Calculations of the interaction of N(1) in **1**(N) and **1**(P) with a proton (vide supra) revealed that electron density is transferred to the proton primarily through orbitals 14 and 16 of **1**(P) and orbitals 14 and 17 (and, to a lesser extent, 15) for **1**(N). Since this interaction is expected to have a greater influence on bonds involving N(1), it should have a greater stabilizing effect on **1**(N) compared to **1**(P) [i.e. the net overlap population for P–N(1) and N(1)–S(1) is –0.025 for orbitals 14 and 16 of **1**(P) and –0.048 for orbitals 14 and 17 of **1**(N)]. Finally, we note that orbitals 14 and 17 for **1**(N) are π-orbitals. The net effect of this interaction would, therefore, appear to be a cancellation of the destabilizing effect on the π-system brought about by the change in ring geometry.

Electronic Spectra of Lewis Acid Adducts of 1 (R = Ph). All the adducts of **1** (R = Ph) exhibit an intense visible absorption band in the region 410–430 nm (Table I). The observed blue shift in the $\pi^*(\text{HOMO}) \rightarrow \pi^*(\text{LUMO})$ transition of $\mathbf{1}^1$ is consistent with the trend in the calculated energy difference $E(\text{LUMO}) - E(\text{HOMO})$ observed for the series $\mathbf{1}(\text{P}) \rightarrow \mathbf{1}(\text{N}) \rightarrow H_2PS_2N_3H^+$ (using the experimental geometry of **5**), viz. 0.066 → 0.063 → 0.075 au. The increase in the transition energy for $H_2PS_2N_3H^+$ is primarily due to stabilization of the HOMO.

Conclusion. The interaction of phosphadithiatriazines with Lewis/Brønsted acids occurs at a nitrogen atom adjacent to the phosphorus atom of the PS_2N_3 ring and is controlled by electrostatic effects. Coordination to an electrophile also imposes a marked perturbation on both the conformation of the ring and the S–N bond lengths. The S–N bond involving the coordinated nitrogen is weakened substantially, and this nitrogen atom moves out of the plane of the other ring atoms, indicating that it is removed from the π-system, which becomes localized in the SNSNP segment of the ring. These effects appear to parallel those found for $S_3N_3^-$.[7] However, in the case of $S_3N_3^-$, a more stable conformation is achieved through ring contraction to give **4** with an S–S bond and the coordinated nitrogen as an exocyclic substituent. For the PS_2N_3 ring this stabilization is attained by the movement of the coordinated nitrogen out of the plane of the other ring atoms rather than by ring contraction, which would involve the formation of an endocyclic P–S bond. The structural changes observed for the PS_2N_3 ring upon adduct formation suggest that electrophiles might be used to promote ring-opening reactions or polymerization via S(2)–N(2) bond cleavage. The formation of π-complexes (η^3, η^4, or η^5) between the adducts and suitable metal acceptors also appears worthy of investigation since coordination to nitrogen should minimize the occurrence of π to σ rearrangements.

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Registry No. **1** (R = H), 112575-73-2; **1** (R = Ph), 76958-87-7; **6**, 112596-25-5; **8**, 112575-74-3; $Ph_2PS_2N_3H^+BF_4^-$, 112596-21-1; $Ph_2PS_2N_3H^+CF_3SO_3^-$, 112575-70-9; $Ph_2PS_2N_3Me^+CF_3SO_3^-$, 112575-72-1; $Ph_2PS_2N_3{\cdot}BCl_3$, 112596-22-2; $Ph_2PS_2N_3{\cdot}SnCl_4$, 112596-23-3.

Supplementary Material Available: Tables listing thermal parameters, the derived hydrogen positions, and all bond lengths and bond angles for **5** and **6** (7 pages); tables of calculated and observed structure factors for **5** and **6** (24 pages). Ordering information is given on any current masthead page.

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Sterically Hindered Magnesium Aryloxides

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Reaction of $MgBu_2$ with sterically hindered phenols such as 2,6-di-*tert*-butyl-4-methylphenol (H-BHT) gives the dimeric bis(phenoxide), $(Mg(BHT)_2)_2$. Reactions with oxygen donors give the monomeric adducts $Mg(BHT)_2L_2$, where L = THF or methyl benzoate. Diethyl ether slowly gives an analogous bis adduct. The X-ray structure of the dimeric species $(Mg(BHB)_2)_2$ (bis(bis(2,6-di-*tert*-butylphenoxy)magnesium)) displays the steric crowding of the *tert*-butyl groups around the Mg_2O_2 core. Crystal data: monoclinic, $C2/c$, $a = 44.629$ (4) Å, $b = 13.922$ (2) Å, $c = 20.067$ (5) Å, $\beta = 97.43°$ at –70 °C.

Introduction

The utility of dialkylmagnesium compounds in synthetic magnesium chemistry has been reported by several investigators.[1-4] Reactions with protic species evolve 2 equiv of the alkane to give the desired species in high yield. Our investigation of the factors that influence the behavior of high activity, high stereospecificity magnesium chloride supported catalysts for 1-olefin polymerization[5] led us to explore magnesium compounds with sterically hindered phenoxide ligands such as 2,6-di-*tert*-butyl-4-methylphenol. (In this paper, butylated hydroxytoluene will be referred to as H-BHT; BHT implies the deprotonated anion.) The chemistry developed here closely parallels chemistry reported for related zinc compounds[6] and is analogous to the chemistry reported for Grignard reagents with the same hindered phenols.[7,8]

Experimental Section

All manipulations were carried out in the nitrogen atmosphere of a Vacuum Atmospheres drybox. Solvents were dried by standard techniques.[9] Dibutylmagnesium in heptane from Alfa and "butylated hydroxytoluene" (H-BHT)(2,6-di-*tert*-butyl-4-methylphenol and "butylated hydroxy benzene" (H-BHB)(2,6-di-*tert*-butylphenol) from Aldrich were used as received. NMR spectra were recorded on NT Series GE spectrometers at 300 or 360 MHz proton frequencies. Chemical shifts (ppm) were referenced to residual protic solvent peaks or internal TMS. Spectra were recorded in standard pulsed FT mode at constant temperature, which was calibrated by using a precalibrated thermocouple. Elemental analyses were performed on all isolated compounds by Galbraith Laboratories, Knoxville, TN, and were satisfactory. Vapor pressure osmometry molecular weight determinations were also

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performed by Galbraith Laboratories.

$(Mg(BHT)_2)_2$. A solution of $MgBu_2$ in pentane (0.7 M, 177 mL, 124 mmol) was slowly added to a solution of H-BHT (54.6 g, 248 mmol) in toluene (200 mL). The addition was exothermic, starting at room temperature and reaching a temperature of 55 °C. Solvent was reduced under vacuum, and the solution was then stored at −35 °C over the weekend. Snow white crystals precipitated. These were collected by vacuum filtration and dried under high vacuum. Yield: 39 g. The compound does not melt but starts to decompose at 102 °C and is black at 156 °C. ^1H NMR (C_6D_6): *t*-Bu, 1.28, 1.62 (s, 36 H); Me, 2.15, 2.30 (s, 6 H); *m*-CH, 7.14, 7.15 (s, 4 H). ^{13}C NMR (C_6D_6): *t*-C, 21.2, 21.5; *t*-Bu, 32.0, 34.3; Me, 35.1, 36.0; *m*-C, 137.7, 138.1; aromatic C, 123.1, 125.9, 129.8, 137.8, 138.1, 153.6, 158.3. IR in Nujol (cm^{-1}, % *T*): 1424, 11; 1348, 40; 1280, 18; 1261, 28; 1223, 26; 1210, 25; 1118, 44; 1026, 48; 918, 49; 860, 31; 817, 38; 799, 33; 779, 40; 644, 48; 621, 48. Anal. Calcd for $C_{60}H_{92}Mg_2O_4$: C, 77.8; H, 10.0. Found: C, 77.6; H, 9.8. Mol wt (C_6H_6): calcd, 926; found, 930.

NMR Experiments with $(Mg(BHT)_2)_2$. Benzene-d_6 solutions of $(Mg(BHT)_2)_2$ (40 mg) were reacted with a variety of donor molecules. Protio species were used for NMR experiments close to stoichiometric conditions, and deuteriated compounds were used in experiments in which a large excess was required. Stoichiometric quantities (4 equiv/$(Mg(BHT)_2)_2$) of acetone, THF, and pyridine caused the resonances of $(Mg(BHT)_2)_2$ to disappear from the spectrum and new resonances attributable to disolvated monomers to grow in. A slight excess of acetonitrile was required to completely eliminate the resonances of the dimer. Diethyl ether and methylene chloride gave resonances very close to those observed in benzene. $Mg(BHT)_2(acetone)_2$: *t*-Bu, 1.65 (s, 36 H); Me_2CO, 1.40 (s, 12 H); Me, 2.22 (s, 6 H); *m*-CH, 7.00 (s, 4 H). $Mg(BHT)_2(THF)_2$: see below. $Mg(BHT)_2(ether)_2$: see below. $Mg(BHT)_2(py)_2$: *t*-Bu, 1.65 (s, 36 H); Me, 2.38 (s, 6 H); *m*-py, 6.45 (t(complex), 4 H); *p*-py, 6.80 (t(complex), 2 H); *m*-CH, 7.22 (s, 4 H); *o*-py, 8.62 (d, 2 H). $Mg(BHT)_2(acetonitrile)_2$: *t*-Bu and MeCN, 1.62 (s, 42 H); Me, 2.25 (s, 6 H); *m*-CH, 7.00 (s, 4 H).

Addition of large excesses of acetone, THF, and acetonitrile caused the BHT resonances to shift slightly, but no new species were observed. The spectrum of $(Mg(BHT)_2)_2$ in methylene-d_2 chloride was shifted considerably from that observed in benzene-d_6, but the basic pattern of the dimer was preserved. As excess pyridine-d_5 is added to the benzene-d_6 solution of $Mg(BHT)_2(py)_2$, two new sets (integration ratio of 3:1) of BHT resonances [(*t*-Bu, 1.70; Me, 2.26; *m*-CH, 7.10) and (*t*-Bu, 1.65; Me, 2.42, *m*-CH, 7.28), respectively] start to grow into the spectra. At 10% pyridine-d_5, the new BHT resonances account for approximately 30% of the BHT integrated intensity. At 50% pyridine-d_5, the new resonances account for 60%, and in pure pyridine-d_5, the new resonances account for about 85% of the BHT intensity, with $Mg(BHT)_2(py)_2$ accounting for the remainder.

$(Mg(BHB)_2)_2$. A pentane solution of $MgBu_2$ (0.7 M, 177 mL, 124 mol) was added slowly to a solution of H-BHB (51.17 g, 0.248 mol) in toluene (200 mL). The reaction was exothermic, and there was considerable gas evolution. The temperature was maintained at 60 °C for an hour, and then the reaction was allowed to cool to room temperature. The off-white precipitate that had formed was collected by vacuum filtration and dried under high vacuum. The material was shown to be pure but to include toluene of solvation by NMR. Analytically pure samples could be prepared by recrystallization from pentane. ^1H NMR (C_6D_6): *t*-Bu, 1.16, 1.54 (s, 36 H); *p*-CH, 6.63, 6.72 (t, *J* = 7.7 and 7.9 Hz, 2 H), *m*-CH, 7.05, 7.16 (d, J = 7.9 and 7.7 Hz, 4 H). Anal. Calcd for $C_{56}H_{84}Mg_2O_4$: C, 77.3; H, 9.7. Found: C, 77.4; H, 9.8.

$Mg(BHT)_2(THF)_2$. A sample of solid $(Mg(BHT)_2)_2$ (4.63 g, 5.0 mmol) was reacted in pentane (25 mL) with THF (4.33 g, 60 mmol). The solid started to dissolve, and then the product began to precipitate so that at no time was the mixture a homogeneous solution. Recrystallized (from THF) yield: 5.90 g, 88%. ^1H NMR (C_6D_6): $OCCH_2$, 1.19 (m, 8 H); *t*-Bu, 1.61 (s, 36 H); Me, 2.41 (s, 6 H); OCH_2, 3.63 (m, 8 H); *m*-CH, 7.25 (s, 4 H). IR in Nujol (cm^{-1}, % *T*): 1425, 4; 1302, 6; 1259, 25; 1218, 40; 1199, 34; 1019, 24; 919, 44; 888, 34; 850, 16; 809, 50; 784, 42; 723, 52; 677, 56. Anal. Calcd for $C_{38}H_{62}MgO_4$: C, 75.2; H, 10.3. Found: C, 75.2; H, 10.4. The molecular weight of this compound was determined by measuring the molecular weight of $(Mg(BHT)_2)_2$ in THF as a solvent. Mol wt (THF): calcd, 607; found, 592.

$Mg(BHT)_2(ether)_2$. Reaction of $(Mg(BHT)_2)_2$ with stoichiometric diethyl ether in benzene gave no visible reaction; the dimer persisted. A sample of $(Mg(BHT)_2)_2$ (4.63 g, 5.0 mmol) was recrystallized from diethyl ether (20 mL) by taking it up in ether at room temperature. The solution was then evaporated, and the white crystalline material was dried under high vacuum overnight. The isolated product was identical with the starting material.

When the dimer was dissolved in neat diethyl-d_{10} ether, there was a reaction with a half-life of about an hour yielding $Mg(BHT)_2(ether\text{-}d_{10})_2$. In an attempt to synthesize and isolate this ether adduct, a sample of $(Mg(BHT)_2)_2$ (2.79 g, 3.0 mmol) was refluxed in diethyl ether (50 mL). The solution was then reduced in volume yielding a white crystalline material that was dried under high vacuum. This new material was considerably less soluble in ether than the dimeric starting material. Yield: 1.94 g, 65%. ^1H NMR (C_6D_6): $OCCH_3$, 0.86 (t, *J* = 7 Hz, 12 H); *t*-Bu, 1.58 (s, 36 H); Me, 2.34 (s, 6 H); OCH_2, 3.28 (q, *J* = 7 Hz, 8 H); *m*-CH, 7.25 (s, 4 H). IR in Nujol (cm^{-1}, % T): 1424, 2; 1364, 34; 1348, 32; 1280, 6; 1261, 13; 1223, 12; 1209, 12; 1118, 38; 1026, 49; 918, 50; 888, 44; 860, 19; 817, 30; 799, 22; 779, 33; 644, 49; 621, 50. Anal. Calcd for $C_{38}H_{66}MgO_4$: C, 74.7; H, 10.9. Found: C, 74.5; H, 10.8.

Table I. Crystal Structure Data for **1** and **2**

	$(Mg(BHB)_2)_2\cdot 1.5C_6H_5CH_3$ (**2**$\cdot 1.5C_6H_5CH_3$)	$(Mg(BHT)_2)_2$ (**1**)
formula	$Mg_4O_8C_{133}H_{192}$	$Mg_2O_4C_{60}H_{92}$
fw	2016.24	1968
space group	*C*2/*c*	P*c*2$_1$*b*
a, Å	44.629 (4)	10.650 (2)
b, Å	13.922 (2)	19.782 (5)
c, Å	20.367 (5)	27.211 (8)
β, deg	97.43 (1)	
V, $Å^3$	12363.4	5733
Z	4	
D(calcd), g cm^{-3}	1.083	
cryst dimens, mm	0.53 × 0.47 × 1.00	
temp, °C	−70	
radiation	Mo Kα[a]	
μ, cm^{-1}	0.79	
2θ limits, deg	1.8–48	
no. of data collcd	10 443	
no. of data with $I \geq 3\sigma(I)$	4847	
final no. variables	658	
final residuals, e $Å^{-3}$	0.14	
R	0.059	
R_w	0.060	

[a] Graphite monochromated, λ = 0.710 69 Å.

$Mg(BHT)_2(MeO_2CC_6H_5)_2$. A sample of $(Mg(BHT)_2)_2$ (4.63 g, 5 mmol) in toluene was reacted with a slight excess of methyl benzoate. There was an immediate color change to an intense yellow. Solvent was removed, yielding an oil that slowly crystallized under high vacuum at room temperature. ^1H NMR (C_6C_6): *t*-Bu, 1.64 (s, 36 H); Me, 2.43 (s, 6 H); OMe, 3.50 (s, 6 H); *m*-CH, 6.85 (t, *J* = 8 Hz, 4 H); *p*-CH, 7.00 (t, *J* = 8 Hz, 2 H); *m*-CH, 7.24 (s, 4 H); *o*-CH, 8.02 (d, *J* = 8 Hz, 4 H). IR in Nujol: (cm^{-1}, % *T*) 1732, 71; 1682, 22; 1648, 12; 1602, 33; 1582, 45; 1423, 12; 1329, 17; 1301, 9; 1220, 45; 1198, 35; 1160, 44; 1135, 42; 1079, 60; 1026, 55; 1003, 57; 973, 63; 950, 57; 887, 63; 864, 49; 840, 33; 809, 67; 784, 58; 723, 14; 688, 64; 676, 69. Anal. Calcd for $C_{46}H_{62}MgO_6$: C, 75.1; H, 8.5. Found: C, 75.2; H, 8.4.

Attempted X-ray Structure Determination of $(Mg(BHT)_2)_2$. Crystals of $(Mg(BHT)_2)_2$ were grown from benzene. While the crystals appeared to be well formed, ω scans were broad. The crystallographic details are given in Table I. The diffraction intensities fell off quickly with increasing 2θ, indicating a disorder problem. Repeated attempts to solve the structure met with failure. A second crystal was mounted in the presence of mother liquor in case the problems were caused by loss of solvent of crystallization. The same problems were encountered with this second data set so the structure determination was abandoned.

X-ray Structure Determination of $(Mg(BHB)_2)_2$. Many of the details of the crystal structure are given in Table I. The procedures are standard for the Du Pont laboratories. Data were collected on a Enraf-Nonius diffractometer by using the ω-scan method. The scan width of 1.80–2.20° in ω was done at scan speeds of 2.20–5.00 deg/min, and a typical half-height peak width was 0.16° in ω. Maximum *h*, *k*, and *l* were 50, 15, and 22, respectively. The two standards, which were collected 103 times, showed a 10% decrease in intensity; the data were adjusted appropriately. Intensity variations in an azimuthal scan were 4.1% so no absorption correction was applied. The structure was solved by direct methods (MULTAN) with some difficulty. Refinement was carried out by full-matrix least squares on *F*, using scattering factors from ref 18, and included anomalous terms for magnesium. All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were fixed, and isotropic thermal parameters of 5.0 were assigned. Both toluene molecules were disordered, and chemically reasonable models could not be refined. The molecules were satisfactorily modeled by inserting atoms at fixed locations and allowing very large anisotropic thermal parameters to account for the ill-defined electron density in the area. Attempts to reduce the high thermal smearing via other models such as inserting

Table II. Fractional Coordinates ($\times 10^5$) and Isotropic Thermal Parameters for Non-Hydrogen Atoms in the Structure of $(Mg(BHB)_2)_2$

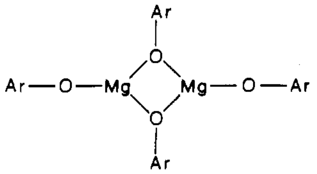
atom	*x*	*y*	*z*	B_{iso},[a] Å^2	atom	*x*	*y*	*z*	B_{iso},[a] Å^2
Mg(1)	1014 (1)	3041 (1)	2701 (1)	2.6 (1)	C(33)	924 (1)	−609 (4)	3897 (3)	5.9 (2)
Mg(2)	1391 (1)	3128 (1)	4030 (1)	2.6 (1)	C(34)	708 (1)	86 (4)	3883 (2)	4.4 (2)
O(1)	783 (1)	2982 (2)	1884 (1)	3.0 (1)	C(35)	768 (1)	1039 (3)	3745 (2)	2.8 (1)
O(2)	1629 (1)	3194 (2)	4837 (1)	2.9 (1)	C(36)	1598 (1)	707 (3)	3371 (2)	3.3 (1)
O(3)	1137 (1)	2198 (2)	3474 (1)	2.2 (1)	C(37)	1550 (1)	851 (4)	2596 (2)	4.9 (2)
O(4)	1263 (1)	3969 (2)	3254 (1)	2.3 (1)	C(37′)	1811 (1)	−147 (4)	3515 (3)	6.3 (2)
C(10)	607 (1)	2962 (3)	1288 (2)	2.6 (1)	C(37″)	1769 (1)	1585 (3)	3684 (2)	3.7 (1)
C(11)	455 (1)	3806 (3)	1033 (2)	2.9 (1)	C(38)	516 (1)	1780 (3)	3809 (2)	3.1 (1)
C(12)	282 (1)	3755 (4)	409 (2)	4.0 (1)	C(39)	564 (1)	2189 (3)	4528 (2)	5.0 (2)
C(13)	250 (1)	2932 (4)	46 (2)	4.5 (2)	C(39′)	498 (1)	2619 (3)	3324 (2)	3.8 (1)
C(14)	393 (1)	2111 (4)	288 (2)	3.9 (1)	C(39″)	204 (1)	1306 (4)	3695 (3)	6.0 (2)
C(15)	573 (1)	2089 (3)	918 (2)	3.0 (1)	C(40)	1364 (1)	4889 (3)	3167 (2)	2.6 (1)
C(16)	737 (1)	1157 (3)	1148 (2)	3.4 (1)	C(41)	1565 (1)	5068 (3)	2689 (2)	3.0 (1)
C(17)	697 (1)	882 (3)	1873 (2)	4.1 (1)	C(42)	1670 (1)	6007 (4)	2660 (2)	5.1 (2)
C(17′)	625 (1)	285 (4)	718 (2)	5.2 (2)	C(43)	1592 (1)	6717 (4)	3064 (3)	6.1 (2)
C(17″)	1074 (1)	1293 (4)	1075 (2)	4.8 (2)	C(44)	1386 (1)	6541 (3)	3502 (2)	4.5 (2)
C(18)	469 (1)	4753 (3)	1425 (2)	3.3 (1)	C(45)	1266 (1)	5635 (3)	3571 (2)	3.0 (1)
C(19)	304 (1)	4613 (3)	2039 (2)	4.7 (2)	C(46)	1688 (1)	4356 (3)	2205 (2)	3.5 (1)
C(19′)	305 (1)	5576 (4)	1017 (3)	6.2 (2)	C(47)	1525 (1)	3406 (3)	2083 (2)	4.5 (2)
C(19″)	790 (1)	5104 (3)	1630 (2)	4.6 (2)	C(47′)	2017 (1)	4137 (5)	2445 (3)	8.3 (2)
C(20)	1829 (1)	3095 (3)	5385 (2)	2.8 (1)	C(47″)	1668 (1)	4796 (4)	1502 (2)	6.7 (2)
C(21)	2106 (1)	3603 (3)	5450 (2)	2.9 (1)	C(48)	1021 (1)	5525 (3)	4046 (2)	3.4 (1)
C(22)	2308 (1)	3469 (3)	6023 (2)	4.1 (1)	C(49)	1022 (1)	6372 (4)	4532 (3)	6.3 (2)
C(23)	2252 (1)	2860 (4)	6533 (2)	4.6 (2)	C(49′)	1053 (1)	4637 (3)	4497 (2)	3.7 (1)
C(24)	1983 (1)	2387 (3)	6473 (2)	3.9 (1)	C(49″)	713 (1)	5493 (4)	3617 (3)	6.1 (2)
C(25)	1759 (1)	2498 (3)	5922 (2)	2.9 (1)	C(51)	1984 (3)	1866 (11)	608 (5)	11.7 (5)
C(26)	1452 (1)	1999 (3)	5910 (2)	3.8 (1)	C(52)	1972 (2)	1079 (9)	1016 (6)	10.7 (4)
C(27)	1385 (1)	1318 (3)	5310 (2)	5.5 (2)	C(53)	2239 (5)	996 (11)	1491 (9)	19.2 (8)
C(27′)	1206 (1)	2763 (3)	5902 (2)	4.6 (2)	C(54)	2502 (5)	1769 (27)	1544 (6)	40.3 (19)
C(27″)	1434 (1)	1394 (3)	6538 (2)	5.4 (2)	C(55)	2432 (4)	2158 (10)	1150 (6)	20.4 (8)
C(28)	2192 (1)	4283 (3)	4902 (2)	3.4 (1)	C(56)	2244 (3)	2414 (6)	681 (6)	11.8 (5)
C(29)	2231 (1)	3725 (4)	4282 (3)	7.3 (2)	C(57)	1789 (2)	2068 (9)	145 (5)	17.3 (5)
C(29′)	2492 (1)	4800 (4)	5105 (3)	6.5 (2)	C(61)	330 (5)	8076 (9)	2481 (13)	17.5 (8)
C(29″)	1959 (1)	5074 (3)	4737 (2)	5.2 (2)	C(62)	133 (6)	8203 (9)	1792 (9)	18.0 (7)
C(30)	1064 (1)	1252 (3)	3602 (2)	2.4 (1)	C(66)	166 (6)	8170 (11)	3054 (9)	17.0 (8)
C(31)	1287 (1)	538 (3)	3591 (2)	3.0 (1)	C(67)	562 (8)	8068 (19)	2149 (24)	28.9 (23)
C(32)	1208 (1)	−390 (3)	3750 (3)	4.8 (2)					

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

additional fixed atoms were unsuccessful. The high correlations in the solvent parameters limit convergence. The largest residual density of 0.14 e/Å^3 was found near carbon atom C(54) of one of the toluene molecules.

Results and Discussion

Synthesis and Structure of Magnesium Bis(phenoxides). Dialkylmagnesium compounds react cleanly with 2 equiv of sterically hindered phenols. This is in contrast to dialkylzinc[10] or trialkylaluminum compounds,[5a,11] which stop at the monoalkyl stage to give $(ZnEt(BHT))_4$ and $AlEt(BHT)_2$, respectively, even with a considerable excess of H-BHT. The resulting products are oxygen bridged dimers (**1**, **2**) in which each metal center is surrounded by three BHT groups.



1: Ar = BHT; bis(bis(2,6-di-*tert*-butyl-4-methylphenoxy)magnesium)
2: Ar = BHB; bis(bis(2,6-di-*tert*-butylphenoxy)magnesium)

Table III. Important Bond Distances (Å) and Angles (deg) in the Structure of $(Mg(BHB)_2)_2$

Interatomic Distances			
Mg(1)–Mg(2)	2.964 (2)	Mg(2)–O(4)	1.971 (3)
Mg(1)–O(1)	1.823 (3)	O(1)–C(10)	1.345 (4)
Mg(1)–O(3)	1.966 (3)	O(2)–C(20)	1.330 (4)
Mg(1)–O(4)	1.951 (3)	O(3)–C(30)	1.386 (5)
Mg(2)–O(2)	1.819 (3)	O(4)–C(40)	1.376 (5)
Mg(2)–O(3)	1.968 (3)		
Intramolecular Angles			
Mg(2)–Mg(1)–O(1)	179.7 (6)	Mg(1)–O(1)–C(10)	178.0 (3)
Mg(2)–Mg(1)–O(3)	41.15 (8)	Mg(2)–O(2)–C(20)	169.1 (3)
Mg(2)–Mg(1)–O(4)	41.16 (8)	Mg(1)–O(3)–C(30)	131.6 (2)
Mg(1)–Mg(2)–O(4)	40.67 (9)	Mg(2)–O(3)–C(30)	130.6 (2)
Mg(1)–Mg(2)–O(2)	178.8 (1)	Mg(1)–O(4)–C(40)	135.5 (2)
Mg(1)–Mg(2)–O(3)	41.09 (8)	Mg(2)–O(4)–C(40)	125.9 (2)
O(1)–Mg(1)–O(4)	139.1 (1)	O(1)–C(10)–C(15)	119.5 (4)
O(1)–Mg(1)–O(3)	138.6 (1)	O(1)–C(10)–C(11)	120.1 (4)
O(3)–Mg(1)–O(4)	82.3 (1)	O(2)–C(20)–C(21)	120.7 (4)
O(2)–Mg(2)–O(4)	138.6 (1)	O(2)–C(20)–C(25)	119.7 (4)
O(2)–Mg(2)–O(3)	139.7 (1)	O(3)–C(30)–C(31)	118.9 (4)
O(3)–Mg(2)–O(4)	81.8 (1)	O(3)–C(30)–C(35)	118.9 (4)
Mg(1)–O(3)–Mg(2)	97.8 (1)	O(4)–C(40)–C(41)	119.8 (4)
Mg(1)–O(4)–Mg(2)	98.2 (1)	O(4)–C(40)–C(45)	118.5 (4)

Evidence of the oligomeric nature of this compound was provided by the proton NMR spectrum, which clearly indicated two different types, presumably terminal and bridging, of phenoxide groups in equal intensity. A molecular weight determination in a nondonor solvent indicated the dimeric nature of the compound, which was confirmed by the X-ray analysis of **2**.

Positional coordinates and isotropic thermal parameters for **2** are given in Table II, and selected bond distances and angles are given in Table III. The atom-labeling scheme is included in the perspective view of the molecule given in Figure 1. The structure of **2** consists of discrete dimeric units in which the primary coordination about each magnesium atom is distorted trigonal planar. Normal coordination numbers for magnesium are four or six, but the three coordination in this system is understandable in light

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(10) Ashby, E. C., Goel, A. B. *Inorg. Chem.* **1979**, *18*, 1306.

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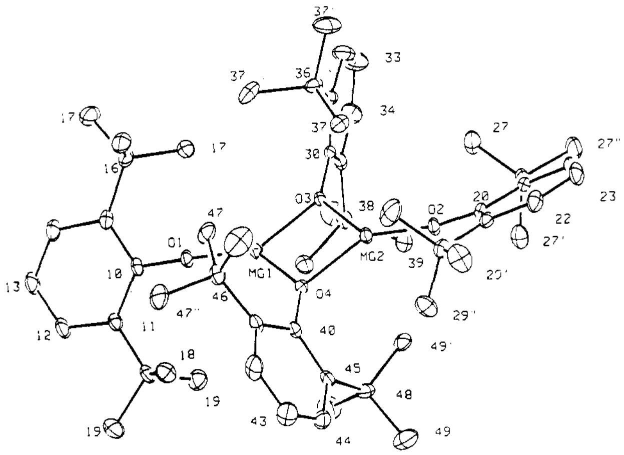
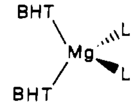


Figure 1. Perspective view of the $(Mg(BHB)_2)_2$ molecule, displaying non-hydrogen atoms.

of the steric bulk of the BHB ligands. The angles about the magnesium atoms are 138.6–139.7° for the four angles involving terminal and bridging oxygens (O_T–Mg–O_B) and 82.3 and 81.8° for O_B–Mg–O_B, indicating a great deal of symmetry about this core. The Mg_2O_2 core is planar (maximum deviation 0.016 Å) and the sum of the internal angles is 360.1°. The four Mg–O_B distances, which range from 1.951 to 1.971 Å are considerably longer than the two Mg–O_T distances. The geometry about the two bridging oxygen atoms is planar with the sums of angles being very close to 360° and the Mg–O_B–C angles being very similar to those found in other main-group phenoxide structures.[6] The Mg–O_T–C angles are surprisingly linear at 178.0 and 169.1°. Angles in the range of 125–150° are expected for main-group structures[6] with angles in the range 160–180° observed only in transition-metal systems where π-interactions become important.[12] The unusual nature of the terminal phenoxides is also reflected in the short C–O_T distances relative to the C–O_B distances; again, distances of this length are normally observed only in transition-metal systems involving π-interactions.

The BHB groups of **2** are rotated with respect to the Mg_2O_2 plane by angles of 53.6–72.7° in order to minimize the steric crowding of the *tert*-butyl groups. This rotation brings four of the *tert*-butyl methyl groups into close proximity of the magnesium atoms. In addition to the primary, oxygen coordination about the magnesium centers, there are also weak agostic interactions with these *tert*-butyl methyl groups of the BHB ligands. The closest interaction (Mg(2)–H(37'') = 2.09 Å) is stronger than the 1.95 Å observed in a related aluminum system if one considers the smaller ionic radius (0.71 versus 0.53 Å) and the observed M–O distances (1.82 for O_T and 1.96 for O_B versus 1.686 Å for O_T). This type of interaction of electron-deficient, early d-block lanthanide and actinide metals with hydrocarbon fragments of coordinated ligands has been noted before.[13] There is a similar short distance on the other side of Mg(2) so its geometry can be considered to be trigonal bipyramidal when these weak hydrogen interactions are included. Mg(1) has a short distance on one side but two somewhat longer interactions from a single methyl group on the other.

Reactions of Magnesium Bis(phenoxides). The NMR spectra of the magnesium dimers are solvent dependent. In nondonor solvents such as benzene or methylene chloride, the spectrum of the dimeric species, **1**, with its two distinct phenoxide ligands is observed. When Lewis base molecules such as THF, acetone, acetonitrile, or pyridine are added to the benzene solutions of $(Mg(BHT)_2)_2$ only one type of BHT ligand is observed. Only 4 equiv of THF, pyridine, or ethyl benzoate is required to cleave the dimeric structure of $(Mg(BHT)_2)_2$ to the monomeric species **3**–**5**. The structure is presumed to be tetrahedral around the magnesium center as has been established for the dietherates of $MgBr_2$,[14] PhMgBr,[15] and EtMgBr.[16] NMR measurements as a function of added ligand indicate that two donor molecules are coordinated to the metal center. Both the THF and methyl benzoate adducts have been isolated and fully characterized. Both the spectroscopic titrations and the NMR spectra of the isolated products indicate only two THF molecules coordinated to the magnesium center. This is in contrast to the octahedral geometry assumed by $MgBr_2$ in THF;[17] presumably the steric bulk of the BHT ligands precludes this higher coordination number.



L = THF (**3**)
pyridine (**4**)
methyl benzoate (**5**)
acetonitrile (**6**)
ether (**7**)

In the $(Mg(BHT)_2)_2$/acetonitrile system, it is likely that the same behavior is obtained, but the coincidence of the acetonitrile and BHT *t*-butyl resonances makes detailed analysis difficult. It is clear that the addition of acetonitrile is an equilibrium reaction and that an excess of acetonitrile is required to obtain all dimer.

When **1** is recrystallized quickly from diethyl ether, there is no reaction; the only product obtained is the starting dimer. This is in spite of the observation of the monomeric ether adduct in ether solution. The rate of formation of the ether adduct observed by a series of NMR spectra of the dimer in ether-d_{10} is much slower that the reactions with the other Lewis bases discussed, taking hours rather than minutes to go to completion. The ether adduct is not observed in a stoichiometric reaction of ether with **1** in benzene solution, presumably due to the very slow rate of formation under low concentrations of ether. Once the ether adduct has been prepared and isolated, NMR spectroscopy indicates that it is stable in benzene at room temperature.

The behavior of the pyridine system at low pyridine concentrations is similar to that observed with the oxygen donor molecules. As the pyridine concentration is increased, the monomeric $Mg(BHT)_2(py)_2$ is replaced in solution by a pair of other BHT-containing species. The observation that these two species grow into the spectra in parallel and that they maintain a 1:3 ratio of BHT–ligand intensities suggests that they arise from the heterolytic disproportionation of eq 1. Pyridine solutions of $(Mg(BHT)_2)_2$ show a conductivity higher than one would expect for molecular species, supporting this supposition, but no further characterization was carried out.

$$2Mg(BHT)_2(py)_2 + 2py \rightleftarrows [Mg(BHT)(py)_5]^+[Mg(BHT)_3(py)]^- \quad (1)$$

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Registry No. **1**, 65277-21-6; **2**, 57570-79-3; **3**, 67825-24-5; **5**, 112596-39-1; **7**, 112596-38-0; $MgBu_2$, 1191-47-5.

Supplementary Material Available: Tables of complete fractional atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, hydrogen atom coordinates, additional bond distances and angles, and nonbonding distances (15 pages); a table of calculated and observed structure factors (13 pages). Ordering information is given on any current masthead page. Inquiries for copies of these materials can also be directed to the indicated author.

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