(Tris(pyrazolyl)hydroborato)magnesium Alkyl Derivatives: Synthetic and Structural Studies

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Received July 23, 1990

A series of solvent-free, 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 (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, $CH(CH_3)_2$, $C(CH_3)_3$, $CH_2(CH_2)_2CH_3$, $CH_2Si(CH_3)_3$, $CH{=}CH_2$, C_6H_5), have been prepared by the reaction of the appropriate dialkylmagnesium compound with either the potassium or thallium derivatives of the respective tris(pyrazolyl)hydroborato ligand. The molecular structures of the complexes $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$, $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH(CH$_3$)$_2$, and $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}$MgCH$_2$Si(CH$_3$)$_3$ have been determined by X-ray diffraction, which shows that in each case the complexes are monomeric with 4-coordinate magnesium centers and η^3-coordinate tris(pyrazolyl)hydroborato ligands. $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ is orthorhombic, *Pnma*, a = 16.362 (4) Å, b = 15.920 (5) Å, c = 9.824 (4) Å, and Z = 4. $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH(CH$_3$)$_2$ is orthorhombic, *Pnma*, a = 17.171 (2) Å, b = 15.893 (7) Å, c = 10.034 (3) Å, and Z = 4. $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}$MgCH$_2$Si(CH$_3$)$_3$ is monoclinic, $C2/c$, a = 23.897 (8) Å, b = 8.010 (2) Å, c = 30.072 (8) Å, and Z = 8. In contrast to the clean reactions of the thallium and potassium tris(pyrazolyl)hydroborato derivatives with R$_2$Mg, the corresponding reactions with Grignard reagents are more complex as a result of competition between Mg-R and Mg-X bond metathesis. The product distribution is dependent upon both RMgX and the tris(pyrazolyl)hydroborato reagent. Thus, for the thallium complex Tl$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$, chloro and bromo Grignard reagents favor alkyl ligand metathesis and the formation of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgX, whereas the iodo Grignard reagent CH$_3$MgI favors halide ligand metathesis and the formation of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$. However, the selectivity of these reactions with Grignard reagents may be altered by the use of the potassium reagent K$\{$HB(3-Bu^{t}pz)$_3\}$, and thus, primary and secondary Grignard reagents react with K$\{$HB(3-Bu^{t}pz)$_3\}$ to give the alkyl derivatives $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgR as the principal products.

Introduction

Organomagnesium complexes and, in particular, Grignard reagents are well-known to be among the most important classes of reagents in synthetic organic and organometallic chemistry. As such, magnesium alkyl derivatives have been the subject of many investigations of which the principal focal points have been reactivity, structure, and composition.[1] These studies have demonstrated that solutions of Grignard reagents consist of a complex mixture of species. A simple indication of the complexity that may arise in solutions of Grignard reagents is provided by the example that "CH_3CH_2MgBr" crystallizes from Et_2O as the disolvated monomer $CH_3CH_2MgBr(OEt_2)_2$,[2] whereas crystallization from Pr^i_2O gives the halogen-bridged dimer $[CH_3CH_2MgBr(OPr^i_2)]_2$.[3] Furthermore, crystallization of the related "CH_3CH_2MgCl" from THF gives tetranuclear $[CH_3CH_2Mg_2Cl_3(THF)_3]_2$, in which the alkyl:halide ratio has deviated from unity.[4] One of the simplest models describing the composition of a Grignard reagent is that described by the well-known Schlenk equilibrium (eq 1).[5] However, this model is complicated by a variety of factors including (i) the formation of dimeric (or higher order) species, (ii) the formation of solvated derivatives of each component, and (iii) the presence of ionic species.[1,6] Although studies on the degree of association demonstrate that many Grignard reagents may be monomeric in dilute solutions, the exact nature of the species present, e.g. the degree of solvation, is uncertain. The influence of solvent on the course of reactions of Grignard reagents is demonstrated by the markedly different reactivity of "solvent-free Grignard reagents", prepared by cocondensation of Mg atoms with alkyl halides at -196 °C.[7] In this regard, an investigation of magnesium alkyl derivatives that are both solvent-free and soluble in noncoordinating hydrocarbon solvents would be particularly helpful in simplifying mechanistic interpretations. This paper describes the use of η^3-tris(pyrazolyl)hydroborato ligands[8] to prepare a series of alkyl derivatives of Mg, in which chelation of the three nitrogen atom donors provides a sterically demanding ligand environment that inhibits oligomerization and, thus, provides a well-defined system. The reactivity of these alkyl derivatives will be reported in a future publication. Some of this work has been communicated.[9]

$$2RMgX \rightleftharpoons R_2Mg + MgX_2 \qquad (1)$$

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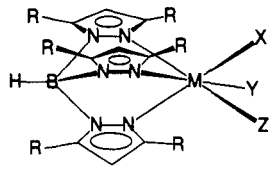


Figure 1. Coordination of the η^3-tris(pyrazolyl)hydroborato ligand to a metal center.

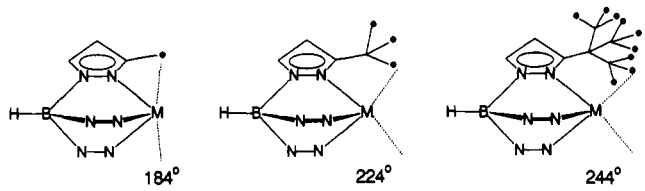


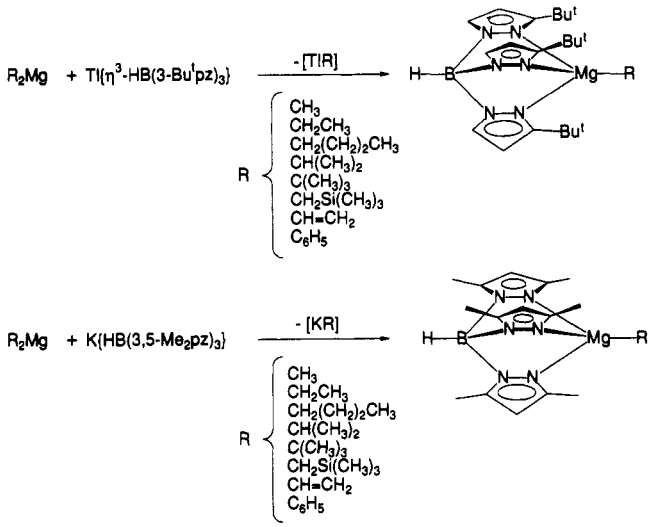
Figure 2. Relative sizes of some η^3-tris(pyrazolyl)hydroborato ligands. (Only one pyrazolyl group is shown for clarity; • = H.)

Results and Discussion

Monomeric, solvent-free, alkyl derivatives of magnesium are comparatively rare. Although the unsolvated bulky dialkyl derivative $Mg\{C(SiMe_3)_3\}_2$[10] has recently been demonstrated to be monomeric by X-ray diffraction, structural studies on other species that have been obtained from solutions of Grignard reagents and dialkylmagnesium complexes include a number of solvated and oligomeric derivatives, e.g. monomeric $CH_3MgBr(THF)_3$,[11] $CH_3CH_2MgBr(OEt_2)_2$,[2] $C_6H_5MgBr(OEt_2)_2$,[12] $(\eta^5\text{-}C_5H_5)MgBr(Et_2NCH_2CH_2NEt_2)$,[13] dimeric $[CH_3CH_2MgBr(OPr^i_2)]_2$,[3] $[CH_3CH_2MgBr(NEt_3)]_2$,[14] and tetranuclear $[CH_3CH_2Mg_2Cl_3(THF)_3]_2$.[1f]

Our approach to isolate a series of monomeric alkyl derivatives of magnesium involved the formation of new alkyl complexes, L_nMgR, by the conceptual substitution of the halide ligand (X) of the Grignard reagent, RMgX, by a sterically demanding ligand (L_n). The expected result of such a substitution would be to inhibit both oligomerization and ligand-exchange processes. We considered that a suitable candidate for L_n would be the η^3-tris(pyrazolyl)hydroborato ligand, shown in Figure 1, which has been used extensively with transition metals[15] and to a lesser extent with the nontransition elements.[16,17] In terms of electron count, the tris(pyrazolyl)hydroborato ligand is formally analogous to η^5-cyclopentadienyl. However, in contrast to cyclopentadienyl ligands, which are notorious for exhibiting a variety of coordination modes with s- and p-block elements,[18] it was anticipated that chelation of the three nitrogen atom donors of a tris(pyrazolyl)hydroborato ligand would provide a well-defined coordination environment for magnesium. Furthermore, the steric demands of the η^3-tris(pyrazolyl)hydroborato ligands may be modified by appropriate substitution at the 3-position of the pyrazolyl group. Thus, cone angles[19] for the ligands η^3-HB(3-Rpz)$_3$ (Rpz = $C_3N_2RH_2$) have been estimated as 244° (R = Bu^t), 224° (R = Me), and 184° (R = H), significantly larger than the cone angles of 100° for η^5-C_5H_5 and 142° for η^5-C_5Me_5 (Figure 2).[20] Additionally, the *tert*-butyl and methyl groups of the η^3-HB(3-Bu^{t}pz)$_3$ and η^3-HB(3,5-Me$_2$pz)$_3$ ligands would be expected to provide a useful and

Scheme I. Synthesis of (Tris(pyrazolyl)hydroborato)magnesium Alkyl Complexes



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invaluable spectroscopic handle for monitoring the reactivity of these complexes.

Conventional methods for the introduction of tris(pyrazolyl)hydroborato ligands generally involve metathesis of metal–halide bonds with either the potassium or thallium derivatives, M{HB(3,5-R_2pz)$_3$} (3,5-R_2pz = 3,5-$C_3N_2R_2H$; M = K, Tl).[15] This suggested that a general approach for the synthesis of a series of alkyl derivatives of the category {η^3-HB(3,5-R_2pz)$_3$}MgR would involve the reaction of M{HB(3,5-R_2pz)$_3$} with Grignard reagents, RMgX (eq 2). However, preliminary studies readily in-

$$RMgX + M\{HB(3,5\text{-}R_2pz)_3\} \longrightarrow \{\eta^3\text{-}HB(3,5\text{-}R_2pz)_3\}MgR + MX \quad (2)$$

dicated that the reactions between M{HB(3,5-R_2pz)$_3$} and RMgX were more complex than originally considered, as the result of the competition between alkyl and halide bond metathesis of RMgX (eq 3). In view of this observed

$$RMgX + M\{HB(3,5\text{-}R_2pz)_3\} \begin{cases} \xrightarrow{-MX} \{\eta^3\text{-}HB(3,5\text{-}R_2pz)_3\}MgR \\ \xrightarrow{-[MR]} \{\eta^3\text{-}HB(3,5\text{-}R_2pz)_3\}MgX \end{cases} \quad (3)$$

reactivity of the magnesium–*alkyl* bonds of RMgX toward M{HB(3,5-R_2pz)$_3$}, we considered that an alternative synthesis for the complexes {η^3-HB(3,5-R_2pz)$_3$}MgR would involve metathesis of the magnesium–alkyl bonds of R_2Mg with M{HB(3,5-R_2pz)$_3$} (M = K, Tl), as shown by eq 4.

$$R_2Mg + M\{HB(3,5\text{-}R_2pz)_3\} \xrightarrow{-[MR]} \{\eta^3\text{-}HB(3,5\text{-}R_2pz)_3\}MgR \quad (4)$$

Here we describe (i) the synthesis and structures of the magnesium alkyl derivatives {η^3-HB(3,5-R_2pz)$_3$}MgR by the reactions of M{HB(3,5-R_2pz)$_3$} with R_2Mg, and (ii) the competition between Mg–alkyl and Mg–halide bond metathesis in the reactions of M{HB(3-Bu^{t}pz)$_3$} with Grignard reagents.

Synthesis and Characterization of {η^3-HB(3,5-R_2pz)$_3$}MgR. The reactions between M{HB(3,5-R_2pz)$_3$} (M = K, Tl) and R_2Mg in a 1:1 molar ratio give good yields of the tris(pyrazolyl)hydroborato magnesium alkyl derivatives {η^3-HB(3,5-R_2pz)$_3$}MgR as white crystalline solids (eq 4). Thus, a series of primary, secondary, tertiary, vinyl, and phenyl derivatives have been obtained, as illustrated in Scheme I. The reactions of the thallium reagents with R_2Mg are also accompanied by the deposition of Tl metal, consistent with the decomposition of [TlR].[21] Although the irreversible decomposition of [TlR] provides an effective driving force for the synthesis of {η^3-HB(3,5-R_2pz)$_3$}MgR, the reactions of the potassium derivatives are also effective. In fact, for the complexes {η^3-HB(3,5-Me_2pz)$_3$}MgR (3,5-Me_2pz = 3,5-$C_3N_2Me_2H$), the potassium derivative K{HB(3,5-Me_2pz)$_3$} is found to be the reagent of choice because the stronger driving force for the thallium reagent may result in disubstitution and the formation of the 6-coordinate magnesium derivative {η^3-HB(3,5-Me_2pz)$_3$}$_2$Mg. Disubstitution is not possible for the more sterically demanding *tert*-butyl-substituted derivatives, for which the complexes {η^3-HB(3-Bu^{t}pz)$_3$}MgR (3-Bu^{t}pz = 3-C_3N_2Bu^{t}H$_2$) may be isolated cleanly by using the thallium reagent. The introduction of tris(pyrazolyl)hydroborato ligands by metathesis of metal–alkyl bonds rather than metal–halide bonds offers an alternative synthetic procedure that may be generally applicable to other systems, and we have already shown that it is suitable for Zn and Al complexes.[22]

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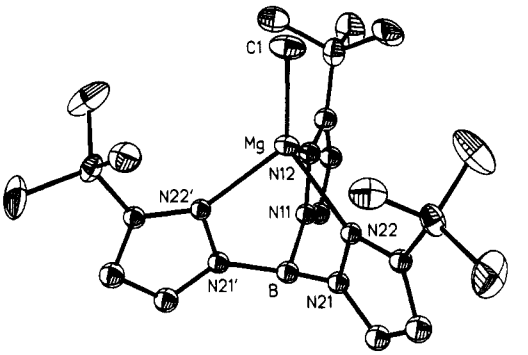

Figure 3. ORTEP drawing of {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_3$.

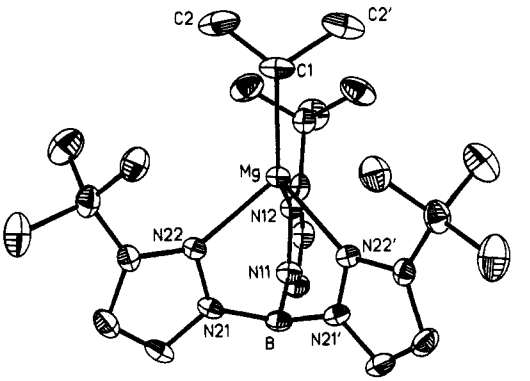

Figure 4. ORTEP drawing of {η^3-HB(3-Bu^{t}pz)$_3$}MgCH(CH$_3$)$_2$.

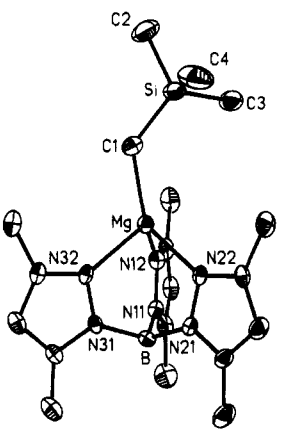

Figure 5. ORTEP drawing of {η^3-HB(3,5-Me_2pz)$_3$}MgCH$_2$Si(CH$_3$)$_3$.

Table I. Selected Bond Lengths (Å) and Angles (deg) for {η^3-HB(3-Bu^{t}pz)$_3$}MgCH$_3$

Bond Lengths			
Mg–N(12)	2.130 (10)	Mg–N(22)	2.137 (7)
Mg–C(1)	2.118 (11)	Mg–N(22′)	2.137 (7)
N(11)–N(12)	1.375 (13)	N(21)–N(22)	1.390 (8)
N(11)–B	1.524 (16)	N(21)–B	1.532 (11)
B–N(21′)	1.532 (11)		
Bond Angles			
N(12)–Mg–N(22)	91.3 (3)	N(12)–Mg–C(1)	122.7 (4)
N(22)–Mg–C(1)	125.4 (2)	N(12)–Mg–N(22′)	91.3 (3)
N(22)–Mg–N(22′)	90.6 (4)	C(1)–Mg–N(22′)	125.4 (2)
N(12)–N(11)–B	122.7 (9)	N(22)–N(21)–B	122.9 (7)
C(11)–N(11)–B	127.9 (9)	Mg–N(12)–N(11)	111.7 (7)
Mg–N(12)–C(13)	142.7 (8)	C(21)–N(21)–B	128.5 (8)
Mg–N(22)–N(21)	110.9 (5)	Mg–N(22)–C(23)	142.3 (5)
N(11)–B–N(21)	109.7 (7)	N(11)–B–N(21′)	109.7 (7)
N(21)–B–N(21′)	108.8 (10)		

Table II. Selected Bond Lengths (Å) and Angles (deg) for {η³-HB(3-Bu^{t}pz)$_3$}MgCH(CH$_3$)$_2$

Bond Lengths			
Mg–C(1)	2.182 (8)	Mg–N(12)	2.157 (6)
Mg–N(22)	2.170 (4)	Mg–N(22′)	2.170 (4)
C(1)–C(2)	1.515 (9)	C(1)–C(2′)	1.515 (9)
N(11)–N(12)	1.377 (8)	N(21)–N(22)	1.375 (5)
N(11)–B	1.541 (11)	N(21)–B	1.537 (6)
B–N(21′)	1.537 (6)		
Bond Angles			
C(1)–Mg–N(12)	124.8 (3)	C(1)–Mg–N(22)	124.0 (2)
N(12)–Mg–N(22)	93.1 (2)	C(1)–Mg–N(22′)	124.0 (2)
N(12)–Mg–N(22′)	93.1 (2)	N(22)–Mg–N(22′)	87.8 (2)
Mg–C(1)–C(2)	119.1 (4)	Mg–C(1)–C(2′)	119.2 (4)
C(2)–C(1)–C(2′)	106.6 (7)	N(12)–N(11)–B	122.5 (6)
N(22)–N(21)–B	122.8 (4)	Mg–N(12)–N(11)	110.5 (4)
Mg–N(22)–N(21)	110.0 (3)	Mg–N(12)–C(13)	144.1 (5)
N(11)–B–N(21)	109.8 (4)	Mg–N(22)–C(23)	144.7 (3)
N(21)–B–N(21′)	110.8 (6)	N(11)–B–N(21′)	109.8 (4)

Table III. Selected Bond Lengths (Å) and Angles (deg) for {η³-HB(3,5-Me$_2$pz)$_3$}MgCH$_2$Si(CH$_3$)$_3$

Bond Lengths			
Mg–N(12)	2.012 (6)	Mg–N(22)	2.119 (6)
Mg–N(32)	2.097 (5)	Mg–C(1)	2.096 (9)
N(11)–N(12)	1.370 (10)	N(11)–B	1.548 (10)
N(21)–N(22)	1.380 (9)	N(21)–B	1.547 (8)
N(31)–N(32)	1.367 (9)	N(31)–B	1.544 (9)
C(1)–Si	1.815 (8)	C(2)–Si	1.851 (12)
C(3)–Si	1.845 (8)	C(4)–Si	1.885 (9)
Bond Angles			
N(12)–Mg–N(22)	88.1 (2)	N(12)–Mg–N(32)	91.7 (2)
N(22)–Mg–N(32)	90.1 (2)	N(12)–Mg–C(1)	124.1 (3)
N(22)–Mg–C(1)	133.5 (2)	N(32)–Mg–C(1)	118.1 (3)
N(12)–N(11)–B	120.5 (6)	Mg–N(12)–N(11)	114.4 (4)
Mg–N(12)–C(11)	138.8 (6)	N(22)–N(21)–B	120.6 (6)
C(23)–N(21)–B	130.3 (7)	Mg–N(22)–N(21)	113.5 (3)
Mg–N(22)–C(21)	140.4 (6)	N(32)–N(31)–C(33)	110.3 (5)
N(32)–N(31)–B	120.2 (5)	Mg–N(32)–N(31)	114.8 (3)
Mg–N(32)–C(31)	138.9 (6)	Mg–C(1)–Si	133.1 (4)
C(1)–Si–C(2)	114.8 (4)	C(1)–Si–C(4)	109.5 (4)
C(1)–Si–C(3)	112.3 (4)	C(3)–Si–C(4)	107.1 (4)
C(2)–Si–C(3)	107.1 (4)	N(11)–B–N(21)	109.1 (5)
C(2)–Si–C(4)	105.6 (5)	N(21)–B–N(31)	108.6 (5)
N(11)–B–N(31)	110.7 (6)		

The molecular structures of the primary and secondary alkyl derivatives {η³-HB(3-Bu^{t}pz)$_3$}MgCH$_3$, {η³-HB(3-Bu^{t}pz)$_3$}MgCH(CH$_3$)$_2$, and {η³-HB(3,5-Me$_2$pz)$_3$}MgCH$_2$Si(CH$_3$)$_3$ have been determined by single-crystal X-ray diffraction (Figures 3–5). Selected bond lengths and angles are presented in Tables I–III. In each case the molecules are monomeric and the tris(pyrazolyl)hydroborato ligand is η³-coordinated. The tris(3-*tert*-butylpyrazolyl)hydroborato derivatives {η³-HB(3-Bu^{t}pz)$_3$}MgCH$_3$ and {η³-HB(3-Bu^{t}pz)$_3$}MgCH(CH$_3$)$_2$ possess trigonally distorted tetrahedral magnesium centers, as evidenced by comparison of the N–Mg–C and N–Mg–N bond angles, which are approximately 125 and 90°, respectively. Specifically, for {η³-HB(3-Bu^{t}pz)$_3$}MgCH$_3$ the bond angles are N–Mg–C (122.7–125.4°) and N–Mg–N (90.6–91.3°) and for {η³-HB(3-Bu^{t}pz)$_3$}MgCH(CH$_3$)$_2$ the bond angles are N–Mg–C (124.0–124.8°) and N–Mg–N (87.8–93.1°). Although the coordination environments around Mg are similar for the two derivatives, the isopropyl group is distorted as a consequence of steric interactions with the *tert*-butyl groups of the ligand, such that the Mg–C–C angle is expanded to almost 120°. In contrast to the regular coordination about Mg in these tris(3-*tert*-butylpyrazolyl)-hydroborato derivatives, the magnesium center of the tris(3,5-dimethylpyrazolyl)hydroborato derivative {η³-HB(3,5-Me$_2$pz)$_3$}MgCH$_2$Si(CH$_3$)$_3$ is noticeably distorted such that, although N–Mg–N bond angles are similar and close to 90° (88.1–91.7°), the C–Mg–N bond angles vary substantially (118.1–133.5°), as illustrated in Figure 5.

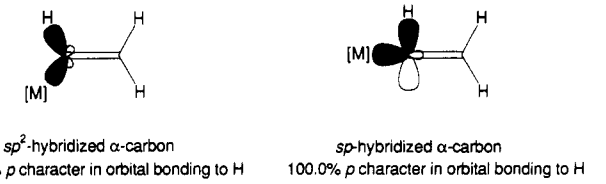

Figure 6. Two extremes for the bonding of metal vinyl derivatives.

The X-ray structures demonstrate that the alkyl derivatives {η³-HB(3,5-R$_2$pz)$_3$}MgR may be readily crystallized free of coordinated solvent. In addition, these complexes are also soluble in noncoordinating hydrocarbon solvents, e.g. benzene, giving well-resolved ^{1}H and ^{13}C NMR spectra. Spectroscopic data for the complexes are provided in the Experimental Section and show that, for example, the methyl derivatives {η³-HB(3-Bu^{t}pz)$_3$}MgCH$_3$ and {η³-HB(3,5-Me$_2$pz)$_3$}MgCH$_3$ are characterized by ^{1}H NMR resonances at δ −0.05 and −0.25 ppm, respectively, that are attributed to the Mg–CH$_3$ groups. Interestingly, particularly low $^1J_{C-H}$ coupling constants are observed for the α-carbon of the vinyl derivatives {η³-HB(3-Bu^{t}pz)$_3$}MgCH=CH$_2$ ($^1J_{C-H}$ = 106 Hz) and {η³-HB(3,5-Me$_2$pz)$_3$}MgCH=CH$_2$ ($^1J_{C-H}$ = 109 Hz) compared with the value of 156 Hz in C$_2$H$_4$. These low $^1J_{C-H}$ coupling constants are not unprecedented for electropositive metal vinyl derivatives and compare well with the values observed for both CH$_2$=CHMgBr ($^1J_{C-H}$ = 104 Hz) and (CH$_2$=CH)$_2$Mg ($^1J_{C-H}$ = 116 Hz).[23] For these systems the low $^1J_{C-H}$ coupling constants presumably reflect changes in hybridization at the α-carbon atom from sp², such that the orbital bonding to Mg is enhanced with s character, accompanied by a concomitant decrease for the orbital bonding to hydrogen. In the extreme, this situation would be represented by sp hybridization at the α-carbon atom, with the H atom bonding to carbon via a p orbital and the magnesium bonding to carbon via an sp hybrid orbital. Such a change in hybridization upon substitution by a highly electropositive substituent would be expected as a consequence of the ability of sp-hybridized carbon to stabilize negative charge effectively (cf. the acidity of terminal acetylenes).[24] Two extremes for bonding representations of metal vinyl derivatives are indicated in Figure 6. A coupling constant of ca. 110 Hz corresponds to ca. 80% p character for the orbital on carbon bonding to hydrogen, midway between the sp² (66.7% p character) and sp (100% p character) hybridized extremes.[25] Conversely, the $^1J_{C-H}$ coupling constant for the α-carbon is known to increase with increasing electronegativity.[26] For example, the $^1J_{C-H}$ coupling constant for the α-carbon for CHF=CH$_2$ is 200 Hz, midway to the $^1J_{C-H}$ coupling constant for HC≡CH

(22) (a) Gorrell, I. B.; Looney, A.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1990**, 220–222. (b) Looney, A.; Parkin, G. *Polyhedron* **1990**, *9*, 265–276.

(23) ^{13}C NMR data for CH$_2$=CHMgBr(THF)$_x$ and (CH$_2$=CH)$_2$MgBr(THF)$_x$ in C$_6$D$_6$: CH$_2$=CHMgBr(THF)$_x$, δ 137.3 ($^1J_{C-H}$ = 144 Hz, β-C), 165.9 ($^1J_{C-H}$ = 104 Hz, α-C); (CH$_2$=CH)$_2$MgBr(THF)$_x$, δ 149.0 ($^1J_{C-H}$ = 144 Hz, β-C), 162.3 ($^1J_{C-H}$ = 116 Hz, α-C).

(24) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*; Allyn and Bacon, Inc.: Boston, MA, 1987.

(25) $^1J_{C-H}$ coupling constants for hydrocarbons correlate with the hybridization (sp^n) of the orbital on carbon that bonds to hydrogen according to the relationship $^1J_{C-H}$ = 500(1/1 + *n*). (a) MacKay, C.; Rosenberg, H. E.; Wolfgang, R. *J. Am. Chem. Soc.* **1962**, *84*, 307–309. (b) Muller, N.; Pritchard, N. *J. Chem. Phys.* **1959**, *31*, 1471–1476.

(26) Abraham, R. J.; Loftus, P. *Proton and Carbon-13 NMR Spectroscopy. An Integrated Approach*; Heyden: London, 1979.

Table IV. Variable-Temperature Behavior of Selected $(RCH_2CH_2)_2Mg$ and $(RCH_2CH_2)MgCl$ Derivatives

R_2Mg	T_t,[a] °C
$CH_3CH_2CH_2CH_2MgCl$[b]	32
$[CH_3CH_2CH_2CH_2]_2Mg$[b]	96
$(CH_3)_2CHCH_2CH_2MgCl$[b]	24
$[(CH_3)_2CHCH_2CH_2]_2Mg$[b]	104
$(CH_3)_3CCH_2CH_2MgCl$[c]	32
$[(CH_3)_3CCH_2CH_2]_2Mg$[c]	110

[a] T_t = temperature at which triplet resonance is observed for α-CH_2 group at 60 MHz. [b] Whitesides, G. M.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 4878–4888. [c] Whitesides, G. M.; Witanowski, M.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 2854–2862.

(248 Hz). Thus, we note that the observation of a particularly low $^1J_{C-H}$ coupling constant for the α-carbon atoms of metal–vinyl systems is not necessarily, per se, an indication of an agostic[27] ground-state structure.[28]

In addition to resonances attributable to the magnesium alkyl groups, each of the complexes $\{\eta^3$-$HB(3,5\text{-}R_2pz)_3\}MgR$ show well-defined resonances for the tris(pyrazolyl)hydroborato ligand that provide a valuable spectroscopic handle for monitoring reactivity. In particular, the complexes $\{\eta^3$-$HB(3\text{-}Bu^tpz)_3\}MgR$ show a single resonance in the range δ 1.34–1.44 for the *tert*-butyl substituents of the η^3-$HB(3\text{-}Bu^tpz)_3$ ligand, consistent with η^3-coordination. In view of the steric interactions that may exist between the $Mg\text{-}C(CH_3)_3$ ligand and the *tert*-butyl substituents of the sterically demanding tris(*tert*-butylpyrazolyl)hydroborato ligand, as evidenced by the distortion of the related isopropyl derivative, $\{\eta^3$-$HB(3\text{-}Bu^tpz)_3\}MgCH(CH_3)_2$, an alternative η^2-coordination mode of the tris(pyrazolyl)hydroborato ligand of $\{HB(3\text{-}Bu^tpz)_3\}MgC(CH_3)_3$ may have been expected. However, variable-temperature ^1H NMR studies were invariant down to −90 °C, so that, in the absence of a crystal structure determination, it is not possible to distinguish between the possibilities $\{\eta^3$-$HB(3\text{-}Bu^tpz)_3\}MgC(CH_3)_3$ or highly fluxional $\{\eta^2$-$HB(3\text{-}Bu^tpz)_3\}MgC(CH_3)_3$.

Previous spectroscopic studies of magnesium alkyl derivatives of the types $(RR'CHCH_2)_2Mg$ and $RR'CHCH_2MgX$ have shown that the form of the resonances due to the α-H substituents are temperature dependent.[29] Thus, the derivatives $(RCH_2CH_2)_2Mg$ and RCH_2CH_2MgX show a complex AA′XX′ pattern at low temperatures for the α-H atoms and a simple triplet A_2X_2 pattern at elevated temperatures. These spectroscopic changes have been proposed to occur as a result of rapid inversion of configuration at the α-carbon atom. For comparison, the temperatures at which the high-temperature A_2X_2 spectrum is obtained for selected primary alkyl derivatives are given in Table IV. The data illustrate that inversion of configuration of the α-carbon is more facile

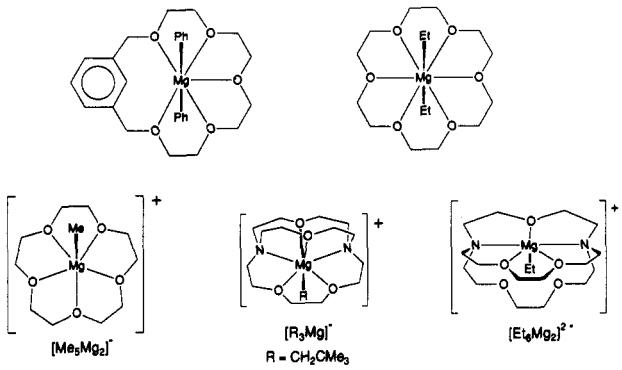

Figure 7. Products derived from the reactions of R_2Mg with crown ethers and cryptands.

for Grignard reagents than for dialkyls and that at room temperature the dialkyl derivatives are configurationally stable on the NMR time scale. Similarly, the tris(pyrazolyl)hydroborato derivative $\{\eta^3$-$HB(3\text{-}Bu^tpz)_3\}MgCH_2(CH_2)_2CH_3$ is also configurationally stable at room temperature and the ^1H NMR resonance of the α-CH_2 group exhibits the AA′ part of an AA′XX′ spectrum. However, variable-temperature ^1H NMR studies show that the form of this resonance does not change significantly between room temperature and 100 °C, indicating a high degree of configurational stability for the complexes $\{\eta^3$-$HB(3\text{-}Bu^tpz)_3\}MgR$.[30]

A second process that has also been detected by using ^1H NMR spectroscopy is alkyl exchange, which is significantly faster than inversion and, thus, occurs primarily with retention of configuration.[29] Our studies have also indicated that the (tris(pyrazolyl)hydroborato)magnesium alkyl derivatives are more stable to ligand-exchange processes than both dialkylmagnesium and Grignard reagents. For example, a mixture of the alkyl derivatives $\{\eta^3$-$HB(3\text{-}Bu^tpz)_3\}MgCH_3$ and $\{\eta^3$-$HB(3,5\text{-}Me_2pz)_3\}MgC(CH_3)_3$ does not result in the formation of crossover products after heating at 80 °C for 3 days (eq 5). Similarly, a mixture

$$\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgCH_3 + \{\eta^3\text{-}HB(3,5\text{-}Me_2pz)_3\}MgC(CH_3)_3 \xrightarrow{\times} \{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgC(CH_3)_3 + \{\eta^3\text{-}HB(3,5\text{-}Me_2pz)_3\}MgCH_3 \quad (5)$$

of the alkyl derivatives $\{\eta^3$-$HB(3\text{-}Bu^tpz)_3\}MgC(CH_3)_3$ and $\{\eta^3$-$HB(3,5\text{-}Me_2pz)_3\}MgCH_2CH_3$ gives no crossover products after 4 days at room temperature.

The above studies have therefore shown that a general series of monomeric magnesium monoalkyl derivatives may be obtained by using tris(pyrazolyl)hydroborato coligands. In this regard, a variety of other uni- and multidentate nitrogen, oxygen, and sulfur ligands, including crown ethers, cryptands, and porphyrins, have also been coordinated to magnesium alkyl derivatives. However, the results of such coordination are invariably the formation of complex species that are either multinuclear or ionic derivatives in which the metal–alkyl moiety is incorporated into both the cation and anion. Thus, replacement of the halogen of RMgX by a unidentate ligand such as OR or NR_2 does not stabilize monomeric derivatives. For example, alkoxide [RMgOR′] and amido $[RMgNR'_2]$ derivatives are also oligomeric,[31] and even the *tert*-butoxide derivatives

(27) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1–124.

(28) Low $^1J_{C-H}$ coupling constants for α-carbon atoms of metal vinyl derivatives have been observed for both main-group and transition-metal systems. See for example: (a) van Dongen, J. P. C. M.; van Dijkman, H. W. D.; de Bie, M. J. A. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 29–32. (b) McDade, C.; Bercaw, J. E. *J. Organomet. Chem.* **1980**, *279*, 281–315. (c) Hyla-Kryspin, I.; Gleiter, R.; Kruger, C.; Zwettler, R.; Erker, G. *Organometallics* **1990**, *9*, 517–523.

(29) (a) Whitesides, G. M.; Roberts, J. *J. Am. Chem. Soc.* **1965**, *87*, 4878–4888. (b) Whitesides, G. M.; Witanowski, M.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 2854–2862. (c) Fraenkel, G.; Dix, D. T. *J. Am. Chem. Soc.* **1966**, *88*, 979–985. (d) House, H. O.; Latham, R. A.; Whitesides, G. M. *J. Org. Chem.* **1967**, *32*, 2481–2496. (e) Fraenkel, G.; Cottrell, C. E.; Dix, D. T. *J. Am. Chem. Soc.* **1971**, *93*, 1704–1708. (f) Allen, P. E. M.; Hagias, S.; Lincoln, S. F.; Mair, C.; Williams, E. H. *Ber. Bunsin-Ges. Phys. Chem.* **1982**, *86*, 515–519. (g) Allen, P. E. M.; Hagias, S.; Lincoln, S. F.; Mair, C.; Williams, E. H. *Ber. Bunsin-Ges. Phys. Chem.* **1984**, *88*, 623–626.

(30) Our investigations were carried out at a higher field (400 MHz) than the previous studies (60 MHz) and so a more detailed comparison of the data is not possible.

(31) (a) Bryce-Smith, D.; Wakefield, B. J. *Proc. Chem. Soc.* **1963**, 376. (b) Bryce-Smith, D.; Wakefield, B. J. *J. Chem. Soc.* **1964**, 2483–2485. (c) House, H. O.; Latham, R. A.; Whitesides, G. M. *J. Org. Chem.* **1967**, *32*, 2481–2496. (d) House, H. O.; Traficante, D. D. *J. Org. Chem.* **1963**, *28*, 355–360. (e) House, H. O.; Respess, W. L. *J. Org. Chem.* **1965**, *30*, 301–303. (f) Bryce-Smith, D.; Graham, I. F. *Chem. Commun.* **1966**, 559–560.

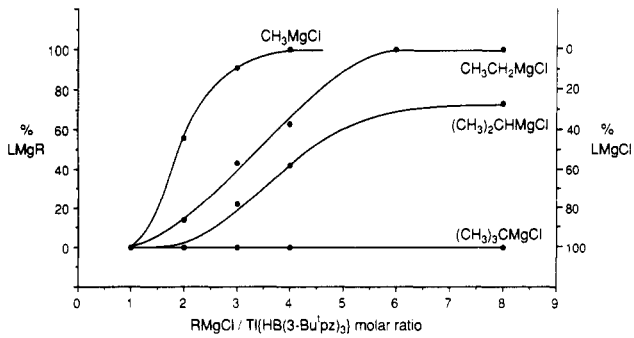

Figure 8. Product distribution of the reactions of RMgCl (R = CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$) with Tl{η³-HB(3-Bu^{t}pz)$_3$} as a function of reactant molar ratio (L = η³-HB(3-Bu^{t}pz)$_3$).

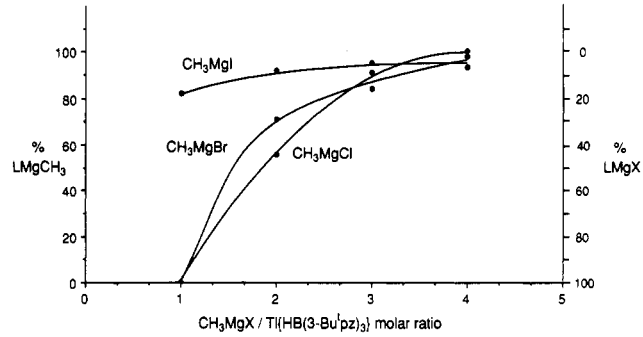

Figure 9. Product distribution of the reactions of CH_3MgX (X = Cl, Br, I) with Tl{η³-HB(3-Bu^{t}pz)$_3$} as a function of reactant molar ratio (L = η³-HB(3-Bu^{t}pz)$_3$).

[RMgOBu^t]$_4$ (R = Me, Et) are tetrameric.[32] Coordination of bidentate chelating agents may stabilize monomeric dialkyl derivatives, and thus, tetramethylethylenediamine gives $R_2Mg(\eta^2\text{-}Me_2NCH_2CH_2NMe_2)$, e.g. R = CH_3, Bu^t, CH_2Bu^t, CH_2SiMe_3, and CH_2CMe_2Ph.[33] Although monomeric monoalkyl complexes derived from the related trimethylethylenediamine ligand have been obtained for sterically demanding alkyl groups, e.g. $(CH_3)_3CMg(\eta^2\text{-}MeNCH_2CH_2NMe_2)$,[34] smaller alkyl substituents on magnesium result in the formation of dimeric complexes, e.g. $[CH_3Mg(\eta^2\text{-}MeNCH_2CH_2NMe_2)]_2$.[33a] Notably, monomeric dialkyl derivatives have been obtained by coordination of a suitable crown ether to R_2Mg, e.g. (18-crown-6)Mg$(CH_2CH_3)_2$[35] and (1,3-xylyl-18-crown-5)Mg$(C_6H_5)_2$.[36] However, systems comprising R_2Mg and either crown ethers or cryptands are complicated by the formation of complex magnesiate anions, $(R_3Mg)_n^{n-}$ (n = 1, 2) or $(R_5Mg_2)^-$, and complexed magnesium alkyl cations, $[L_nMgR]^+$, in addition to the neutral complexed magnesium dialkyl.[35-38] Indeed, solutions comprising these magnesiate anions are considerably more reactive than the parent dialkylmagnesium. Some of the products of the reactions of R_2Mg with crown ethers and cryptands that have been structurally characterized are illustrated in Figure 7. Thus, although monomeric magnesium alkyl derivatives may be obtained by a *selected* combination of alkyl group and coligand, the formation of well-defined monomeric, neutral, magnesium alkyl complexes using tris(pyrazolyl)hydroborato coligands appears to be entirely general.

Reactions of M{HB(3-Bu^{t}pz)$_3$} (M = K, Tl) with Grignard Reagents: Competitive Alkyl and Halide Bond Metathesis. The reactions between M{HB(3-Bu^{t}pz)$_3$} (M = K, Tl) and Grignard reagents are more complex than with R_2Mg as a result of competition between metathesis of the Mg–R and Mg–X bonds. The products obtained depend upon the choice of Grignard reagent and reactant ratio.

Chloro and bromo Grignard reagents RMgX [RMgX = CH_3MgCl, CH_3MgBr, CH_3CH_2MgCl, $(CH_3)_2CHMgCl$, $(CH_3)_3CMgCl$] react with Tl{η³-HB(3-Bu^{t}pz)$_3$} in a 1:1 molar ratio in Et_2O to give {η³-HB(3-Bu^{t}pz)$_3$}MgX by metathesis of the Mg–R bond, in preference to that of the Mg–X bond (eq 6). In contrast, the analogous reaction

$$\text{RMgX} + \text{Tl}\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\} \xrightarrow[-[\text{TlR}]]{\text{Et}_2\text{O}} \{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgX} \quad (6)$$

with CH_3MgI results in preferential metathesis of the Mg–I bond to give the methyl complex {η³-HB(3-Bu^{t}pz)$_3$}$MgCH_3$ as the major product (eq 7). Furthermore, increasing the

$$\text{CH}_3\text{MgI} + \text{Tl}\{\text{HB(3-Bu}^t\text{pz)}_3\} \xrightarrow[-\text{TlI}]{(80\%)} \{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgCH}_3 \quad (7)$$
$$\xrightarrow[-[\text{TlCH}_3]]{(20\%)} \{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgI}$$

molar ratio of the reactants RMgX and Tl{HB(3-Bu^{t}pz)$_3$} from unity also results in the formation of the alkyl derivative {η³-HB(3-Bu^{t}pz)$_3$}MgR (Figures 8 and 9). The formation of {η³-HB(3-Bu^{t}pz)$_3$}MgR is clearly hindered for the more sterically demanding alkyl substituents (Figure 8). For example, the proportion of {η³-HB(3-Bu^{t}pz)$_3$}MgR in the product mixture of the reaction of a 4:1 molar ratio of RMgCl and Tl{η³-HB(3-Bu^{t}pz)$_3$} in Et_2O decreases from 100% for R = CH_3, to ca. 60% for R = CH_2CH_3, to ca. 40% for R = $CH(CH_3)_2$, and to 0% for R = $C(CH_3)_3$. Figure 9 illustrates the effect of the halide ligand on the product distribution for CH_3MgX (X = Cl, Br, I). These results suggest that the products obtained in the reactions with greater than 1:1 reactant molar ratios are a result of an equilibrium between the initially formed halide derivative {η³-HB(3-Bu^{t}pz)$_3$}MgX and RMgX (eq 8). For the

$$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgX} + \text{RMgX} \rightleftharpoons \{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgR} + \text{MgX}_2 \quad (8)$$

reaction with CH_3MgCl, this reversibility has been verified by the observation that {η³-HB(3-Bu^{t}pz)$_3$}$MgCH_3$ reacts with excess $MgCl_2$ to give {η³-HB(3-Bu^{t}pz)$_3$}MgCl (eq 9).

$$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgCH}_3 + \text{MgCl}_2 \longrightarrow \{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgCl} + \text{CH}_3\text{MgCl} \quad (9)$$

Although the alkyl derivatives {η³-HB(3-Bu^{t}pz)$_3$}MgR [R = CH_3, CH_2CH_3, $CH(CH_3)_2$] are formed by the reaction of Tl{η³-HB(3-Bu^{t}pz)$_3$} with excess Grignard reagent, this method is not useful for their preparation. Furthermore, even in the presence of a large excess of Grignard reagent, the reaction between Tl{η³-HB(3-Bu^{t}pz)$_3$} and the tertiary Grignard reagent, $(CH_3)_3CMgCl$, gave specifically {η³-HB-

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$(3\text{-}Bu^tpz)_3\}MgCl$ to the total exclusion of $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgC(CH_3)_3$. Hence, R_2Mg compounds are the most useful reagents for the synthesis of the complexes $\{\eta^3\text{-}HB(3,5\text{-}R_2pz)_3\}MgR$.

We now consider in more detail the initial reaction between $Tl\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}$ and RMgX to give either $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgR$ or $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgX$. The results clearly indicate that the order of observed metathesis is Mg–I > Mg–CH_3 > Mg–X (X = Cl, Br). However, we need to consider the origin of this sequence and in particular address the question whether this sequence corresponds to a kinetic or thermodynamic preference. In order to assess whethr the observed metathesis order is determined by kinetic or thermodynamic factors, it is necessary to examine the pathways that may lead to the formation of both $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgR$ and $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgX$. Alkyl and halide ligands in solutions of Grignard reagents are kinetically labile, as evidenced by the Schlenk equilibrium (eq 1), and the position and rate of reestablishment of this equilibrium, for which relatively little quantitative information is available,[1] may be expected to have a critical effect on the product distribution. As a result of this complexity, there is a manifold of reaction pathways that may independently lead to the products $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgX$ and $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgR$, of which the competitive metathesis of the Mg–R and Mg–X bonds of RMgX is the most direct, and simplest, pathway. If we restrict our discussion to the reactive species in solution as consisting of only RMgX, R_2Mg, and MgX_2, then the product $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgX$ may arise via reaction with either RMgX (eqs 10) or MgX_2 (eqs 11). The independent

$$RMgX + Tl\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\} \longrightarrow \{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgX + [TlR] \quad (10a)$$

$$[TlR] \longrightarrow Tl + \text{decomposition} \quad (10b)$$

$$RMgX + Tl\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\} \longrightarrow \{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgX + Tl + \text{dec.} \quad (10c)$$

$$MgX_2 + Tl\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\} \longrightarrow \{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgX + TlX \quad (11a)$$

$$TlX + RMgX \longrightarrow [TlR] + MgX_2 \quad (11b)$$

$$[TlR] \longrightarrow Tl + \text{decomposition} \quad (11c)$$

$$RMgX + Tl\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\} \longrightarrow \{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgX + Tl + \text{dec.} \quad (11d)$$

reaction of $Tl\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}$ with $MgCl_2$ is notably slower than the reactions with RMgCl, thus suggesting that the reaction between $Tl\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}$ and RMgX does not proceed via reaction with MgX_2 that is generated by the Schlenk equilibrium; i.e., eqs 11a–d do not operate.[39] This observation supports the view that the formation of $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgX$ is a result of direct metathesis between $Tl\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}$ and RMgX (eqs 10a–c). However, given that the formation of $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgX$ may proceed via the species RMgX, the observation of this product does not, per se, indicate that Mg–R bond metathesis is kinetically favored over Mg–X bond metathesis, since the Mg–R bond metathesis reaction may be rapidly reversible (eq 12) and the product $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgX$

$$RMgX + Tl\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\} \rightleftharpoons \{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgR + TlX \quad (12)$$

formed as a result of the driving force of the irreversible decomposition of unstable [TlR] (eq 13). Thus, if the

$$RMgX + Tl\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\} \longrightarrow \{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgX + Tl + \text{dec.} \quad (13)$$

above hypothesis was correct, then it would be necessary

(39) We can not exclude the possibility that the solvated form of $MgCl_2$ that is generated as a result of the Schlenk equilibrium may lead to higher concentrations of "$MgCl_2$" existing in solutions of Grignard reagents than in their absence.

Table V. Comparison of Alkyl and Halide Bond Metathesis in the Reactions of RMgX (1 Equiv) with $Tl\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}$ and $K\{HB(3\text{-}Bu^tpz)_3\}$

	% $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgR$	
RMgX	$Tl\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}$	$K\{HB(3\text{-}Bu^tpz)_3\}$
CH_3MgCl	≈0	90
CH_3CH_2MgCl	≈0	90
$(CH_3)_2CHMgCl$	≈0	75
$(CH_3)_3CMgCl$	≈0	35
CH_3MgCl	≈0	90
CH_3MgBr	≈0	95
CH_3MgI	80	85

for $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgR$ to react with TlCl to give $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgCl$ (eq 14). However, TlCl does not react

$$\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgR + TlCl \rightleftharpoons RMgCl + Tl\{HB(3\text{-}Bu^tpz)_3\} \longrightarrow \{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgCl + Tl + \text{dec.} \quad (14)$$

with $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgCH_3$ under similar conditions to give $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgCl$, which therefore suggests that the formation of $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgX$ in the reactions of $Tl\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}$ with RMgX are a result of kinetically favored Mg–R bond metathesis. Other evidence mitigating against preferential Mg–X (X = Cl, Br) bond metathesis and the formation of $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgR$ on the reaction pathway to $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgX$ is that $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgR$ also does not react with excess RMgX to give $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgX$ (eq 15). In contrast,

$$\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgR + RMgX \longrightarrow \{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgX + R_2Mg \quad (15)$$

the above studies have shown that $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgX$ reacts with excess RMgX to give $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgR$ (eq 16).[40]

$$\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgX + RMgX \longrightarrow \{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgR + MgX_2 \quad (16)$$

The preferential formation of $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgCH_3$ in the reaction of $Tl\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}$ with CH_3MgI may likewise be explained by kinetically favored Mg–I bond metathesis over Mg–CH_3 bond metathesis. Support for this statement is a consequence of the irreversible decomposition of $[TlCH_3]$ that would accompany the formation of $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgI$.[41] Thus, the observed products of the reactions of the Grignard reagents CH_3MgX with $Tl\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}$ are most consistently explained by the metathesis sequence Mg–I > Mg–CH_3 > Mg–X (X = Cl, Br) representing a kinetic preference.

The selectivity of the reactions with Grignard reagents is markedly dependent on the choice of tris(pyrazolyl)-hydroborato derivative. A comparison of the product distributions obtained from the reactions of the potassium and thallium derivatives $K\{HB(3\text{-}Bu^tpz)_3\}$ and $Tl\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}$ with Grignard reagents is presented in Table V. The results clearly indicate that use of the potassium derivative $K\{HB(3\text{-}Bu^tpz)_3\}$ results in significantly greater yields of the alkyl derivatives $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgR$. For example, whereas the reaction of $Tl\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}$ with CH_3MgCl (1 equiv) gives selectively $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgCl$, the corresponding reaction with $K\{HB(3\text{-}Bu^tpz)_3\}$ gives predominantly $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgCH_3$. The origin of this inversion of selectivity presumably reflects the

(40) Furthermore, although $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgR$ reacts with $MgCl_2$ to give $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgCl$, this reaction is sufficiently slow that it is unlikely that this process can be responsible for the formation of $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgCl$.

(41) The alternative possibility involving formation of $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgCH_3$, as a result of reaction with $(CH_3)_2Mg$ generated by the Schlenk equilibrium, could only be operative if unstable $[TlCH_3]$ was effectively trapped by CH_3MgI before it decomposed.

establishment of an equilibrium situation for the potassium derivatives, in contrast to the kinetic control that was proposed for the thallium derivatives as a result of the irreversible decomposition of [TlR]. Thus, it is likely that the product distribution is a consequence of the position of equilibrium for the ligand-exchange reaction shown in eq 17. Steric interactions between the magnesium–alkyl

$$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgR} + \text{KX} \rightleftharpoons \{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgX} + \text{KR} \quad (17)$$

group and substituents on the pyrazolyl rings would suggest that the above equilibrium would be shifted in favor of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgX}$ for the larger alkyl groups. In accord with this suggestion, the yield of alkyl product $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgR}$ from the reaction of $\text{K}\{\text{HB(3-Bu}^t\text{pz)}_3\}$ with RMgX decreases from 90% for CH_3MgCl to 35% for $(CH_3)_3CMgCl$.

Conclusions

The above studies have demonstrated that a series of monomeric 4-coordinate magnesium alkyl complexes $\{\eta^3\text{-HB(3,5-R}_2\text{pz)}_3\}\text{MgR}$ may be readily synthesized in good yield by metathesis of the magnesium–alkyl bonds of R_2Mg with either the potassium or thallium derivatives of tris(pyrazolyl)hydroborato ligands. The molecular structures of the derivatives $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgCH}_3$, $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgCH(CH}_3)_2$, and $\{\eta^3\text{-HB(3,5-Me}_2\text{pz)}_3\}\text{MgCH}_2\text{Si(CH}_3)_3$ have been determined by X-ray diffraction techniques, which confirm the monomeric nature and η^3-coordination mode of the tris(pyrazolyl)hydroborato ligand. In addition to providing a stable coordination environment for the investigation of monomeric magnesium alkyl derivatives, the alkyl substituents of the tris(pyrazolyl)hydroborato ligand provide a valuable spectroscopic handle for mechanistic and reactivity studies. Furthermore, the introduction of tris(pyrazolyl)hydroborato ligands by metathesis of metal–alkyl bonds, rather than the more conventional metathesis of metal–halide bonds, offers an alternative synthetic procedure that may be generally applicable, and we have already demonstrated that it is suitable for Zn and Al derivatives. In contrast to the clean reactions of $\text{M}\{\text{HB(3,5-R}_2\text{pz)}_3\}$ with R_2Mg, the corresponding reactions with Grignard reagents are more complex as a result of competition between Mg–R and Mg–X bond metathesis, and the product distribution is dependent upon both RMgX and the tris(pyrazolyl)hydroborato reagent. Thus, for the thallium complex $\text{Tl}\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$, chloro and bromo Grignard reagents favor alkyl metathesis and the formation of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_2\}\text{MgX}$, whereas the iodo Grignard reagent CH_3MgI favors halide metathesis and the formation of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgCH}_3$. However, the selectivity of these reactions with Grignard reagents may be dramatically altered by the use of the potassium reagent $\text{K}\{\text{HB(3-Bu}^t\text{pz)}_3\}$, and thus, primary and secondary Grignard reagents react with $\text{K}\{\text{HB(3-Bu}^t\text{pz)}_3\}$ to give the alkyl derivatives $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgR}$ as the principal products.

Experimental Section

General Considerations. All manipulations were performed by using a combination of glovebox, high-vacuum, or Schlenk techniques.[42] Solvents were purified and degassed by standard procedures. ^1H and ^{13}C NMR spectra were measured on Varian VXR 200, 300, and 400 spectrometers. IR spectra were recorded as Nujol mulls on a Perkin-Elmer 1420 spectrophotometer. All J values are in hertz. Mass spectra were obtained on a Nermag R10-10 mass spectrometer using chemical ionization techniques. Elemental analyses were measured with a Perkin-Elmer 2400 CHN elemental analyzer.

$\text{K}\{\text{HB(3,5-Me}_2\text{pz)}_3\}$,[43] $\text{K}\{\text{HB(3-Bu}^t\text{pz)}_3\}$,[20a] and $\text{Tl}\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$[20a] were prepared as described previously, and $\text{Tl}\{\eta^3\text{-HB(3,5-Me}_2\text{pz)}_3\}$ was prepared from $\text{K}\{\text{HB(3,5-Me}_2\text{pz)}_3\}$ by an analogous procedure. $(CH_3)_2Mg$ and $(CH_3CH_2)_2Mg$ were obtained from Alfa, and other dialkylmagnesium derivatives were prepared directly from the Grignard reagents (Aldrich) and standardized prior to use.

Synthesis of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgR}$ Derivatives. $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgCH}_3$. Method A. A solution of $(CH_3)_2Mg$ (11.4 mL of 0.6 M in Et_2O, 6.8 mmol) was added dropwise to $\text{Tl}\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$ (4.0 g, 6.8 mmol) in THF (120 mL), resulting in the immediate formation of a black deposit of Tl metal. The mixture was stirred for 10 min at room temperature and filtered. The filtrate was concentrated to ca. 30 mL and placed at 0 °C giving a crop of colorless crystals. The crystals of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgCH}_3$ were isolated by filtration and dried in vacuo (0.73 g). Further crops of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgCH}_3$ were obtained from the mother liquor by a similar procedure. Total yield of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgCH}_3$: 2.29 g (80%). Anal. Found for $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgCH}_3$: C, 62.5; H, 8.9; N, 19.9. Calcd: C, 62.8; H, 8.9; N, 20.0. IR data (Nujol mull, KBr plates, cm^{-1}): 2500 (ν_{B-H}). MS: m/e 421 ($M^+ + H$). ^1H NMR: δ 1.42 [27 H, s, η^3-HB{$C_3N_2H_2C(CH_3)_3$}$_3$], 5.81 [3 H, d, $^3J_{H-H}$ = 2.2, η^3-HB{$C_3N_2H_2C(CH_3)_3$}$_3$], 7.35 [3 H, d, $^3J_{H-H}$ = 2.2, η^3-HB{$C_3N_2H_2C(CH_3)_3$}$_3$], −0.05 [3 H, s, $MgCH_3$]. ^{13}C NMR: δ 31.0 [q, $^1J_{C-H}$ = 126; spt (partial res), $^3J_{C-H}$ = 5; η^3-HB{$C_3N_2H_2C(CH_3)_3$}$_3$], 32.0 [dct (partial res), $^2J_{C-H}$ = 5, η^3-HB{$C_3N_2H_2C(CH_3)_3$}$_3$], 102.1 [d, $^1J_{C-H}$ = 176; d, $^2J_{C-H}$ = 9; η^3-HB{$C_3N_2H_2C(CH_3)_3$}$_3$], 136.3 [d, $^1J_{C-H}$ = 185; d, $^2J_{C-H}$ = 6, η^3-HB{$C_3N_2H_2C(CH_3)_3$}$_3$], 165.7 [s, η^3-HB{$C_3N_2H_2C(CH_3)_3$}$_3$], −5.2 [q, $^1J_{C-H}$ = 109, $MgCH_3$].

Method B. A solution of $(CH_3)_2Mg$ (4 mL of 0.6 M in Et_2O, 2.4 mmol) was added dropwise to $\text{K}\{\text{HB(3-Bu}^t\text{pz)}_3\}$ (1.0 g, 2.40 mmol) in Et_2O (60 mL). The mixture was stirred for 30 min at room temperature and filtered. The filtrate was concentrated to ca. 20 mL and placed at 0 °C, giving a crop of colorless crystals. The crystals of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgCH}_3$ were isolated by filtration and dried in vacuo (0.70 g, 70%).

$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgCH}_2\text{CH}_3$. A solution of $(CH_3CH_2)_2Mg$ (2.3 mL of 1.5 M in Et_2O, 3.5 mmol) was added dropwise to $\text{Tl}\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$ (2.0 g, 3.4 mmol) in THF (70 mL), resulting in the immediate formation of a black deposit of Tl metal. The mixture was stirred for 10 min at room temperature and filtered. The filtrate was concentrated to ca. 20 mL and placed at 0 °C, giving a crop of colorless crystals. The crystals of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgCH}_2\text{CH}_3$ were isolated by filtration and dried in vacuo (0.74 g). A further crop of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgCH}_2\text{CH}_3$ was obtained from the mother liquor by a similar procedure. Total yield of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgCH}_2\text{CH}_3$: 0.87 g (59%). Anal. Found for $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgCH}_2\text{CH}_3$: C, 63.2; H, 9.4; N, 19.6. Calcd: C, 63.6; H, 9.0; N, 19.3. IR data (Nujol mull, KBr plates, cm^{-1}): 2490 (ν_{B-H}). ^1H NMR: δ 1.41 [27 H, s, η^3-HB{$C_3N_2H_2C(CH_3)_3$}$_3$], 5.81 [3 H, d, $^3J_{H-H}$ = 2.2, η^3-HB{$C_3N_2H_2C(CH_3)_3$}$_3$], 7.34 [3 H, d, $^3J_{H-H}$ = 2.2, η^3-HB{$C_3N_2H_2C(CH_3)_3$}$_3$], 0.65 [2 H, q, $^3J_{H-H}$ = 8.0, $MgCH_2CH_3$], 2.03 [3 H, t, $^3J_{H-H}$ = 8.0, $MgCH_2CH_3$]. ^{13}C NMR: δ 31.0 [q, $^1J_{C-H}$ = 126; spt (partial res), $^3J_{C-H}$ = 5; η^3-HB{$C_3N_2H_2C(CH_3)_3$}$_3$], 32.0 [dct (partial res), $^2J_{C-H}$ = 4, η^3-HB{$C_3N_2H_2C(CH_3)_3$}$_3$], 102.0 [d, $^1J_{C-H}$ = 176; d, $^2J_{C-H}$ = 9; η^3-HB{$C_3N_2H_2C(CH_3)_3$}$_3$], 136.3 [d, $^1J_{C-H}$ = 184; d, $^2J_{C-H}$ = 7, η^3-HB{$C_3N_2H_2C(CH_3)_3$}$_3$], 165.8 [s, η^3-HB{$C_3N_2H_2C(CH_3)_3$}$_3$], 5.7 [t, $^1J_{C-H}$ = 106; q, $^2J_{C-H}$ = 3; $MgCH_2CH_3$], 14.0 [q, $^1J_{C-H}$ = 122; t, $^2J_{C-H}$ = 5; $MgCH_2CH_3$].

$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgCH}_2(\text{CH}_2)_2\text{CH}_3$. A solution of $[CH_3(CH_2)_3]_2Mg$ (25 mL of 0.07 M in Et_2O/THF, 1.8 mmol) was added dropwise to $\text{Tl}\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$ (1.0 g, 1.7 mmol) in Et_2O (10 mL), resulting in the immediate formation of a black deposit of Tl metal. The mixture was stirred for 10 min at room temperature and filtered. The filtrate was concentrated to ca. 15 mL and placed

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at 0 °C, giving a crop of colorless crystals. The crystals of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_2$(CH$_2$)$_2$CH$_3$ were isolated by filtration and dried in vacuo (0.64 g, 81%). Anal. Found for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_2$(CH$_2$)$_2$CH$_3$: C, 64.8; H, 9.5; N, 18.3. Calcd: C, 64.9; H, 9.4; N, 18.2. IR data (Nujol mull, KBr plates, cm^{-1}): 2489 (ν_{B-H}). ^{1}H NMR: δ 1.40 [27 H, s, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 5.81 [3 H, d, $^3J_{H-H}$ = 2.2, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}$], 7.34 [3 H, d, $^3J_{H-H}$ = 2.2, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 0.60 [2 H, m, MgCH_2CH$_2$CH$_2$CH$_3$], 2.20 [2 H, m, MgCH$_2$CH_2CH$_2$CH$_3$], 1.94 [2 H, m, MgCH$_2$CH$_2$CH_2CH$_3$], 1.37 [3 H, t, $^3J_{H-H}$ = 7.2, MgCH$_2$CH$_2$CH$_2$CH_3]. ^{13}C NMR: δ 31.1 [q, $^1J_{C-H}$ = 126; spt (partial res), $^3J_{C-H}$ = 5; η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 32.0 [s, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 102.1 [d, $^1J_{C-H}$ = 176; d, $^2J_{C-H}$ = 9; η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 136.3 [d, $^1J_{C-H}$ = 185; d, $^2J_{C-H}$ = 7; η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 165.9 [s, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 15.0 [t, $^1J_{C-H}$ = 106, MgCH$_2$CH$_2$CH$_2$CH$_3$], 32.7 [t, $^1J_{C-H}$ = 122; t, $^2J_{C-H}$ = 4; MgCH$_2$(CH$_2$)$_2$CH$_3$], 33.0 [t, $^1J_{C-H}$ = 120; t, $^2J_{C-H}$ = 4; MgCH$_2$-(CH$_2$)$_2$CH$_3$], 14.5 [q, $^1J_{C-H}$ = 123; t, $^2J_{C-H}$ = 4; MgCH$_2$CH$_2$CH$_2$CH$_3$].

$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_2$Si(CH$_3$)$_3$. A solution of [(CH$_3$)$_3$-SiCH$_2$]$_2$Mg (29 mL of 0.06 M in Et$_2$O, 1.7 mmol) was added dropwise to Tl$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$ (1.0 g, 1.7 mmol) in Et$_2$O (10 mL), resulting in the immediate formation of a black deposit of Tl metal. The mixture was stirred for 10 min at room temperature and filtered. The filtrate was concentrated to ca. 15 mL and placed at 0 °C, giving a crop of colorless crystals. The crystals of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_2$Si(CH$_3$)$_3$ were isolated by filtration and dried in vacuo (0.51 g, 61%). Anal. Found for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$-MgCH$_2$Si(CH$_3$)$_3$: C, 60.1; H, 8.8; N, 17.1. Calcd: C, 60.9; H, 9.2; N, 17.1. IR data (Nujol mull, KBr plates, cm^{-1}): 2482 (ν_{B-H}). ^{1}H NMR: δ 1.40 [27 H, s, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 5.80 [3 H, d, $^3J_{H-H}$ = 2.2, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}$], 7.33 [3 H, d, $^3J_{H-H}$ = 2.2, η^3-HB-$\{C_3N_2H_2C(CH_3)_3\}_3$], -0.49 [2 H, s, MgCH_2Si(CH$_3$)], 0.54 [9 H, s, MgCH$_2$Si(CH_3)$_3$]. ^{13}C NMR: δ 31.6 [q, $^1J_{C-H}$ = 126; spt (partial res), $^3J_{C-H}$ = 5; η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 32.1 [dct (partial res), $^2J_{C-H}$ = 4, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 102.3 [d, $^1J_{C-H}$ = 176; d, $^2J_{C-H}$ = 9; η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 136.7 [d, $^1J_{C-H}$ = 185; d, $^2J_{C-H}$ = 6, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 166.1 [s, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], -0.3 [t, $^1J_{C-H}$ = 96, MgCH$_2$Si(CH$_3$)$_3$], 5.4 [q, $^1J_{C-H}$ = 117, MgCH$_2$Si(CH_3)$_3$].

$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH(CH$_3$)$_2$. A solution of [(CH$_3$)$_2$CH]$_2$Mg (10 mL of 0.09 M in Et$_2$O, 0.9 mmol) was added dropwise to Tl$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$ (0.5 g, 0.9 mmol) in Et$_2$O (50 mL), resulting in the immediate formation of a black deposit of Tl metal. The mixture was stirred for 10 min at room temperature and filtered. The filtrate was concentrated to ca. 15 mL and placed at 0 °C, giving a crop of colorless crystals. The crystals of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH(CH$_3$)$_2$ were isolated by filtration and dried in vacuo (0.15 g). Further crops of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH(CH$_3$)$_2$ were obtained from the mother liquor by a similar procedure. Total yield of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH(CH$_3$)$_2$: 0.25 g (66%). Anal. Found for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH(CH$_3$)$_2$: C, 63.5; H, 8.9; N, 19.0. Calcd: C, 64.2; H, 9.2; N, 18.7. IR data (Nujol mull, KBr plates, cm^{-1}): 2490 (ν_{B-H}). ^{1}H NMR: δ 1.39 [27 H, s, η^3-HB$\{C_3N_2H_2C$-$(CH_3)_3\}_3$], 5.82 [3 H, d, $^3J_{H-H}$ = 2.2, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}$], 7.35 [3 H, d, $^3J_{H-H}$ = 2.2, η^3-HB$\{\eta_3N_2H_2C(CH_3)_3\}_3$], 0.98 [1 H, spt, $^3J_{H-H}$ = 7.8, MgCH(CH$_3$)$_2$], 2.01 [6 H, d, $^3J_{H-H}$ = 7.8, MgCH(CH_3)$_2$]. ^{13}C NMR: δ 31.2 [q, $^1J_{C-H}$ = 126; spt (partial res), $^3J_{C-H}$ = 5; η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 32.1 [dct (partial res), $^2J_{C-H}$ = 6, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 102.2 [d, $^1J_{C-H}$ = 176; d, $^2J_{C-H}$ = 9; η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 136.7 [d, $^1J_{C-H}$ = 185; d, $^2J_{C-H}$ = 8, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 166.2 [s, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 12.2 [d, $^1J_{C-H}$ = 107, MgCH(CH$_3$)$_2$], 26.5 [q, $^1J_{C-H}$ = 123, MgCH(CH_3)$_2$].

$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgC(CH$_3$)$_3$. A solution of [(CH$_3$)$_3$C]$_2$Mg (25 mL of 0.07 M in Et$_2$O, 1.8 mmol) was added dropwise to Tl$\{\eta^3$-HB(3-Bu^{5}pz)$_3\}$ (1.0 g, 1.7 mmol) in Et$_2$O (10 mL), resulting in the immediate formation of a black deposit of Tl metal. The mixture was stirred for 10 min at room temperature and filtered. The filtrate was concentrated to ca. 15 mL and placed at 0 °C, giving a crop of colorless crystals. The crystals of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgC(CH$_3$)$_3$ were isolated by filtration and dried in vacuo (0.35 g, 44%). Anal. Found for $\{\eta^3$-HB(3-Bu^{5}pz)$_3\}$MgC(CH$_3$)$_3$: C, 64.2; H, 9.5; N, 17.8. Calcd: C, 64.9; H, 9.4; N, 18.2. IR data (Nujol mull, KBr plates, cm^{-1}): 2493 (ν_{B-H}). ^{1}H NMR: δ 1.37 [27 H, s, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 5.83 [3 H, d, $^3J_{H-H}$ = 2.2, η^3-HB[$C_3N_2H_2C(CH_3)_3$]], 7.36 [3 H, d, $^3J_{H-H}$ = 2.2, η^3-HB-$\{C_3N_2H_2C(CH_3)_3\}_3$], 1.75 [9 H, s, MgC(CH_3)$_3$]. ^{13}C NMR: δ 31.6 [q, $^1J_{C-H}$ = 126; spt (partial res), $^3J_{C-H}$ = 5; η^3-HB$\{C_3N_2H_2C$-$(CH_3)_3\}_3$], 32.1 [dct (partial res), $^2J_{C-H}$ = 4, η^3-HB$\{C_3N_2H_2C$-$(CH_3)_3\}_3$], 102.3 [d, $^1J_{C-H}$ = 176; d, $^2J_{C-H}$ = 9; η^3-HB$\{C_3N_2H_2C$-$(CH_3)_3\}_3$], 137.1 [d, $^1J_{C-H}$ = 185, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 166.8 [s, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 37.6 [q, $^1J_{C-H}$ = 121, MgC(CH_3)$_3$], 17.8 [s, MgC(CH$_3$)$_3$].

$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH=CH$_2$. A solution of (CH$_2$=CH)$_2$Mg (29 mL of 0.06 M in Et$_2$O, 1.7 mmol) was added dropwise to Tl$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$ (1.0 g, 1.7 mmol) in Et$_2$O (15 mL), resulting in the immediate formation of a black deposit of Tl metal. The mixture was stirred for 10 min at room temperature and filtered. The filtrate was concentrated to ca. 15 mL and placed at 0 °C, giving a crop of colorless crystals. The crystals of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH=CH$_2$ were isolated by filtration and dried in vacuo (0.15 g, 20%). Anal. Found for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH=CH$_2$: C, 63.2, H, 8.5; N, 19.0. Calcd: C, 63.8; H, 8.6; N, 19.4. IR data (Nujol mull, KBr plates, cm^{-1}): 2489 (ν_{B-H}). ^{1}H NMR: δ 1.44 [27 H, s, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 5.80 [3 H, d, $^3J_{H-H}$ = 2.2, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}$], 7.34 [3 H, d, $^3J_{H-H}$ = 2.2, η^3-HB-$\{C_3N_2H_2C(CH_3)_3\}_3$], 7.85 [1 H, d, $^3J_{H-H(trans)}$ = 22.4; d, $^3J_{H-H(cis)}$ = 17.7; MgCH=CH$_2$], 7.23 [1 H (cis), d, $^3J_{H-H(cis)}$ = 17.7; d, $^2J_{H-H}$ = 6.5; MgCH=CH_2], 6.56 [1 H (trans), d, $^3J_{H-H(trans)}$ = 22.4; d, $^2J_{H-H}$ =6.5; MgCH=CH_2]. ^{13}C NMR: δ 31.2 [q, $^1J_{C-H}$ = 126; spt (partial res), $^3J_{C-H}$ = 5; η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 32.2 [s, η^3-HB-$\{C_3N_2H_2C(CH_3)_3\}_3$], 102.1 [d, $^1J_{C-H}$ = 176; d, $^2J_{C-H}$ = 9; η^3-HB-$\{C_3N_2H_2C(CH_3)_3\}_3$], 136.4 [d, $^1J_{C-H}$ = 185; d, $^2J_{C-H}$ = 7; η^3-HB-$\{C_3N_2H_2C(CH_3)_3\}_3$], 165.9 [s, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 167.2 [d, $^1J_{C-H}$ = 106; t, $^2J_{C-H}$ = 7; MgCH=CH$_2$], 133.8 [d, $^1J_{C-H}$ = 147; d, $^1J_{C-H}$ = 150; d, $^2J_{C-H}$ = 10; MgCH=CH$_2$].

$\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgC$_6$H$_5$. A solution of (C$_6$H$_5$)$_2$Mg (29 mL of 0.06 M in Et$_2$O, 1.7 mmol) was added dropwise to Tl(η^3-HB-(3-Bu^{t}pz)$_3\}$ (1.0 g, 1.7 mmol) in Et$_2$O (15 mL), resulting in the immediate formation of a black deposit of Tl metal. The mixture was stirred for 10 min at room temperature and filtered. The filtrate was concentrated to ca. 15 mL and placed at 0 °C, giving a crop of colorless crystals. The crystals of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$-MgC$_6$H$_5$ were isolated by filtration and dried in vacuo (0.26 g). Further cropts of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgC$_6$H$_5$ were obtained from the mother liquor by a similar procedure. Total yield of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgC$_6$H$_5$: 0.36 g (44%). Anal. Found for $\{\eta^3$-HB-(3-Bu^{t}pz)$_3\}$MgC$_6$H$_5$: C, 66.9; H, 8.1; N, 17.1. Calcd: C, 67.2; H, 8.1; N, 17.4. IR data (Nujol mull, KBr plates, cm^{-1}): 2493 (ν_{B-H}). ^{1}H NMR: δ 1.34 [27 H, s, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 5.83 [3 H, d, $^3J_{H-H}$ = 2.2, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}$], 7.38 [3 H, d, $^3J_{H-H}$ = 2.2, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 8.46 [2 H (ortho), m, MgC$_6H_5$], 7.54 [2 H (meta), m, MgC$_6H_5$], 7.40 [1 H (para), m, MgC$_6H_5$]. ^{13}C NMR: δ 31.2 [q, $^1J_{C-H}$ = 126; spt (partial res), $^3J_{C-H}$ = 5; η^3-HB-$\{C_3N_2H_2C(CH_3)_3\}_3$], 32.2 [s, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 102.5 [d, $^1J_{C-H}$ = 176; d, $^2J_{C-H}$ = 9; η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 137.0 [d, $^1J_{C-H}$ = 185; d, $^2J_{C-H}$ = 6, η^3-HB$\{C_3N_2H_2C(CH_3)_3\}_3$], 166.4 [s, η^3-HB-$\{C_3N_2H_2C(CH_3)_3\}_3$], 160.0 [1 C (ipso), s, MgC$_6$H$_5$], 126.8 [2 C (ortho), d, $^1J_{C-H}$ = 153; d, $^2J_{C-H}$ = 6; MgC$_6$H$_5$], 142.5 [2 C (meta), d, $^1J_{C-H}$ = 151; d, $^2J_{C-H}$ = 11; d, $^2J_{C-H}$ = 7; MgC$_6$H$_5$], 125.6 [1 C (para), d, $^1J_{C-H}$ = 157; t, $^2J_{C-H}$ = 7; MgC$_6$H$_5$].

Synthesis of $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}$MgR Derivatives. **$\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}$MgCH$_3$.** A solution of (CH$_3$)$_2$Mg (2 mL of 0.8 M in Et$_2$O, 1.6 mmol) was added dropwise to K$\{$HB(3,5-Me$_2$pz)$_3\}$ (0.5 g, 1.5 mmol) in Et$_2$O (70 mL). The mixture was stirred for 30 min at room temperature and filtered. The filtrate was concentrated to ca. 20 mL and placed at 0 °C, giving a crop of colorless crystals. The crystals of $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}$MgCH$_3$ were isolated by filtration and dried in vacuo (0.17 g, 34%). Anal. Found for $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}$MgCH$_3$: C, 57.1; H, 8.0; N, 24.6. Calcd: C, 57.1; H, 7.5; N, 25.0. IR data (Nujol mull, KBr plates, cm^{-1}): 2530 (ν_{B-H}). ^{1}H NMR: δ 2.11 [9 H, s, η^3-HB$\{C_3N_2H(CH_3)_2\}_3$], 2.20 [9 H, s, η^3-HB$\{C_3N_2H(CH_3)_2\}_3$], 5.47 [3 H, s, η^3-HB$\{C_3N_2H(CH_3)_2\}_3$], -0.25 [3 H, s, MgCH_3]. ^{13}C NMR: δ 12.5 [q, $^1J_{C-H}$ = 128, η^3-HB$\{C_3N_2H(CH_3)_2\}_3$], 13.1 [q, $^1J_{C-H}$ = 128, η^3-HB$\{C_3N_2H(CH_3)_2\}_3$], 105.3 [d, $^1J_{C-H}$ = 172; spt (partial res), $^3J_{C-H}$ = 3; η^3-HB$\{C_3N_2H$-$(CH_3)_2\}_3$], 145.2 [dq, $^2J_{C-H}$ = 6, η^3-HB$\{C_3N_2H(CH_3)_2\}_3$], 149.7 [dq, $^2J_{C-H}$ = 6, η^3-HB$\{C_3N_2H(CH_3)_2\}_3$], -17.1 [q, $^1J_{C-H}$ = 109, MgCH$_3$].

$\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}$MgCH$_2$CH$_3$. A solution of (CH$_3$CH$_2$)$_2$Mg (1 mL of 1.5 M in Et$_2$O, 1.5 mmol) was added dropwise to K-$\{$HB(3,5-Me$_2$pz)$_3\}$ (0.5 g, 1.5 mmol) in Et$_2$O (80 mL). The mixture was stirred for 30 min at room temperature and filtered. The

filtrate was concentrated to ca. 20 mL and placed at 0 °C, giving a crop of colorless crystals. The crystals of {η³-HB(3,5-$Me_2pz)_3$}$MgCH_2CH_3$ were isolated by filtration and dried in vacuo (0.26 g, 50%). Anal. Found for {η³-HB(3,5-$Me_2pz)_3$}$MgCH_2CH_3$: C, 58.3; H, 7.4; N, 23.6. Calcd: C, 58.3; H, 7.8; N, 24.0. IR data (Nujol mull, KBr plates, cm^{-1}): 2515 (ν_{B-H}). ^1H NMR: δ 2.11 [9 H, s, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 2.20 [9 H, s, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 5.46 [3 H, s, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 0.57 [2 H, q, $^3J_{H-H}$ = 8.3, $MgCH_2CH_3$], 2.14 [3 H, t, $^3J_{H-H}$ = 8.3, $MgCH_2CH_3$]. ^{13}C NMR: δ 12.5 [q, $^1J_{C-H}$ = 128, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 13.1 [q, $^1J_{C-H}$ = 128, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 105.3 [d, $^1J_{C-H}$ = 172, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 145.2 [dq, $^2J_{C-H}$ = 6, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 149.6 [dq, $^2J_{C-H}$ = 6, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], −3.0 [t, $^1J_{C-H}$ = 107, $MgCH_2CH_3$], 14.1 [q, $^1J_{C-H}$ = 123, $MgCH_2CH_3$].

{η³-HB(3,5-$Me_2pz)_3$}$MgCH_2(CH_2)_2CH_3$. A solution of [$CH_3(CH_2)_3]_2Mg$ (26 mL of 0.07 M in Et_2O/THF, 1.8 mmol) was added dropwise to K{HB(3,5-$Me_2pz)_3$} (0.6 g, 1.8 mmol) in Et_2O (120 mL). The mixture was stirred for 30 min at room temperature and filtered. The filtrate was concentrated to ca. 20 mL and placed at 0 °C, giving a crop of colorless crystals. The crystals of {η³-HB(3,5-$Me_2pz)_3$}$MgCH_2(CH_2)_2CH_3$ were isolated by filtration and dried in vacuo (0.35 g, 52%). Anal. Found for {η³-HB(3,5-$Me_2pz)_3$}$MgCH_2(CH_2)_2CH_3$: C, 59.4; H, 8.1; N, 22.0. Calcd: C, 60.3; H, 8.3; N, 22.2. IR data (Nujol mull, KBr plates, cm^{-1}): 2519 (ν_{B-H}). ^1H NMR: δ 2.11 [9 H, s, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 2.21 [9 H, s, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 5.46 [3 H, s, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 0.60 [2 H, m, $MgCH_2CH_2CH_2CH_3$], 2.35 [2 H, m, $MgCH_2CH_2CH_2CH_3$], 1.91 [2 H, m, $MgCH_2CH_2CH_2CH_3$], 1.32 [3 H, t, $^3J_{H-H}$ = 7.2, $MgCH_2CH_2CH_2CH_3$]. ^{13}C NMR: δ 12.5 [q, $^1J_{C-H}$ = 128, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 13.2 [q, $^1J_{C-H}$ = 128, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 105.3 [d, $^1J_{C-H}$ = 172, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 145.2 [dq, $^2J_{C-H}$ = 6, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 149.6 [dq, $^2J_{C-H}$ = 6, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 7.1 [t, $^1J_{C-H}$ = 106; t, $^2J_{C-H}$ = 4; $MgCH_2CH_2CH_2CH_3$], 32.6 [t, $^1J_{C-H}$ = 122; t, $^2J_{C-H}$ = 4; $MgCH_2(CH_2)_2CH_3$], 33.3 [t, $^1J_{C-H}$ = 120; t, $^2J_{C-H}$ = 4; $MgCH_2(CH_2)_2CH_3$], 14.7 [q, $^1J_{C-H}$ = 122, $MgCH_2CH_2CH_2CH_3$].

{η³-HB(3,5-$Me_2pz)_3$}$MgCH_2Si(CH_3)_3$. A solution of [$(CH_3)_3SiCH_2]_2Mg$ (50 mL of 0.06 M in Et_2O, 3.0 mmol) was added dropwise to K{HB(3,5-$Me_2pz)_3$} (1.0 g, 3.0 mmol) in Et_2O (20 mL). The mixture was stirred for 30 min at room temperature and filtered. The filtrate was concentrated at ca. 20 mL and placed at 0 °C, giving a crop of colorless crystals. The crystals of {η³-HB(3,5-$Me_2pz)_3$}$MgCH_2Si(CH_3)_3$ were isolated by filtration and dried in vacuo (0.63 g). Further crops of {η³-HB(3,5-$Me_2pz)_3$}-$MgCH_2Si(CH_3)_3$ were obtained from the mother liquor by a similar procedure. Total yield of {η³-HB(3,5-$Me_2pz)_3$}$MgCH_2Si(CH_3)_3$: 0.88 g (72%). Anal. Found for {η³-HB(3,5-$Me_2pz)_3$}$MgCH_2Si(CH_3)_3$: C, 55.4; H, 8.3; N, 20.6. Calcd: C, 55.8; H, 8.1; N, 20.6. IR data (Nujol mull, KBr plates, cm^{-1}): 2543 (ν_{B-H}). ^1H NMR: δ 2.10 [9 H, s, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 2.23 [9 H, s, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 5.44 [3 H, s, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], −0.64 [2 H, s, $MgCH_2Si(CH_3)_3$], 0.51 [9 H, s, $MgCH_2Si(CH_3)_3$]. ^{13}C NMR: δ 12.5 [q, $^1J_{C-H}$ = 128, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 13.6 [q, $^1J_{C-H}$ = 127, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 105.5 [d, $^1J_{C-H}$ = 173, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 145.2 [dq, $^2J_{C-H}$ = 6, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 149.7 [dq, $^2J_{C-H}$ = 6, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], −8.9 [t, $^1J_{C-H}$ = 103, $MgCH_2Si(CH_3)_3$], 5.0 [q, $^1J_{C-H}$ = 116, $MgCH_2Si(CH_3)_3$].

{η³-HB(3,5-$Me_2pz)_3$}$MgCH(CH_3)_2$. A solution of [$(CH_3)_2CH]_2Mg$ (20 mL of 0.09 M in Et_2O, 1.8 mmol) was added dropwise to K{HB(3,5-$Me_2pz)_3$} (0.6 g, 1.8 mmol) in Et_2O (100 mL). The mixture was stirred for 30 min at room temperature and filtered. The filtrate was concentrated to ca. 20 mL and placed at 0 °C, giving a crop of colorless crystals. The crystals of {η³-HB(3,5-$Me_2pz)_3$}$MgCH(CH_3)_2$ were isolated by filtration and dried in vacuo (0.35 g, 54%). Anal. Found for {η⁵-HB(3-Bu^{t}pz)$_3$}$MgCH(CH_3)_2$: C, 58.1; H, 8.0; N, 22.3. Calcd: C, 59.3; H, 8.0; N, 23.1. IR data (Nujol mull, KBr plates, cm^{-1}): 2519 (ν_{B-H}). ^1H NMR: δ 2.11 [9 H, s, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 2.21 [9 H, s, η³-HB[{$C_3N_2H(CH_3)_2$}$_3$], 5.45 [3 H, s, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 0.82 [1 H, spt, $^3J_{H-H}$ = 7.8, $MgCH(CH_3)_2$], 2.12 [6 H, d, $^3J_{H-H}$ = 7.8, $MgCH(CH_3)_2$]. ^{13}C NMR: δ 12.5 [q, $^1J_{C-H}$ = 128, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 13.2 [q, $^1J_{C-H}$ = 128, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 105.4 [d, $^1J_{C-H}$ = 173, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 145.2 [dq, $^2J_{C-H}$ = 6, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 149.6 [dq, $^2J_{C-H}$ = 6, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 8.5 [d, $^1J_{C-H}$ = 107, $MgCH(CH_3)_2$], 25.7 [q, $^1J_{C-H}$ = 121, $MgCH(CH_3)_2$].

{η³-HB(3,5-$Me_2pz)_3$}$MgC(CH_3)_3$. A solution of [$(CH_3)_3C]_2Mg$ (26 mL of 0.07 M in Et_2O, 1.8 mmol) was added dropwise to K{HB(3,5-$Me_2pz)_3$} (0.6 g, 1.8 mmol) in Et_2O (100 mL). The mixture was stirred for 30 min at room temperature and filtered. The filtrate was concentrated to ca. 30 mL and placed at 0 °C, giving a crop of colorless crystals. The crystals of {η³-HB(3,5-$Me_2pz)_3$}$MgC(CH_3)_3$ were isolated by filtration and dried in vacuo (0.34 g, 50%). Anal. Found for {η³-HB(3,5-$Me_2pz)_3$}$MgC(CH_3)_3$: C, 60.9; H, 8.9; N, 21.0. Calcd: C, 60.3; H, 8.3; N, 22.2. IR data (Nujol mull, KBr plates, cm^{-1}): 2544 (ν_{B-H}). ^1H NMR: δ 2.11 [9 H, s, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 2.22 [9 H, s, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 5.43 [3 H, s, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 1.77 [9 H, s, $MgC(CH_3)_3$]. ^{13}C NMR: δ 12.5 [q, $^1J_{C-H}$ = 128, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 13.5 [q, $^1J_{C-H}$ = 128, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 105.6 [d, $^1J_{C-H}$ = 174, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 145.2 [dq, $^2J_{C-H}$ = 5, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 149.7 [dq, $^2J_{C-H}$ = 6, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 14.5 [s, $MgC(CH_3)_3$], 34.9 [q, $^1J_{C-H}$ = 120; spt (partial res), $^3J_{C-H}$ = 7; $MgC(CH_3)_3$].

{η³-HB(3,5-$Me_2pz)_3$}$MgCH{=}CH_2$. A solution of ($CH_2{=}CH)_2Mg$ (20 mL of 0.06 M in Et_2O, 1.2 mmol) was added dropwise to K{HB(3,5-$Me_2pz)_3$} (0.39 g, 1.2 mmol) in Et_2O (100 mL). The mixture was stirred for 30 min at room temperature and filtered. The filtrate was concentrated to ca. 15 mL and placed at 0 °C, giving a crop of colorless crystals. the crystals of {η³-HB(3,5-$Me_2pz)_3$}$MgCH{=}CH_2$ were isolated by filtration and dried in vacuo (0.10 g, 25%). Anal. Found for {η³-HB(3,5-$Me_2pz)_3$}-$MgCH{=}CH_2$: C, 57.2; H, 7.4; N, 23.3. Calcd: C, 58.6; H, 7.2; N, 24.1. IR data (Nujol mull, KBr plates, cm^{-1}): 2518 (ν_{B-H}). ^1H NMR: δ 2.11 [9 H, s, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 2.24 [9 H, s, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 5.46 [3 H, s, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 7.78 [1 H, d, $^3J_{H-H(trans)}$ = 23.2; d, $^3J_{H-H(cis)}$ = 17.2; $MgCH{=}CH_2$], 7.33 [1 H (cis), d, $^3J_{H-H(cis)}$ = 17.2; d, $^2J_{H-H}$ = 7.2; $MgCH{=}CH_2$], 6.44 [1 H (trans), d, $^3J_{H-H(trans)}$ = 23.2; d, $^2J_{H-H}$ = 7.2; $MgCH{=}CH_2$]. ^{13}C NMR: δ 12.5 [q, $^1J_{C-H}$ = 128, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 13.2 [q, $^1J_{C-H}$ = 128, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 105.3 [d, $^1J_{C-H}$ = 172, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 145.3 [dq, $^2J_{C-H}$ = 6, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 149.9 [dq, $^2J_{C-H}$ = 6, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 164.3 [d, $^1J_{C-H}$ = 109; d, $^2J_{C-H}$ = 9; d, $^2J_{C-H}$ = 5; $MgCH{=}CH_2$], 134.8 [d, $^1J_{C-H}$ = 145; d, $^1J_{C-H}$ = 150; d, $^2J_{C-H}$ = 9; $MgCH{=}CH_2$].

{η³-HB(3,5-$Me_2pz)_3$}MgC_6H_5. A solution of $(C_6H_5)_2Mg$ (30 mL of 0.06 M in Et_2O, 1.8 mmol) was added dropwise to K{HB(3,5-$Me_2pz)_3$} (0.60 g, 1.8 mmol) in Et_2O (60 mL). The mixture was stirred for 30 min at room temperature and filtered. The filtrate was concentrated to ca. 30 mL and placed at 0 °C, giving a crop of colorless crystals. The crystals of {η³-HB(3,5-$Me_2pz)_3$}MgC_6H_5 were isolated by filtration and dried in vacuo (0.46 g). Further crops of {η³-HB(3,5-$Me_2pz)_3$}MgC_6H_5 were obtained from the mother liquor by a similar procedure. Total yield of {η³-HB-(3,5-$Me_2pz)_3$}MgC_6H_5: 0.54 g (76%). Anal. Found for {η³-HB-(3,5-$Me_2pz)_3$}MgC_6H_5: C, 63.2; H, 6.7; N, 21.2. Calcd: C, 63.3; H, 6.8; N, 21.1. IR data (Nujol mull, KBr plates, cm^{-1}): 2517 (ν_{B-H}). ^1H NMR: δ 2.12 [9 H, s, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 2.17 [9 H, s, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 5.46 [3 H, s, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 8.38 [2 H (ortho), m, MgC_6H_5], 7.62 [2 H (meta), m, MgC_6H_5], 7.52 [1 H (para), m, MgC_6H_5]. ^{13}C NMR: δ 12.5 [q, $^1J_{C-H}$ = 128, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 13.4 [q, $^1J_{C-H}$ = 128, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 105.5 [d, $^1J_{C-H}$ = 173, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 145.5 [dq, $^2J_{C-H}$ = 6, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 150.0 [dq, $^2J_{C-H}$ = 6, η³-HB{$C_3N_2H(CH_3)_2$}$_3$], 163.1 [1 C (ipso), s, MgC_6H_5], 127.2 [2 C (ortho), d, $^1J_{C-H}$ = 155, MgC_6H_5], 141.5 [2 C (meta), d, $^1J_{C-H}$ = 151, MgC_6H_5], 126.2 [1 C (para), d, $^1J_{C-H}$ = 157, MgC_6H_5].

Reactions of M{HB(3-Bu^{t}pz)$_3$} (M = K, Tl) with Grignard Reagents. The reactions were typically carried out by addition of the appropriate Grignard reagent to solutions of M{HB(3-Bu^{t}pz)$_3$} (50 mg) in Et_2O (15 mL) at room temperature, followed by filtration and removal of the solvent under reduced pressure. The product distribution was analyzed by comparison of the ^1H NMR spectrum with that of authentic samples of [η³-HB(3-Bu^{t}pz)$_3$]MgR, as described above, and {η³-HB(3-Bu^{t}pz)$_3$}MgX (X = Cl, Br, I).[44] Product distributions are given in Table V and Figure 8 and 9 and are not markedly affected by prolonged reaction times.

Reaction of {η³-HB(3-Bu^{t}pz)$_3$}$MgCH_3$ with $MgCl_2$. A solution of {η³-HB(3-Bu^{t}pz)$_3$}$MgCH_3$ (55 mg, 0.13 mmol) in Et_2O

(44) Han, R.; Parkin, G. Manuscript in preparation.

(30 mL) was stirred with $MgCl_2$ (120 mg, 1.26 mmol) for 24 h at room temperature. The mixture was filtered and the solvent removed under reduced pressure, giving $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCl (35 mg, 61%).

Reaction of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ with TlCl. A solution of $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$ (60 mg, 0.14 mmol) in Et_2O (30 mL) was stirred with TlCl (170 mg, 0.71 mmol) for 18 h at room temperature. The mixture was filtered and the solvent removed under reduced pressure, giving starting material $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$.

X-ray Structure Determinations. Details of the crystal data, data collection, and refinement parameters are available as supplementary material.

Acknowledgment is made to the National Science Foundation (Grant CHE 90-07512) and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Supplementary Material Available: Complete tables of crystal and intensity collection data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters and ORTEP drawings for $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH(CH$_3$)$_2$, $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$MgCH$_3$, and $\{\eta^3$-HB(3,5-Me$_2$pz)$_3\}$MgCH$_2$Si(CH$_3$)$_3$ (21 pages); listings of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

Synthesis, Structures, and Reactivity of Cationic Carbonyl α-Ketoacyl Complexes of Platinum(II). Crystal Structures of *trans*-[Pt(COCOOMe)(CO)(PPh$_3$)$_2$](BF$_4$), *trans*-Pt(COCOOMe)(COOMe)(PPh$_3$)$_2$, *trans*-Pt(COCOOMe)(CONEt$_2$)(PPh$_3$)$_2$, and *trans*-Pt(COCOPh)(CONEt$_2$)(PPh$_3$)$_2$

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Received August 15, 1990

The abstraction of the chloride ligand from *trans*-Pt(COCOR)(Cl)(PPh$_3$)$_2$ (R = Ph (**1a**), OMe (**1b**)) by a Ag(I) ion in the presence of CO leads to the formation of the cationic carbonyl α-ketoacyl complexes *trans*-[Pt(CO)(COCOR)(PPh$_3$)$_2$](BF$_4$) (R = Ph (**2a**), OMe (**2b**)). The crystal structure of **2b** determined by X-ray diffraction, shows trans square-planar geometry, with its α-ketoacyl carbonyls being in the *s*-trans configuration. The rather long distance of the Pt–C(O) bond is 1.96 (1) Å. Complexes **2a** and **2b** suffer from nucleophilic attack by NaOMe and Et_2NH to give *trans*-Pt(COCOR)(COOMe)(PPh$_3$)$_2$ (R = Ph (**3a**), OMe (**3b**)) and *trans*-Pt(COCOR)(CONEt$_2$)(PPh$_3$)$_2$ (R = Ph (**4a**), OMe (**4b**)). The X-ray crystal structures of **3b**, **4a**, and **4b** were also determined. The spontaneous decarbonylation of complex **2a** in solutions neatly yields *trans*-[Pt(CO)(COPh)(PPh$_3$)$_2$](BF$_4$) (**9a**). The reactions of equimolar MeCN or PPh$_3$ with **2a** and **2b** cause the replacement of the carbonyl ligand to give *trans*-[Pt(COCOR)(NCMe)(PPh$_3$)$_2$](BF$_4$) (R = Ph (**6a**), OMe (**6b**)) and *trans*-[Pt(COCOR)(PPh$_3$)$_3$](BF$_4$) (R = Ph (**7a**), OMe (**7b**)), respectively. In contrast, no substitution was observed when 10 equiv of THF or 1 atm ethylene was added to the complexes. The kinetic results indicate that the substitution reactions are independent of the entering ligands and their concentrations and presumably undergo a reversible mechanism. The reaction of chelating DPPE with **2a** leads to the replacement of the CO ligand and a PPh$_3$ to form *cis*-[Pt(COCOPh)(PPh$_3$)(DPPE)](BF$_4$) (**8a**).

Introduction

The carbonyl ligands in the complexes of palladium(II) and platinum(II) have long been known to play important roles in many carbonylation reactions.[1-4] Palladium(II) carbonyls are generally too unstable to be isolated.[5] The chemically resembling platinum(II) carbonyls are therefore employed for the model study. Although quite a variety of the Pt(II) complexes containing coordinated CO has been intensively investigated,[6] curiously, only a very small

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