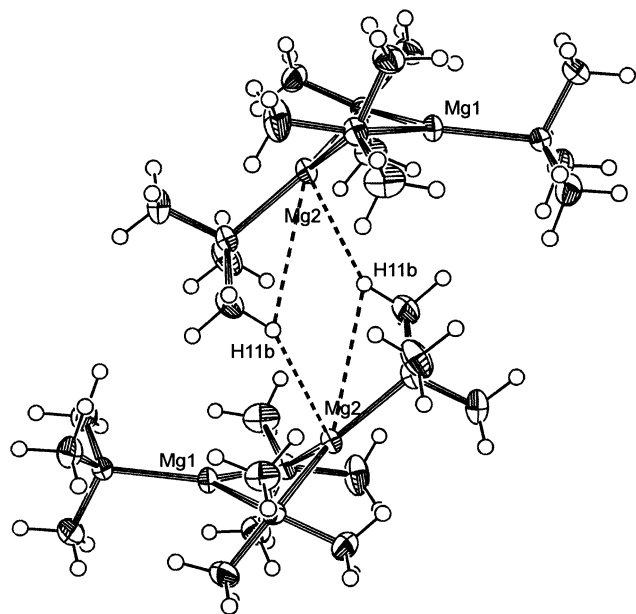
(27) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

Figure 2. View of the weakly bonded dimmer of [$^tBu_2$-Mg]$_2$ based on the C−H⋯Mg agostic interactions with 50% probability thermal ellipsoids.

the shift of electron density to the external side of the folded bridge, but the planarity of the three-coordinate MgC$_3$ metal center remains unchanged. It is worthwhile that, to our knowledge, [$^tBu_2Mg$]$_2$ is the first example of a structurally authenticated three-coordinated homoleptic magnesium compound substituted with alkyl groups; the only other known dimer bridged by carbons, but of the phenyl rings, is [(2,6-Et$_2$Ph)$_2$Mg]$_2$.[11]

The reported results demonstrate that contrary to low-alkyl substituents, which form nonterminated associates with four-coordinated magnesium, or sterically strongly encumbered groups, which form monomeric two-coordinate R$_2$Mg compounds, *tert*-butyl groups allow only the formation of dimeric species with three-coordinated magnesium. This shows that the *tert*-butyl groups are insufficiently bulky to prevent association. The size of the *tert*-butyl group and the presence of agostic magnesium−methyl group interactions exclude the formation of polymeric structures. Furthermore, the complex Mg⋯H$_\beta$ interaction rationalizes the low thermal stability of [$^tBu_2Mg$]$_2$ (visible elimination of CH$_2$=C(CH$_3$)$_2$ even below 50 °C). This is explained by the very small activation energy in a cyclic synchronic reaction of the β-elimination of isobutylene. While the C−H⋯Mg interactions give a simple explanation for the low thermal stability of [$^tBu_2Mg$]$_2$, its slow decomposition even at room temperature, when exposed to sunlight, cannot find a simple explanation. To solve the problem, we tentatively assume that in the butterfly conformation of the dimer p$_z$ orbitals of the neighboring magnesium centers interact substantially and contribute to the lowering of the LUMO. Thus, the light-induced homolytic cleavage of the Mg−C bond leads to the electron promotion into the LUMO and the formation of a single-electron Mg−Mg transannular bond. The resulting species are unstable and further react, decomposing to magnesium and the earlier mentioned hydrocarbons. It is worth noting that one-electron σ-bonding is a rapidly emerging field that has been

investigated in group 13, 14, and 15 chemistry;[28] however, to our knowledge, it has not been considered for the group 2 elements.

Scheme 1. Schematic Representation of Both the Exchange of the Terminal and Bridging *tert*-butyl Groups and the Rotation of the Methyl Groups for [$^tBu_2Mg$]$_2$ in Solution
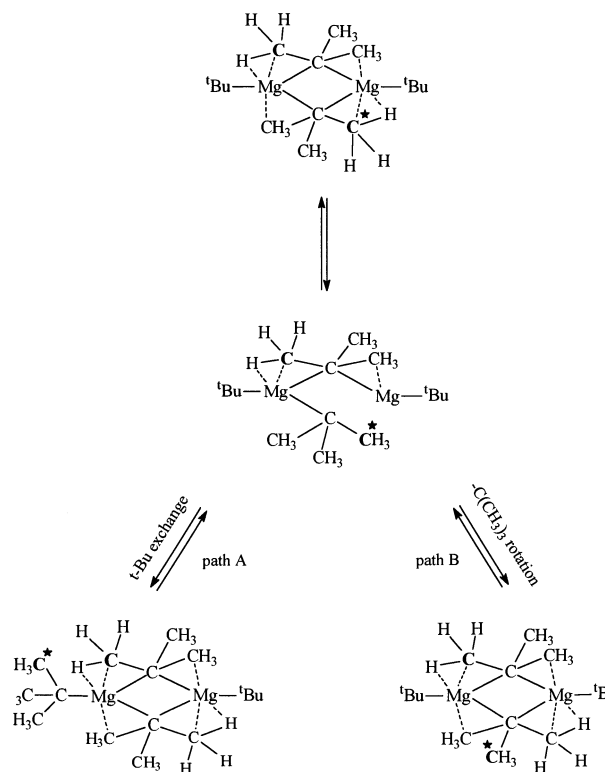
The dimeric structure of di-*tert*-butylmagnesium is retained in solution, as found from both a cryometric molecular weight determination in benzene and NMR studies. The ^{1}H NMR spectrum of [$^tBu_2Mg$]$_2$ displayed one signal (1.15 ppm) at ambient temperature. However, the spectroscopic details are apparent at low temperatures (Figure 3), and the data indicate that the dimeric structure, found in the solid state, is maintained in solution. With a decrease in temperature the signal associated with the ^tBu-Mg protons broadened (below −65 °C) and split into two well-separated resonances at −75 °C (1.53 and 0.95 ppm), which corresponds to the terminal and bridging *tert*-butyl group protons in [$^tBu_2Mg$]$_2$. This result can be best interpreted in terms of a dissociative process (with ΔG_{-187} = 44.0 kJ/mol) in which the Mg(μ-^tBu)Mg bridging bond undergoes cleavage, giving rise to the interchange of the terminal and bridging groups (Scheme 1, path A). Below −80 °C the higher field signal decoalesced to a 1:2 ratio of signals and appears as well-resolved peaks at 0.96 and 0.94 ppm (Scheme 1, path B). This splitting is apparently consistent with the folded structure of dimeric [$^tBu_2Mg$]$_2$ in solution similar to that observed in the solid. Because the decoalescence appears at nearly the

(28) (a) Glidewell, C. Rhodes, C. J. *J. Organomet. Chem.* **1994**, *471*, 71. Canac, Y.; Bourissou, D.; Baceiredo, A.; Gorntzka, H.; Schoeller, W. W.; Bertrand, G. *Science* **1998**, *279*, 2080. (b) Hoefelmeyer, J. D.; Gabbai, F. P. *J. Am. Chem. Soc.* **2000**, *122*, 9054. (c) Cataldo, L.; Choua, S.; Berclaz, T.; Geoffroy, M.; Mezailles, N.; Ricard, L.; Mathey, F.; Le Floch, P. *J. Am. Chem. Soc.* **2001**, *123*, 6654.
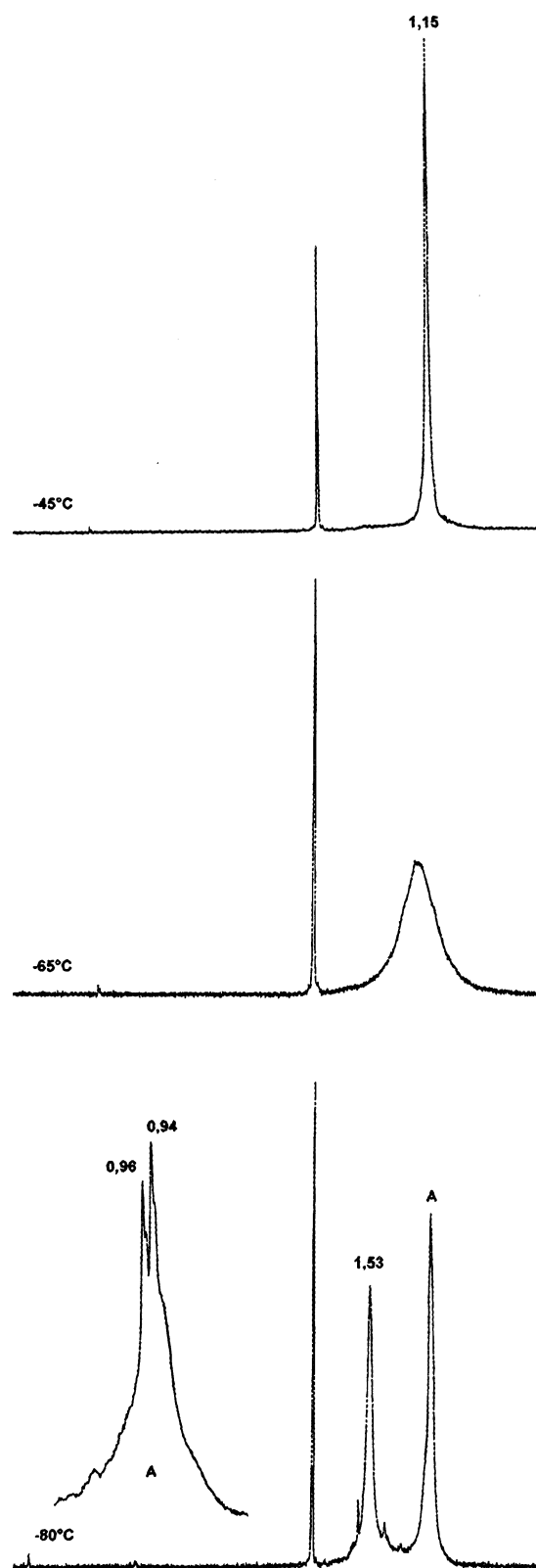
Figure 3. Variable-temperature ^{1}H NMR spectra of [^{t}Bu$_2$-Mg]$_2$ in toluene-d_8.

same temperature as the exchange of terminal−bridging groups, the rotation of methyl groups is slow when the splitting of the Mg(μ-^{t}Bu)$_2$Mg bridging bond is restrained.

The ^{13}C NMR spectroscopic behavior is similar to that observed in the ^{1}H NMR spectrum. The sharp peak of

the β-carbon atoms at 32.8 ppm splits at −80 °C into two broad signals at about 30 and 34 ppm. The weak peak of the α-carbon atoms at 16.5 ppm formed at −80 °C a very broad absorption with inclination for splitting into two maxima at about 16.4 and 15.5 ppm. Such a spectrum is consistent with the dimeric structure of ^{t}Bu$_2$Mg.

In conclusion, crystalline di-*tert*-butylmagnesium exists as a dimer with a folded bridge bonded through α-carbon atoms, which indicates that the *tert*-butyl groups are insufficiently bulky to prevent aggregation. The structure is stabilized by short C−H···Mg interactions on the outer side of the bridge, and additionally two dimer units are weakly connected through weak intermolecular C−H···Mg interactions. The molecular weight measurements and the variable-temperature NMR studies revealed that the dimeric structure of di-*tert*-butylmagnesium found in the solid state is maintained in solution.

Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques in dry, oxygen-free solvents. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury-400 (500 MHz) spectometer. Molecular weight measurements were carried out cryoscopically in benzene. Magnesium turnings were purchased from commercial suppliers. ^{t}BuLi was synthesized by literature procedures.[29,30]

Synthesis of ^{t}BuMgCl. Magnesium turnings (24 g, 1 mol) were activated by stirring with iodine (0.25 g) at 200 °C. They were then treated with ^{t}BuCl (5 g, 0.05 mol) in Et$_2$O (500 cm^3) at reflux temperature. After 1 h the remaining ^{t}BuCl (65 g, 0.7 mol) was added dropwise. After 24 h the clear Grignard solution was decanted. The concentration was 1.02 mol/dm^3. Yield: 89%.

Synthesis of ^{t}Bu$_2$Mg. To a well-stirred Grignard solution (100 cm^3, 0.1 mol) was added dropwise a ^{t}BuLi solution (60 cm^3 pentane, 0.11 mol) at 0 °C. After 2 h the whole amount of ^{t}BuLi was added and the temperature was slowly increased to room temperature. The temperature of the mixture was increased to boiling and kept for some minutes to improve the precipitation. The next day the clear solution was decanted. The solvents were removed under high vacuum (10^{-6} Torr) at 20 °C. Then ^{t}Bu$_2$Mg was sublimed not exceeding 50 °C, maintaining the vacuum. Yield: 39%. Molecular weight measurements (cryoscopically in benzene, 2.4 wt %): calcd 277.09 (dimer), found 278.

X-ray Structure Determination. Single crystals of [^{t}Bu$_2$Mg]$_2$, suitable for X-ray diffraction studies, were placed in thin-walled capillary tubes (Lindemann glass 0.5 mm) in an inert atmosphere. The tubes were plugged with grease, then flame-sealed and mounted on a goniometer head. Crystal data for [^{t}Bu$_2$Mg]$_2$, C$_{16}$H$_{36}$Mg$_2$: $M = 277.07$, crystal dimensions 0.50 × 0.40 × 0.20 mm^3, monoclinic, space group $P2_1/c$ (no. 14), $a = 8.90190(10)$ Å, $b = 11.17700(10)$ Å, $c = 18.9204(2)$ Å, $\beta = 91.4151(5)°$, $U = 1881.92(3)$ Å^3, $Z = 4$, $F(000) = 624$, $D_c = 0.978$ g m^3, $T = 150(2)$ K, μ(Mo Kα) = 4.19 mm^{-1}, Nonius Kappa-CCD diffractometer, $\theta_{max} = 30.03°$, 5515 unique reflections, which were used in all calculations. The structure was solved by direct methods using the SHELXS-97 program[31] and was refined by full matrix least-squares on F^2 using the program SHELXL-97.[32] H atoms were included in idealized positions and refined isotropically. In final cycles all geometrical parameters and isotropic temperature factors of H atoms were

(29) Kottke, T.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 580.
(30) Giancaspro, C.; Sleiter, G. *J. Prakt. Chem.* **1979**, *321*, 876.
(31) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

refined. Refinement converged at R1 = 0.0424, wR2 = 0.0941 for all data and 307 parameters (R1 = 0.0346, wR2 = 0.0905 for 4930 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal to 1.074. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density was equal to $+0.242/-0.178$ e Å^{-3}.

Supporting Information Available: Full details of the X-ray structural analysis of [^{t}Bu$_2$Mg]$_2$, including complete tables of crystal data, atomic coordinates, bond lengths and angles, and positional and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030091J

(32) Sheldrick, G. M. *SHELXL 97, Program for Refinement of Crystal Structures*; University of Göttingen, 1993.