6-Fluoro-1,4,5,6-tetradeoxy-1,5-imino-D-lyxitol (15): Hydrogenolysis of **11** resulted in a mixture of **14** (52% yield) and **15** (11% yield) after column chromatography on silica gel (^{i}PrOH/H_2O/NH_4OH, 14:1:1); ^{1}H NMR (D_2O) δ 1.50 (app q, J = 12.0, 1 H, H-3a), 1.66 (app dt, J = 3.8, 12.4, 1 H, H-3e), 2.69 (dd, J = 1.3, 14.3, 1 H, H-6a), 2.91–2.83 (dddd, J = 3.0, 5.7, 12.2, 25.3, 1 H, H-2), 3.03 (dd, J = 2.8, 14.3, 1 H, H-6e), 3.80 (ddd, J = 3.0, 7.7, 11.6, 1 H, H-4), 3.84–3.81 (m, 1 H, H-5), 4.37 (ddd, J = 5.7, 9.7, 47.2, 1 H, H-1), 4.46 (ddd, J = 3.0, 9.7, 47.2, 1 H, H-1); ^{13}C NMR (D_2O) δ 29.4 (C-3), $^3J_{C-F}$ = 5.9), 49.2 (C-6), 54.6 (C-2, $^2J_{C-F}$ = 18.1), 67.6, 69.8 (C-4, C-5), 87.00 (C-1, $^1J_{C-F}$ = 165.3); HRMS (M − H)$^+$ calcd 150.0930, found 150.0923.

(2*S*)-Methyl-1,2,5-trideoxy-1,5-imino-D-ribitol (16): 90% yield; ^{1}H NMR (D_2O) δ 0.91 (d, J = 7.0, 3 H, CH_3), 1.77–1.82 (m, 1 H, H-2), 2.45 (t, J = 12.4, 1 H, H-1a), 2.67 (t, J = 11.7, 1 H, H-5a), 2.70 (dd, J = 4.8, 12.4, 1 H, H-1e), 2.90 (dd, J = 4.6, 11.9, 1 H, H-5e), 3.72 (ddd, J = 3.0, 5.1, 11.7, 1 H, H-4), 3.85 (br s, 1 H, H-3); ^{13}C NMR (D_2O) δ 15.4 (CH_3), 35.5 (C-2), 44.8, 45.7 (C-1, C-5), 67.0, 72.6 (C-3, C-4); HRMS (M − Cs)$^+$ calcd 264.0001, found 264.0003.

1,2,5-Trideoxy-1,5-imino-D-erythritol (17): 97% yield; ^{1}H NMR (D_2O) δ 1.51 (m, 2 H, H-2), 2.55 (ddd, J = 4.8, 7.6, 13.1, 1 H, H-1), 2.67 (dd, J = 3.0, 13.4, 1 H, H-5), 2.90 (dd, J = 5.7, 13.4, 1 H, H-5), 2.86–2.96 (m, 1 H, H-1), 3.67 (dt, J = 2.5, 5.9, 1 H, H-4), 3.74 (ddd, J = 3.0, 4.6, 7.6, 1 H, H-3); ^{13}C NMR (D_2O) δ 29.9 (C-2), 41.9 (C-1), 48.1 (C-5), 68.8, 69.3 (C-3, C-4); HRMS (M$^+$) calcd 117.0790, found 117.0785.

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[Tris(pyrazolyl)hydroborato]magnesium Alkyl Derivatives: Reactivity Studies

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Abstract: The reactivity of a series of 4-coordinate [tris(pyrazolyl)hydroborato]magnesium alkyl derivatives, $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgR and $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}$MgR (3-Bu^{t}pz = 3-C_3N_2Bu^tH_2, 3,5-Me$_2$pz = 3,5-$C_3N_2Me_2H$; R = CH_3, CH_2CH_3, $(CH_2)_3CH_3$, $CH(CH_3)_2$, $C(CH_3)_3$, CH=CH_2, C_6H_5, CH_2SiMe_3), has been investigated. The complexes $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}$MgR undergo ligand redistribution reactions, analogous to the Schlenk equilibrium, to give the 6-coordinate sandwich complex $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}_2$Mg. In contrast, the 4-coordinate magnesium alkyl derivatives supported by the more sterically demanding tris(3-*tert*-butylpyrazolyl)hydroborato ligand, $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgR, are stable with respect to the formation of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}_2$Mg. The alkyl complexes $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgR are useful precursors for a variety of other 4-coordinate complexes, including $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgX (X = C≡CC_6H_5, C≡CSiMe$_3$, OEt, OPr^i, OBu^t, OPh, OCH$_2$SiMe$_3$, OSiMe$_3$, OOBu^t, NHPh, SH, SCH$_3$, Cl, Br, I, NCO, NCS). CO_2 inserts into the Mg–C bond of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ to give the η^1-acetato complex $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$Mg$\{\eta^1$-OC(O)CH$_3\}$. In contrast, the reactions with the ketones $CH_3C(O)CH_3$ and $CH_3C(O)$Bu^t do not result in insertion to give the alkoxide derivatives, but preferentially give the enolate complexes $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$Mg$\{\eta^1$-OC(=CH$_2$)CH$_3\}$ and $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$Mg$\{\eta^1$-OC(=CH$_2$)Bu$^t\}$, accompanied by the elimination of methane. Insertion of O_2 into the Mg–R bond of the complexes $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgR (R = CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$) results in formation of the alkylperoxo derivatives $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgOOR, which have been characterized by the use of ^{17}O NMR spectroscopy. In contrast, the reaction of the magnesium (trimethylsilyl)methyl complex $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_2$SiMe$_3$ with O_2 gives the trimethylsiloxide derivative $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgOSiMe$_3$ as a result of facile cleavage of the Si–C bond upon autoxidation. The molecular structures of $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}_2$Mg and $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCl have been determined by X-ray diffraction. $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}_2$Mg is triclinic, $P\bar{1}$ (No. 2), a = 8.837 (3) Å, b = 10.223 (3) Å, c = 10.773 (2) Å, α = 63.92 (3)°, β = 85.24 (2)°, γ = 79.87 (2)°, V = 860.4 (4) Å^3, Z = 1. $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCl is orthorhombic, *Pnma* (No. 62), a = 16.048 (7) Å, b = 16.006 (3) Å, c = 9.840 (1) Å, V = 2527 (1) Å^3, Z = 4.

Introduction

We have recently reported the syntheses and structures of a series of 4-coordinate organomagnesium complexes $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgR (A) and $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}$MgR (B) (3-Bu^{t}pz = 3-C_3N_2Bu^tH_2; 3,5-Me$_2$pz = 3,5-$C_3N_2Me_2H$)[1] that are stabilized by coordination of tris(pyrazolyl)hydroborato ligands,[2] as illustrated in Figure 1.

In contrast to Grignard reagents, which are well-known to (i) exist in solution as a complex mixture of species (e.g., the Schlenk equilibrium) and (ii) exhibit a variety of structures in the solid state,[3] the organomagnesium complexes illustrated in Figure 1 exist as well-defined 4-coordinate monomeric complexes both in the solid state and in solution. Furthermore, the solvent-free [tris(pyrazolyl)hydroborato]magnesium alkyl derivatives are soluble in noncoordinating hydrocarbon solvents (e.g., benzene) and possess valuable spectroscopic handles, in the form of the resonances due to the tris(pyrazolyl)hydroborato ligands, that are ideal for monitoring reactions. Here we report our studies of

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[3] The simple model of the Schlenk equilibrium ($2RMgX \rightleftarrows R_2Mg + MgX_2$) for describing the composition of Grignard reagents is complicated by a variety of factors including (i) the formation of complexes of each component with either solvent, reactant, or product, (ii) the formation of dimeric (or higher order) species, and (iii) the presence of ionic species. (a) Kharasch, M. S.; Reinmuth, O. *Grignard Reactions of Nonmetallic Substances*; Prentice-Hall: New York, 1954. (b) Ashby, E. C. *Pure Appl. Chem.* **1980**, *52*, 545–569. (c) Ashby, E. C. *Q. Rev.* **1967**, 259–285. (d) Ashby, E. C.; Laemmle, J.; Neumann, H. M. *Acc. Chem. Res.* **1974**, *7*, 272–280. (e) Wakefield, B. J. *Pure Appl. Chem.* **1966**, *1*, 131–156. (f) Toney, J.; Stucky, G. D. *J. Organomet. Chem.* **1971**, *28*, 5–20. (g) Ashby, E. C.; Smith, M. G. *J. Am. Chem. Soc.* **1964**, *86*, 4363–4370. (h) Ashby, E. C.; Becker, W. E. *J. Am. Chem. Soc.* **1963**, *85*, 118–119. (i) Guggenberger, L. J.; Rundle, R. E. *J. Am. Chem. Soc.* **1968**, *90*, 5375–5378. (j) Spek, A. L.; Voorbergen, P.; Schat, G.; Blomberg, C.; Bickelhaupt, F. *J. Organomet. Chem.* **1974**, *77*, 147–151. (k) Schlenk, W.; Schlenk, W., Jr. *Ber.* **1929**, *62B*, 920–924. (l) Evans, W. V.; Pearson, R. *J. Am. Chem. Soc.* **1942**, *64*, 2865–2871. (m) Dessy, R. E.; Handler, G. S. *J. Am. Chem. Soc.* **1958**, *80*, 5824–5826.

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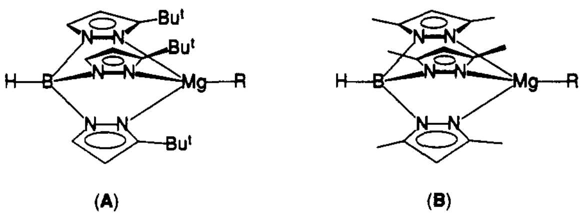


Figure 1. Monomeric [tris(pyrazolyl)hydroborato]magnesium alkyl complexes.

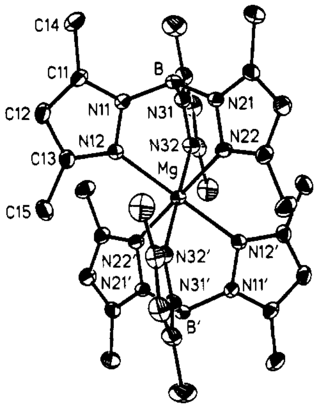


Figure 2. Molecular structure of $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}_2$Mg.

[tris(pyrazolyl)hydroborato]magnesium alkyl derivatives in order to assess the reactivity of the magnesium–carbon bond in a well-defined 4-coordinate environment.

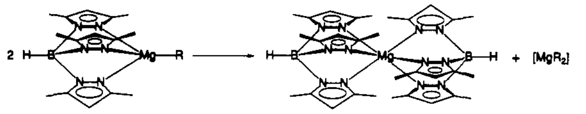
Results and Discussion

The monomeric [tris(pyrazolyl)hydroborato]magnesium alkyl derivatives $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgR and $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}$MgR (R = CH_3, CH_2CH_3, $(CH_2)_3CH_3$, $CH(CH_3)_2$, $C(CH_3)_3$, CH_2SiMe_3, CH=CH$_2$, C_6H_5) were obtained as described previously by the metathesis of R_2Mg with M$\{$HB(3,5-R$_2$pz)$_3\}$ (3,5-R$_2$pz = 3-Bu^{t}pz, 3,5-Me$_2$pz; M = K, Tl), as shown in eq 1.[1]

$$\mathrm{R_2Mg + M\{HB(3,5\text{-}R_2pz)_3\}} \xrightarrow[(\mathrm{M = K, Tl})]{-[\mathrm{MR}]} \{\eta^3\text{-}\mathrm{HB(3,5\text{-}R_2pz)_3}\}\mathrm{MgR} \quad (1)$$

The reactivity of the complexes $\{\eta^3$-HB(3,5-R$_2$pz)$_3\}$MgR is described below under the general classifications of (i) ligand redistribution, (ii) metathesis, and (iii) insertion reactions.

Ligand Redistribution Reactions. In view of the fact that Grignard reagents exist in solution as a complex mixture of species as a result of facile ligand redistribution reactions, e.g., the Schlenk equilibrium,[3] we have investigated the possibility of similar ligand redistribution reactions for the [tris(pyrazolyl)hydroborato]magnesium alkyl complexes, $\{\eta^3$-HB(3,5-R$_2$pz)$_3\}$MgR. Thus, we have observed that although solutions of the tris(3,5-dimethylpyrazolyl)hydroborato derivatives $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}$MgR (R = CH_3, CH_2CH_3, $(CH_2)_3CH_3$, CH_2SiMe_3, $CH(CH_3)_2$, $C(CH_3)_3$, CH=CH$_2$, C_6H_5) are stable at room temperature, heating to 80–120 °C results in ligand redistribution and the formation of the 6-coordinate sandwich complex $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}_2$Mg (eq 2).



(2)

The reactions only proceed to ca. 90% completion, presumably arriving at equilibrium. The molecular structure of $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}_2$Mg has been determined by X-ray diffraction, as shown in Figure 2. Selected bond lengths and angles are presented in Tables I and II. The two tris(pyrazolyl)hydroborato ligands adopt a mutually staggered conformation, and the overall coordination geometry about the centrosymmetric magnesium center is trigonally distorted octahedral. $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}_2$Mg can also be readily prepared by the reaction of K$\{$HB(3,5-Me$_2$pz)$_3\}$ with $MgBr_2$. Thus, coordination of two tris(dimethylpyrazolyl)hydroborato ligands to magnesium does not result in particularly excessive steric interactions, which accounts for the facile redistribution reaction described above.

Table I. Selected Bond Lengths for $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}_2$Mg (Å)

Mg-N(12)	2.192 (2)	Mg-N(22)	2.169 (2)
Mg-N(32)	2.197 (3)	Mg-N(12')	2.192 (2)
Mg-N(22')	2.169 (2)	Mg-N(32')	2.197 (3)
N(11)-N(12)	1.375 (3)	N(11)-C(11)	1.353 (3)
N(11)-B	1.547 (4)	N(12)-C(13)	1.341 (3)
N(21)-N(22)	1.375 (3)	N(21)-C(21)	1.353 (3)
N(21)-B	1.544 (4)	N(22)-C(23)	1.337 (4)
N(31)-N(32)	1.375 (3)	N(31)-C(31)	1.348 (5)
N(31)-B	1.543 (4)	N(32)-C(33)	1.340 (5)
C(11)-C(12)	1.368 (4)	C(11)-C(14)	1.505 (4)
C(12)-C(13)	1.386 (4)	C(13)-C(15)	1.496 (4)
C(21)-C(22)	1.355 (5)	C(21)-C(24)	1.494 (4)
C(22)-C(23)	1.383 (4)	C(23)-C(25)	1.493 (5)
C(31)-C(32)	1.370 (5)	C(31)-C(34)	1.497 (5)
C(32)-C(33)	1.376 (6)	C(33)-C(35)	1.499 (4)

Table II. Selected Bond Angles for $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}_2$Mg (deg)

N(12)-Mg-N(22)	85.6 (1)	N(12)-Mg-N(32)	87.0 (1)
N(22)-Mg-N(32)	85.6 (1)	N(12)-Mg-N(12')	180.0
N(22)-Mg-N(12')	94.4 (1)	N(32)-Mg-N(12')	93.0 (1)
N(12)-Mg-N(22')	94.4 (1)	N(22)-Mg-N(22')	180.0
N(32)-Mg-N(22')	94.4 (1)	N(12')-Mg-N(22')	85.6 (1)
N(12)-Mg-N(32')	93.0 (1)	N(22)-Mg-N(32')	94.4 (1)
N(32)-Mg-N(32')	180.0	N(12')-Mg-N(32')	87.0 (1)
N(22')-Mg-N(32')	85.6 (1)		

In contrast to the facile formation of $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}_2$Mg from $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}$MgR, solutions of the tris(3-*tert*-butylpyrazolyl)hydroborato derivatives $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgR in benzene are thermally stable. For example, solutions of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ show no evidence of decomposition after 7 days at 120 °C. This marked difference between $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgR and $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}$MgR derivatives is undoubtedly a consequence of the sterically demanding environment created by the η^3-HB(3-Bu^{t}pz)$_3$ ligand that disfavors the formation of the bis complex $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}_2$Mg. Indeed, the tris(3-*tert*-butylpyrazolyl)hydroborato ligand has been described as a "tetrahedral enforcer" due to its ability to effectively restrict a metal center to a maximum of 4-coordination.[4] Thus, whereas the complexes $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}$MgR undergo ligand redistribution reactions that are analogous to the Schlenk equilibrium, the more sterically demanding tris(3-*tert*-butylpyrazolyl)hydroborato derivatives $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgR are not subject to such transformations. Such an observation is of particular relevance with regard to other studies (vide infra), and hence we have concentrated our efforts on the more sterically demanding $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgR system.

Metathesis Reactions. The alkyl derivatives $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgR are useful precursors to a wide variety of other derivatives as a result of metathesis of the magnesium–alkyl bond. Reactions of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgR with protic reagents, e.g., RC≡CH (R = Ph, SiMe$_3$), ROH (R = Et, Pr^i, Bu^t, Ph, CH$_2$SiMe$_3$, SiMe$_3$), Bu^{t}OOH, PhNH$_2$, CH$_3$SH, H$_2$S and HCl, are accompanied by elimination of the alkane and the formation of the corresponding magnesium derivative as shown in Scheme

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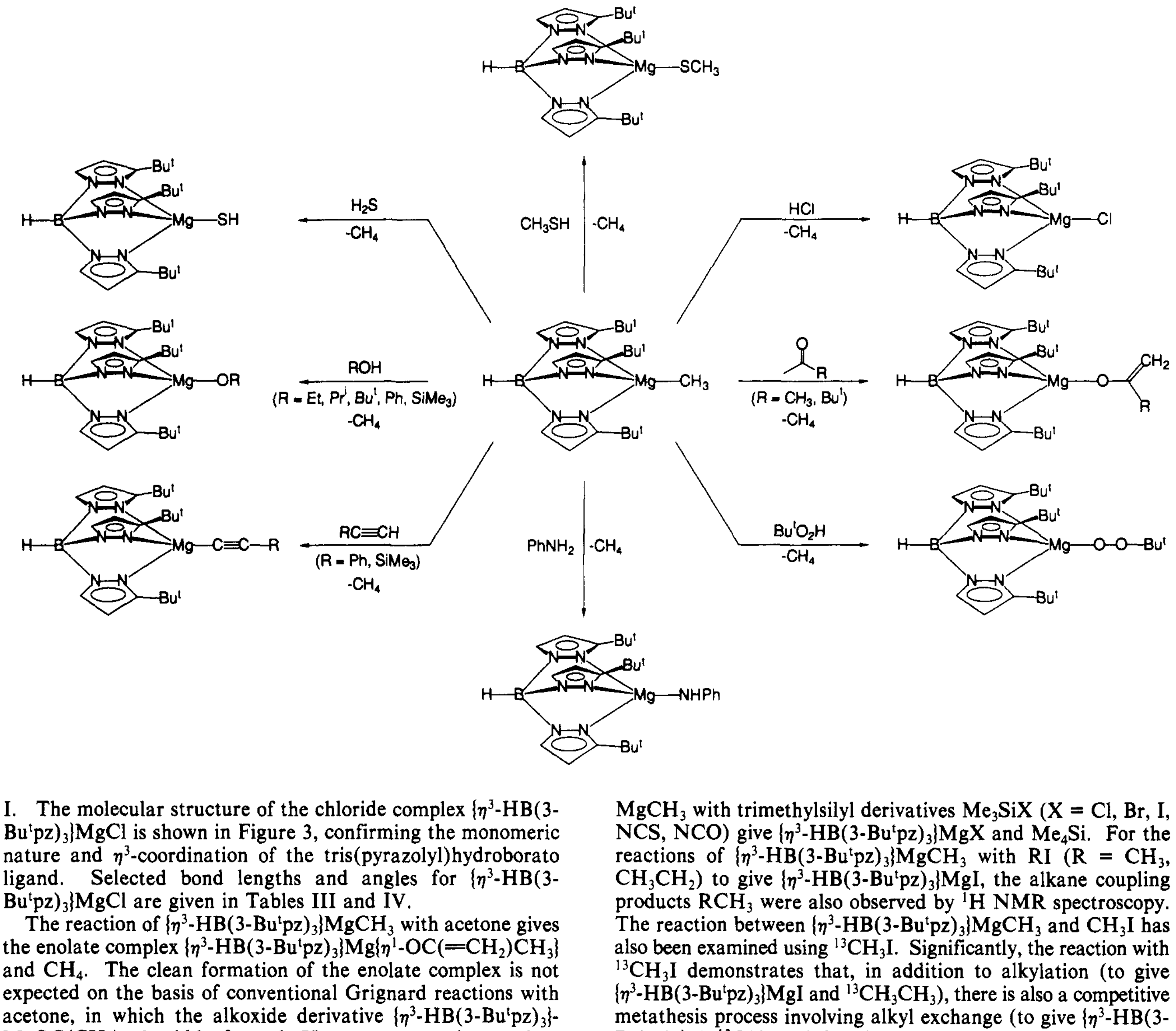
(4) The "tetrahedral enforcer" nature of the η^3-HB(3-Bu^{t}pz)$_3$ ligand was suggested for metals of similar size to the first-row transition elements.[4a] Although this is generally observed, we note that there are exceptions to this suggestion, namely $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$Co(η^2-O$_2$),[4b] $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$-Cu(η^2-O$_2$NO),[4c] and $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$Ni(η^2-O$_2$NO).[4c] (a) Trofimenko, S.; Calabrese, J. C.; Thompson, J. S. *Inorg. Chem.* **1987**, *26*, 1507–1514. (b) Egan, J. W., Jr.; Haggerty, B. S.; Rheingold, A. L.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1990**, *112*, 2445–2446. (c) Han, R.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 9707–9708.

Scheme I



I. The molecular structure of the chloride complex {η^3-HB(3-Bu^{t}pz)$_3$}MgCl is shown in Figure 3, confirming the monomeric nature and η^3-coordination of the tris(pyrazolyl)hydroborato ligand. Selected bond lengths and angles for {η^3-HB(3-Bu^{t}pz)$_3$}MgCl are given in Tables III and IV.

The reaction of {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_3$ with acetone gives the enolate complex {η^3-HB(3-Bu^{t}pz)$_3$}Mg{η^1-OC(=CH$_2$)CH$_3$} and CH$_4$. The clean formation of the enolate complex is not expected on the basis of conventional Grignard reactions with acetone, in which the alkoxide derivative {η^3-HB(3-Bu^{t}pz)$_3$}MgOC(CH$_3$)$_3$ should be formed. However, magnesium enolate complexes have previously been isolated for ketones with sterically demanding substituents, e.g., Bu^{t}C(O)Et[5] and (2,4,6-Me$_3$C$_6$H$_2$)C(O)CH$_3$.[6] The formation of {η^3-HB(3-Bu^{t}pz)$_3$}Mg{η^1-OC(=CH$_2$)(CH$_3$)} represents a unique example of a magnesium enolate derived from acetone. Similarly, the reaction of {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_3$ with CH$_3$C(O)Bu^t gives the enolate complex {η^3-HB(3-Bu^{t}pz)$_3$}Mg{η^1-OC(=CH$_2$)(Bu^t)}. The NMR and IR data of {η^3-HB(3-Bu^{t}pz)$_3$}Mg{η^1-OC(=CH$_2$)(CH$_3$)} and {η^3-HB(3-Bu^{t}pz)$_3$}Mg{η^1-OC(=CH$_2$)(Bu^t)} are particularly characteristic of enolate derivatives. Specifically for {η^3-HB(3-Bu^{t}pz)$_3$}Mg{η^1-OC(=CH$_2$)(CH$_3$)}, $\nu_{C=C}$ is observed at 1620 cm^{-1} in the IR spectrum and the olefinic resonances {OC(=*C*H$_2$)(CH$_3$)} and {O*C*(=CH$_2$)(CH$_3$)} are observed at δ 83.1 and 161.9, respectively, in the ^{13}C NMR spectrum.

Metathesis reactions are also observed with nonprotic reagents such as dimethyl disulfide, alkyl halides, trimethylsilyl derivatives, and halogens as shown in Scheme II. Thus, {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_3$ reacts with a variety of alkyl and aralkyl halides (RX) at ca. 100–140 °C to give the halide derivative {η^3-HB(3-Bu^{t}pz)$_3$}MgX. Similarly, the reactions of {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_3$ with trimethylsilyl derivatives Me$_3$SiX (X = Cl, Br, I, NCS, NCO) give {η^3-HB(3-Bu^{t}pz)$_3$}MgX and Me$_4$Si. For the reactions of {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_3$ with RI (R = CH$_3$, CH$_3$CH$_2$) to give {η^3-HB(3-Bu^{t}pz)$_3$}MgI, the alkane coupling products RCH$_3$ were also observed by ^{1}H NMR spectroscopy. The reaction between {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_3$ and CH$_3$I has also been examined using ^{13}CH$_3$I. Significantly, the reaction with ^{13}CH$_3$I demonstrates that, in addition to alkylation (to give {η^3-HB(3-Bu^{t}pz)$_3$}MgI and ^{13}CH$_3$CH$_3$), there is also a competitive metathesis process involving alkyl exchange (to give {η^3-HB(3-Bu^{t}pz)$_3$}Mg^{13}CH$_3$ and CH$_3$I), as shown in Scheme III.

The observation of competitive alkyl exchange is supported by the reaction of {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_2$CH$_3$ and CH$_3$I, in which alkyl exchange giving {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_3$ is observed to occur concomitant with the irreversible formation of {η^3-HB(3-Bu^{t}pz)$_3$}MgI. To our knowledge, alkyl exchange has not previously been observed to occur between Grignard reagents and simple alkyl halides[7] although there is indirect evidence for alkyl exchange (as determined by the *organic* products after quenching with CO$_2$) with more complex derivatives.[8] The observation of alkyl exchange in the reaction of {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_3$ with CH$_3$I is reminiscent of the σ-bond metathesis exchange process reported for (η^5-C$_5$Me$_5$)$_2$ScCH$_3$.[9]

The reactions of {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_3$ with aralkyl halides C$_6$H$_5$CH$_2$X (X = Cl, Br, I) also result in the clean formation of {η^3-HB(3-Bu^{t}pz)$_3$}MgX. However, significant quantities of bibenzyl (C$_6$H$_5$CH$_2$CH$_2$C$_6$H$_5$) are observed in addition to the product of coupling with the methyl group (C$_6$H$_5$CH$_2$CH$_3$), indicative of radical processes.[10] Support for this suggestion is

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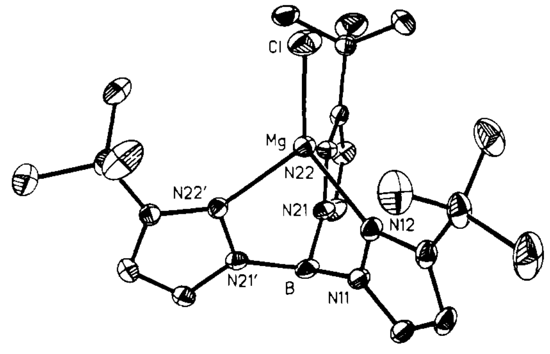


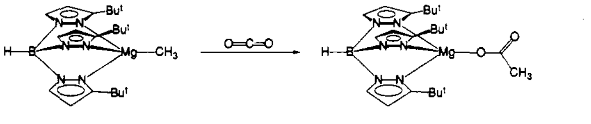
Figure 3. Molecular structure of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCl.

Table III. Selected Bond Lengths for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCl (Å)

Mg–Cl	2.262 (2)	Mg–N(12)	2.097 (5)
Mg–N(22)	2.100 (3)	Mg–N(22′)	2.101 (3)
N(11)–N(12)	1.379 (6)	N(11)–C(11)	1.338 (8)
N(11)–B	1.542 (8)	N(12)–C(13)	1.351 (7)
N(21)–N(22)	1.376 (4)	N(21)–C(21)	1.328 (5)
N(21)–B	1.538 (5)	N(22)–C(23)	1.345 (5)
C(11)–C(12)	1.357 (10)	C(12)–C(13)	1.375 (10)
C(13)–C(14)	1.510 (9)	C(14)–C(15)	1.530 (9)
C(14)–C(16)	1.535 (7)	C(14)–C(16′)	1.535 (7)
C(21)–C(22)	1.363 (6)	C(22)–C(23)	1.387 (6)
C(23)–C(24)	1.518 (6)	C(24)–C(25)	1.525 (6)
C(24)–C(26)	1.536 (7)	C(24)–C(27)	1.512 (7)
B–N(21′)	1.538 (5)		

provided by the observation that the reaction of cyclopropylmethyl bromide with $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ results in ring opening and the formation of the homoallyl derivative $\mathrm{CH_2{=}CHCH_2CH_2Br}$.[11] The formation of products derived from ring-opening reactions of cyclopropylmethyl halide derivatives has previously been proposed to be a test for radical processes.[12] In addition to the nature of the products of the reactions of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ with alkyl and aralkyl halides, the qualitative rates of the reactions are also consistent with radical processes. Thus, for the alkyl iodides ($\mathrm{CH_3I}$, $\mathrm{CH_3CH_2I}$, $\mathrm{(CH_3)_2CHI}$, $\mathrm{(CH_3)_3CI}$) the increasing order of reactivity is primary < secondary < tertiary, and for the benzyl halides $\mathrm{C_6H_5CH_2X}$ the order is chloride < bromide ≈ iodide.[13]

Insertion Reactions. Although the anticipated insertion reaction, typical of Grignard reactivity, was not observed between $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ and acetone to give the alkoxide derivative η^3-HB(3-Bu^{t}pz)$_3\}$MgOBu^t, clean insertion of CO$_2$ to give the acetato complex was observed (eq 3). However, this reaction s significantly slower than the reactions of Grignard reagents with CO$_2$. Characterization of the acetato product is provided by the reaction with ^{13}CO$_2$ which allows the $J_{\text{C–C}}$ coupling constant in η^3-HB(3-Bu^{t}pz)$_3\}$Mg(η^1-O$_2$^{13}CCH$_3$) to be determined, a value of 53 Hz being clearly indicative of a one-bond coupling. Furthermore, support for the η^1-coordination mode of the acetato ligand is provided by the X-ray diffraction study of the zinc analogue, $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$Zn(η^1-O$_2$CCH$_3$).[14]

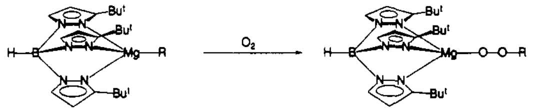


(3)

Table IV. Selected Bond Angles for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCl (deg)

Cl–Mg–N(12)	121.4 (2)	Cl–Mg–N(22)	123.4 (1)
N(12)–Mg–N(22)	93.7 (1)	Cl–Mg–N(22′)	123.4 (1)
N(12)–Mg–N(22′)	93.7 (1)	N(22)–Mg–N(22′)	93.3 (2)

Insertion reactions of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgR are also observed with dioxygen. Thus, treatment of the alkyl complexes $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgR (R = CH$_3$, CH$_2$CH$_3$, CH(CH$_3$)$_2$, C(CH$_3$)$_3$) with excess O$_2$ at room temperature results in formation of the alkylperoxo complexes $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgOOR (eq 4). The



(4)

reactions of the derivatives $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgR (R = CH$_2$CH$_3$, CH(CH$_3$)$_2$, C(CH$_3$)$_3$) with O$_2$ are both instantaneous (<10 min) and quantitative, as judged by ^{1}H NMR spectroscopy. In contrast, the reaction of O$_2$ with the methyl complex $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ is significantly slower (>1 day at room temperature) than for the other alkyl derivatives.[15]

The ^{17}O-labeled alkyperoxo complexes $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$Mg^{17}O^{17}OR, obtained from the reactions of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgR with ^{17}O$_2$ (41%), have been investigated by ^{17}O NMR spectroscopy. Specifically, each complex shows two ^{17}O NMR resonances in the ranges δ 102–183 and 323–427 for the peroxo (Mg–O–O–R) moiety as shown in Table V and Figure 4. Interestingly, Figure 4 illustrates that the ^{17}O NMR resonances for the two oxygen atoms of the alkylperoxo group shift in opposite directions upon changing of the alkyl substituent. On the basis of the observed trend for the ^{17}O NMR resonances of the corresponding alcohols (also shown in Figure 4), we suggest that the set of resonances at higher field correspond to the β-O atoms and that the set of resonances at lower field correspond to the α-O atoms of the alkylperoxo moiety. The Mg–O–O–R group is further characterized by IR absorption bands in the ranges 889–935 cm^{-1} ($\nu_{\text{O–O}}$) and 608–660 cm^{-1} ($\nu_{\text{Mg–O}}$) that are assigned on the basis of the shifts observed for the isotopomers $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$Mg^{18}O^{18}OR.[16] Other supporting evidence that the products are alkylperoxo complexes is provided by the observation that the *tert*-butylperoxo derivative $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgOOC(CH$_3$)$_3$ may be synthesized independently by the reaction of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ with the hydroperoxide (CH$_3$)$_3$COOH as shown in Scheme I.

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(10) For the reactions of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ with PhCH$_2$X, the ratios of the products PhCH$_2$CH$_3$ to PhCH$_2$CH$_2$Ph are approximately 40:60 (X = Cl), 50:50 (X = Br), and 10:90 (X = I).

(11) Ring-opening of *c*-C$_3$H$_5$CH$_2$Br to CH$_2$=CHCH$_2$CH$_2$Br is, in fact, faster than the formation of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgBr, presumably suggesting that the CH$_2$=CHCH$_2$CH$_2^\bullet$ radical is more reactive toward excess *c*-C$_3$H$_5$CH$_2$Br than $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgR.

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(13) Although the reactions are not kinetically well behaved and thus prevent a detailed analysis, an estimate of the second-order rate constants for he reactions of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ with RX under similar conditions provides an indication of the relative reactivity of RX. k (mol^{-1} L s^{-1} at 100 °C): CH$_3$I, ≈10^{-4}; CH$_3$CH$_2$I ≈10^{-5}; (CH$_3$)$_2$CHI, ≈10^{-4}; (CH$_3$)$_3$CI, ≈10^{-3}; C$_6$H$_5$CH$_2$Cl, ≈10^{-5}; C$_6$H$_5$CH$_2$Br, ≈10^{-3}; C$_6$H$_5$CH$_2$I, ≈10^{-3}.

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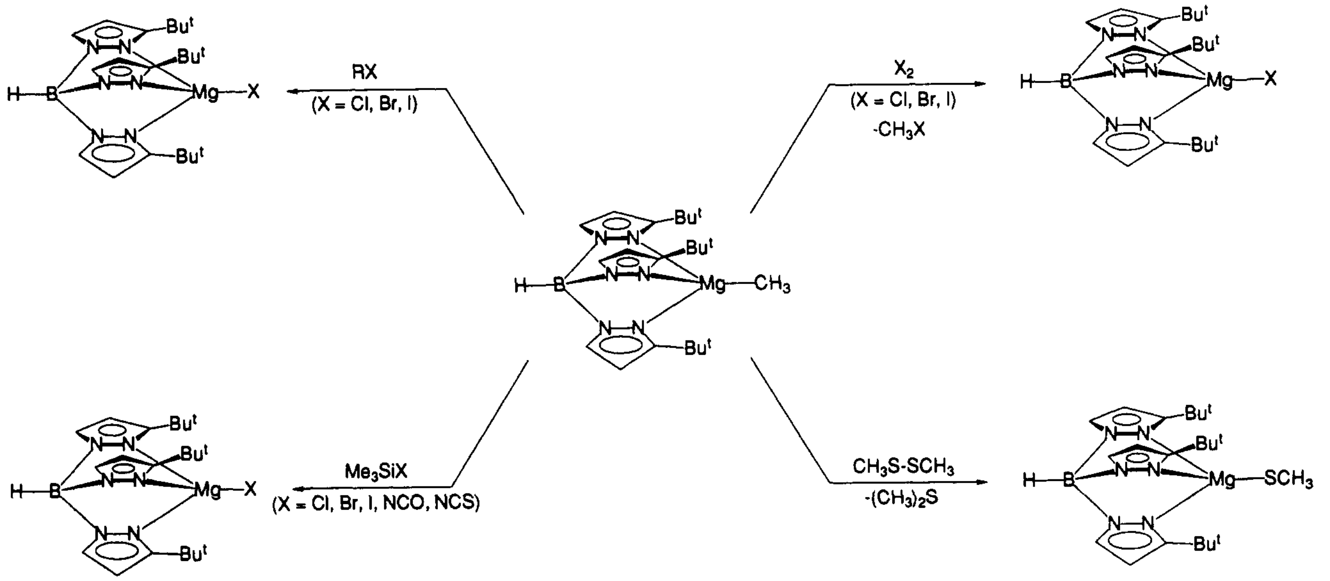
Scheme II



Scheme III

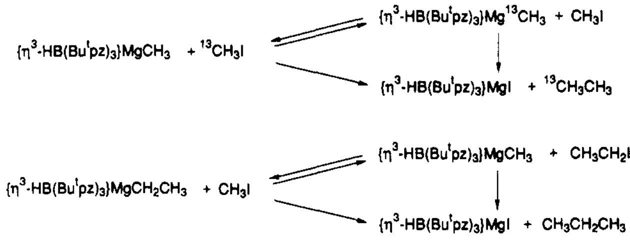


Table V. ^{17}O NMR Data[a]

	δ(Mg*O*OR)	δ(MgO*O*R)
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}MgOOCH_3$	427	102
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}MgOOCH_2CH_3$	407	130
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}MgOOCH(CH_3)_2$	373	159
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}MgOOC(CH_3)_3$	323	183

[a] Relative to H_2O.

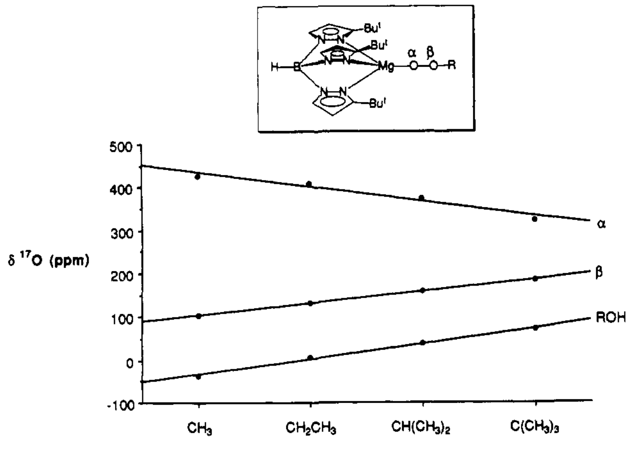


Figure 4. ^{17}O NMR shifts for $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}MgOOR$ and ROH.

The reactions of molecular oxygen with metal alkyl derivatives are of fundamental importance in view of the role that metal-based oxidations play in systems as diverse as industrial and biological processes.[17] However, the reactions of organometallic derivatives with oxygen often produce complex mixtures, in part as a result of the indiscriminate reactivity of radical intermediates, and relatively few reactions result in the formation of single products.[18] In this regard the isolation of discrete products by the reaction of dioxygen with metal alkyl derivatives and investigation of their subsequent reactivity have provided major challenges. Although a number of well-characterized examples of reactions of dioxygen with metal alkyl complexes have been reported, isolated products are commonly alkoxo derivatives, $[L_nMOR]$,[19] with relatively few examples involving isolation of alkylperoxo complexes, $[L_nMOOR]$.[20] The selective formation of alkylperoxo complexes in the reactions of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}MgR$ with O_2 is presumably a consequence of the sterically demanding ligand environment that hinders bimolecular oxygen atom abstraction from the alkylperoxo complex by alkyl derivative, which is the commonly suggested pathway for the formation of alkoxo derivatives (eq 5). In support

$$L_nMOOR + L_nMR \rightarrow 2L_nMOR \qquad (5)$$

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of this suggestion, {η^3-HB(3-Bu^{t}pz)$_3$}MgOOCH(CH$_3$)$_2$ and {η^3-HB(3-Bu^{t}pz)$_3$}MgCH(CH$_3$)$_2$ do not react rapidly at room temperature to give the alkoxo derivative {η^3-HB(3-Bu^{t}pz)$_3$}MgOCH(CH$_3$)$_2$, but rather require heating to 80 °C to effect this transformation (eq 6). The alkoxo derivatives {η^3-HB(3-Bu^{t}pz)$_3$}MgOR (R = CH$_3$, CH$_2$CH$_3$, CH(CH$_3$)$_2$, C(CH$_3$)$_3$) are also obtained upon treatment of {η^3-HB(3-Bu^{t}pz)$_3$}MgOOR with PPh$_3$ (eq 7).

$$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgOOPr}^i + \{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgPr}^i \xrightarrow{80\ ^\circ\text{C}} 2\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgOPr}^i \tag{6}$$

$$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgOOR} + \text{PPh}_3 \rightarrow \{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgOR} + \text{Ph}_3\text{PO} \tag{7}$$

In marked contrast to the above reactions of molecular oxygen with the alkyl derivatives {η^3-HB(3-Bu^{t}pz)$_3$}MgR to give alkylperoxo complexes, the analogous reaction of the (trimethylsilyl)methyl derivative {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_2$SiMe$_3$ with O$_2$ is accompanied by facile Si–C bond cleavage and the formation of the trimethylsiloxide derivative {η^3-HB(3-Bu^{t}pz)$_3$}MgOSiMe$_3$ (eq 8).[21] Formaldehyde was also observed by ^{1}H NMR spectroscopy as a product of this reaction. Identification of the trimethylsiloxide derivative {η^3-HB(3-Bu^{t}pz)$_3$MgOSiMe$_3$ is also supported by the independent syntheses using the reactions of (i) {η^3-HB(3-Bu^{t}pz)$_3$}MgCl and KOSiMe$_3$ and also (ii) {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_3$ with Me$_3$SiOH (Scheme I).

$$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgCH}_2\text{SiMe}_3 \xrightarrow{\text{O}_2} \{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgOSiMe}_3 + (\text{CH}_2\text{O})_n \tag{8}$$

Organic products arising from facile cleavage of Si–C bonds of other (trialkylsilyl)metal derivatives upon autoxidation have been previously observed and thus provide a precedent for the reactions described here. For example, treatment of the Grignard reagent Me$_3$SiCH$_2$MgCl with O$_2$, followed by hydrolysis, gave significant quantities of Me$_3$SiOH, (Me$_3$Si)$_2$O, and CH$_2$O.[22] Therefore, these observations provide further evidence that such cleavage reactions may be a general feature of (trimethylsilyl)methyl derivatives upon autoxidation.

The mechanism of the reactions of oxygen with metal alkyl derivatives is of considerable interest since the direct insertion of ground-state triplet oxygen into metal–carbon bonds is considered to be unlikely. Evidence for mechanisms involving radical intermediates in the reactions of metal–alkyls with O$_2$ has been previously suggested by the observations of alkyl group rearrangement and racemization, and also inhibition of autoxidation by radical traps.[23] Thus, radical chain processes of the type illustrated by eqs 9–11 have been proposed for the autoxidation of metal–alkyl derivatives. We have monitored the reactions of the magnesium alkyl derivatives {η^3-HB(3-Bu^{t}pz)$_3$}MgR by ^{1}H NMR spectroscopy. Although the insertion of O$_2$ into the Mg–C bonds of the derivatives {η^3-HB(3-Bu^{t}pz)$_3$}MgR (R = CH$_2$CH$_3$, CH(CH$_3$)$_2$, C(CH$_3$)$_3$) is too rapid to be studied, the reaction of the methyl derivative may be conveniently monitored by ^{1}H NMR spectroscopy over a period of several days at room temperature. Monitoring the reaction of two samples of {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_3$ and O$_2$ prepared under identical conditions, with the exception of prior addition of a small quantity (≈2 mol %) of the radical trap galvinoxyl to one of them, indicated that the reaction of {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_3$ with O$_2$ was inhibited by the galvinoxyl. Although more detailed kinetic information could not be obtained from this study due to the occurrence of other decomposition pathways, this observation supports the above radical chain sequence for formation of the alkylperoxo complexes {η^3-HB(3-Bu^{t}pz)$_3$}MgOOR. Further evidence for a radical chain process is provided by the observation of crossover products using two different tris(pyrazolyl)hydroborato ligands. For example, the reaction of O$_2$ with a mixture of {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_3$ and {η^3-HB(3,5-Me$_2$pz)$_3$}MgC(CH$_3$)$_3$ results in the formation of, inter alia, the crossover product {η^3-HB(3-Bu^{t}pz)$_3$}MgOOC(CH$_3$)$_3$ (eq 12). We note that the alkyl exchange between {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_3$ and {η^3-HB(3,5-Me$_2$pz)$_3$}MgC(CH$_3$)$_3$ does *not* occur in the absence of O$_2$ over a period of more than 1 month at 80 °C.

$$\text{L}_n\text{M–R} + \text{O}_2 \rightarrow \text{L}_n\text{MOO}^\bullet + \text{R}^\bullet \text{ (initiation)} \tag{9}$$

$$\text{R}^\bullet + \text{O}_2 \rightarrow \text{ROO}^\bullet \tag{10}$$

$$\text{L}_n\text{M–R} + \text{ROO}^\bullet \rightarrow \text{L}_n\text{MOOR} + \text{R}^\bullet \tag{11}$$

$$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgCH}_3 + \{\eta^3\text{-HB(3,5-Me}_2\text{pz)}_3\}\text{MgC(CH}_3)_3 \xrightarrow{\text{O}_2} \{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgOOC(CH}_3)_3 + \ldots \tag{12}$$

Similarly, we suggest that the reaction of {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_2$SiMe$_3$ with O$_2$ also involves a radical chain process, and a proposed mechanism for the formation of {η^3-HB(3-Bu^{t}pz)$_3$}MgOSiMe$_3$ involves the generation of Me$_3$SiO$^\bullet$ as a result of the rearrangement of the radical intermediate Me$_3$SiCH$_2$O$_2$$^\bullet$ (eq 13).

(13)

The formation of a strong Si–O bond would be expected to provide an effective driving force for such a transformation. Support for a radical chain process is also provided by the observation of (i) mild inhibition of the reaction of {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_2$SiMe$_3$ with O$_2$ in the presence of galvinoxyl and (ii) crossover products using two different tris(pyrazolyl)hydroborato ligands. Thus, the reaction of O$_2$ with a mixture of {η^3-HB(3,5-Me$_2$pz)$_3$}MgCH$_2$SiMe$_3$ and {η^3-HB(3-Bu^{t}pz)$_3$}MgC(CH$_3$)$_3$ results in the formation of both {η^3-HB(3-Bu^{t}pz)$_3$}MgOOC(CH$_3$)$_3$ and {η^3-HB(3-Bu^{t}pz)$_3$}MgOSiMe$_3$ (eq 14).[24]

$$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgC(CH}_3)_3 + \{\eta^3\text{-HB(3,5-Me}_2\text{pz)}_3\}\text{MgCH}_2\text{SiMe}_3 \xrightarrow{\text{O}_2} \{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgOSiMe}_3 + \{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgOOC(CH}_3)_3 + \ldots \tag{14}$$

Conclusion

In summary, the reactivity of a series of 4-coordinate magnesium alkyl derivatives {η^3-HB(3-Bu^{t}pz)$_3$}MgR and {η^3-HB(3,5-Me$_2$pz)$_3$}MgR stabilized by tris(pyrazolyl)hydroborato ligation has been investigated. The complexes {η^3-HB(3,5-Me$_2$pz)$_3$}MgR undergo ligand redistribution reactions, analogous to the Schlenk equilibrium, to give the sandwich complex {η^3-HB(3,5-Me$_2$pz)$_3$}$_2$Mg. In contrast, magnesium alkyl derivatives of the more sterically demanding tris(3-*tert*-butylpyrazolyl)hydroborato ligand, {η^3-HB(3-Bu^{t}pz)$_3$}MgR, are stable with respect to the formation of {η^3-HB(3-Bu^{t}pz)$_3$}$_2$Mg. The alkyl complexes {η^3-HB(3-Bu^{t}pz)$_3$}MgR are useful precursors for a variety of other 4-coordinate complexes, including {η^3-HB(3-Bu^{t}pz)$_3$}MgX (X = C≡CR, OR, OOR, NHPh, SH, SCH$_3$, Cl, Br, I, NCO, NCS),

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[21] Over a period of days at room temperature, the minor product, which may be tentatively assigned as the (trimethylsilyl)peroxo derivative {η^3-HB(3-Bu^{t}pz)$_3$}MgOOCH$_2$SiMe$_3$ is slowly converted to {η^3-HB(3-Bu^{t}pz)$_3$}MgOSiMe$_3$.

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[24] In view of the decomposition that arises as a result of the reaction of {η^3-HB(3,5-Me$_2$pz)$_3$}MgR derivatives with O$_2$, only the {η^3-HB(3-Bu^{t}pz)$_3$}MgX derivatives can be definitively identified as crossover products.

Table VI. Selected ^{1}H and ^{13}C NMR Data[a]

^{1}H NMR			^{13}C NMR		
assignment	δ (ppm)	coupling (Hz)	assignment	δ (ppm)	coupling (Hz)
$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCCPh					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3\mathrm{)_3}\}_3$	1.56	s	η^3-HB$\{\mathrm{C_3N_2H_2C(}C\mathrm{H_3)_3}\}_3$	31.3	q, $^1J_{\mathrm{C-H}}$ = 126
$\mathrm{MgCCC_6}H_5$			$\mathrm{MgCC}C_6\mathrm{H_5}$		
2 o-H	7.78	m	1 ipso-C	128.6	t, $^2J_{\mathrm{C-H}}$ = 8
2 m-H	7.15	m	2 o-C	128.3	d, $^1J_{\mathrm{C-H}}$ = 159
1 p-H	7.03	m			d, $^2J_{\mathrm{C-H}}$ = 8
			2 m-C	131.9	d, $^1J_{\mathrm{C-H}}$ = 160
					d, $^2J_{\mathrm{C-H}}$ = 7
			1 p-C	126.2	d, $^1J_{\mathrm{C-H}}$ = 160
					d, $^2J_{\mathrm{C-H}}$ = 8
			$\mathrm{Mg}C_2\mathrm{C_6H_5}$		
			1 C	113.6	s
			1 C	121.8	s
$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCCSi(CH$_3$)$_3$					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3\mathrm{)_3}\}_3$	1.54	s	η^3-HB$\{\mathrm{C_3N_2H_2C(}C\mathrm{H_3)_3}\}_3$	31.5	q, $^1J_{\mathrm{C-H}}$ = 126
$\mathrm{MgCCSi(C}H_3\mathrm{)_3}$	0.40	s	$\mathrm{Mg}CC\mathrm{Si(CH_3)_3}$	120.0	s
				146.7	s
			$\mathrm{MgCCSi(}C\mathrm{H_3)_3}$	1.35	q, $^1J_{\mathrm{C-H}}$ = 119
$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgSH					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3\mathrm{)_3}\}_3$	1.47	s	η^3-HB$\{\mathrm{C_3N_2H_2C(}C\mathrm{H_3)_3}\}_3$	31.4	q, $^1J_{\mathrm{C-H}}$ = 126
Mg–SH	−1.02	s			
$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgSCH$_3$					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3\mathrm{)_3}\}_3$	1.49	s	η^3-HB$\{\mathrm{C_3N_2H_2C(}C\mathrm{H_3)_3}\}_3$	31.2	q, $^1J_{\mathrm{C-H}}$ = 126
$\mathrm{MgSC}H_3$	2.59	s	$\mathrm{MgS}C\mathrm{H_3}$	10.2	q, $^1J_{\mathrm{C-H}}$ = 137
$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgOCH$_2$CH$_2$					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3\mathrm{)_3}\}_3$	1.48	s	η^3-HB$\{\mathrm{C_3N_2H_2C(}C\mathrm{H_3)_3}\}_3$	30.7	q, $^1J_{\mathrm{C-H}}$ = 126
$\mathrm{MgOC}H_2\mathrm{CH_3}$	4.63	q, $^3J_{\mathrm{H-H}}$ = 6.8	$\mathrm{MgO}C\mathrm{H_2CH_3}$	59.3	t, $^1J_{\mathrm{C-H}}$ = 133
$\mathrm{MgOCH_2C}H_3$	1.72	t, $^3J_{\mathrm{H-H}}$ = 6.8	$\mathrm{MgOCH_2}C\mathrm{H_3}$	23.4	q, $^1J_{\mathrm{C-H}}$ = 123
$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgOCH(CH$_3$)$_2$					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3\mathrm{)_3}\}_3$	1.48	s	η^3-HB$\{\mathrm{C_3N_2H_2C(}C\mathrm{H_3)_3}\}_3$	31.0	q, $^1J_{\mathrm{C-H}}$ = 126
$\mathrm{MgOC}H\mathrm{(CH_3)_2}$	4.84	spt, $^3J_{\mathrm{H-H}}$ = 6.0	$\mathrm{MgO}C\mathrm{H(CH_3)_2}$	64.2	d, $^1J_{\mathrm{C-H}}$ = 134
$\mathrm{MgOCH(C}H_3\mathrm{)_2}$	1.65	d, $^3J_{\mathrm{H-H}}$ = 6.0	$\mathrm{MgOCH(}C\mathrm{H_3)_2}$	30.2	q, $^1J_{\mathrm{C-H}}$ = 123
$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgOBu^t					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3\mathrm{)_3}\}_3$	1.50	s	η^3-HB$\{\mathrm{C_3N_2H_2C(CH_3)_3}\}_3$	31.6	q, $^1J_{\mathrm{C-H}}$ = 126
$\mathrm{MgOC(C}H_3\mathrm{)_3}$	1.75	s	$\mathrm{MgOC(}C\mathrm{H_3)_3}$	35.7	q, $^1J_{\mathrm{C-H}}$ = 127
			$\mathrm{MgO}C\mathrm{(CH_3)_3}$	68.1	s
$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgOCH$_2$Si(CH$_3$)$_3$					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3\mathrm{)_3}\}_3$	1.48	s	η^3-HB$\{\mathrm{C_3N_2H_2C(}C\mathrm{H_3)_3}\}_3$	30.7	q, $^1J_{\mathrm{C-H}}$ = 126
$\mathrm{MgOC}H_2\mathrm{Si(CH_3)_3}$	4.20	s	$\mathrm{MgO}C\mathrm{H_2Si(CH_3)_3}$	58.2	t, $^1J_{\mathrm{C-H}}$ = 122
$\mathrm{MgOCH_2Si(C}H_3\mathrm{)_3}$	0.37	s	$\mathrm{MgOCH_2Si(}C\mathrm{H_3)_3}$	−2.1	q, $^1J_{\mathrm{C-H}}$ = 118
$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgOPh[b]					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3\mathrm{)_3}\}_3$	1.40	s	η^3-HB$\{\mathrm{C_3N_2H_2C(}C\mathrm{H_3)_3}\}_3$	30.7	q, $^1J_{\mathrm{C-H}}$ = 126
$\mathrm{Mg\text{-}OC_6}H_5$			$\mathrm{MgO}C_6\mathrm{H_5}$		
2 o-H	7.28	d, $^3J_{\mathrm{H-H}}$ = 7.5	1 ipso-C	163.3	t, $^2J_{\mathrm{C-H}}$ = 9
2 m-H	7.52	t, $^3J_{\mathrm{H-H}}$ = 7.5	2 o-C	129.0	d, $^1J_{\mathrm{C-H}}$ = 155
1 p-H	6.96	t, $^3J_{\mathrm{H-H}}$ = 7.5			d, $^2J_{\mathrm{C-H}}$ = 9
			2 m-C	120.2	d, $^1J_{\mathrm{C-H}}$ = 154
					d, $^2J_{\mathrm{C-H}}$ = 8
					d, $^2J_{\mathrm{C-H}}$ = 5
			1 p-C	114.5	d, $^1J_{\mathrm{C-H}}$ = 160
					t, $^2J_{\mathrm{C-H}}$ = 7
$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgOSi(CH$_3$)$_3$					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3\mathrm{)_3}\}_3$	1.44	s	η^3-HB$\{\mathrm{C_3N_2H_2C(}C\mathrm{H_3)_3}\}_3$	31.2	q, $^1J_{\mathrm{C-H}}$ = 126
$\mathrm{MgOSi(C}H_3\mathrm{)_3}$	0.53	s	$\mathrm{MgOSi(}C\mathrm{H_3)_3}$	4.9	q, $^1J_{\mathrm{C-H}}$ = 116
$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgOOCH$_3$					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3\mathrm{)_3}\}_3$	1.45	s	η^3-HB$\{\mathrm{C_3N_2H_2C(}C\mathrm{H_3)_3}\}_3$	30.6	q, $^1J_{\mathrm{C-H}}$ = 126
$\mathrm{MgOOC}H_3$	4.06	s	$\mathrm{MgOO}C\mathrm{H_3}$	64.0	q, $^1J_{\mathrm{C-H}}$ = 142
$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgOOCH$_2$CH$_3$					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3\mathrm{)_3}\}_3$	1.46	s	η^3-HB$\{\mathrm{C_3N_2H_2C(}C\mathrm{H_3)_3}\}_3$	30.8	q, $^1J_{\mathrm{C-H}}$ = 126
$\mathrm{MgOOC}H_2\mathrm{CH_3}$	4.32	q, $^3J_{\mathrm{H-H}}$ = 6.8	$\mathrm{MgOO}C\mathrm{H_2CH_3}$	71.6	t, $^1J_{\mathrm{C-H}}$ = 143
$\mathrm{MgOOCH_2C}H_3$	1.50	t, $^3J_{\mathrm{H-H}}$ = 6.8	$\mathrm{MgOOCH_2}C\mathrm{H_3}$	14.4	q, $^1J_{\mathrm{C-H}}$ = 126
$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgOOCH(CH$_3$)$_2$					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3\mathrm{)_3}\}_3$	1.48	s	η^3-HB$\{\mathrm{C_3N_2H_2C(}C\mathrm{H_3)_3}\}_3$	30.9	q, $^1J_{\mathrm{C-H}}$ = 126
$\mathrm{MgOOC}H\mathrm{(CH_3)_2}$	4.50	spt, $^3J_{\mathrm{H-H}}$ = 6.2	$\mathrm{MgOO}C\mathrm{H(CH_3)_2}$	76.5	d, $^1J_{\mathrm{C-H}}$ = 143
$\mathrm{MgOOCH(C}H_3\mathrm{)_2}$	1.52	d, $^3J_{\mathrm{H-H}}$ = 6.2	$\mathrm{MgOOCH(}C\mathrm{H_3)_2}$	21.6	q, $^1J_{\mathrm{C-H}}$ = 126
$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgOOC(CH$_3$)$_3$					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3\mathrm{)_3}\}_3$	1.48	s	η^3-HB$\{\mathrm{C_3N_2H_2C(}C\mathrm{H_3)_3}\}_3$	30.9	q, $^1J_{\mathrm{C-H}}$ = 126
$\mathrm{MgOOC(C}H_3\mathrm{)_3}$	1.61	s	$\mathrm{MgOO}C\mathrm{(CH_3)_3}$	78.3	s
			$\mathrm{MgOOC(}C\mathrm{H_3)_3}$	27.4	q, $^1J_{\mathrm{C-H}}$ = 126

Table VI (Continued)

^{1}H NMR			^{13}C NMR		
assignment	δ (ppm)	coupling (Hz)	assignment	δ (ppm)	coupling (Hz)
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$MgNHPh					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3)_3\}_3$	1.36	s	η^3-HB$\{\mathrm{C_3N_2H_2C(}C\mathrm{H_3)_3}\}_3$	31.0	q, $^1J_{\mathrm{C\text{-}H}} = 126$
MgNHC$_6$$H_5$			MgNHC_6H$_5$		
2 o-H	6.86	m	1 ipso-C	157.7	m
2 m-H	7.28	m	2 o-C	129.4	d, $^1J_{\mathrm{C\text{-}H}} = 153$
1 p-H	6.70	m			d, $^2J_{\mathrm{C\text{-}H}} = 9$
MgNHC$_6$H$_5$	3.64	broad	2 m-C	118.1	d, $^1J_{\mathrm{C\text{-}H}} = 150$
					dd, $^2J_{\mathrm{C\text{-}H}} = 8, 14$
			1 p-C	112.6	d, $^1J_{\mathrm{C\text{-}H}} = 159$
					t, $^2J_{\mathrm{C\text{-}H}} = 7$
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$MgOC(=CH$_2$)CH$_3$					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3)_3\}_3$	1.45	s	η^3-HB$\{\mathrm{C_3N_2H_2C(}C\mathrm{H_3)_3}\}_3$	30.9	q, $^1J_{\mathrm{C\text{-}H}} = 126$
MgOC(CH_2)CH$_3$			MgOC(CH$_2$)CH$_3$	26.4	q, $^1J_{\mathrm{C\text{-}H}} = 128$
1 H	4.29	s (broad)	MgOC(CH$_2$)CH$_3$	83.1	t, $^1J_{\mathrm{C\text{-}H}} = 155$
1 H	4.32	d, $^2J_{\mathrm{H\text{-}H}} = 1.4$	MgOC(CH$_2$)CH$_3$	161.9	s
MgOC(CH$_2$)CH_3	2.28	s			
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$MgOC(=CH$_2$)Bu^t					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3)_3\}_3$	1.45	s	η^3-HB$\{\mathrm{C_3N_2H_2C(}C\mathrm{H_3)_3}\}_3$	31.0	q, $^1J_{\mathrm{C\text{-}H}} = 126$
MgOC(CH_2)C(CH$_3$)$_3$			MgOC(CH$_2$)C(CH$_3$)$_3$	172.4	s
1 H	3.84	s	MgOC(CH$_2$)C(CH$_3$)$_3$	82.1	dd, $^1J_{\mathrm{C\text{-}H}} = 149, 156$
1 H	4.42	s	MgOC(CH$_2$)C(CH$_3$)$_3$	37.8	s
MgO(CH$_2$)C(CH_3)$_3$	1.54	s	MgOC(CH$_2$)C(CH$_3$)$_3$	29.7	q, $^1J_{\mathrm{C\text{-}H}} = 125$
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$Mg($\eta^1$-O$_2CCH_3$)					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3)_3\}_3$	1.44	s	η^3-HB$\{\mathrm{C_3N_2H_2C(}C\mathrm{H_3)_3}\}_3$	30.6	q, $^1J_{\mathrm{C\text{-}H}} = 126$
MgO$_2$CCH_3	2.19	s^c	MgO$_2$CCH$_3$	22.5	q, $^1J_{\mathrm{C\text{-}H}} = 128^c$
			MgO$_2$$CCH_3$	187.0	s
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$MgCl					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3)_3\}_3$	1.49	s	η^3-HB$\{\mathrm{C_3N_2H_2C(}C\mathrm{H_3)_3}\}_3$	31.0	q, $^1J_{\mathrm{C\text{-}H}} = 126$
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$MgBr					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3)_3\}_3$	1.50	s	η^3-HB$\{\mathrm{C_3N_2H_2C(}C\mathrm{H_3)_3}\}_3$	31.3	q, $^1J_{\mathrm{C\text{-}H}} = 126$
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$MgI					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3)_3\}_3$	1.52	s	η^3-HB$\{\mathrm{C_3N_2H_2C(}C\mathrm{H_3)_3}\}_3$	31.8	q, $^1J_{\mathrm{C\text{-}H}} = 126$
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$MgNCS					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3)_3\}_3$	1.34	s	η^3-HB$\{\mathrm{C_3N_2H_2C(}C\mathrm{H_3)_3}\}_3$	30.6	q, $^1J_{\mathrm{C\text{-}H}} = 126$
			MgNCS	145.1	s
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$MgNCO					
η^3-HB$\{\mathrm{C_3N_2H_2C(C}H_3)_3\}_3$	1.37	s	η^3-HB$\{\mathrm{C_3N_2H_2C(}C\mathrm{H_3)_3}\}_3$	30.7	q, $^1J_{\mathrm{C\text{-}H}} = 126$
$\{\eta^3\text{-HB(3,5-Me}_2\text{pz)}_3\}_2$Mg					
η^3-HB$\{\mathrm{C_3N_2H(C}H_3)_2\}_3$			η^3-HB$\{\mathrm{C_3N_2H(}C\mathrm{H_3)_2}\}_3$		
3 CH$_3$	1.65	s	3 C	12.5	q, $^1J_{\mathrm{C\text{-}H}} = 128$
3 CH$_3$	2.29	s	3 C	13.0	q, $^1J_{\mathrm{C\text{-}H}} = 127$
η^3-HB$\{\mathrm{C_3N_2}H\mathrm{(CH_3)_2}\}_3$	5.66	s	η^3-HB$\{C_3\mathrm{N_2H(CH_3)_2}\}_3$		
			3 C	105.2	d, $^1J_{\mathrm{C\text{-}H}} = 170$
			3 C	143.6	dq, $^2J_{\mathrm{C\text{-}H}} = 7$
			3 C	149.7	dq, $^2J_{\mathrm{C\text{-}H}} = 6$

[a] In C$_6$D$_6$ unless stated otherwise. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, spt = septet. For brevity, only the *tert*-butyl resonances of the η^3-HB(3-Bu^{t}pz)$_3$ ligand are listed. [b] ^{13}C NMR spectrum in CDCl$_3$. [c] Additional couplings [d, $^2J_{\mathrm{C\text{-}H}}$ = 6.4 Hz, d $^1J_{\mathrm{C\text{-}C}}$ = 53 Hz] are observed for the isotopomer $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$Mg($\eta^1$-O$_2^{13}CCH_3$).

and studies of the reactions with alkyl halides and O$_2$ suggest that radical processes are involved. Furthermore, the reactions of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$MgCH$_3$ with ketones, resulting in the selective formation of enolate rather than alkoxide derivatives, demonstrate that the reactivity of the Mg–R bond in these well-defined 4-coordinate complexes is not typical of Grignard reagents.

Experimental Details

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, and Schlenk techniques.[25] Solvents were purified and degassed by standard procedures. ^{1}H, ^{13}C, and ^{17}O NMR spectra were measured on Varian VXR 200, 300, and 400 spectrometers. IR spectra were recorded as Nujol mulls between KBr disks on a Perkin-Elmer 1420 spectrophotometer (cm^{-1}). Mass spectra were obtained on a Nermag R10-10 mass spectrometer using chemical ionization (NH$_3$ or CH$_4$) techniques. Elemental analyses were measured using a Perkin-Elmer 2400 CHN elemental analyzer. $\{\eta^3\text{-HB(3,5-Me}_2\text{pz)}_3\}$MgR and $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$MgR were prepared by the literature method.[1] Me$_3$SiOH was prepared by a modification of a literature method.[26] Selected ^{1}H and ^{13}C NMR data are presented in Table VI, and a complete table of data is available as supplementary material.

Synthesis of $\{\eta^3\text{-HB(3,5-Me}_2\text{pz)}_3\}_2$Mg. A solution of K{HB(3,5-Me$_2$pz)$_3$} (235 mg, 0.70 mmol) in THF (20 mL) was added dropwise to a stirred solution of MgBr$_2$ (65 mg, 0.35 mmol) in THF (15 mL). The mixture was stirred for 2 h at room temperature and filtered. The filtrate was concentrated to ca. 10 mL and placed at 0 °C, giving colorless crystals of $\{\eta^3\text{-HB(3,5-Me}_2\text{pz)}_3\}_2$Mg which were isolated by filtration and dried in vacuo (120 mg, 56%). Anal. Calcd for $\{\eta^3\text{-HB(3,5-Me}_2\text{pz)}_3\}_2$Mg: C, 58.2; H, 7.2; N, 27.2. Found: C, 58.4; H, 7.2; N, 26.9. IR: 2520 ($\nu_{\mathrm{B\text{-}H}}$).

Ligand Redistribution Reactions. Solutions of $\{\eta^3\text{-HB(3,5-Me}_2\text{pz)}_3\}$MgR (R = CH$_3$, CH$_2CH_3$, (CH$_2$)$_3CH_3$, CH$_2$SiMe$_3$, CH(CH$_3$)$_2$, C(CH$_3$)$_3$, CH=CH$_2$, C$_6H_5$; ca. 20 mg) in benzene-$d_6$ were heated at 80–120 °C. The formation of $\{\eta^3\text{-HB(3,5-Me}_2\text{pz)}_3\}_2$Mg over a period of days was

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[25] (a) McNally, J. P.; Leong, V. S.; Cooper, N. J. *ACS Symp. Ser.* **1987**, *357*, 6–23. (b) Burger, B. J.; Bercaw, J. E. *ACS Symp. Ser.* **1987**, *357*, 79–97.

[26] A solution of Me$_3$SiCl (20 mL) in Et$_2$O (100 mL) was added dropwise to a mixture of ET$_2$O (100 mg) and H$_2$O (100 g) at 0 °C (maintained at pH 7 using phosphate buffer). The ether and aqueous layers were separated, and the Me$_3$SiOH was obtained by removing the Et$_2$O by distillation. We thank Dr. R. Colborn for this advice. George, P. D.; Sommer, L. H.; Whitmore, F. C. *J. Am. Chem. Soc.* **1953**, *75*, 1585–1588.

demonstrated by ^{1}H NMR spectroscopy. A similar experiment was carried out for the complex $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$, which showed no reaction after 7 days at 120 °C.

Reaction of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ with ROH. A solution of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ (150 mg, 0.36 mmol) in benzene (20 mL) was treated with C$_6$H$_5$OH (40 mg, 0.43 mmol). The mixture was concentrated to ca. 2 mL and placed at 0 °C, giving a white precipitate of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgOC$_6$H$_5$ which was filtered and dried in vacuo (60 mg, 34%). Similar procedures were carried out for the reactions of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ with ROH (R = CH$_2$CH$_3$, CH(CH$_3$)$_2$, CH$_2$SiMe$_3$, C(CH$_3$)$_3$, SiMe$_3$). Anal. Calcd for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgOCH$_2$CH$_3$: C, 61.3; H, 8.7; N, 18.7. Found: C, 60.3; H, 8.4; N, 18.2. IR: 2480 ($\nu_{\text{B-H}}$). Anal. Calcd for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgOCH(CH$_3$)$_2$: C, 62.0; H, 8.9; N, 18.1. Found: C, 62.1; H, 8.6; N, 17.7. IR: 2490 ($\nu_{\text{B-H}}$). Anal. Calcd for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgOC(CH$_3$)$_3$: C, 62.7; H, 9.1; N, 17.6. Found: C, 62.0; H, 9.1; N, 17.1. IR: 2500 ($\nu_{\text{B-H}}$). Anal. Calcd for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgOC$_6$H$_5$: C, 65.0; H, 7.9; N, 16.9. Found: C, 66.0; H, 8.1; N, 16.6. IR: 2510 ($\nu_{\text{B-H}}$). Anal. Calcd for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgOSiMe$_3$: C, 58.3; H, 8.8; N, 17.0. Found: C, 59.2; H, 8.0; N, 16.1. IR: 2495 ($\nu_{\text{B-H}}$). Anal. Calcd for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgOCH$_2$SiMe$_3$: C, 59.0; H, 8.9; N, 16.5. Found: C, 57.9; H, 8.8; N, 15.8. IR: 2480 ($\nu_{\text{B-H}}$).

Reaction of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ with H$_2$S. A solution of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ (150 mg, 0.36 mmol) in benzene (15 mL) was treated with H$_2$S (1 atm). The mixture was stirred at room temperature for 2 h, concentrated to ca. 2 mL, and cooled giving $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgSH as a white solid (90 mg, 57%). Anal. Calcd for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgSH: C, 57.5; H, 8.0; N, 19.2. Found: C, 56.8; H, 7.6; N, 18.4. IR: 2500 ($\nu_{\text{B-H}}$).

Reaction of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ with CH$_3$SH. A solution of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ (40 mg, 0.1 mmol) in benzene (1 mL) was treated with CH$_3$SH (1 atm) and left for 10 min at room temperature. The volatile components were removed under reduced pressure, giving $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgSCH$_3$ as a white solid (40 mg, 93%). Anal. Calcd for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgSCH$_3$: C, 58.4; H, 8.2; N, 18.6. Found: C, 57.9; H, 8.4; N, 17.9. IR: 2480 ($\nu_{\text{B-H}}$).

Reaction of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ with X$_2$ (X = Cl, Br, I). A solution of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ (100 mg, 0.24 mmol) in benzene (15 mL) was titrated with a solution of X$_2$ (X = Br, I) in C$_6$H$_6$ until the solution became pale yellow. The solution was concentrated to ca. 2 mL, and the solid that separated was filtered. The solid was redissolved in benzene, filtered, and concentrated to ca. 2 mL, giving $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgX which was isolated by filtration and dried in vacuo (ca. 50%). The reaction between $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ and Cl$_2$ was monitored by ^{1}H NMR spectroscopy. A solution of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ (20 mg, 0.05 mmol) in benzene-d_6 (0.7 mL) was treated with Cl$_2$ (1 atm). ^{1}H NMR spectroscopy demonstrated that $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCl was formed quantitatively after 10 min at room temperature. However, $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCl is more conveniently prepared by the method described below. Anal. Calcd for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgBr: C, 52.0; H, 7.1; N, 17.3. Found: C, 51.2; H, 6.8; N, 15.6. IR: 2520 ($\nu_{\text{B-H}}$). MS: *m/e* 487 (M$^+$ + 1). Anal. Calcd for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgI: C, 47.4; H, 6.4; N, 15.8. Found: C, 49.1; H, 6.3; N, 14.4. IR: 2500 ($\nu_{\text{B-H}}$). MS: *m/e* 533 (M$^+$ + 1).

Reaction of Bu^{t}MgCl with Tl$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$. A solution of Bu^{t}MgCl (1.7 mL, 3.4 mmol, 2.0 M in Et$_2$O) was added dropwise to a solution of Tl$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$ (2.0 g, 3.4 mmol) in THF (60 mL), resulting in the immediate formation of a black deposit of Tl metal. The mixture was stirred for 20 min at room temperature and filtered. The filtrate was concentrated to ca. 15 mL and placed at 0 °C to give a crop of colorless crystals. The crystals of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCl were isolated by filtration and dried in vacuo (0.63 g, 42%). Anal. Calcd for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCl: C, 57.2; H, 7.8; N, 19.1. Found: C, 57.0; H, 7.9; N, 19.0. IR: 2520 ($\nu_{\text{B-H}}$). MS: *m/e* 441 (M$^+$ + 1).

Reaction of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ with HCl. A solution of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ (20 mg, 0.05 mmol) in benzene-d_6 (0.7 mL) was treated with HCl (1 atm) and left at room temperature for 30 min. The products were identified as $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCl and CH$_4$ by ^{1}H NMR spectroscopy.

Reaction of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ with C$_6$H$_5$NH$_2$. A solution of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ (40 mg, 0.1 mmol) in benzene (1 mL) was treated with C$_6$H$_5$NH$_2$ (9 μL, 0.1 mmol) and heated at 60 °C for 1 day. The volatile components were removed under reduced pressure, giving $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgNHPh (ca. 40 mg, 85%). Anal. Calcd for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgNHPh: C, 65.2; H, 8.1; N, 19.7. Found: C, 64.3; H, 7.8; N, 20.4. IR: 2510 ($\nu_{\text{B-H}}$).

Reaction of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ with RC≡CH. A solution of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ (40 mg, 0.1 mmol) in benzene (1 mL) was treated with RC≡CH (R = C$_6$H$_5$, SiMe$_3$; 0.1 mmol) and heated at 110 °C for 5 h. The volatile components were removed under reduced pressure, giving $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgC$_2$R (ca. 90%). Anal. Calcd for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgC$_2$C$_6$H$_5$: C, 68.7; H, 7.8; N, 16.6. Found: C, 67.6; H, 7.9; N, 15.7. IR: 2510 ($\nu_{\text{B-H}}$). Anal. Calcd for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgC$_2$SiMe$_3$: C, 62.1; H, 8.6; N, 16.7. Found: C, 61.1; H, 7.3; N, 16.1. IR: 2480 ($\nu_{\text{B-H}}$).

Reaction of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ with Me$_3$SiX (X = Cl, Br, I, NCO, NCS). A solution of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ (40 mg, 0.1 mmol) in benzene (1 mL) was treated with Me$_3$SiX (X = Cl, Br, I, NCO, NCS; 0.1 mmol). Although Me$_3$SiI reacted rapidly (ca. 5 h at room temperature), the other derivatives required heating at ca. 120 °C for 2 weeks for completion. The volatile components were removed under reduced pressure, giving $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgX (ca. 90%). Anal. Calcd for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgNCS: C, 57.0; H, 7.4; N, 21.1. Found: C, 56.1; H, 7.5; N, 20.8. IR: 2520 ($\nu_{\text{B-H}}$), 2060 (ν_{NCS}). MS: *m/e* 464 (M$^+$ + 1). Anal. Calcd for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgNCO: C, 59.0; H, 7.7; N, 21.9. Found: C, 57.8; H, 8.0; N, 21.1. IR: 2510 ($\nu_{\text{B-H}}$), 2230 (ν_{NCO}). MS: *m/e* 448 (M$^+$ + 1).

Reaction of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ with RX. A solution of $\{\eta^3$-HB(3-Bu^{t}pz)$_3$MgCH$_3$ (20 mg, 0.05 mmol) in benzene-d_6 (0.7 mL) was treated with RX (RX = CH$_3$I, CH$_3$CH$_2$I, (CH$_3$)$_2$CHI, (CH$_3$)$_3$CI, C$_6$H$_5$CH$_2$Cl, C$_6$H$_5$CH$_2$Br, C$_6$H$_5$CH$_2$I) and heated at 100–140 °C. The reactions were monitored by ^{1}H NMR spectroscopy which demonstrated the formation of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgX over a period of days. For the reactions with C$_6$H$_5$CH$_2$X (X = Cl, Br, I) the relative amounts of PhCH$_2$CH$_2$Ph and PhCH$_2$CH$_3$ in the products were measured by ^{1}H NMR spectroscopy.

Alkyl Exchange Experiments. A solution of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ (8.4 mg, 0.02 mmol) in benzene-d_6 (0.7 mL) was treated with ^{13}CH$_3$I (2.5 μL, 0.04 mmol) and heated at 140 °C. Evidence for the formation of the alkyl exchange product $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$Mg^{13}CH$_3$ during the course of the reaction was provided by the observation of a doublet ($^1J_{\text{C-H}}$ = 108 Hz) in the ^{1}H NMR spectrum at δ −0.05 due to the magnesium methyl group of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$Mg^{13}CH$_3$. Similarly, a solution of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_2$CH$_3$ (25 mg, 0.06 mmol) in benzene-d_6 (0.7 mL) was treated with CH$_3$I (5 μL, 0.08 mmol) and heated at 110 °C. ^{1}H NMR spectroscopy demonstrated the formation of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ during the course of the reaction.

Ring Opening of Cyclopropylmethyl Bromide. A solution of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ (10 mg, 0.02 mmol) in benzene-d_6 (0.7 mL) was treated with c-C$_3$H$_5$CH$_2$Br (4 μL, 0.04 mmol) and heated at 110 °C. The reaction was monitored by ^{1}H NMR spectroscopy. Over a period of 5 days the c-C$_3$H$_5$CH$_2$Br had completely isomerized to the ring-opened isomer CH$_2$=CHCH$_2$CH$_2$Br, while only ca. 25% $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgBr had been formed. Complete conversion to $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgBr required heating at 110 °C for 1 month.

Reaction of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ with CH$_3$SSCH$_3$. A solution of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ (20 mg, 0.05 mmol) in benzene-d_6 (0.7 mL) was treated with CH$_3$SSCH$_3$ (5 μL, 0.06 mmol) and heated at 140 °C for 2 weeks. $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgSCH$_3$ and (CH$_3$)$_2$S were identified as the products by ^{1}H NMR spectroscopy.

Reaction of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ with CO$_2$. A solution of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ (40 mg, 0.1 mmol) in benzene (1 mL) was treated with CO$_2$ (1 atm) and heated at 80 °C for 4 h. The volatile components were removed under reduced pressure, giving $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$Mg(η^1-O$_2$CCH$_3$) as a white solid (40 mg, 91%). Anal. Calcd for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$Mg(η^1-O$_2$CCH$_3$): C, 59.5; H, 8.0; N, 18.1. Found: C, 58.6; H, 7.9; N, 17.4. IR: 2480 ($\nu_{\text{B-H}}$), 1555 (ν_{CO_2}) [1515 ($\nu_{^{13}\text{CO}_2}$)].

Reaction of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ with RCOCH$_3$ (R = CH$_3$, C(CH$_3$)$_3$). A solution of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ (40 mg, 0.1 mmol) in benzene (1 mL) was treated with RCOCH$_3$ (0.1 mmol) and left at room temperature (R = CH$_3$, 5 min; R = Bu^t, 5 h). The volatile components were removed under reduced pressure, giving $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$Mg$\{\eta^1$-OC(=CH$_2$)R$\}$ as a white solid in quantitative (by ^{1}H NMR) yield. Anal. Calcd for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$Mg$\{\eta^1$-OC(=CH$_2$)CH$_3\}$: C, 62.3; H, 8.5; N, 18.2. Found: C, 59.3; H, 8.3; N, 16.4. IR: 2490 ($\nu_{\text{B-H}}$), 1620 ($\nu_{\text{C=C}}$). Anal. Calcd for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$Mg$\{\eta^1$-OC(=CH$_2$)Bu$^t\}$: C, 64.2; H, 9.0; N, 16.7. Found: C, 63.5; H, 8.7; N, 17.4. IR: 2505 ($\nu_{\text{B-H}}$), 1615 ($\nu_{\text{C=C}}$).

Reaction of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgR with O$_2$. A solution of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgR (R = CH$_2$CH$_3$, CH(CH$_3$)$_2$, C(CH$_3$)$_3$; ca. 40 mg, ca. 0.1 mmol) in benzene (1 mL) was treated with O$_2$ (1 atm). The volatile components were removed under reduced pressure after 10 min, giving $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgO$_2$R in quantitative yield (by ^{1}H NMR). The reaction of the methyl derivative $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ proceeded similarly with the exception that the reaction required ca. 2 days to go to completion and was accompanied by ca. 25% decomposition. Anal. Calcd for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgO$_2$Bu^t: C, 60.7; H, 8.8; N, 17.0. Found: C, 60.3; H, 8.6; N, 17.2. IR: 2491 ($\nu_{\text{B-H}}$), 889 ($\nu_{\text{O-O}}$) [866 ($\nu_{^{18}\text{O}-^{18}\text{O}}$)], 660 ($\nu_{\text{Mg-O}}$) [618 ($\nu_{\text{Mg}-^{18}\text{O}}$)]. Anal. Calcd for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgO$_2$Pr^i: C, 60.0; H, 8.6; N, 17.5. Found: C, 56.7; H, 8.4; N, 16.6. IR: 2485

(ν_{B-H}), 931 (ν_{O-O}) [912 ($\nu_{^{18}O-^{18}O}$)], 631 (ν_{Mg-O}) [611 ($\nu_{Mg-^{18}O}$)]. Anal. Calcd for {η^3-HB(3-Bu^{t}pz)$_3$}MgO$_2$Et: C, 59.2; H, 8.4; N, 18.0. Found: C, 59.3; H, 7.7; N, 16.8. IR: 2481 (ν_{B-H}), 902 (ν_{O-O}) [885 ($\nu_{^{18}O-^{18}O}$)], 611 (ν_{Mg-O}) [580 ($\nu_{Mg-^{18}O}$)]. IR for {η^3-HB(3-Bu^{t}pz)$_3$}MgO$_2$CH$_3$: 2505 (ν_{B-H}), 935 (ν_{O-O}) [929 ($\nu_{^{18}O-^{18}O}$)], 608 (ν_{Mg-O}) [582 ($\nu_{Mg-^{18}O}$)].

Galvinoxyl Inhibition Experiment. A solution of {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_3$ (0.7 mL, 34 mM in benzene-d_6) was placed in two NMR tubes, and a solution of galvinoxyl (0.1 mL, 5 mM in benzene-d_6) was added to one of the tubes. Both NMR tubes were exposed to the same O$_2$ source (1 atm), and the reactions were monitored by ^{1}H NMR spectroscopy. After 35 h at room temperature the reaction in the absence of galvinoxyl had proceeded to completion, whereas the reaction in the presence of galvinoxyl had proceeded to only ≈60% completion.

Crossover Experiment. A solution of a mixture of {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_3$ and {η^3-HB(3,5-Me$_2$pz)$_3$}MgC(CH$_3$)$_3$ (0.7:1.0 molar ratio) in benzene-d_6 (0.7 mL) was treated with O$_2$ (1 atm), and the reaction was monitored by ^{1}H NMR spectroscopy. After 5 min at room temperature the crossover product {η^3-HB(3-Bu^{t}pz)$_3$}MgO$_2$C(CH$_3$)$_3$ was one of the major species present.

Reaction of {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_3$ with Bu^{t}O$_2$H. A solution of {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_3$ (40 mg, 0.1 mmol) in benzene (1 mL) was treated with Bu^{t}O$_2$H (34 μL, 3.0 M solution in 2,2,4-trimethylpentane, 0.1 mmol). The volatile components were removed under reduced pressure after 10 min at room temperature, giving η^3-HB(3-Bu^{t}pz)$_3$}MgO$_2$Bu^t as a white solid (40 mg, 85%).

Reaction of {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_2$SiMe$_3$ with O$_2$. A solution of {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_2$SiMe$_3$ (ca. 20 mg, 0.04 mmol) in benzene-d_6 (0.7 mL) was treated with O$_2$ (1 atm), and the reaction was monitored by ^{1}H NMR spectroscopy. After 2 days at room temperature the major product was {η^3-HB(3-Bu^{t}pz)$_3$}MgOSiMe$_3$ (ca. 90%). Formaldehyde was also present.

Crossover Experiment. A solution of a mixture of {η^3-HB(3-Bu^{t}pz)$_3$}MgC(CH$_3$)$_3$ and {η^3-HB(3,5-Me$_2$pz)$_3$}MgCH$_2$SiMe$_3$ (0.8:1 molar ratio) in benzene-d_6 (0.7 mL) was treated with O$_2$ (1 atm), and the reaction was monitored by ^{1}H NMR spectroscopy. After 2 h at room temperature the main products were {η^3-HB(3-Bu^{t}pz)$_3$}MgO$_2$C(CH$_3$)$_3$ and the crossover product {η^3-HB(3-Bu^{t}pz)$_3$}MgOSiMe$_3$.

Reaction of {η^3-HB(3,5-Me$_2$pz)$_3$}MgR with O$_2$. A solution of {η^3-HB-(3,5-Me$_2$pz)$_3$}MgR (R = CH(CH$_3$)$_2$, C(CH$_3$)$_2$; 0.05 mmol) in benzene-d_6 (0.7 mL) was treated with O$_2$ (1 atm). The reactions were monitored by ^{1}H NMR spectroscopy. After 30 min a mixture of products was obtained, of which {η^3-HB(3,5-Me$_2$pz)$_3$}$_2$Mg was the major component (ca. 40%).

Reaction of {η^3-HB(3-Bu^{t}pz)$_3$}MgO$_2$Pr^i with {η^3-HB(3-Bu^{t}pz)$_3$}MgPr^i. {η^3-HB(3-Bu^{t}pz)$_3$}MgPr^i (ca. 20 mg, 0.04 mmol) was added to a solution of {η^3-HB(3-Bu^{t}pz)$_3$}MgO$_2$Pr^i (ca. 20 mg, 0.04 mmol) in benzene-d_6 (0.7 mL). No immediate reaction was observed by ^{1}H NMR spectroscopy. The sample was heated overnight at 80 °C, giving {η^3-HB(3-Bu^{t}pz)$_3$}MgOPr^i, as demonstrated by ^{1}H NMR spectroscopy.

Reaction of {η^3-HB(3-Bu^{t}pz)$_3$}MgO$_2$R with PPh$_3$. PPh$_3$ (ca. 15 mg, 0.06 mmol) was added to solutions of {η^3-HB(3-Bu^{t}pz)$_3$}MgO$_2$R (R = CH$_3$, CH$_2$CH$_3$, CH(CH$_3$)$_2$, C(CH$_3$)$_3$; ca. 0.05 mmol) in benzene-d_6 (0.7 mL), and the sample was monitored by ^{1}H NMR spectroscopy. In each case the products {η^3-HB(3-Bu^{t}pz)$_3$}MgOR and Ph$_3$PO were formed within 2 h at room temperature.

X-ray Structure Determination of {η^3-HB(3-Bu^{t}pz)$_3$}MgCl. Crystal data, data collection, and refinement parameters are summarized in Table VII. A single crystal of {η^3-HB(3-Bu^{t}pz)$_3$}MgCl was mounted in a glass capillary and placed on a Nicolet R3m diffractometer. The unit cell was determined by the automatic indexing of 25 centered reflections and confirmed by examination of the axial photographs. Intensity data were collected using graphite-monochromated Mo Kα X-radiation (λ = 0.71073 Å). Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization, and absorption effects. The structure was solved using direct methods and standard difference map techniques on a Data General NOVA 4 computer using SHELXTL.[27] Systematic absences were consistent with the space groups *Pnma* or *Pna*2$_1$, but consideration of the *E*-value statistics suggested the choice *Pnma* (No. 62). Most of the hydrogen atoms were located in the difference map after all the non-hydrogen atoms were located and refined anisotropically, but hydrogens on carbon were allowed to refine in calculated positions (d_{C-H} = 0.96 Å; $U_{iso}(H) = 1.2U_{iso}(C)$). Block-diagonal least-squares refinement converged to R = 0.0517 (R_w = 0.0590). Selected bond distances and angles are listed in Tables III and IV.

Table VII. Crystal and Intensity Collection Data for {η^3-HB(3-Bu^{t}pz)$_3$}MgCl and {η^3-HB(3,5-Me$_2$pz)$_3$}$_2$Mg

	{η^3-HB(3-Bu^{t}pz)$_3$}MgCl	{η^3-HB(3,5-Me$_2$pz)$_3$}$_2$Mg
formula	C$_{21}$H$_{34}$N$_6$BMgCl	C$_{30}$H$_{44}$N$_{12}$B$_2$Mg
formula weight	441.2	618.7
lattice	orthorhombic	triclinic
cell constants	a = 16.048 (7) Å b = 16.006 (3) Å c = 9.840 (1) Å V = 2527 (1) Å^3	a = 8.837 (3) Å b = 10.223 (3) Å c = 10.773 (1) Å α = 63.92 (3)° β = 85.24 (2)° γ = 79.87 (2)° V = 860.4 (4) Å^3
Z	4	1
space group	*Pnma* (No. 62)	$P\bar{1}$ (No. 2)
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
ρ(calcd)	1.16 g cm^{-3}	1.19 g cm^{-3}
μ(Mo Kα)	2.0 cm^{-1}	1.0 cm^{-1}
goodness of fit	1.450	1.630
R	0.0517	0.0579
R_w	0.0590	0.0765

X-ray Structure Determination of {η^3-HB(3,5-Me$_2$pz)$_3$}$_2$Mg. Crystal data, data collection, and refinement parameters are summarized in Table VII, and general procedures are as for {η^3-HB(3-Bu^{t}pz)$_3$}MgCl. Systematic absences were consistent with the space groups *P*1 or $P\bar{1}$, but successful solution was found in $P\bar{1}$ (No. 2). Most of the hydrogen atoms were located in the difference map after all the non-hydrogen atoms were located and refined anisotropically, but hydrogens on carbon were allowed to refine in calculated positions (d_{C-H} = 0.96 Å; $U_{iso}(H) = 1.2U_{iso}(C)$). Block-diagonal least-squares refinement converged to R = 0.0579 (R_w = 0.0765). Selected bond distances and angles are listed in Tables I and II.

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Registry No. A (R = OPh), 122519-78-2; A (R = OEt), 125950-47-2; A (R = OPr-*i*), 125950-48-3; A (R = OBu-*t*), 122519-77-1; A (R = OTMS), 131931-53-8; A (R = OCH$_2$TMS), 137743-91-0; A (R = SH), 122519-79-3; A (R = SMe), 137743-92-1; A (R = Br), 122519-81-7; A (R = I), 122519-74-8; A (R = NHPh), 137743-93-2; A (R = C$_2$Ph), 137743-94-3; A (R = C$_2$TMS), 137743-95-4; A (R = NCS), 137743-96-5; A (R = NCO), 137743-97-6; A (R = OAc), 122519-80-6; A (R = OC(CH$_3$)=CH$_2$, 122519-76-0; A (R = OC(=CH$_2$)C(CH$_3$)$_3$, 137743-98-7; A (R = O$_2$Bu-*t*), 125950-45-0; A (R = O$_2$Pr-*i*), 125950-44-9; A (R = O$_2$Et), 125950-43-8; A (R = O$_2$Me), 125950-42-7; A (R = Cl), 122519-75-9; A (R = Me), 122519-72-6; A (R = Et), 122519-82-8; A (R = Pr-*i*), 125950-40-5; A (R = Bu-*t*), 125950-41-6; B (R = Me), 122539-41-7; B (R = Et), 130950-97-9; B (R = Bu), 130949-85-8; B (R = CH$_2$TMS), 131931-52-7; B (R = Pr-*i*), 130949-86-9; B (R = Bu-*t*), 130949-87-0; B (R = CH=CH$_2$), 130949-88-1; B (R = Ph), 130949-89-2; {η^3-HB(3,5-Me$_2$pz)$_3$}$_2$Mg, 130949-90-5; c-C$_3$H$_5$CH$_2$Br, 7051-34-5; CH$_2$=CHCH$_2$CH$_2$Br, 5162-44-7.

Supplementary Material Available: Listings of crystal and intensity collection data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters, ORTEP drawings for {η^3-HB(3-Bu^{t}pz)$_3$}MgCl and {η^3-HB(3,5-Me$_2$pz)$_3$}$_2$Mg, and complete tables of spectroscopic data (29 pages); listings of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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[27] Sheldrick, G. M. *SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*; University of Göttingen: Göttingen, Federal Republic of Germany, 1981.