± 0.010 mm s^{-1}) is well resolved and is consistent with the expected low axial symmetry at the tin coordination center.

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Supplementary Material Available: Complete listings of crystallographic details, anisotropic thermal parameters, and bond lengths and angles (9 pages); a listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page. A complete MSC structure report (No. 87158) is available on request from the Indiana University Chemistry Library.

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[Tris(3-*tert*-butylpyrazolyl)hydroborato]beryllium Hydride: Synthesis, Structure, and Reactivity of a Terminal Beryllium Hydride Complex

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The terminal beryllium hydride complex {η^3-HB(3-Bu^{t}pz)$_3$}BeH (3-Bu^{t}pz = 3-C_3N_2Bu^tH_2) has been synthesized by the reactions of either {η^3-HB(3-Bu^{t}pz)$_3$}BeCl or {η^3-HB(3-Bu^{t}pz)$_3$}BeBr with $LiAlH_4$. The molecular structure of {η^3-HB(3-Bu^{t}pz)$_3$}BeH has been investigated by X-ray diffraction, thus determining d(Be–H) = 1.23 (7) Å. ^{1}H NMR studies on {η^3-HB(3-Bu^{t}pz)$_3$}BeH have determined the magnitude of $^1J_{^9\text{Be–H}}$ to be 28 Hz, the first report of $^1J_{^9\text{Be–H}}$ for a terminal beryllium hydride moiety. IR studies demonstrate that the Be–H stretching frequency is observed at 1865 cm^{-1} and shifts to 1410 cm^{-1} (ν_H/ν_D = 1.32) upon deuterium substitution. Other half-sandwich [tris(pyrazolyl)hydroborato]beryllium complexes of the series {η^3-HB(3-Bu^{t}pz)$_3$}BeX (X = Cl, Br, I, SH) have also been synthesized, and the molecular structure of the bromide derivative {η^3-HB(3-Bu^{t}pz)$_3$}BeBr has been determined by X-ray diffraction. The series of complexes {η^3-HB(3-Bu^{t}pz)$_3$}BeX (X = H, Cl, Br, I, SH) have been investigated by ^{9}Be NMR spectroscopy and are characterized by ^{9}Be resonances in the range δ 1–4 ppm (relative to $[Be(H_2O)_4]^{2+}$). {η^3-HB(3-Bu^{t}pz)$_3$}BeH is rhombohedral, $R3m$ (No. 160), with a = 15.739 (3) Å, b = 15.739(3) Å, c = 8.228 (3) Å, α = 90.0°, β = 90.0°, γ = 120.0°, V = 1765.3 (8) Å^3, and Z = 3. {η^3-HB(3-Bu^{t}pz)$_3$}BeBr is monoclinic, Pn (No. 7), with a = 8.455 (1) Å, b = 15.242(3) Å, c = 9.643 (2) Å, β = 100.54 (1)°, V = 1221.8 (4) Å^3, and Z = 2.

Introduction

Our recent investigations have described the use of the sterically demanding tris(3-*tert*-butylpyrazolyl)hydroborato ligand, [HB(3-Bu^{t}pz)$_3$]$^-$ (3-Bu^{t}pz = 3-C_3N_2Bu^tH_2),[1] to provide a well-defined coordination environment for zinc and magnesium, which has allowed an investigation of the synthesis and reactivity of 4-coordinate monomeric zinc and magnesium alkyl and hydride derivatives {η^3-HB(3-Bu^{t}pz)$_3$}MR (M = Zn, Mg) and {η^3-HB(3-Bu^{t}pz)$_3$}ZnH.[2-4] Here we report the first tris(pyrazolyl)hydroborato complexes of beryllium and, in particular, the synthesis and characterization of the terminal hydride complex {η^3-HB(3-Bu^{t}pz)$_3$}BeH.

Results

The [tris(pyrazolyl)hydroborato]beryllium halide complexes {η^3-HB(3-Bu^{t}pz)$_3$}BeCl and {η^3-HB(3-Bu^{t}pz)$_3$}BeBr are readily obtained by reaction of Tl{η^3-HB(3-Bu^{t}pz)$_3$} with $BeCl_2 \cdot xH_2O$ and $BeBr_2(OEt_2)_2$, respectively (eq 1). The molecular structure of

$$BeX_2 + Tl\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\} \xrightarrow{Et_2O} \{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}BeX + TlX \quad (1)$$

the bromide derivative {η^3-HB(3-Bu^{t}pz)$_3$}BeBr has been determined by X-ray diffraction, as shown in Figure 1. Selected bond lengths and angles are presented in Tables I and II, with atomic coordinates in Table III.

The hydride derivative {η^3-HB(3-Bu^{t}pz)$_3$}BeH is obtained by metathesis of either {η^3-HB(3-Bu^{t}pz)$_3$}BeCl or {η^3-HB(3-Bu^{t}pz)$_3$}BeBr with $LiAlH_4$ in Et_2O at room temperature (Scheme I). However, the reaction of $LiAlH_4$ with {η^3-HB(3-Bu^{t}pz)$_3$}BeBr proceeded faster than that with {η^3-HB(3-Bu^{t}pz)$_3$}BeCl. The deuteride derivative {η^3-HB(3-Bu^{t}pz)$_3$}BeD was obtained by the corresponding reaction with $LiAlD_4$ in benzene. The molecular structure of {η^3-HB(3-Bu^{t}pz)$_3$}BeH has also been determined by X-ray diffraction, as shown in Figure 2. Selected bond lengths and angles are presented in Tables IV and V, with atomic coordinates in Table VI.

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

Be–Br	2.122 (7)	Be–N(12)	1.793 (8)
Be–N(22)	1.788 (8)	Be–N(32)	1.810 (7)
N(11)–N(12)	1.377 (6)	N(11)–B	1.506 (7)
N(21)–N(22)	1.386 (6)	N(21)–B	1.541 (8)
N(31)–N(32)	1.382 (6)	N(31)–B	1.534 (8)

Table II. Selected Bond Angles (deg) for {η^3-HB(3-Bu^{t}pz)$_3$}BeBr

Br–Be–N(12)	117.2 (3)	Br–Be–N(22)	117.2 (4)
Br–Be–N(32)	114.1 (4)	N(12)–Be–N(22)	100.7 (4)
N(12)–Be–N(32)	102.2 (4)	N(22)–Be–N(32)	103.2 (4)
N(12)–N(11)–B	121.6 (4)	Be–N(12)–N(11)	107.3 (4)
N(22)–N(21)–B	119.5 (4)	Be–N(22)–N(21)	108.5 (4)
N(32)–N(31)–B	120.2 (4)	Be–N(32)–N(31)	107.7 (4)
N(11)–B–N(21)	107.6 (4)	N(11)–B–N(31)	107.5 (5)
N(21)–B–N(31)	104.6 (4)		

The reactivity of {η^3-HB(3-Bu^{t}pz)$_3$}BeH, leading to the formation {η^3-HB(3-Bu^{t}pz)$_3$}BeI and {η^3-HB(3-Bu^{t}pz)$_3$}BeSH, is illustrated in Scheme I. The series of complexes {η^3-HB(3-Bu^{t}pz)$_3$}BeX (X = H, Cl, Br, I, SH) have been investigated by ^{9}Be NMR spectroscopy, and the data are presented in Table VII, while ^{1}H and ^{13}C NMR data on all new compounds are presented in Table VIII.

Discussion

The cyclopentadienyl ligand has played a central role in the development of the organometallic chemistry of the transition metals due to its ability to stabilize well-defined coordination environments.[5] However, the cyclopentadienyl ligand frequently exhibits a variety of coordination modes with s- and p-block

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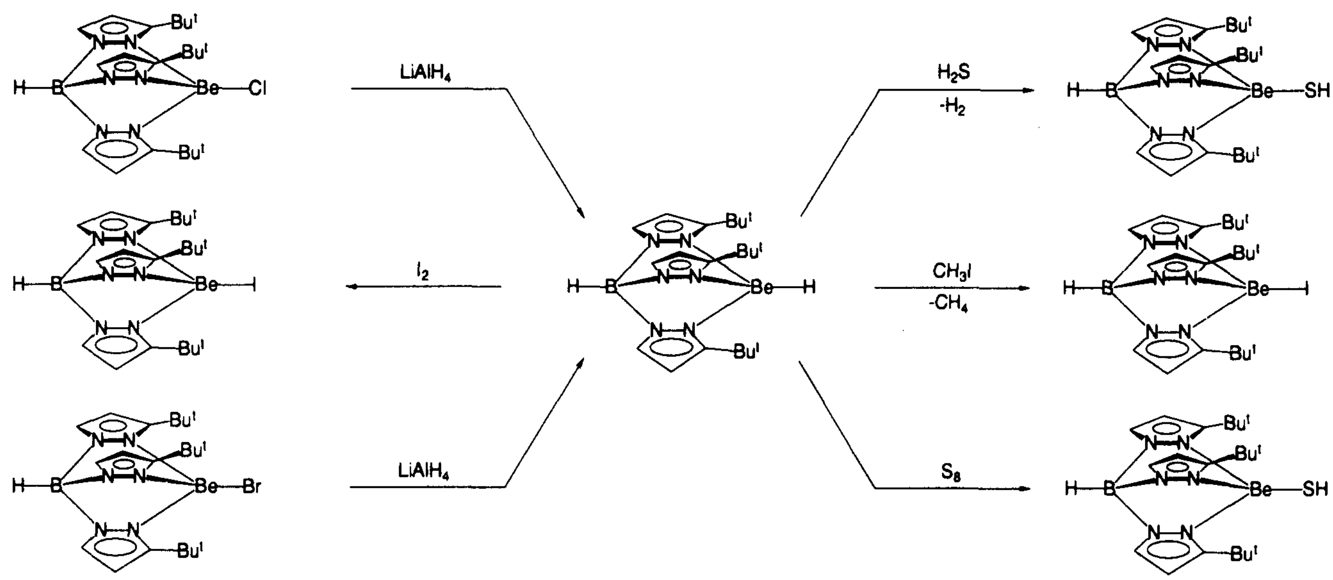
Scheme I



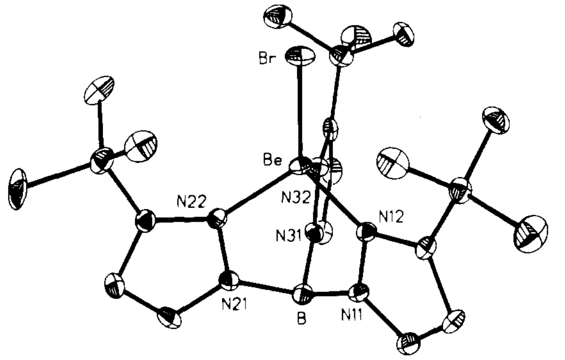


Figure 1. Molecular structure of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{BeBr}$.

Table III Atom Coordinates ($\times 10^4$) and Temperature Factors ($\text{Å}^2 \times 10^3$) for $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{BeBr}$

atom	*x*	*y*	*z*	U^a
Be	10336 (8)	7606 (5)	9964 (7)	33 (2)
Br	8007	7939 (1)	10320	49 (1)
N(11)	12119 (5)	6518 (3)	8924 (4)	34 (1)
N(12)	10509 (5)	6638 (3)	8945 (4)	32 (1)
N(21)	12866 (5)	8078 (3)	8998 (4)	36 (1)
N(22)	11336 (5)	8389 (3)	9048 (4)	32 (1)
N(31)	13249 (5)	7227 (3)	11169 (4)	33 (1)
N(32)	11785 (5)	7399 (3)	11558 (4)	32 (1)
C(11)	12292 (7)	5788 (4)	8193 (6)	45 (2)
C(12)	10831 (7)	5430 (4)	7721 (6)	44 (2)
C(13)	9713 (7)	5964 (3)	8185 (5)	36 (2)
C(14)	7889 (6)	5831 (4)	7939 (6)	39 (2)
C(15)	7389 (7)	5610 (4)	9352 (6)	55 (2)
C(16)	7443 (8)	5056 (4)	6934 (7)	70 (3)
C(17)	7012 (7)	6634 (4)	7217 (6)	53 (2)
C(21)	13661 (7)	8670 (4)	8374 (6)	46 (2)
C(22)	12696 (7)	9371 (4)	7975 (6)	47 (2)
C(23)	11237 (8)	9180 (4)	8417 (6)	38 (2)
C(24)	9740 (8)	9779 (4)	8161 (6)	49 (2)
C(25)	8308 (8)	9282 (4)	7342 (6)	60 (2)
C(26)	9436 (9)	10109 (4)	9571 (7)	65 (3)
C(27)	10077 (11)	10572 (5)	7272 (9)	83 (4)
C(31)	14398 (6)	7123 (4)	12331 (6)	45 (2)
C(32)	13680 (7)	7223 (4)	13471 (6)	49 (2)
C(33)	12049 (7)	7383 (3)	12986 (5)	37 (2)
C(34)	10789 (8)	7508 (4)	13878 (6)	52 (2)
C(35)	9469 (9)	6796 (4)	13503 (7)	65 (3)
C(36)	11542 (10)	7381 (5)	15447 (6)	82 (3)
C(37)	10066 (9)	8445 (5)	13716 (7)	68 (3)
B	13371 (7)	7164 (4)	9605 (7)	38 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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

Be–H(1)	1.228 (70)	B–H(2)	1.011 (82)
Be–N(12)	1.778 (3)	Be–N(12′)	1.778 (4)
Be–N(12″)	1.778 (3)	B–N(11)	1.530 (3)
B–N(11′)	1.530 (4)	B–N(11″)	1.530 (3)
N(11)–N(12)	1.368 (3)		

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

H(1)–Be–N(12)	117.6 (2)	H(2)–B–N(11)	111.8 (2)
N(12)–Be–N(12′)	100.2 (2)	N(12)–Be–N(12″)	100.2 (2)
N(12′)–Be–N(12″)	100.2 (2)	N(11)–B–N(11′)	107.1 (2)
N(11)–B–N(11″)	107.1 (2)	N(11′)–B–N(11″)	107.1 (2)

Table VI. Atom Coordinates ($\times 10^4$) and Temperature Factors ($\text{Å}^2 \times 10^3$) for $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{BeH}$

atom	*x*	*y*	*z*	*U*
Be	0	0	−0 (6)	36 (1)^a
B	0	0	3343 (6)	55 (1)^a
N(11)	−1043 (2)	−521 (1)	2654	51 (1)^a
N(12)	−1156 (2)	−578 (1)	1002 (3)	42 (1)^a
C(11)	−1923 (3)	−961 (1)	3343 (5)	65 (1)^a
C(12)	−2628 (2)	−1314 (1)	2176 (5)	67 (1)^a
C(13)	−2125 (2)	−1063 (1)	701 (4)	50 (1)^a
C(14)	−2553 (2)	−1276 91)	−994 (4)	55 (1)^a
C(15)	−3679 (3)	−1839 (1)	−915 (8)	98 (2)^a
C(16)	−2224 (2)	−320 (2)	−1920 (4)	72 (1)^a
H(1)	0	0	−1492 (85)	83 (19)
H(2)	0	0	4572 (100)	98 (23)
H(11)	−1984 (30)	−992 (15)	4465 (42)	67 (10)
H(12)	−3255 (33)	−1628 (16)	2316 (46)	70 (10)
H(15a)	−4028 (58)	−2014 (29)	−2202 (85)	161 (24)
H(15b)	−3854 (29)	−1373 (30)	−298 (43)	119 (12)
H(16a)	−2524 (25)	−473 (25)	−3036 (35)	89 (9)
H(16b)	−1532 (24)	82 (23)	−1952 (34)	76 (8)
H(16c)	−2426 (30)	110 (27)	−1271 (39)	100 (10)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VII. ^{9}Be NMR Data

compd	δ^a	$W_{1/2}$,^{b}
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{BeH}$	2.7	61
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{BeCl}$	2.7	1
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{BeBr}$	2.4	1
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{BeI}$	1.3	2
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{BeSH}$	4.0	6
$\text{BeBr}_2(\text{OEt}_2)_2$	1.2	1

[a] In C_6D_6; relative to δ 0 for $[\text{Be(H}_2\text{O)}_4]^{2+}$ in aqueous $\text{Be(NO}_3)_2$. [b] Width at half-height.

Table VIII. ^{1}H and ^{13}C NMR Data[a–f]

	^{1}H NMR			^{13}C NMR		
compd	assgnt	δ	coupling, Hz	assgnt	δ	coupling, Hz
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{BeH}$[a,d]	$\eta^3\text{-HB}\{\mathrm{C_3N_2H_2C(C}\mathit{H}_3)_3\}_3$	1.61	s	$\eta^3\text{-HB}\{\mathrm{C_3N_2H_2C(}\mathit{C}\mathrm{H_3)_3}\}_3$	30.7	q, $^1J_{C-H} = 126$
	$\eta^3\text{-HB}\{\mathrm{C_3N_2}\mathit{H}_2\mathrm{C(CH_3)_3}\}_3$			$\eta^3\text{-HB}\{\mathrm{C_3N_2H_2}\mathit{C}\mathrm{(CH_3)_3}\}_3$	32.2	s
	1 H	5.78	d, $^3J_{H-H} = 2.2$	$\eta^3\text{-HB}\{\mathit{C}_3\mathrm{N_2H_2C(CH_3)_3}\}_3$		
	1 H	7.20	d, $^3J_{H-H} = 2.2$	1 C	101.9	d, $^1J_{C-H} = 176$
	$\eta^3\text{-}\mathit{H}\mathrm{B}\{\mathrm{C_3N_2H_2C(CH_3)_3}\}_3$	4.47	q, $^1J_{B-H} = 113$[f]			d, $^2J_{C-H} = 9$
	BeH	5.00	q, $^1J_{Be-H} = 28$[f]	1 C	133.2	d, $^1J_{C-H} = 185$
						d, $^2J_{C-H} = 7$
				1 C	163.3	s
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{BeCl}$[b,d]	$\eta^3\text{-HB}\{\mathrm{C_3N_2H_2C(C}\mathit{H}_3)_3\}_3$	1.52	s	$\eta^3\text{-HB}\{\mathrm{C_3N_2H_2C(}\mathit{C}\mathrm{H_3)_3}\}_3$	30.9	q, $^1J_{C-H} = 126$
	$\eta^3\text{-HB}\{\mathrm{C_3N_2}\mathit{H}_2\mathrm{C(CH_3)_3}\}_3$			$\eta^3\text{-HB}\{\mathrm{C_3N_2H_2}\mathit{C}\mathrm{(CH_3)_3}\}_3$	32.4	s
	1 H	6.04	d, $^3J_{H-H} = 2.2$	$\eta^3\text{-HB}\{\mathit{C}_3\mathrm{N_2H_2C(CH_3)_3}\}_3$		
	1 H	7.48	d, $^3J_{H-H} = 2.2$	1 C	103.2	d, $^1J_{C-H} = 177$
	$\eta^3\text{-}\mathit{H}\mathrm{B}\{\mathrm{C_3N_2H_2C(CH_3)_3}\}_3$	not obsd				d, $^2J_{C-H} = 9$
				1 C	133.7	d, $^1J_{C-H} = 186$
						d, $^2J_{C-H} = 7$
				1 C	165.4	s
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{BeBr}$[b,d]	$\eta^3\text{-HB}\{\mathrm{C_3N_2H_2C(C}\mathit{H}_3)_3\}_3$	1.56	s	$\eta^3\text{-HB}\{\mathrm{C_3N_2H_2C(}\mathit{C}\mathrm{H_3)_3}\}_3$	31.4	q, $^1J_{C-H} = 126$
	$\eta^3\text{-HB}\{\mathrm{C_3N_2}\mathit{H}_2\mathrm{C(CH_3)_3}\}_3$			$\eta^3\text{-HB}\{\mathrm{C_3N_2H_2}\mathit{C}\mathrm{(CH_3)_3}\}_3$	32.5	s
	1 H	6.07	d, $^3J_{H-H} = 2.2$	$\eta^3\text{-HB}\{\mathit{C}_3\mathrm{N_2H_2C(CH_3)_3}\}_3$		
	1 H	7.50	d, $^3J_{H-H} = 2.2$	1 C	103.6	d, $^1J_{C-H} = 177$
	$\eta^3\text{-}\mathit{H}\mathrm{B}\{\mathrm{C_3N_2H_2C(CH_3)_3}\}_3$	not obsd				d, $^2J_{C-H} = 9$
				1 C	134.0	d, $^1J_{C-H} = 187$
						d, $^2J_{C-H} = 7$
				1 C	165.8	s
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{BeI}$[a,c]	$\eta^3\text{-HB}\{\mathrm{C_3N_2H_2C(C}\mathit{H}_3)_3\}_3$	1.73	s	$\eta^3\text{-HB}\{\mathrm{C_3N_2H_2C(}\mathit{C}\mathrm{H_3)_3}\}_3$	32.6	q, $^1J_{C-H} = 126$
	$\eta^3\text{-HB}\{\mathrm{C_3N_2}\mathit{H}_2\mathrm{C(CH_3)_3}\}_3$			$\eta^3\text{-HB}\{\mathrm{C_3N_2H_2}\mathit{C}\mathrm{(CH_3)_3}\}_3$	33.0	s
	1 H	5.79	d, $^3J_{H-H} = 2.2$	$\eta^3\text{-HB}\{\mathit{C}_3\mathrm{N_2H_2C(CH_3)_3}\}_3$		
	1 H	7.13	d, $^3J_{H-H} = 2.2$	1 C	104.5	d, $^1J_{C-H} = 177$
	$\eta^3\text{-}\mathit{H}\mathrm{B}\{\mathrm{C_3N_2H_2C(CH_3)_3}\}_3$	not obsd				d, $^2J_{C-H} = 8$
				1 C	134.3	d, $^1J_{C-H} = 187$
						d, $^2J_{C-H} = 6$
				1 C	166.9	s
$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{BeSH}$[a,c]	$\eta^3\text{-HB}\{\mathrm{C_3N_2H_2C(C}\mathit{H}_3)_3\}_3$	1.65	s	$\eta^3\text{-HB}\{\mathrm{C_3N_2H_2C(}\mathit{C}\mathrm{H_3)_3}\}_3$	31.7	q, $^1J_{C-H} = 126$
	$\eta^3\text{-HB}\{\mathrm{C_3N_2}\mathit{H}_2\mathrm{C(CH_3)_3}\}_3$			$\eta^3\text{-HB}\{\mathrm{C_3N_2H_2}\mathit{C}\mathrm{(CH_3)_3}\}_3$	32.7	s
	1 H	5.81	d, $^3J_{H-H} = 2.2$	$\eta^3\text{-HB}\{\mathit{C}_3\mathrm{N_2H_2C(CH_3)_3}\}_3$		
	1 H	7.18	d, $^3J_{H-H} = 2.2$	1 C	103.9	d, $^1J_{C-H} = 177$
	$\eta^3\text{-}\mathit{H}\mathrm{B}\{\mathrm{C_3N_2H_2C(CH_3)_3}\}_3$	not obsd				d, $^2J_{C-H} = 9$
	BeSH	–0.10	s	1 C	133.9	d, $^1J_{C-H} = 186$
						d, $^2J_{C-H} = 7$
				1 C	166.0	s

[a] ^{1}H NMR in C_6D_6. [b] ^{1}H NMR in $CDCl_3$. [c] ^{13}C NMR in C_6D_6. [d] ^{13}C NMR in $CDCl_3$. [e] s = singlet, d = doublet, t = triplet, q = quartet. [f] At 100 °C in toluene-d_8.

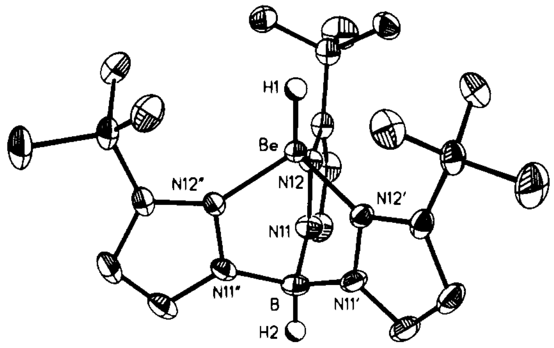


Figure 2. Molecular structure of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{BeH}$.

elements. For example, $(C_5H_5)_2Be$ possesses one η^1-C_5H_5 and one η^5-C_5H_5 ligand,[6] $(C_5H_5)_2Mg$ possesses two η^5-Cp ligands,[7] and in $(C_5H_5)_2Ca$ each Ca is bonded to *four* Cp ligands with two η^5-C_5H_5, one η^3-C_5H_5, and one η^1-C_5H_5 bonding modes.[8] Nevertheless, the cyclopentadienyl ligand has allowed the synthesis of a series of half-sandwich complexes of beryllium, including $(C_5H_5)BeX$ (X = F, Cl, Br, I, H, R, BH_4).[9] More recently, the pentamethylcyclopentadienyl congeners $(C_5Me_5)BeCl$[10] and $(C_5Me_5)BePBu^t_2$[11] have been reported. In terms of electron count, the tris(pyrazolyl)hydroborato ligand is formally analogous to η^5-cyclopentadienyl, and we anticipated that chelation of the three nitrogen atom donors of a tris(pyrazolyl)hydroborato ligand would provide a well-defined coordination environment for the synthesis of a new series of half-sandwich complexes of beryllium.

A convenient synthetic entry to [tris(pyrazolyl)hydroborato]beryllium complexes is provided by reactions of $BeCl_2 \cdot xH_2O$ and $BeBr_2(OEt_2)_2$ with $Tl\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$, which give the halide derivatives $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{BeCl}$ and $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{BeBr}$, respectively (eq 1). We note that the corresponding derivatives of less sterically demanding tris(3,5-dimethylpyrazolyl)hydroborato ligand are not readily prepared by this method. The molecular structure of the bromide derivative $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{BeBr}$ has been determined by X-ray diffraction (Figure 1), confirming both the monomeric nature of the complex and also the η^3-coordination mode of the tris(pyrazolyl)hydroborato ligand. The Be–Br bond length in $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{BeBr}$ [2.122 (7) Å] is close to the sum of the covalent radii (2.03 Å)[12] and slightly longer than that determined for $(C_5H_5)BeBr$ by gas-phase electron diffraction [1.943 (15) Å].[13]

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The hydride derivative $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$BeH is readily obtained from either $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$BeCl or $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$BeBr by reaction with $LiAlH_4$ in Et_2O (Scheme I). Repeated attempts to prepare the deuteride derivative $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$BeD by the corresponding reaction with $LiAlD_4$ in Et_2O were unsuccessful in that the *hydride* derivative was the major product! However, the use of benzene as the reaction solvent did allow the deuteride derivative to be obtained cleanly. The origin of the exchange process that results in the formation of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$BeH in Et_2O is unknown, since isolated $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$BeD *does not* exchange with Et_2O.[14]

$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$BeH provides a well-defined example of a complex containing a terminal beryllium-hydride ligand. In this regard, both BeH_2[15] and M_2BeH_4 (M = Li, Na)[16] are polymeric materials. Furthermore, other than the cyclopentadienyl derivatives $(C_5H_5)BeH$[9] and $(C_5Me_5)BeH$,[17] alkylberyllium hydride complexes, e.g. $[CH_3Be(OEt_2)]_2(\mu\text{-H})_2$,[18] $[C_6H_5Be(NMe_3)]_2(\mu\text{-H})_2$,[19] and $[(Et_2O)NaHBeEt_2]_n$,[20] are also oligomeric. Significantly, $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$BeH is the first terminal Be–H complex to be studied by X-ray diffraction (Figure 2), and the Be–H bond length was determined to be 1.23 (7) Å, close to the sum of the covalent radii (1.26 Å).[12] The closest nonbonding interactions of the hydride ligand are intramolecular with the nitrogen [d(H(1)···N(12)) = 2.59 Å] and hydrogen atoms [d(H(1)···H(16b)) = 2.51 Å] of the tris(3-*tert*-butylpyrazolyl)borate ligand. The only other report of a terminal Be–H bond length is for $(C_5H_5)BeH$ as measured in the gas phase by microwave spectroscopy [d(Be–H) = 1.32 (1) Å].[21,22] Terminal Be–H bond lengths have also been theoretically calculated for a series of hypothetical beryllium-hydride derivatives and are estimated to be in the range 1.25–1.29 Å.[23] As expected, these terminal Be–H bond lengths are shorter than the Be–H distance (1.4 Å) reported for the bridging structure of $[(Et_2O)NaHBeEt_2]_n$.[24]

The coordination environments about beryllium in $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$BeH and $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$BeBr are almost identical, even though there is a significant difference in size between H and Br. Thus, $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$BeH and $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$BeBr possess average Be–N bond distances of 1.778 (3) and 1.80 (1) Å and average N–Be–N bond angles of 100.2 (2) and 102 (1)°, respectively. Furthermore, the H–Be–N [117.6 (2)°] and Br–Be–N(av) [116 (1)°] bond angles are also very similar.

Characterization of the terminal Be–H moiety in $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$BeH is also provided by NMR and IR studies. At room temperature the Be–H resonance in the ^1H NMR spectrum is observed as two broad peaks at δ 5.0 ppm, close to that for the B–H group at δ 4.5 ppm (in C_6D_6). The relative assignments have been confirmed by ^2H NMR spectroscopy on the isotopomer $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$BeD. Although the Be–H and B–H resonances are quadrupolar broadened at room temperature, at higher temperatures quadrupolar relaxation is reduced and the expected 1:1:1:1 quartet structure may be observed for each resonance, thus allowing determination of the one-bond $^1J_{^9Be\text{-}H}$ and $^1J_{^{11}B\text{-}H}$ coupling constants of 28 and 113 Hz, respectively.[25] $^1J_{Be\text{-}H}$ (28 Hz) is

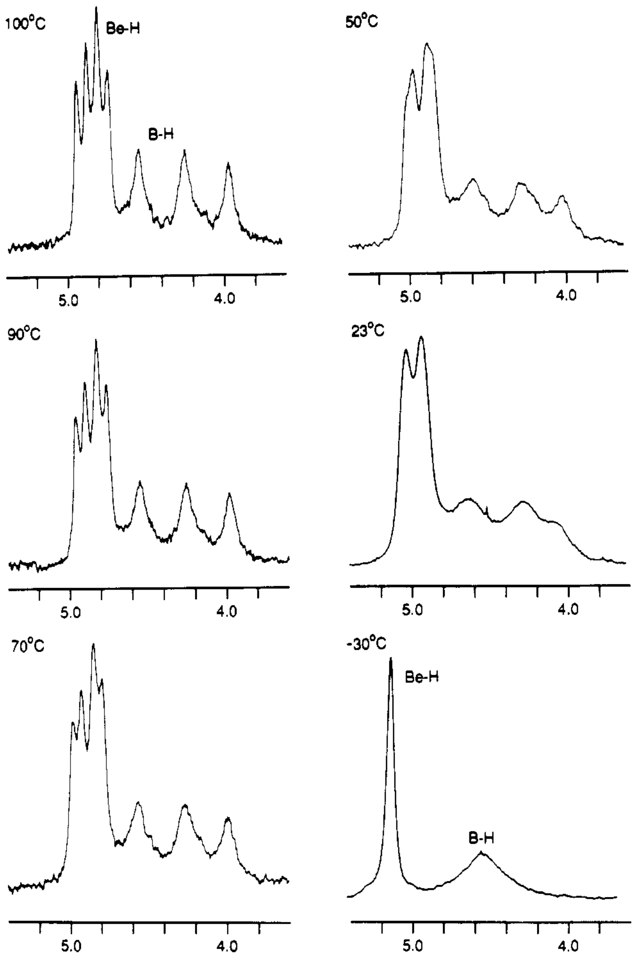

Figure 3. Variable temperature ^1H NMR spectra of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$BeH in toluene-$d_8$.

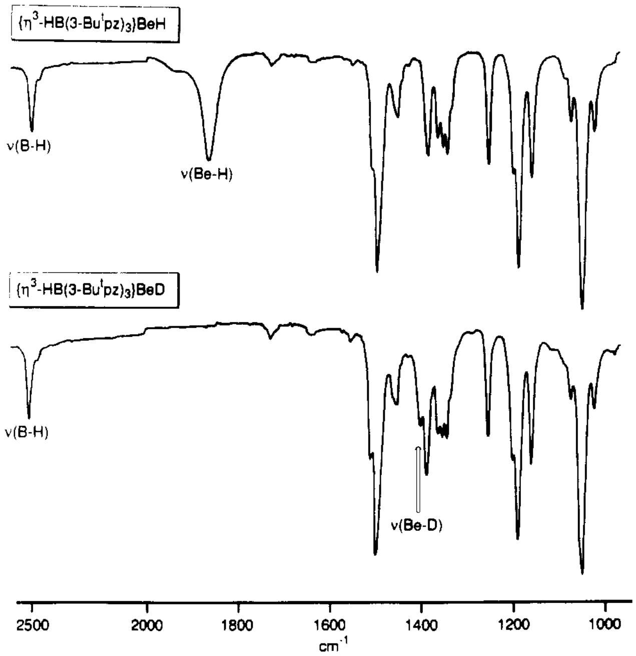

Figure 4. IR spectra of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$BeH and $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$BeD.

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(14) A possible mechanism for the H/D exchange during the synthesis with $LiAlH_4$ may involve a process in which a reactive species is formed via hydride abstraction, e.g. $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}BeHAlH_3 \rightarrow [\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}Be]^+[AlH_4]^-$. However, we have no data that support this suggestion.

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(22) A Be–H bond length of 1.306 (6) Å determined by electron diffraction for $(C_5H_5)BeH$ has also been cited in ref 9. However, ref 21 reveals that the compound had partially decomposed and that a quantitative structure determination by this method was not possible.

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(25) For reference, terminal boron–hydrogen bonds normally exhibit $^1J_{^{11}B\text{-}H}$ in the range 100–190 Hz, whereas when a hydrogen bridge is involved, $^1J_{^{11}B\text{-}H}$ is usually less than 80 Hz: Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*; Academic Press: New York, 1978.

the first coupling constant to be measured for a terminal Be–H group, since the corresponding resonance could not be observed for (C_5H_5)BeH.[26] For comparison, the hydride ligands in (C_5H_5)Be(η^2-H_2BH_2), which are fluxional at −80 °C, exhibit smaller coupling constants: $J_{^9\text{Be–H}} = 10.2$ Hz and $J_{^{11}\text{B–H}} = 84$ Hz ($J_{^{10}\text{B–H}} = 28$ Hz).[25,27]

The complete variable-temperature behavior of the ^{1}H NMR spectrum of the Be–H and B–H groups is illustrated in Figure 3. Notably, the broad singlet resonances observed at low temperatures due to rapid relaxation transform to a 1:1:1:1 quartet at high temperatures. At intermediate temperatures the resonances have more complicated appearances, as has been theoretically calculated for spin $I = {}^1/_2$ coupled to $I = {}^3/_2$ systems.[28]

The IR spectra of {η^3-HB(3-Bu^{t}pz)$_3$}BeH and {η^3-HB(3-Bu^{t}pz)$_3$}BeD are shown in Figure 4. Comparison of the two spectra reveal that ν(Be–H) is observed at 1865 cm^{-1} in the IR spectrum and shifts to 1410 cm^{-1} ($\nu_H/\nu_D = 1.32$) upon deuterium substitution. Note that the Be–H absorption is significantly more intense than the B–H absorption observed at 2500 cm^{-1}. The IR spectrum of (C_5H_5)BeH has been reported in both the gas and solid phases.[9] In the gas phase the Be–H stretching frequency is observed at ν(Be–H) = 2030 cm^{-1}, with ν(Be–D) = 1535 cm^{-1} ($\nu_H/\nu_D = 1.32$). However, in the solid state the absorptions are observed at lower frequencies, with ν(Be–H) = 1720 cm^{-1} and ν(Be–D) = 1275 cm^{-1} ($\nu_H/\nu_D = 1.35$), possibly suggesting some degree of association.[29] In accord with this suggestion, the Be–H stretching frequency of the more sterically demanding derivative (C_5Me_5)BeH, which is less prone to association, is observed to be significantly higher (1948 cm^{-1}) in the solid state.[17]

Some reactions of {η^3-HB(3-Bu^{t}pz)$_3$}BeH are shown in Scheme I. {η^3-HB(3-Bu^{t}pz)$_3$}BeH reacts with CH_3I at room temperature to give the iodide derivative {η^3-HB(3-Bu^{t}pz)$_3$}BeI and CH_4. Interestingly, the cyclopentadienyl analogue (η^5-C_5H_5)BeH was reported to be unreactive toward CH_3I under these conditions.[9] The iodide derivative {η^3-HB(3-Bu^{t}pz)$_3$}BeI is also obtained by the reation of {η^3-HB(3-Bu^{t}pz)$_3$}BeH with I_2. The reaction of {η^3-HB(3-Bu^{t}pz)$_3$}BeH with H_2S results in the formation of the thiol derivative {η^3-HB(3-Bu^{t}pz)$_3$}BeSH, which can also be obtained by the direct insertion of elemental sulfur into the Be–H bond.

We have also investigated the series of complexes {η^3-HB(3-Bu^{t}pz)$_3$}BeX (X = H, Cl, Br, I, SH) using ^{9}Be NMR spectroscopy, since the isostructural nature of this series would allow meaningful comparison of substituent effects upon the ^{9}Be NMR resonance. The results presented in Table VII show that, with the exception of the hydride derivative, which exhibited a broad resonance with a width at half-height $W_{1/2} = 61$ Hz, all derivatives possess relatively sharp resonances with $W_{1/2}$ in the range 1–6 Hz. The ^{9}Be chemical shifts for the complexes {η^3-HB(3-Bu^{t}pz)$_3$}BeX and $BeBr_2(OEt_2)_2$ shown in Table VII are in the range δ 1–4 (relative to $[Be(H_2O)_4]^{2+}$). The present range of ^{9}Be chemical shifts is ca. +20 to −20 ppm, with typical extremes represented by the cyclopentadienyl derivatives (C_5H_5)BeX (δ_X: δ_{BH_4} −22.2, δ_{CH_3} −20.4, δ_{Cl} −19.1) and the three-coordinate derivatives $(CH_3)_2BeNMe_2$ (δ 19.9) and $(CH_3)_2Be(OEt_2)$ (δ 20.8).[27,30] The ^{9}Be chemical shifts for the complexes {η^3-HB(3-Bu^{t}pz)$_3$}BeX and $BeBr_2(OEt_2)_2$ (δ 1–4) are close to those observed[27,30] for $[BeF_4]^{2-}$ (δ ca. −2), $[Be(H_2O)_4]^{2+}$ (δ 0.0), $[Be(NH_3)_4]^{2+}$ (δ 1.7), $BeCl_2(OEt_2)_2$ (δ 3.1), $(CH_3)_2Be(PMe_3)_2$ (δ 3.6), $CH_3BeCl(SMe_2)_2$ (δ 4.2), and $Be(C_6H_4OCO_2)(OH_2)_2$ (δ 3.0),[31] thus suggesting that the range δ −2 to +6 is typical for well-defined 4-coordinate beryllium. Examination of the chemical shifts for the halide series {η^3-HB(3-Bu^{t}pz)$_3$}BeX (X = Cl, Br, I) confirms that increasing the electronegativity of the substituent on the beryllium shifts the ^{9}Be resonance to lower field, consistent with previously reported data.[27,30]

Experimental Section

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, and Schlenk techniques.[32] Solvents were purified and degassed by standard procedures. ^{1}H, ^{2}H, and ^{13}C NMR spectra were recorded on Varian VXR 200, 300, and 400 spectrometers. ^{9}Be NMR spectra were obtained on a Varian VXR 300 spectrometer at 42.16 MHz. IR spectra were recorded as KBr pellets or Nujol mulls between KBr disks on a Perkin-Elmer 1420 spectrophotometer and are reported in 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. $BeCl_2 \cdot xH_2O$ and $BeBr_2(OEt_2)_2$ were received as gifts from Professor R. Breslow and Professor R. A. Andersen, respectively. {η^3-HB(3-Bu^{t}pz)$_3$}Tl was prepared by the literature method.[1] *CAUTION*! Beryllium and thallium complexes are extremely toxic and should be handled with due care. ^{1}H and ^{13}C NMR data are presented in Table VIII.

Synthesis of {η^3-HB(3-Bu^{t}pz)$_3$}BeCl. A solution of {η^3-HB(3-Bu^{t}pz)$_3$}Tl (1.2 g, 2.1 mmol) in Et_2O (ca. 50 mL) was added to a suspension of $BeCl_2 \cdot xH_2O$ (0.31 g) in Et_2O (ca. 15 mL). A white precipitate of TlCl was immediately deposited. The mixture was stirred at room temperature for 2 h and filtered. The filtrate was concentrated to ca. 10 mL and placed at 0 °C, giving colorless crystals of {η^3-HB(3-Bu^{t}pz)$_3$}BeCl, which were isolated by filtration and dried in vacuo (0.45 g, 51%). Anal. Calcd. for {η^3-HB(3-Bu^{t}pz)$_3$}BeCl: C, 59.2; H, 8.1; N, 19.7. Found: C, 59.1; H, 8.5; N, 17.5. IR: 2550 cm^{-1} (ν_{B-H}). MS: *m/e* 426 ($M^+ + 1$).

Synthesis of {η^3-HB(3-Bu^{t}pz)$_3$}BeBr. A solution of {η^3-HB(3-Bu^{t}pz)$_3$}Tl (2.0 g, 3.4 mmol) in Et_2O (ca. 70 mL) was added to a solution of $BeBr_2(OEt_2)_2$ (1.1 g, 3.5 mmol) in Et_2O (ca. 80 mL). A white precipitate of TlBr was immediately deposited. The mixture was stirred at room temperature for 40 min and filtered. The filtrate was concentrated to ca. 15 mL and placed at 0 °C giving colorless crystals of {η^3-HB(3-Bu^{t}pz)$_3$}BeBr, which were isolated by filtration and dried in vacuo (0.9 g, 56%). Anal. Calcd. for {η^3-HB(3-Bu^{t}pz)$_3$}BeBr: C, 53.6; H, 7.3; N, 17.9. Found: C, 53.4; H, 7.3; N, 17.4. IR: 2550 cm^{-1} (ν_{B-H}). MS: *m/e* 470 ($M^+ + 1$).

Synthesis of {η^3-HB(3-Bu^{t}pz)$_3$}BeH. (I) A suspension of {η^3-HB(3-Bu^{t}pz)$_3$}BeCl (0.90 g, 2.1 mmol) in Et_2O (ca. 60 mL) was treated with a solution of $LiAlH_4$ in Et_2O (4.0 mL of 1.0 M, 4.0 mmol), and the mixture was stirred for 7 days at room temperature. The mixture was filtered, and the filtrate was concentrated to ca. 5 mL and placed at 0 °C. Colorless crystals of {η^3-HB(3-Bu^{t}pz)$_3$}BeH were deposited and were isolated by filtration and dried in vacuo (0.55 g, 67%). Anal. Calcd. for {η^3-HB(3-Bu^{t}pz)$_3$}BeH: C, 64.5; H, 9.0; N, 21.5. Found: C, 64.1; H, 8.8; N, 20.7. IR: 2500 (ν_{B-H}), 1865 cm^{-1} (ν_{Be-H}) [1410 cm^{-1} (ν_{Be-D})].

(II) A solution of {η^3-HB(3-Bu^{t}pz)$_3$]BeBr (0.30 g, 0.64 mmol) in Et_2O (ca. 40 mL) was treated with a solution of $LiAlH_4$ in Et_2O (0.9 mL of 1.0 M, 0.9 mmol). A small amount of a brown-black cloudy deposit was observed. The mixture was stirred for 4 h at room temperature and filtered. The filtrate was concentrated to ca. 5 mL and placed at 0 °C, giving colorless crystals of {η^3-HB(3-Bu^{t}pz)$_3$}BeH, which were isolated by filtration and dried in vacuo (0.11 g, 44%).

Synthesis of {η^3-HB(3-Bu^{t}pz)$_3$}BeD. A mixture of {η^3-HB(3-Bu^{t}pz)$_3$}BeBr (50 mg, 0.11 mmol) and $LiAlD_4$ (5 mg, 0.12 mmol) was heated in C_6H_6 (ca. 1.5 mL) at 120 °C for 15 h. The mixture was filtered and the solvent removed in vacuo, giving {η^3-HB(3-Bu^{t}pz)$_3$}BeD.

Synthesis of {η^3-HB(3-Bu^{t}pz)$_3$}BeI. A solution of {η^3-HB(3-Bu^{t}pz)$_3$}BeH (50 mg, 0.13 mmol) in C_6H_6 (ca. 10 mL) was titrated with a solution of I_2 in C_6H_6 (ca. 1.3 M) until the solution became pale yellow. The solution was concentrated to ca. 2 mL and cooled, giving colorless crystals of {η^3-HB(3-Bu^{t}pz)$_3$}BeI, which were isolated by filtration and dried in vacuo (30 mg, 45%). Anal. Calcd for {η^3-HB(3-Bu^{t}pz)$_3$}BeI: C, 48.8; H, 6.6; N, 16.3. Found: C, 49.5; H, 6.6; N, 15.3. IR: 2510 cm^{-1} (ν_{B-H}).

Reaction of {η^3-HB(3-Bu^{t}pz)$_3$}BeH with CH_3I. A solution of {η^3-HB(3-Bu^{t}pz)$_3$}BeH (20 mg, 0.05 mmol) in benzene-d_6 (0.7 mL) was treated with CH_3I (5 μL, 0.08 mmol). The reaction was monitored by ^{1}H NMR spectroscopy, which demonstrated the quantitative formation of {η^3-HB(3-Bu^{t}pz)$_3$}BeI and CH_4 over a period of 1 week at room temperature.

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Table IX. Crystal and Intensity Collection Data

	{η^3-HB(3-Bu^{t}pz)$_3$}BeBr	{η^3-HB(3-Bu^{t}pz)$_3$}BeH
formula	$C_{21}H_{34}N_6BBeBr$	$C_{21}H_{35}N_6BBe$
fw	470.3	391.4
lattice	monoclinic	rhombohedral
cell consts		
a, Å	8.455 (1)	15.739 (3)
b, Å	15.242 (3)	15.739 (3)
c, Å	9.643 (2)	8.228 (3)
α, deg	90.0	90.0
β, deg	100.54 (1)	90.0
γ, deg	90.0	120.0
V, Å^3	1221.8 (4)	1765.3 (8)
Z	2	3
space group	*Pn* (No. 7)	*R*3*m* (No. 160)
radiation (λ,Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
ρ(calcd), g cm^{-3}	1.28	1.10
μ(Mo Kα), cm^{-1}	18.0	0.7
goodness of fit	1.148	1.351
R	0.0355	0.0404
R_w[a]	0.0346	0.0433

[a] Weighting scheme: $w = [\sigma^2(F) + gF^2]^{-1}$.

Synthesis of {η^3-HB(3-Bu^{t}pz)$_3$}BeSH. A solution of {η^3-HB(3-Bu^{t}pz)$_3$}BeH (30 mg, 0.08 mmol) in benzene (ca 1 mL) was treated with H_2S (1 atm) and heated at 50 °C for 10 days. The solvent was removed under reduced pressure, giving {η^3-HB(3-Bu^{t}pz)$_3$}BeSH as a white solid (30 mg, 90%). Anal. Calcd for {η^3-HB(3-Bu^{t}pz)$_3$}BeSH: C, 59.6; H, 8.3; N, 19.9. Found: C, 58.5; H, 7.9; N, 19.0. IR: 2510 cm^{-1} (ν_{B-H}).

Reaction of {η^3-HB(3-Bu^{t}pz)$_3$}BeH with S_8. A solution of {η^3-HB(3-Bu^{t}pz)$_3$}BeH (20 mg, 0.05 mmol) in benzene-d_6 (0.7 mL) was treated with S_8 (2 mg) and heated at 110 °C overnight. The reaction was monitored by ^{1}H NMR spectroscopy, which demonstrated the quantitative formation of {η^3-HB(3-Bu^{t}pz)$_3$}BeSH.

X-ray Structure Determination of {η^3-HB(3-Bu^{t}pz)$_3$}BeBr. Crystal data, data collection, and refinement parameters are summarized in Table IX. A single crystal of {η^3-HB(3-Bu^{t}pz)$_3$}BeBr 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.[33] Systematic absences were consistent with the space groups *Pn* and *P*2/*n*, but consideration of the *E*-value statistics and the molecular symmetry suggested the choice *Pn* (No. 7). 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* = 0.0355 (R_w = 0.0346). Inversion of configuration indicated the correct choice of enantiomorph. Atomic coordinates and thermal parameters for non-hydrogen atoms are listed in Table III, and selected bond distances and angles are listed in Tables I and II.

X-ray Structure Determination of {η^3-HB(3-Bu^{t}pz)$_3$}BeH. Crystal data, data collection, and refinement parameters are summarized in Table IX, and the general procedure is as described for {η^3-HB(3-Bu^{t}pz)$_3$}BeBr. Systematic absences were consistent with the space groups *R*3, *R*$\bar{3}$, *R*32, *R*3*m*, and *R*$\bar{3}$*m*, but consideration of the *E*-value statistics, the axial photographs (*a* and *b* axis mirror symmetry), and the molecular symmetry strongly suggested the choice *R*3*m* (No. 160). All the hydrogen atoms were located in the difference map after all the non-hydrogen atoms were located and refined anisotropically and were refined isotropically. Block-diagonal least-squares refinement converged to *R* = 0.0404 (R_w = 0.0433). Inversion of configuration indicated the correct choice of enantiomorph. Atomic coordinates and thermal parameters for all non-hydrogen atoms and selected hydrogen atoms are listed in Table VI, and selected bond distances and angles are listed in Tables IV and V.

Conclusion

In summary, the sterically demanding tris(3-*tert*-butylpyrazolyl)hydroborato ligand has allowed isolation of a series of half-sandwich beryllium complexes {η^3-HB(3-Bu^{t}pz)$_3$}BeX (X = Cl, Br, I, H, SH). The terminal hydride complex {η^3-HB(3-Bu^{t}pz)$_3$}BeH has been investigated both structurally by X-ray diffraction and spectroscopically by NMR and IR techniques, thus allowing characterization of the Be–H moiety in this complex with the parameters *d*(Be-H) = 1.23 (7) Å, $^1J_{^9\text{Be-H}}$ = 28 Hz, and ν(Be–H) = 1865 cm^{-1}.

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Supplementary Material Available: Tables SI–SXII, giving crystal and intensity collection data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters, and ORTEP drawings for {η^3-HB(3-Bu^{t}pz)$_3$}BeBr and {η^3-HB(3-Bu^{t}pz)$_3$}BeH (12 pages); listings of calculated and observed structure factors (15 pages). Ordering information is given on any current masthead page.

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(33) Sheldrick, G. M. *SHELXTL: An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*; University of Göttingen: Göttingen, Germany, 1981.