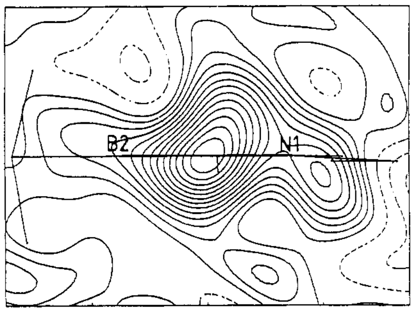

Figure 9. Difference electron density perpendicular to the NBN plane in **4b** through the N1-B2 bond. Contour lines are in e/Å^3; min = -0.17, max = 0.32. Distance: positive 0.025 e/Å^3, negative 0.05 e/Å^3 (dotted). Reference line: first solid line.

atoms. The bonding electrons of the B-C, B-N, and the C-C bonds are situated in the calculated plane. The highest calculated density is 0.37 e/Å.^{3} The maxima are found a little outside of the ring, as could be expected for sp^2-hybridized N atoms. But, there are some doubts if this finding is really significant.

Figure 6 shows the deformation electron density perpendicular to the N-B-N plane along one of the B-N bonds in **4a**. The elliptic inclination of the electron density perpendicular to the B-N bond is caused by the B-N π-back-bonding.

As can be seen from Figure 7, the maxima of the bonding electrons in the NBN plane of 1,3-diethyl-2-methyl-1,3,2-diazaborolidine (**2a**) are found exactly on the connecting line of the N(1)-B(2), B(2)-N(3), C(4)-C(5), and B(2)-C(8) nuclei. Again, the maxima in the B-N bonds are shifted toward the N atoms, due to their higher electronegativity.

The electronic difference between the saturated 1,3,2-diazaborolidines **4a** and the "aromatic" system of 1*H*-1,3,2-diazaboroles is elucidated in Figure 8. The difference electron density in the NBN plane of **4b** is similar in all five bonds. The shift of the maxima in the B-N bonds toward the nitrogen atoms cannot be observed to the same extent as in the diazaborolidines, due to the extensive delocalization of the π electrons.

Supplementary Material Available: Listings of thermal parameters, atomic coordinates, detailed crystallographic descriptions, and all bond lengths and angles (26 pages); tables of calculated and observed structure factors (110 pages). Ordering information is given on any current masthead page.

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Steric Effects in Polypyrazolylborates: Mixed Complexes M(HB(3-isopropyl-4-bromopyrazolyl)$_3$)L

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The stable, tetrahedral M(HB(3-isopropyl-4-bromopyrazolyl)$_3$)Cl, (= ML*Cl) complexes react with uninegative polydentate ligands L, forming mixed species ML*L, the structure of which depends on the nature of L. With L = [HB(pyrazolyl)$_3$]$^-$ or [HB(3,5-Me$_2$pyrazolyl)$_3$]$^-$, octahedral complexes are obtained, as was established by the paramagnetic NMR spectra of the Co(II) derivatives and an X-ray crystallographic structure determination of NiL*(HB(pyrazolyl)$_3$). This complex, $C_{39}H_{47}B_2Br_3N_{12}Ni$, crystallizes in the monoclinic space group $P2_1/m$ with two molecules per unit cell of dimensions $a = 9.764$ (2) Å, $b = 16.804$ (4) Å, $c = 13.673$ (5) Å, and $\beta = 96.35$ (2)°, at -70 °C. Least-squares refinement of 280 variables led to a value of the conventional R index (on F) of 0.044 and of R_w of 0.042 for 2546 reflections with $I > 3.0\sigma(I)$. The Ni(II) ion is coordinated to six pyrazolyl nitrogen atoms from two different ligands. The reaction with [HB(3-Phpyrazolyl)$_3$]$^-$ produced ML*L complexes where L was coordinated via two 3-phenylpyrazolyl groups and an agostic B-H-M bond, as was established by X-ray crystallography for the Co(II) compound. This complex, $C_{51}H_{53}B_2Br_3CoN_{12}$, crystallizes in the orthorhombic space group *Pbca* with eight molecules per unit cell of dimensions $a = 22.269$ (3) Å, $b = 22.299$ (3) Å, and $c = 21.216$ (5) Å, at -70 °C. Least-squares refinement of 607 variables led to a value of the conventional R index (on F) of 0.062 and of R_w of 0.047 for 2722 reflections with $I > 3.0\sigma(I)$. The Co(II) ion is coordinated to five pyrazolyl nitrogen atoms from two ligands and a hydrogen atom from the [HB(3-Phpyrazolyl)$_3$]$^-$ group. Bidentate dipyrazolylborates [H$_2$B(pyrazolyl)$_2$]$^-$ and [H$_2$B(3,5-Me$_2$pyrazolyl)$_2$]$^-$ produced ML*L complexes where L coordinated through two pyrazolyl groups, and through an agostic B-H-M bond, as was established by X-ray crystallography for CoL*(H$_2$B(3-Ph-pyrazolyl)$_2$). This complex, $C_{48}H_{53}B_2Br_3CoN_{10}$, crystallizes in the triclinic space group $P\bar{1}$ with two molecules per unit cell of dimensions $a = 11.343$ (1) Å, $b = 11.426$ (1) Å, $c = 20.716$ (6) Å, $\alpha = 80.74$ (1)°, $\beta = 80.80$ (1)°, and $\gamma = 74.25$ (1)°, at -70 °C. Least-squares refinement of 577 variables led to a value of the conventional R index (on F) of 0.064 and of R_w of 0.068 for 5695 reflections with $I > 3.0\sigma(I)$. The Co(II) ion is coordinated to five pyrazolyl groups from two ligands and a hydrogen atom from the [H$_2$B(3-Phpyrazolyl)$_2$]$^-$ ligand. The complex CoL*(Ph$_2$B(pyrazolyl)$_2$) was shown to lack an agostic interaction. This complex, $C_{48}H_{53}B_2Br_3CoN_{10}$, crystallizes in the monoclinic space group $P2_1/m$ with two molecules in a unit cell of dimensions $a = 10.570$ (1) Å, $b = 16.717$ (4) Å, $c = 14.918$ (4) Å, and $\beta = 108.35$ (1)°, at -70 °C. Least-squares refinement of 316 variables led to a value of the conventional R index (on F) of 0.055 and of R_w of 0.045 for 2064 reflections with $I > 3.0\sigma(I)$. The Co(II) ion is coordinated to five pyrazolyl groups from two ligands. With L = [B(3-Phpyrazolyl)$_4$]$^-$, the ML*L complex with M = Ni(II) had a five-coordinate structure, while that for M = Co(II) was tetrahedral. Simple bidentate ions such as acetylacetonate, tropolonate, and diethyldithiocarbamate produced five-coordinate ML*L species, whereas the oxalate ion gave the binuclear, bis(five-coordinate), M$_2$(L*)$_2$(C$_2$O$_4$) complex.

Introduction

The ability to synthesize, in controlled fashion, transition-metal complexes containing several different ligands is an important desideratum in coordination chemistry. From that point of view, a gap existed in the area of polypyrazolylborate ligands, where among the plethora of reported complexes[1] only a few ML*L compounds are represented, containing one [RB(pz*)$_3$]$^-$ (=L*) and a different polydentate ligand, L. No examples have been reported for first-row transition metals,[2] and examples for second row metals as, for instance, Ru(B(pz)$_4$)(η^6-C$_6$H$_6$)$^+$ and Rh(HB-(pz)$_3$)(η^5-C$_5$H$_5$)$^+$ contain only carbocyclic π-donors as L.[3] They

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(1) (a) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115-210. (b) Trofimenko, S. *Chem. Rev.* **1972**, *72*, 497-509. (c) Trofimenko, S. *Acc. Chem. Res.* **1971**, *4*, 17-22.

(2) Two compounds, Cu(HB(3,5-Me$_2$pz)$_3$)(R$_2$NCS$_2$) (Thompson, J. S.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4180-4192) and Co(*p*-BrC$_6$H$_4$B(pz)$_3$)(HB(3,5Me$_2$pz)$_3$) (cited in ref 1a as a personal communication) have been mentioned, but not structural proof or experimental data were given.

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Table I. Properties of ML*L Complexes (L = Other Polypyrazolylborate Ligands)

complex	color	anal. calcd (found), % C	H	N	mp, °C	IR, cm^{-1}
CoL*(HB(pz)$_3$)	yellow	38.2 (38.3)	4.13 (4.24)	19.8 (20.0)	above 275	2490, sh 2508, 2450, sh 2460
NiL*(HB(pz)$_3$)	lilac	38.2 (38.4)	4.13 (4.00)	19.8 (20.1)	above 275	2490, sh 2508, 2450, sh 2460
ZnL*(HB(pz)$_3$)	white	37.9 (38.3)	4.10 (4.40)	19.7 (20.1)	254–256	2490, sh 2508, 2450, sh 2460
FeL*(HB(pz)$_3$)	white	38.3 (38.5)	4.14 (4.32)	19.9 (19.7)	260 dec	2490, sh 2508, 2450, sh 2460
CoL*(HB(3,5-Me$_2$pz)$_3$)	yellow	42.5 (42.4)	5.04 (5.27)	18.0 (18.3)	302–305	2520, 2475
NiL*(HB(3,5-Me$_2$pz)$_3$)	lilac	42.5 (42.6)	5.04 (5.26)	18.0 (18.5)	301–304	2520, 2470
CoL*(HB(3-Phpz)$_3$)	wine red	50.2 (50.1)	4.37 (4.58)	15.6 (15.8)	142–146	2490 (br), 2290, 2175
NiL*(HB(3-Phpz)$_3$)	green	50.2 (50.4)	4.37 (4.65)	15.6 (15.9)	197–201	2490 (br), 2150, 2120
CoL*(H$_2$B(pz)$_2$)	wine red	36.8 (36.9)	4.22 (4.26)	17.9 (17.7)	208–214, turns blue	2460, 2440, 2430, 2360, 2330, 2275, 2240
NiL*(H$_2$B(pz)$_2$)	greenish blue	36.8 (36.6)	4.22 (4.24)	17.9 (18.1)	261–263, turns red	2460, 2440, 2430, 2360, 2330, 2275, 2240
CoL*(H$_2$B(3,5-Me$_2$pz)$_2$)	wine red	40.1 (40.4)	4.89 (5.07)	16.8 (16.8)	219–221	2470 (vs), 2355, 2310, 2265, 2225
NiL*(H$_2$B(3,5-Me$_2$pz)$_2$)	pale blue	40.1 (40.4)	4.89 (5.10)	16.8 (16.9)	269–272	2470 (vs), 2355, 2310, 2260, 2220
CoL*(H$_2$B(3-Phpz)$_2$)	wine red	46.3 (46.5)	4.39 (4.44)	15.0 (15.3)	190–192	2480 (vs), 2230, 2195, 2160
NiL*(H$_2$B(3-Phpz)$_2$)	greenish blue	46.3 (46.6)	4.39 (4.47)	15.0 (15.0)	125–127, turns red	2470 (vs), 2180, 2140, 2120, 2060
CoL*(Ph$_2$B(pz)$_2$)	wine red	46.1 (46.5)	4.38 (4.49)	14.9 (14.9)	238–240	2495, 2480
NiL*(Ph$_2$B(pz)$_2$)	lilac blue	46.1 (46.4)	4.38 (4.46)	14.9 (14.8)	286–289	2495, 2480
CoL*(B(3-Phpz)$_4$)	deep violet	53.2 (53.4)	4.35 (4.42)	16.1 (16.3)	155–159	
NiL*(B(3-Phpz)$_4$)	pale green	53.2 (53.5)	4.35 (4.47)	16.1 (16.2)	2510	

Table II. Properties of ML*L Complexes (L = Acetylacetonate, Tropolonate, Diethyldithiocarbamate, and 0.5 Oxalate)

complex	color	anal. calcd (found), % C	H	N	mp, °C	IR, cm^{-1}
CoL*(AcAc)	wine red	37.6 (37.9)	4.36 (4.51)	11.4 (11.5)	149–151	2490, 2465, 2450
NiL*(AcAc)	green	37.6 (37.7)	4.36 (4.41)	11.4 (11.2)	210–212	2490, 2470
NiL*(tropolonate)	lime green	39.7 (40.1)	3.97 (4.00)	11.1 (11.3)	230–232	2490 (br)
NiL*(Et$_2$NCS$_2$)	green	35.3 (35.6)	4.47 (4.45)	12.5 (12.4)	sinters 240, melts above 280	2490, 2470
(NiL*)$_2$(C$_2$O$_4$)	green	33.6 (33.9)	3.69 (3.79)	12.4 (12.6)	255–265	2490, 2470

were prepared by the reaction of a polypyrazolylborate ion with MLX (L = C_5H_5, C_5Me_5, a diene, or η^3-allyl). No ML*L complexes were reported where L would be another bi- or tridentate polypyrazolylborate or, for that matter, any other heteroatom-coordinated polydentate ligand. The reason for this lack of ML*L complexes is the absence of stable polypyrazolylborate ML*X (X = leaving group, usually halide) complexes, which could react, in a controlled fashion, with L to produce ML*L species. Attempts to prepare ML*L either led immediately to ML^*_2 complexes, or to unstable ML*X dimers, which readily underwent ligand-exchange reactions to form ML^*_2 and MX_2. On the other hand, the very stable M(HB(3-*t*-Bupz)$_3$)X complexes[4] were too unreactive to be useful.

A good candidate for L* should, first of all, be easily obtainable in pure form, such as a K or Tl salt; it should be reluctant to form ML^*_2, while producing readily stable ML*X complexes with sufficient accessibility of the metal ion to permit displacement of X by L. All these requirements are met by L* = [HB(3-*i*-Pr-4-Br-pz)$_3$]$^-$.[5] Its K and Tl salts are crystalline and convenient to work with (unlike their 4-H analogues), it forms stable tetrahedral ML*Cl complexes, which show no noticeable tendency for ligand-exchange reactions to form ML^*_2 and MCl_2, and at the same time, the metal is readily accessible to donor molecules, forming ML*Cl·Solv$_n$ complexes of varying lability. It appeared, therefore, that compounds ML*Cl might be excellent starting materials for synthesizing ML*L species, with a high degree of specificity.

We report here a representative variety of such mixed complexes, which have been characterized by spectroscopic techniques as well as by X-ray crystallography of key compounds. The emphasis here is primarily on mixed polypyrazolylborate complexes ML*(HB(pz*)$_3$), ML*(H$_2$B(pz*)$_2$), ML*(B(pz*)$_4$), and ML*(Ph$_2$B(pz)$_2$), although complexes where L was any of several simple bidentate ligands are also reported. Although we chose to limit ourselves to ML*L complexes of first-row metals, the same approach should also be valid for those of lower rows.

Experimental Section

The complexes ML*Cl,[5] and the ligands KH$_2$B(pz)$_2$, KHB(pz)$_3$, KB(pz)$_4$,[6] KH$_2$B(3,5-Me$_2$pz)$_2$, KHB(3,5-Me$_2$pz)$_3$,[7] KH$_2$B(3-Phpz)$_2$, KHB(3-Phpz)$_3$, KB(3-Phpz)$_4$,[4] and KPh$_2$B(pz)$_2$[8] were prepared by literature procedures. All the other chemicals were reagent grade, and used as received. Elemental analyses were done by Microanalysis, Inc., Wilmington, DE. Infrared spectra were obtained as Nujol mulls with a Perkin-Elmer 283-B infrared spectrophotometer. Proton NMR spectra were obtained with a Nicolet NT360WB spectrometer. Diamagnetic compounds were studied with typical conditions of 16K data points, a sweep width of 3000-4000 Hz, 90° pulse angles, and a recycle time of 4-5 s. Paramagnetic compounds were studied with 64K data points, a sweep width of 100 KHz, 45° pulse angles, and a recycle time of 1.2 s.

Synthesis of ML*L Complexes (M = Fe, Co, Ni, Zn; L = Other Polypyrazolylborate Ligands). An equimolar mixture of ML*Cl and of the appropriate KL or TlL salt was stirred at room temperature in dichloromethane. Except for L = [HB(3,5-Me$_2$pz)$_3$]$^-$, which required stirring overnight, the reactions were complete in less than 0.5 h, as manifested by a change of color from that characteristic of the tetrahedral ML*Cl species to that of ML*L. The mixtures were filtered through a bed of Celite and alumina to remove KCl or TlCl, and the filtrates were then evaporated to dryness. The residues were purified by chromatography on alumina and then by recrystallization from heptane or toluene–heptane mixtures. In the case of L = [HB(3,5-Me$_2$pz)$_3$]$^-$, the ML*L complex was too insoluble in dichloromethane; the reaction mixture had to be evaporated to dryness, and the residue was boiled in toluene and filtered to remove TlCl. Properties of these products are listed in Table I.

NMR Spectra of ML*L Complexes (ppm, Relative Ratios, Assignments). CoL*(HB(pz)$_3$): 108.4, 106.8, 86.2, 84.5, 42.3, −35.2, −96.3, −126.1; 1:1:1:1:1:6:1:1 (BH, BH', 5H, 5H', 4H, *i*-Pr-Me, 3H, *i*-Pr-H).

CoL*(HB(3,5-Me$_2$pz)$_3$): 94.8, 94.0, 75.4, 50.1, 40.8, −28.5, −67.1, −104.5; 1:1:1:1:3:6:3:1 (BH, BH', 5H, 4H, 5Me, *i*-Pr-Me, 3Me, *i*-Pr-H).

ZnL*(HB(pz)$_3$): d, 7.68; s, 7.56; d, 7.21; t, 6.03; septet, 1.86; d, 0.83 (1:1:1:1:1:6).

Synthesis of ML*L Complexes (M = Co, Ni, Zn; L = Acetylacetonate, Tropolonate, Diethyldithiocarbamate, $^1/_2$ Oxalate). An equimolar mixture of ML*Cl and HL (HL = acetylacetone, tropolone, oxalic acid) was stirred in dichloromethane, and an equivalent amount of triethylamine was added in one portion. The color changed rapidly to that of the five-coordinate species (Co, blue to wine-red; Ni, red to green). An equal

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Table III. Crystal Data for Ni(HB(3-*i*-Pr-4-Br-pz)$_3$)(HB(pz)$_3$) (I), [Co(HB(3-*i*-Pr-4-Br-pz)$_3$)(HB(3-Phpz)$_3$)](C_6H_6) (II), [Co(HB(3-*i*-Pr-4-Br-pz)$_3$)(H_2B(3-Phpz)$_2$)](C_6H_6)$_2$ (III), and Co(HB(3-*i*-Pr-4-Br-pz)$_3$)(Ph_2B(pz)$_2$) (**IV**)

	I	II	III	IV
mol formula	$C_{39}H_{47}B_2Br_3N_{12}Ni$	$C_{51}H_{53}B_2Br_3CoN_{12}$	$C_{48}H_{53}B_2Br_3CoN_{10}$	$C_{48}H_{53}B_2Br_3CoN_{10}$
M_r	1003.95	1154.35	1090.30	1090.30
a, Å	9.764 (2)	22.269 (3)	11.343 (1)	10.570 (1)
b, Å	16.804 (4)	22.299 (3)	11.426 (1)	16.717 (4)
c, Å	13.673 (5)	21.216 (5)	20.716 (6)	14.918 (4)
α, deg	90	90	80.74 (1)	90
β, deg	96.35 (2)	90	80.80 (1)	108.35 (1)
γ, deg	90	90	74.25 (1)	90
V, Å^3	2229.6	10535.4	2531.3	2501.9
Z	2	8	2	2
space group	$P2_1/m$	$Pbca$	$P\bar{1}$	$P2_1/m$
radiation (λ, Å)		Mo Kα (0.71069) from graphite monochromator		
temp, °C	−70	−70	−70	−70
abs coeff, cm^{-1}	31.41	26.24	27.25	27.57
R	0.044	0.062	0.064	0.055
R_w	0.042	0.047	0.068	0.045

volume of water was added, and after the mixture was stirred, the organic layer was separated and passed through a short alumina column. The eluate was evaporated to dryness, and the residue was recrystallized from heptane. For diethyldithiocarbamate derivatives, the commercial sodium salt was used in the first step. Properties of these complexes are listed in Table II.

X-ray Data Collection and Structure Solution and Refinement. [Ni(HB(3-*i*-Pr-4-Br-pz)$_3$)(HB(pz)$_3$)](C_6H_6)$_2$ (I). Crystals suitable for diffraction were obtained by evaporation of solvent from a benzene solution of the compound. The crystal was encapsulated in a glass capillary, then was placed on the Enraf-Nonius CAD4 diffractometer, and was shown to be suitable for diffraction on the basis of ω-scans, which showed the peak width at half-height to be ca. 0.20° at −70 °C. The cell parameters were then refined on the basis of 25 reflections chosen from diverse regions of reciprocal space. These parameters and other crystallographic data are summarized in Table III. Intensity data collection by the ω-scan technique, intensity measurements of standard reflections, empirical corrections for absorption, and data processing were performed as described elsewhere.[9]

The structure was solved by automated Patterson analysis (PHASE). The function minimized is given elsewhere.[9] Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[10] Hydrogen atom positions were calculated with C–H and B–H distances of 0.95 Å. Least-squares refinement converged to $R = 0.044$ and R_w 0.042 (R_w and w are described elsewhere[4]). All peaks in the final difference Fourier map were less than or equal to 0.48 e/Å^3.

The final positional and thermal parameters of the refined atoms appear in Table IV. Tables of general temperature factors, calculated hydrogen atom positions, and structure factor amplitudes, a complete listing of bond distances and angles, and a complete listing of crystallographic data are available (see paragraph at end of paper regarding supplementary material).

[Co(HB(3-*i*-Pr-4-Br-pz)$_3$)(HB(3-Phpz)$_3$)](C_6H_6) (II). Crystals suitable for diffraction studies were obtained by vapor diffusion of hexane into a benzene solution of the compound. The crystal was handled as described above, placed on a Enraf-Nonius CAD4 diffractometer, and shown to be suitable for diffraction studies on the basis of ω-scans, which showed the peak width at half-height to be 0.15° in ω at −70 °C. The cell parameters were refined on the basis of 25 reflections chosen from diverse regions of reciprocal space. These parameters and other crystallographic data are summarized in Table III. Intensity data collection, intensity measurements of standard reflections, and data processing were performed as described above. Data were adjusted for a 5% decrease in intensity. An empirical absorption correction was carried out (DIFABS).

The structure was solved by direct methods (Multan) and refined as described above. The asymmetric unit consists of the complex with one molecule of benzene, each in a general position. The atoms were refined anisotropically except for several carbon atoms on the pyrazolyl phenyl groups (C(34), C(43), C(52'), and C(65)) and the H atoms, which were idealized with C–H distances of 0.95 Å and B–H distances of 1.0 Å. Atom C(65') was successfully refined as two half-weighted atoms in its highly anisotropic phenyl ring. Least-squares refinement converged to values of $R = 0.062$ and $R_w = 0.047$. All peaks in the final difference map were less than or equal to 0.72 e/Å^3, with the largest residual density near Co(1).

Table IV. Fractional Coordinates (×10^4) and Isotropic Thermal Parameters for Ni(HB(3-*i*-Pr-4-Br-pz)$_3$)(HB(pz)$_3$) (I)

atom	x	y	z	B_{eq},[a] Å^2
Br(1)	6677.3 (6)	−439.1 (3)	1432.7 (5)	3.2 (1)
Br(2)	1490.5 (13)	2500.0	−3233.7 (7)	5.6 (1)
Ni(1)	2935.9 (10)	2500.0	1286.4 (7)	1.5 (1)
N(11)	5407 (4)	1752 (2)	595 (3)	1.8 (1)
N(12)	4494 (4)	1620 (2)	1265 (3)	1.8 (1)
N(21)	3957 (6)	2500	−708 (4)	1.7 (2)
N(22)	2731 (6)	2500	−316 (4)	1.6 (2)
N(31)	402 (4)	1760 (2)	1894 (3)	1.9 (1)
N(32)	1405 (4)	1655 (2)	1289 (3)	1.8 (1)
N(41)	1805 (7)	2500	3214 (4)	2.3 (2)
N(42)	3027 (6)	2500	2811 (4)	2.2 (2)
C(13)	4764 (5)	890 (3)	1653 (4)	2.0 (1)
C(14)	5859 (5)	568 (3)	1197 (4)	2.1 (1)
C(15)	6224 (5)	1112 (3)	550 (4)	2.2 (1)
C(16)	4001 (6)	558 (3)	2457 (4)	2.6 (2)
C(17)	4946 (7)	469 (4)	3412 (4)	4.2 (2)
C(18)	3323 (6)	−241 (3)	2171 (5)	3.5 (2)
C(23)	1742 (8)	2500	−1061 (5)	1.9 (2)
C(24)	2362 (9)	2500	−1949 (5)	2.4 (2)
C(25)	3740 (8)	2500	−1691 (6)	2.4 (2)
C(26)	223 (8)	2500	−938 (5)	2.2 (2)
C(27)	−503 (6)	1756 (4)	−1383 (4)	3.2 (2)
C(33)	1113 (5)	981 (3)	803 (4)	2.2 (1)
C(34)	−88 (6)	646 (3)	1088 (4)	2.7 (2)
C(35)	−496 (6)	1156 (3)	1775 (4)	2.5 (1)
C(43)	4027 (8)	2500	3557 (6)	2.7 (2)
C(44)	3459 (10)	2500	4436 (6)	3.6 (3)
C(45)	2091 (9)	2500	4205 (6)	3.0 (3)
C(51)	8880 (9)	−474 (5)	4756 (8)	6.4 (3)
C(52)	9342 (10)	−331 (5)	5713 (7)	6.2 (3)
C(53)	9547 (12)	−131 (6)	4040 (6)	6.7 (3)
C(61)	3285 (8)	7098 (4)	3780 (5)	5.3 (2)
C(63)	2636 (9)	6692 (4)	4453 (6)	5.6 (3)
C(64)	1998 (7)	7094 (4)	5129 (5)	5.5 (2)
B(1)	5344 (9)	2500	−51 (6)	1.9 (2)
B(2)	457 (9)	2500	2562 (6)	2.1 (2)

[a] $B_{eq} = {}^4/_3\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$.

The final positional parameters for the non-hydrogen atoms appear in Table V. Tables of general temperature factors, calculated hydrogen atom positions, and structure factor amplitudes, a complete listing of bond distances and angles, and a complete listing of crystallographic data are available (see paragraph at end of paper regarding supplementary material).

[Co(HB(3-*i*-Pr-4-Br-pz)$_3$)(H_2B(3-Phpz)$_2$)](C_6H_6)$_2$ (III). Crystals suitable for diffraction studies were obtained by evaporation of a benzene solution of the compound. The crystal was handled as described above, placed on an Enraf-Nonius CAD4 diffractometer, and shown to be suitable for diffraction studies on the basis of ω-scans, which showed the peak width at half-height to be 0.14° in ω at −70 °C. The cell parameters were refined on the basis of 25 reflections chosen from diverse regions of reciprocal space. These parameters and other crystallographic data

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(9) Thompson, J. S.; Harlow, R. L.; Whitney, J. F. *J. Am. Chem. Soc.*, **1983**, *105*, 3522–3527.

(10) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV: (a) Table 2.2B; (b) Table 2.31.

Table V. Fractional Coordinates (×10^4) and Isotropic Thermal Parameters for [Co(HB(3-*i*-Pr-4-Br-pz)$_3$)(HB(3-Phpz)$_3$)](C$_6$H$_6$) (II)

atom	x	y	z	B_{eq},[a] Å^2
Br(1)	1446 (1)	2536 (1)	−254 (1)	5.7 (1)
Br(2)	2860 (1)	6396 (1)	712 (1)	8.8 (1)
Br(3)	4196 (1)	2663 (1)	2713 (1)	6.6 (1)
Co(1)	1950 (1)	4148 (1)	2045 (1)	1.9 (1)
N(11)	2394 (5)	3659 (5)	814 (5)	2.8 (4)
N(12)	1910 (5)	3606 (4)	1200 (4)	1.9 (3)
N(21)	2781 (5)	4663 (5)	1137 (5)	2.7 (4)
N(22)	2357 (5)	4843 (5)	1544 (5)	2.5 (4)
N(31)	3172 (5)	3722 (5)	1654 (5)	2.7 (4)
N(32)	2795 (4)	3693 (4)	2163 (4)	1.9 (3)
N(41)	752 (5)	4034 (4)	2479 (5)	2.3 (3)
N(42)	1020 (4)	4344 (4)	1997 (5)	2.3 (3)
N(51)	1547 (5)	4073 (4)	3313 (5)	2.3 (3)
N(52)	1963 (5)	4411 (4)	3019 (4)	1.8 (3)
N(61)	823 (5)	3194 (5)	3271 (5)	2.1 (3)
N(62)	442 (5)	3348 (5)	3737 (5)	3.0 (4)
C(13)	1518 (6)	3243 (6)	916 (6)	2.2 (4)
C(14)	1769 (6)	3049 (6)	365 (7)	2.7 (4)
C(15)	2306 (7)	3316 (6)	306 (6)	2.5 (4)
C(17)	897 (6)	2400 (6)	1351 (6)	3.9 (5)
C(18)	404 (6)	3243 (6)	807 (7)	4.3 (5)
C(23)	2310 (6)	5429 (7)	1475 (6)	2.7 (5)
C(24)	2719 (8)	5623 (6)	1036 (7)	3.5 (5)
C(25)	3000 (6)	5131 (9)	828 (6)	4.0 (5)
C(26)	1882 (7)	5799 (6)	1860 (6)	3.3 (5)
C(27)	1470 (7)	6197 (6)	1472 (7)	5.3 (5)
C(28)	2196 (8)	6203 (7)	2323 (7)	7.0 (6)
C(33)	3078 (6)	3352 (5)	2600 (5)	1.9 (4)
C(34)	3619 (6)	3171 (5)	2346 (6)	2.4 (3)*
C(35)	3660 (6)	3403 (6)	1762 (6)	3.4 (5)
C(36)	2799 (6)	3223 (6)	3221 (6)	2.6 (4)
C(37)	2656 (5)	2558 (6)	3291 (6)	3.9 (4)
C(38)	3197 (6)	3450 (5)	3756 (6)	4.0 (5)
C(41′)	645 (6)	4947 (6)	1084 (6)	2.3 (4)
C(42′)	1098 (6)	4851 (6)	667 (7)	2.7 (4)
C(43)	566 (7)	4596 (6)	1665 (6)	2.4 (3)
C(43′)	1130 (6)	5176 (7)	115 (7)	4.0 (5)
C(44)	22 (6)	4458 (6)	1940 (6)	3.2 (5)
C(44′)	713 (8)	5616 (6)	−3 (7)	4.1 (5)
C(45)	151 (6)	4110 (6)	2452 (7)	3.5 (5)
C(45′)	258 (7)	5709 (7)	414 (8)	4.1 (5)
C(46′)	221 (6)	5384 (7)	937 (6)	3.3 (5)
C(51′)	2795 (6)	5102 (6)	3357 (6)	2.6 (4)
C(52′)	3185 (6)	5015 (5)	2868 (6)	2.6 (3)*
C(53)	2276 (6)	4708 (6)	3460 (7)	2.1 (4)
C(53′)	3655 (7)	5406 (7)	2779 (7)	4.9 (5)
C(54)	2038 (7)	4545 (6)	4047 (6)	3.2 (5)
C(54′)	3737 (7)	5881 (8)	3192 (10)	5.9 (7)
C(55)	1601 (6)	4142 (6)	3935 (6)	2.6 (4)
C(55′)	3363 (8)	5965 (7)	3654 (9)	4.8 (6)
C(56′)	2888 (7)	5594 (7)	3741 (6)	3.3 (5)
C(61′)	−268 (6)	2872 (7)	4420 (6)	2.9 (5)
C(62′)	−272 (7)	3319 (7)	4844 (7)	4.2 (5)
C(63)	175 (6)	2850 (7)	3917 (6)	1.9 (4)
C(63′)	−686 (9)	3349 (8)	5315 (8)	6.2 (7)
C(64)	359 (6)	2367 (6)	3561 (6)	2.8 (4)
C(64′)	−1111 (8)	2893 (10)	5387 (7)	5.4 (7)
C(65)	783 (6)	2598 (6)	3161 (6)	2.7 (4)
C(65′)	−1069 (19)	2337 (17)	4880 (18)	3.3 (11)*
C(65″)	−1147 (18)	2520 (20)	5012 (20)	2.9 (9)*
C(71)	627 (10)	5354 (12)	3380 (13)	7.7 (9)
C(72)	445 (12)	5832 (12)	3062 (9)	8.5 (9)
C(73)	−107 (15)	6048 (10)	3200 (15)	9.6 (11)
C(74)	−435 (12)	5785 (17)	3692 (19)	12.1 (15)
C(75)	−245 (14)	5304 (12)	3939 (14)	10.7 (11)
C(76)	277 (15)	5084 (11)	3832 (15)	10.4 (11)
B(1)	2946 (7)	3999 (7)	1033 (7)	3.0 (6)
B(2)	1172 (7)	3645 (7)	2912 (7)	2.3 (5)

[a] B_{eq} defined in Table IV. Values marked with an asterisk are B_{iso} values for atoms refined isotropically, here and in subsequent tables.

are summarized in Table III. Intensity data collection, intensity measurements of standard reflections, and data processing were performed as described above. Data were adjusted for a 12% decrease in intensity. No absorption correction was applied.

Table VI. Fractional Coordinates (×10^4) and Isotropic Thermal Parameters for [Co(HB(3-*i*-Pr-4-Br-pz)$_3$)(H$_2$B(3-Phpz)$_2$)](C$_6$H$_6$)$_2$ (III)

atom	x	y	z	B_{eq},[a] Å^2
Br(1)	−3621 (1)	6291 (1)	2640 (1)	4.6 (1)
Br(2)	1811 (1)	−1898 (1)	3181 (1)	5.1 (1)
Br(3)	1318.5 (9)	3848.2 (9)	−785.2 (4)	3.5 (1)
Co(1)	1843.5 (5)	3426.7 (9)	2168.1 (5)	1.3 (1)
N(11)	−812 (5)	3526 (5)	2112 (3)	1.4 (2)
N(12)	−110 (5)	4224 (5)	2283 (3)	1.4 (2)
N(21)	638 (5)	1414 (5)	2205 (3)	1.6 (2)
N(22)	1603 (5)	1634 (5)	2456 (3)	1.5 (2)
N(31)	595 (5)	2811 (5)	1138 (3)	1.4 (2)
N(32)	1484 (5)	3399 (5)	1175 (3)	1.5 (2)
N(41)	4117 (6)	4102 (6)	1882 (3)	2.0 (2)
N(42)	3784 (5)	3049 (5)	1845 (3)	1.6 (2)
N(51)	2773 (6)	4738 (5)	2916 (3)	2.1 (2)
N(52)	2009 (6)	3967 (5)	3075 (3)	1.7 (2)
C(13)	−935 (7)	5217 (7)	2499 (3)	1.6 (2)
C(14)	−2129 (7)	5157 (7)	2466 (4)	2.0 (2)
C(15)	−1997 (7)	4053 (7)	2227 (4)	1.9 (2)
C(16)	−496 (7)	6200 (7)	2738 (4)	2.0 (2)
C(17)	−791 (9)	7413 (8)	2265 (5)	3.9 (3)
C(18)	−1027 (9)	6398 (8)	3434 (4)	3.5 (3)
C(23)	2136 (7)	601 (7)	2811 (4)	1.7 (2)
C(24)	1494 (7)	−270 (6)	2783 (4)	2.2 (2)
C(25)	582 (7)	265 (7)	2411 (4)	2.0 (2)
C(26)	3213 (8)	486 (7)	3172 (4)	2.6 (3)
C(27)	2903 (9)	247 (8)	3913 (5)	3.9 (3)
C(28)	4335 (8)	−501 (9)	2944 (5)	4.0 (3)
C(33)	1878 (7)	3807 (6)	562 (4)	1.7 (2)
C(34)	1232 (7)	3450 (7)	131 (4)	2.0 (2)
C(35)	455 (7)	2840 (6)	507 (4)	1.9 (2)
C(36)	2899 (7)	4478 (7)	408 (4)	2.2 (2)
C(37)	2382 (8)	5820 (7)	141 (4)	2.8 (3)
C(38)	3958 (7)	3837 (7)	−54 (4)	2.8 (3)
C(41′)	4805 (8)	1105 (8)	1369 (4)	2.5 (3)
C(42′)	3757 (8)	811 (7)	1250 (4)	3.0 (3)
C(43)	4769 (7)	2330 (7)	1532 (4)	2.1 (2)
C(43′)	3816 (10)	−358 (9)	1111 (5)	4.4 (4)
C(44)	5735 (7)	2915 (8)	1371 (4)	2.7 (3)
C(44′)	4912 (13)	−1206 (9)	1080 (6)	5.9 (5)
C(45)	5252 (8)	4032 (8)	1599 (4)	2.7 (3)
C(45′)	5975 (11)	−929 (10)	1165 (6)	6.1 (4)
C(46′)	5925 (8)	209 (9)	1323 (5)	3.8 (3)
C(51′)	900 (8)	3129 (7)	4103 (4)	2.4 (3)
C(52′)	54 (8)	2770 (7)	3812 (4)	2.5 (3)
C(53)	1747 (7)	3847 (7)	3735 (4)	2.1 (2)
C(53′)	−720 (8)	2103 (8)	4160 (4)	3.2 (3)
C(54)	2365 (8)	4543 (8)	3993 (4)	2.8 (3)
C(54′)	−648 (10)	1746 (9)	4822 (5)	4.5 (4)
C(55)	2980 (8)	5073 (7)	3472 (4)	2.6 (3)
C(55′)	151 (11)	2089 (11)	5123 (5)	5.2 (4)
C(56′)	914 (9)	2767 (9)	4776 (4)	3.7 (3)
C(61)	687 (10)	356 (10)	−561 (5)	4.5 (4)
C(62)	590 (11)	−695 (9)	498 (5)	4.5 (4)
C(62′)	1259 (9)	−334 (10)	−68 (6)	4.2 (4)
C(71)	6874 (14)	1090 (15)	3070 (6)	6.3 (5)
C(72)	5934 (12)	1983 (12)	3250 (7)	5.5 (5)
C(73)	5473 (10)	2002 (10)	3890 (7)	5.7 (5)
C(74)	5952 (12)	1076 (12)	4342 (5)	5.5 (5)
C(75)	6906 (12)	174 (11)	4157 (7)	5.7 (5)
C(76)	7373 (12)	148 (11)	3528 (8)	6.1 (5)
C(81)	4885 (39)	4092 (25)	5437 (11)	9.1 (10)
C(82)	5910 (26)	3958 (21)	5039 (17)	8.6 (8)
C(83)	6022 (25)	4908 (40)	4571 (12)	9.4 (10)
B(1)	−167 (8)	2393 (8)	1762 (5)	1.8 (3)
B(2)	3127 (9)	5115 (9)	2188 (5)	2.5 (3)

[a] Defined as in Table IV.

The structure was solved by automated Patterson analysis (PHASE), and refinement was performed as described above. The asymmetric unit requires two half-molecules of benzene and one in a general position per Co atom. C–H and B–H bond lengths were idealized at 0.95 Å. Least-squares refinement converged to values of $R = 0.064$ and $R_w = 0.068$. All peaks in the final difference map were less than or equal to 1.14 e/Å^3, with the largest residual density near Co(1).

The final positional parameters for the non-hydrogen atoms appear in Table VI. Tables of general temperature factors, calculated hydrogen

Table VII. Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters for Co(HB(3-*i*-Pr-4-Br-pz)$_3$)(Ph$_2$B(pz)$_2$) (IV)

atom	x	y	z	B_{eq},^{a} Å^2
Br(1)	9528 (1)	2500	5600 (1)	7.5 (1)
Br(2)	994.9 (9)	121.0 (5)	2955.1 (7)	6.2 (1)
Co(1)	4500 (1)	2500	2171 (1)	2.3 (1)
N(11)	5613 (7)	2500	4267 (6)	2.5 (3)
N(12)	6015 (7)	2500	3476 (6)	2.2 (3)
N(21)	3443 (5)	1763 (3)	3593 (4)	2.4 (2)
N(22)	3382 (5)	1678 (3)	2662 (4)	2.6 (2)
N(31)	5647 (5)	3246 (3)	749 (4)	3.0 (2)
N(32)	5252 (5)	3352 (3)	1529 (4)	2.8 (2)
C(13)	7349 (10)	2500	3782 (8)	2.9 (4)
C(14)	7802 (10)	2500	4773 (8)	3.7 (4)
C(15)	6665 (10)	2500	5035 (7)	3.1 (3)
C(16)	8117 (9)	2500	3070 (7)	3.2 (3)
C(17)	9004 (7)	1754 (5)	3184 (6)	5.2 (3)
C(23)	2551 (6)	1070 (4)	2305 (5)	2.9 (2)
C(24)	2136 (6)	751 (4)	3030 (6)	3.0 (2)
C(25)	2686 (6)	1200 (4)	3810 (5)	2.9 (2)
C(26)	2150 (7)	882 (5)	1279 (6)	4.0 (3)
C(27)	2401 (8)	15 (5)	1068 (6)	5.7 (3)
C(33)	5672 (7)	4073 (5)	1889 (5)	3.9 (3)
C(34)	6287 (9)	4450 (5)	1324 (7)	5.6 (4)
C(35)	6260 (9)	3925 (5)	627 (6)	5.3 (3)
C(41)	6118 (10)	2500	−620 (7)	3.0 (3)
C(42)	5557 (11)	2500	−1568 (9)	5.6 (5)
C(43)	6311 (14)	2500	−2180 (9)	8.1 (7)
C(44)	7612 (13)	2500	−1886 (9)	5.9 (5)
C(45)	8249 (11)	2500	−933 (10)	5.3 (5)
C(46)	7501 (12)	2500	−324 (9)	4.9 (5)
C(51)	3686 (10)	2500	−453 (7)	3.6 (4)
C(52)	3008 (9)	1800 (7)	−764 (6)	7.7 (4)
C(53)	1733 (11)	1798 (13)	−1368 (9)	12.9 (8)
C(54)	1119 (18)	2500	−1679 (17)	18.8 (22)
C(61)	4317 (28)	66 (18)	5955 (17)	12.2 (12)
C(62)	3164 (45)	−317 (10)	5589 (12)	13.9 (16)
C(63)	2048 (21)	0 (17)	5713 (17)	11.9 (10)
C(64)	2161 (19)	644 (16)	6204 (15)	9.1 (8)
C(65)	3298 (33)	992 (7)	6563 (9)	9.6 (7)
C(66)	4412 (17)	687 (17)	6447 (16)	10.9 (8)
B(1)	4121 (11)	2500	4164 (8)	2.6 (4)
B(2)	5241 (12)	2500	81 (8)	2.8 (4)

^{a} As defined in Table IV.

atom positions, and structure factor amplitudes, a complete listing of bond distances and angles, and a complete listing of crystallographic data are available (see paragraph at end of paper regarding supplementary material).

[Co(HB(3-*i*-Pr-4-Br-pz)$_3$)(Ph$_2$B(pz)$_2$)](C$_6$H$_6$)$_2$ (IV). Crystals suitable for diffraction studies were obtained by evaporation of a benzene solution of the compound. The crystal was handled as described above, placed on an Enraf-Nonius CAD4 diffractometer, and shown to be suitable for diffraction studies on the basis of ω-scans, which showed the peak width at half-height to be 0.15° in ω at −70 °C. The cell parameters were refined on the basis of 25 reflections chosen from diverse regions of reciprocal space. These parameters and other crystallographic data are summarized in Table III. Intensity data collection, intensity measurements of standard reflections, and data processing were preformed as described above. Data were adjusted for a 15% decrease in intensity. An empirical absorption correction was carried out (DIFABS).

The structure was solved by automated Patterson analysis (PHASE). The structure refinement was performed as described above. Hydrogen atom positions were calculated with C–H and B–H distances of 0.95 Å. Least-squares refinement converged to values of R = 0.055 and R_w = 0.045. All peaks in the final difference map were less than or equal to 0.56 e/Å^3, with the largest residual density near Br(1).

The final positional parameters for the non-hydrogen atoms appear in Table VII. Tables of general temperature factors, calculated hydrogen atom positions, and structure factor amplitudes, a complete listing of bond distances and angles, and a complete listing of crystallographic data are available (see paragraph at end of paper regarding supplementary material).

Results

The reaction of ML*Cl with [HB(pz)$_3$]$^-$ rapidly produced compounds having colors characteristic of octahedral complexes (Co, yellow; Ni, pale lilac; Fe, very pale green). Their IR spectra were superimposable, and had two sets of sharp BH doublets at 2490 and 2450 cm^{-1}, assigned to [HB(pz)$_3$]$^-$ and L*, respectively. The NMR spectrum of ZnL*(HB(pz)$_3$) showed presence of both ligands, and was consistent with a static or, more likely, dynamic C_{3v} symmetry of the molecule. Stronger support for this structure was obtained from the NMR spectrum of the paramagnetic CoL*(HB(pz)$_3$) complex (Figure 1), which spanned almost 200 ppm and which accounted for every proton of each ligand. Finally, the structure of the isomorphous NiL*(HB(pz)$_3$) was determined by X-ray crystallography to be octahedral and of C_{3v} symmetry (vide infra).

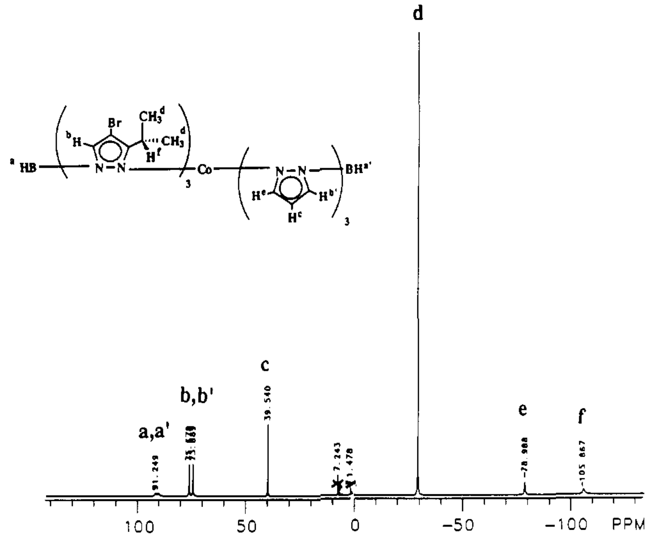

Figure 1. NMR spectrum of Co(HB(3-*i*-Pr-4-Br-pz)$_3$)(HB(pz)$_3$).

When ML*Cl was treated with the more hindered [HB(3,5-Me$_2$pz)$_3$]$^-$ ion, the same type of octahedral structure was obtained, as judged from the colors of the complexes, although the reaction proceeded much more slowly. The BH stretching bands in the IR spectrum were less sharp than in the ML*(HB(pz)$_3$) analogues and were at 2520 and 2490 cm^{-1}. Support for an octahedral structure of C_{3v} symmetry was obtained from the NMR spectrum of ZnL*L, and also from the paramagnetic NMR spectrum of the Co(II) complex CoL*L.

The bidentate ligand [H$_2$B(pz)$_2$]$^-$ also reacted rapidly with ML*Cl to yield ML*L complexes. The Co(II) derivative was wine red, suggesting formation of a five-coordinate complex, but the Ni(II) analogue was bluish lilac, similar in color to octahedral Ni-polypyrazolylborate complexes and quite different from the green color of five-coordinate Ni(II) complexes. The IR spectra had a very complex BH stretching pattern ranging from 2200 to 2500 cm^{-1}. The NMR spectrum of the Zn(II) derivative supported the ML*L structure. The mixed complexes derived from L = [H$_2$B(3,5-Me$_2$pz)$_2$]$^-$ had much simpler IR spectra (as compared with the unmethylated analogues) in the BH stretching region, characterized by a very strong peak at 2470 cm^{-1} and much weaker peaks in the 2200–2360-cm^{-1} range, presumably because of the agostic B–H–M interaction. Similar IR spectra were also obtained for ML*(H$_2$B(3-Phpz)$_2$) complexes. Here, the Co(II) complex still had the pale wine red color, but the Ni complex was bluish green. The question of whether there is an agostic B–H–M interaction was answered affirmatively in the case of the Co(II) complex by an X-ray structure determination, which established that such an interaction does indeed exist, with a Co–H distance of 2.36 Å.

It was of interest to find out what sort of coordination will be present in ML*(Ph$_2$B(pz)$_2$), since compounds involving the [Ph$_2$B(pz)$_2$]$^-$ ligand have the pseudoaxial phenyl group positioned at right angles to the coordinated metal and are thus incapable of any agostic interaction. This type of coordination had been found in the structure determinations of Ni(Ph$_2$B(pz)$_2$)$_2$[11] and Mo(Ph$_2$B(pz)$_2$)(η^3-allyl)(CO)$_2$.[12] With L*, one could consider

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(11) Cotton, F. A.; Murillo, C. A. *Inorg. Chim. Acta* **1976**, *17*, 121–124.

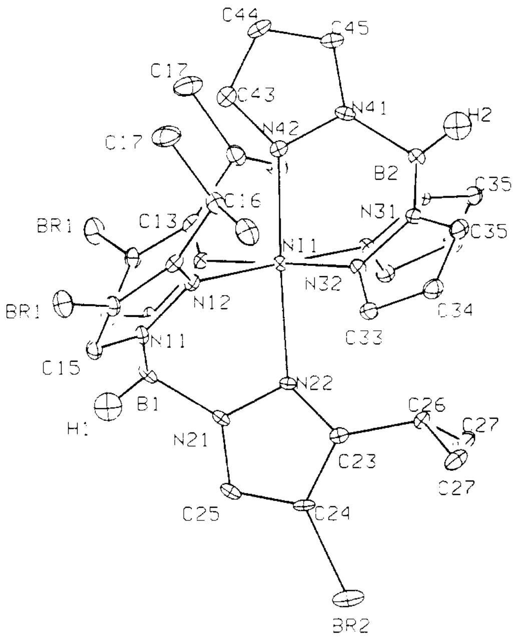

Figure 2. View of $[Ni(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)(HB(pz)_3)](C_6H_6)_2$ (I). The vibrational ellipsoids are drawn at the 50% level in this and the other figures.

Table VIII. Selected Bond Distances (Å) and Angles (deg) for $[Ni(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)(HB(pz)_3)](C_6H_6)_2$ (I)

Ni(1)–N(12)	2.124 (4)	N(31)–N(32)	1.361 (6)
Ni(1)–N(22)	2.177 (6)	N(31)–C(35)	1.339 (6)
Ni(1)–N(32)	2.061 (4)	N(32)–C(33)	1.329 (6)
Ni(1)–N(42)	2.076 (6)	C(33)–C(34)	1.395 (7)
N(11)–N(12)	1.365 (5)	C(34)–C(35)	1.362 (7)
N(11)–C(15)	1.344 (6)	N(11)–B(1)	1.534 (6)
N(12)–C(13)	1.351 (6)	N(21)–B(1)	1.540 (11)
C(13)–C(14)	1.404 (6)	N(31)–B(2)	1.541 (6)
C(13)–C(16)	1.502 (7)	N(41)–B(2)	1.506 (11)
C(14)–C(15)	1.348 (7)	Br(1)–C(14)	1.883 (5)
C(16)–C(17)	1.520 (8)	Br(2)–C(24)	1.865 (5)
C(16)–C(18)	1.529 (8)		
N(12)–Ni(1)–N(12)[a]	88.3 (2)	C(14)–C(13)–C(16)	130.2 (5)
N(12)–Ni(1)–N(22)	88.4 (2)	C(13)–C(14)–C(15)	107.4 (5)
N(12)–Ni(1)–N(32)[a]	179.1 (4)	C(13)–C(16)–C(17)	111.2 (5)
N(12)–Ni(1)–N(32)	92.4 (2)	C(13)–C(16)–C(18)	112.0 (5)
N(12)–Ni(1)–N(42)	93.6 (2)	C(17)–C(16)–C(18)	109.8 (5)
N(22)–Ni(1)–N(32)	90.9 (2)	N(31)–N(32)–C(33)	106.5 (4)
N(22)–Ni(1)–N(42)	177.2 (2)	N(32)–N(31)–C(35)	109.5 (4)
N(32)–Ni(1)–N(32)[a]	87.0 (2)	C(33)–C(34)–C(35)	105.0 (5)
Ni(1)–N(12)–N(11)	114.7 (3)	Br(1)–C(14)–C(13)	126.8 (4)
Ni(1)–N(32)–N(31)	118.9 (3)	Br(1)–C(14)–C(15)	125.8 (4)
N(12)–N(11)–C(15)	109.6 (4)	N(11)–B(1)–N(21)	108.2 (4)
N(11)–N(12)–C(13)	107.3 (4)	N(31)–B(2)–N(41)	108.8 (4)

[a] Symmetry operation $x, {}^1/_2 - y, z$.

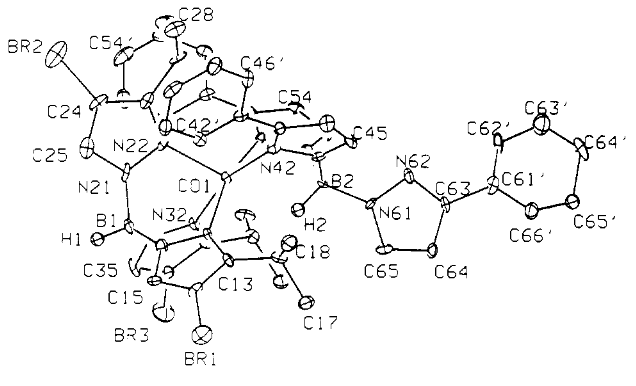

Figure 3. View of $[Co(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)(HB(3\text{-}Phpz)_3)](C_6H_6)$ (II).

the possibility that steric interactions might be reduced if the phenyl group were oriented between the two pz* rings, and this arrangement might lead to an agostic interaction. The complexes $ML^*(Ph_2B(pz)_2)$ for M = Co and Ni were prepared with ease and had colors similar to those of $ML^*(H_2B(pz)_2)$ complexes, where agostic interaction was established. Their IR spectra showed a broad band at 2480 cm^{-1} but gave otherwise no indication of agostic bonding. The absence of such bonding was finally confirmed by an X-ray structure determination for CoL*L, which showed the pseudoaxial phenyl group to be remote from the metal center and L to have the same configuration as previously found.[11,12]

The complex $ML^*(HB(3\text{-}Phpz)_3)$, in contrast to those where L = $[HB(pz)_3]^-$ or $[HB(3,5\text{-}Me_2pz)_3]^-$, had colors similar to those of $ML^*(H_2B(3\text{-}Phpz)_2)$ compounds, suggesting structures other than octahedral. An X-ray structure determinination of $CoL^*(HB(3\text{-}Phpz)_3)$ did show a pseudooctahedral structure, with the sixth coordination site on Co containing an agostic B–H–Co bond of 2.26 Å, even shorter than in the case of L = $[H_2B(3\text{-}Phpz)_2]^-$, and the third 3-Phpz group positioned away from the Co(II) ion.

We next sought to answer the question as to what the structure of ML*L will be when both octahedral coordination *and* the agostic option were ruled out. To this end, $[B(3\text{-}Phpz)_4]^-$ was chosen as L, and ML*L complexes for M = Co(II) and Ni(II) were prepared. While the Ni complex was green, like other five-coordinate ML*L complexes, the Co(II) complex was deep purple, resembling tetrahedral bis-bidentate species. The IR spectra of the Ni(II) and Co(II) derivatives were quite different, indicating different structures. We are, therefore, assigning a five-coordinate structure to NiL*L, similar to that of $NiL^*(Ph_2B(pz)_2)$, whereas for CoL*L both L* and L may be coordinated in bidentate fashion.

A variety of ML*L complexes was also prepared where L was a simple bidentate ligand, devoid of the coordination ambiguities present in the polypyrazolylborate systems. Examples of L were acetylacetonate, tropolonate, diethyldithiocarbamate, and oxalate ion, the latter forming binuclear $M_2L^*_2(C_2O_4)$ complexes. In all instances, the product colors were consistent with a five-coordinate structure.

Description of the Structure of $[Ni(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)(HB(pz)_3)](C_6H_6)_2$ (I). The overall structure of this Ni(II) complex is apparent in the drawing of the molecule (Figure 2) and consists of well-separated neutral monomeric complexes $Ni(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)(HB(pz)_3)$ and two solvent molecules. This structure establishes the formation of a mixed-ligand complex containing two different polypyrazolylborate ligands with a first-row transition-metal ion. The two ligands coordinate to the Ni(II) ion through the nitrogen atom in the 2-position of the pyrazolyl rings to produce an octahedrally coordinated complex. Figure 2 also shows that the substituted ligand has the isopropyl group in the 3-position of each of the rings and the bromine atom in the 4-position; this mode of coordination is seen with all of the structures reported here. This arrangement is in contrast to the structure reported previously, which showed a rearranged polypyrazolylborate ligand: $Co(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_2(5\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz))_2$.[5]

Selected bond distances and angles are presented in Table VIII. The Ni–N distances and angles are typical of first-row transition-metal ions with this ligand. There are no unusual features in this regard. The steric repulsion of the isopropyl groups elongates the Ni–N distances of the substituted ligand compared with those of $[HB(pz)_3]^-$.

Description of the Structure of $[Co(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)(HB(3\text{-}Phpz)_3)](C_6H_6)$ (II). The overall structure of the molecule is apparent in the drawing of molecule (Figure 3) and consists of well-separated neutral, monomeric $Co(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)(HB(3\text{-}Phpz)_3)$ molecules and a solvent molecule. The Co(II) ion is coordinated to two different types of polypyrazolylborate complexes to yield an octahedral complex. The $[HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3]^-$ ligand coordinates to the Co(II) ion through the nitrogen

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(12) Cotton, F. A.; Frenz, B. A.; Murillo, C. A.; *J. Am. Chem. Soc.* **1975**, *97*, 2118–2122.

Table IX. Selected Bond Distances (Å) and Angles (deg) for $[Co(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)(HB(3\text{-}Phpz)_3)](C_6H_6)$ (II)

Co(1)–N(12)	2.164 (9)	N(41)–N(42)	1.371 (11)
Co(1)–N(22)	2.087 (10)	N(41)–C(45)	1.348 (13)
Co(1)–N(32)	2.152 (9)	N(42)–C(43)	1.354 (14)
Co(1)–N(42)	2.117 (9)	C(41′)–C(42′)	1.358 (16)
Co(1)–N(52)	2.149 (10)	C(41′)–C(43)	1.471 (16)
N(11)–N(12)	1.359 (11)	C(41′)–C(46′)	1.392 (16)
N(11)–C(15)	1.334 (14)	C(42′)–C(43′)	1.378 (17)
N(12)–C(13)	1.333 (14)	C(43)–C(44)	1.381 (16)
C(13)–C(14)	1.366 (15)	C(43′)–C(44′)	1.374 (17)
C(13)–C(16)	1.484 (16)	C(44)–C(45)	1.365 (16)
C(14)–C(15)	1.341 (15)	C(44′)–C(45′)	1.360 (18)
C(16)–C(17)	1.517 (16)	C(45′)–C(46′)	1.327 (16)
C(16)–C(18)	1.512 (16)	B(1)–N(11)	1.519 (17)
C(14)–Br(1)	1.884 (13)	B(2)–N(41)	1.572 (16)

N(12)–Co(1)–N(22)	90.6 (4)	Co(1)–N(42)–N(41)	106.7 (8)
N(12)–Co(1)–N(32)	82.5 (4)	Co(1)–N(42)–C(43)	147 (1)
N(12)–Co(1)–N(42)	92.0 (4)	N(42)–N(41)–C(45)	110 (1)
N(12)–Co(1)–N(52)	161.8 (4)	N(41)–N(42)–C(43)	106 (1)
N(22)–Co(1)–N(32)	91.7 (4)	C(42′)–C(41′)–C(43)	123 (1)
N(22)–Co(1)–N(42)	104.4 (4)	C(42′)–C(41′)–C(46′)	118 (1)
N(22)–Co(1)–N(52)	106.4 (4)	C(43)–C(41′)–C(46′)	119 (1)
N(32)–Co(1)–N(42)	163.2 (4)	C(41′)–C(42′)–C(43′)	121 (1)
N(32)–Co(1)–N(52)	90.3 (4)	C(41′)–C(43)–C(44)	125 (1)
N(42)–Co(1)–N(52)	90.2 (4)	C(42′)–C(43′)–C(44′)	120 (1)
Co(1)–N(12)–N(11)	114.7 (8)	C(43)–C(44)–C(45)	106 (1)
Co(1)–N(12)–C(13)	138 (1)	C(43′)–C(44′)–C(45′)	120 (1)
N(12)–C(13)–C(14)	108 (1)	C(44′)–C(45′)–C(46′)	120 (1)
N(12)–C(13)–C(16)	123 (1)	C(41′)–C(46′)–C(45′)	122 (1)
N(11)–C(15)–C(14)	108 (1)	N(11)–B(1)–N(21)	109 (1)
C(14)–C(13)–C(16)	129 (1)	N(11)–B(1)–N(31)	109 (1)
C(13)–C(14)–C(15)	108 (1)	N(21)–B(1)–N(31)	110 (1)
C(13)–C(16)–C(17)	114 (1)	N(41)–B(2)–N(51)	108 (1)
C(13)–C(16)–C(18)	113 (1)	N(41)–B(2)–N(61)	111 (1)
C(17)–C(16)–C(18)	109 (1)	N(51)–B(2)–N(61)	115 (1)
C(13)–C(14)–Br(1)	129 (1)		
C(15)–C(14)–Br(1)	123 (1)		

atom in the 2-position of the pyrazolyl rings, whereas the $[HB(3\text{-}Phpz)_3]^-$ ligand coordinates through the nitrogen atom in the 2-position of two of the three pyrazolyl rings and the hydrogen atom attached to the central boron atom. The overall geometry about the Co(II) ion is octahedral, consistent with the spectroscopic properties of the complex and the color in the solid state. The third pyrazolyl group from the $[HB(3\text{-}Phpz)_3]^-$ ligand is not coordinated to a metal ion.

Selected bond distances and angles are presented in Table IX. The Co(II)–N(pyrazolyl) distances and bond angles are typical of Co(II) complexes with ligands of this type. The Co(II)–H distance of 2.26 Å is in the range of values observed for other agostic hydrogen interactions in Co(II) complexes (2.166–2.26 Å),[13] including that described below (2.37 Å). The coordination of the hydride group to the Co(II) ion leads to a distortion of the octahedral geometry, as evidenced by the nonlinear axial N–Co–H angle of 150.7°. It can be seen in Figure 3 that this Co–H interaction avoids the steric interactions that would be enforced by coordination of three 3-phenylpyrazolyl groups.

Description of the Structure of $[Co(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)(H_2B(3\text{-}Phpz)_2)](C_6H_6)_2$ (III). The overall structure of this Co(II) complex is apparent in the drawing of the molecule (Figure 4) and consists of well-separated neutral monomeric $Co(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)(H_2B(3\text{-}Phpz)_2)$ molecules as well as two well-separated solvent molecules. As in the structure determinations of I and II, the Co(II) ion here is coordinated to two different types of polypyrazolylborate ligands to yield an octahedral complex. The Co(II) coordination sphere is the same as that described above for II. As in that structure, the coordination sphere of the metal ion consists of five pyrazolyl nitrogen atoms and a hydrogen atom from the $[H_2B(3\text{-}Phpz)_2]^-$ ligand.

Selected bond distances and angles are presented in Table X. Co–N(pyrazolyl) and Co–H distances are nearly identical with those for II. There are no other unusual features.

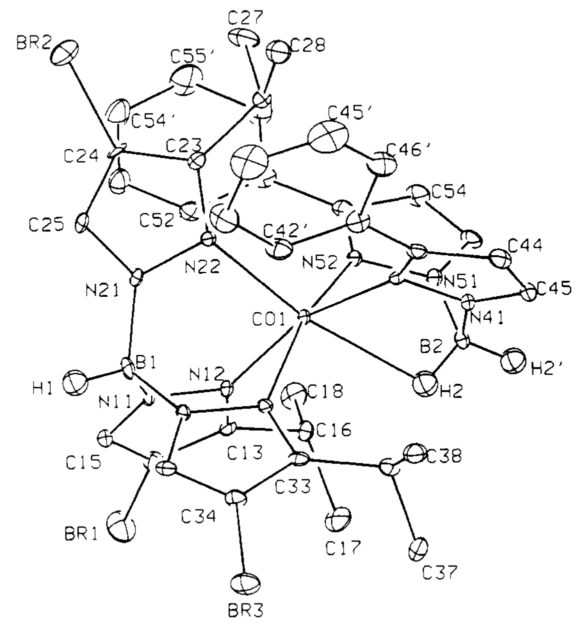

Figure 4. View of $[Co(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)(H_2B(3\text{-}Phpz)_2)](C_6H_6)_2$ (III).

Table X. Selected Bond Distances (Å) and Angles (deg) for $[Co(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)(H_2B(3\text{-}Phpz)_2)](C_6H_6)_2$ (III)

Co(1)–N(12)	2.145 (6)	N(41)–N(42)	1.372 (8)
Co(1)–N(22)	2.117 (6)	N(41)–C(45)	1.314 (9)
Co(1)–N(32)	2.167 (6)	N(42)–C(43)	1.337 (9)
Co(1)–N(42)	2.142 (6)	C(43)–C(44)	1.403 (10)
Co(1)–N(52)	2.120 (6)	C(44)–C(45)	1.373 (11)
N(11)–N(12)	1.387 (7)	C(43)–C(41′)	1.480 (11)
N(11)–C(15)	1.315 (9)	C(41′)–C(42′)	1.387 (11)
N(12)–C(13)	1.347 (9)	C(41′)–C(46′)	1.399 (11)
C(13)–C(14)	1.389 (10)	C(42′)–C(43′)	1.393 (12)
C(13)–C(16)	1.521 (10)	C(43′)–C(44′)	1.352 (14)
C(14)–C(15)	1.390 (10)	C(44′)–C(45′)	1.370 (16)
C(16)–C(17)	1.553 (11)	C(45′)–C(46′)	1.375 (14)
C(16)–C(18)	1.500 (11)	B(1)–N(11)	1.535 (10)
C(14)–Br(1)	1.854 (7)	B(2)–N(41)	1.518 (12)

N(12)–Co(1)–N(22)	92.1 (2)	Co(1)–N(42)–N(41)	105.5 (4)
N(12)–Co(1)–N(32)	81.2 (2)	Co(1)–N(42)–C(43)	147.4 (5)
N(12)–Co(1)–N(42)	164.2 (2)	N(42)–N(41)–C(45)	110.2 (7)
N(12)–Co(1)–N(52)	91.1 (2)	N(41)–N(42)–C(43)	105.8 (6)
N(22)–Co(1)–N(32)	91.2 (2)	N(42)–C(43)–C(41′)	124.0 (7)
N(22)–Co(1)–N(42)	101.3 (2)	N(42)–C(43)–C(44)	110.3 (7)
N(22)–Co(1)–N(52)	102.5 (2)	N(41)–C(45)–C(44)	109.6 (7)
N(32)–Co(1)–N(42)	90.1 (2)	C(43)–C(44)–C(45)	104.2 (7)
N(32)–Co(1)–N(52)	164.6 (2)	C(44)–C(43)–C(41′)	125.7 (8)
N(42)–Co(1)–N(52)	94.0 (2)	C(43)–C(41′)–C(42′)	122.1 (7)
Co(1)–N(12)–N(11)	114.8 (4)	C(43)–C(41′)–C(46′)	119.8 (8)
Co(1)–N(12)–C(13)	140.0 (5)	C(42′)–C(41′)–C(46′)	118.1 (8)
N(12)–N(11)–C(15)	110.8 (6)	C(41′)–C(42′)–C(43′)	120.7 (8)
N(11)–N(12)–C(13)	105.1 (6)	C(42′)–C(43′)–C(44′)	119 (1)
N(12)–C(13)–C(14)	110.5 (6)	C(43′)–C(44′)–C(45′)	121 (1)
N(12)–C(13)–C(16)	120.2 (6)	C(44′)–C(45′)–C(46′)	120 (1)
N(11)–C(15)–C(14)	108.4 (6)	C(41′)–C(46′)–C(45′)	120 (1)
C(14)–C(13)–C(16)	129.3 (7)	N(11)–B(1)–N(21)	111.3 (6)
C(13)–C(14)–C(15)	105.1 (7)	N(11)–B(1)–N(31)	107.6 (6)
C(13)–C(16)–C(17)	110.3 (6)	N(21)–B(1)–N(31)	111.1 (6)
C(13)–C(16)–C(18)	112.2 (6)	N(41)–B(2)–N(51)	111.3 (7)
C(17)–C(16)–C(18)	111.2 (7)	C(15)–C(14)–Br(1)	124.8 (6)
C(13)–C(14)–Br(1)	130.0 (6)		

Description of the Structure of $[Co(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)(Ph_2B(pz)_2)](C_6H_6)_2$ (IV). The overall structure of this Co(II) complex is apparent in the drawing of the molecule (Figure 5) and consists of well-separated neutral monomeric $Co(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)(Ph_2B(pz)_2)$ molecules with associated solvent molecules. This structure determination establishes that the complex consists of a Co(II) ion coordinated to two different

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[13] Trofimenko, S.; Calabrese, J. C.; Thompson, J. S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 205–206.

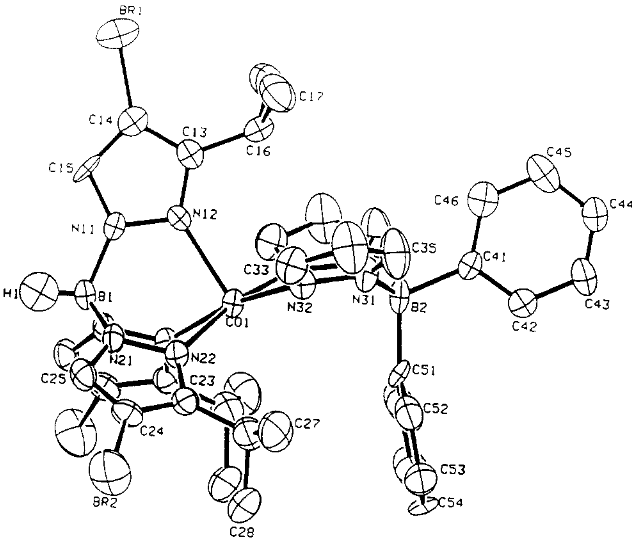

Figure 5. View of Co(HB(3-*i*-Pr-4-Br-pz)$_3$)(Ph$_2$B(pz)$_2$) (IV).

Table XI. Selected Bond Distances (Å) and Angles (deg) for [Co(HB(3-*i*-Pr-4-Br-pz)$_3$)(Ph$_2$B(pz)$_2$)](C$_6$H$_6$)$_2$ (IV)

Co(1)–N(12)	2.095 (8)	N(31)–N(32)	1.365 (7)
Co(1)–N(22)	2.088 (5)	N(31)–C(35)	1.348 (8)
Co(1)–N(32)	2.014 (5)	N(32)–C(33)	1.337 (8)
N(11)–N(12)	1.375 (9)	C(33)–C(34)	1.370 (10)
N(12)–C(13)	1.338 (11)	C(34)–C(35)	1.355 (10)
C(13)–C(14)	1.403 (13)	B(1)–N(11)	1.535 (12)
C(13)–C(16)	1.527 (13)	B(1)–N(21)	1.540 (8)
C(14)–C(15)	1.376 (13)	B(2)–N(31)	1.570 (9)
C(16)–C(17)	1.536 (9)	B(2)–C(41)	1.602 (14)
C(14)–Br(1)	1.854 (10)	B(2)–C(51)	1.585 (15)

N(12)–Co(1)–N(22)	91.5 (2)	N(31)–N(32)–Co(1)	125.9 (4)
N(12)–Co(1)–N(32)	98.1 (2)	N(31)–N(31)–C(33)	107.9 (6)
N(22)–Co(1)–N(22)^a	82.2 (3)	N(32)–N(31)–C(35)	107.2 (6)
N(22)–Co(1)–N(32)^a	93.1 (2)	C(33)–N(32)–Co(1)	125.2 (5)
N(22)–Co(1)–N(32)	169.5 (2)	N(32)–C(33)–C(34)	109.3 (7)
N(32)–Co(1)–N(32)^a	89.9 (3)	N(31)–C(35)–C(34)	109.7 (7)
N(11)–N(12)–Co(1)	116.4 (5)	C(33)–C(34)–C35)	105.9 (7)
N(11)–N(12)–C(13)	106.5 (8)	B(1)–N(11)–N(12)	120.0 (8)
N(12)–N(11)–C(15)	109.9 (8)	B(1)–N(21)–N(22)	120.3 (6)
N(12)–C(13)–C(14)	109 (1)	B(2)–N(31)–N(32)	123.2 (6)
N(12)–C(13)–C(16)	120 (1)	N(11)–B(1)–N(21)	109.9 (5)
N(11)–C(15)–C(14)	109 (1)	N(31)–B(2)–C(41)	108.4 (6)
C(14)–C(13)–C(16)	131 (1)	N(31)–B(2)–C(51)	110.6 (6)
C(13)–C(14)–C(15)	105 (1)	Br(1)–C(14)–C(13)	129.8 (9)
C(13)–C(16)–C(17)	111.3 (6)	Br(1)–C(14)–C(15)	125 (1)
C(17)–C(16)–C(17)^a	108.4 (8)		

^{a}Symmetry operation, x, $^1/_2 - y$, z.

polypyrazolylborate ligands. In this case the Co(II) ion has a five-coordinate geometry. Formation of an agostic Co–H–phenyl interaction would require an unacceptable interaction of the phenyl group with the pyrazolyl hydrogen atoms.

Selected bond distances and angles are presented in Table XI. The bond distances and angles are typical of Co(II)–polypyrazolylborate complexes. There are no unusual features.

Discussion

The reduced propensity of [HB(3-*i*-Pr-4-Br-pz)$_3$]$^-$ to form ML*$_2$ species and the enhanced stability of ML*X complexes, as compared with their 4-H analogues, may result from the electron-withdrawing effect of the 4-Br substituent. Despite its relative bulk, the Br atom does not prevent free rotation of the *i*-Pr group. We have examples of structures in which the 3-*i*-Pr group points the methyl groups toward the metal ion (such as with CoL*NCS) or away from it (as with Co(HB(3-*i*-Pr-4-Br-pz)$_2$-(5-*i*-Pr-4-Br-pz))$_2$). In each case, the methyl groups straddle the pyrazolyl plane. The isopropyl rotamer with its methyl groups toward the metal is probably also present in ML*Cl, but upon reaction with a polydentate ligand, the methyl groups are swung away from the metal ion. This orientation yields the less hindered form, which permits the largest substituent size possible in the second polypyrazolylborate ligand L.

The ability of first-row transition-metal ions to form octahedral complexes with polypyrazolylborate ligands depends, inter alia, on the nature of the two sets of 3-R groups forming the equatorial belt of the molecule. Clearly, six methyls can be accommodated (as in M(HB(3,5-Me$_2$pz)$_3$)$_2$), but not six isopropyl groups, so that the ligand [HB(3-*i*-Pr-pz)$_3$]$^-$ must isomerize to produce, ultimately, M(HB(3-*i*-Pr-pz)$_2$(5-*i*-Pr-pz))$_2$ complexes.[5] From the present work we see that three isopropyl groups and three hydrogens or three methyl groups can be accommodated in an octahedral structure. Three isopropyl groups and two (but not three) phenyl groups can also be accommodated, because of a distortion in L* which opens up two of the angles between the pz* planes, constricting the third, and permits the sixth coordination site to be occupied by an agostic B–H–M bond.

That the reaction of ML*Cl with [HB(pz)$_3$]$^-$ is rapid, but that with [HB(3,5-Me$_2$pz)$_3$]$^-$ very slow, suggests that the former can react regardless of the orientation of the isopropyl groups, but the latter requires for bond formation that *two* isopropyl groups, flanking the coordination site, be in the least hindered conformation. Although in the crystal structure determination of ML*Cl all the isopropyl groups are found with their methyl groups toward the metal, they should be rotating freely in solution.

The formation of agostic B–H–M bonding in ML*(H$_2$B(pz*)$_2$) complexes is unusual, in that no such bonding was previously found with first-row transition metals, except for a suggestion of it in Cu(H$_2$B(pz)$_2$)PR$_3$.[14] In the three examples where the structures were determined by X-ray crystallography: Ni(H$_2$B(pz)$_2$)$_2$,[15] the Co analogue,[16] and the Cr analogue,[17] the B–H–M distances were between 3.0 and 3.1 Å and thus were out of the bonding range. By contrast, there are several examples of such bonding with lower row metals as, for instance, in Mo(H$_2$B(3,5-Me$_2$pz)$_2$)(η^3-allyl)(CO)$_2$,[18] Ta(H$_2$B(3,5-Me$_2$pz)$_2$)ClMe$_3$,[19] and Pt(H$_2$B(pz)$_2$)-Me$_3$.[20]

The agostic B–H–M bonding may occur in ML*(H$_2$B(pz*)$_2$) because the steric effect of 3-*i*-Pr groups in L* forces the pz* rings of the L ligand to fit rigidly between the pz* planes of L*, in an arrangement akin to that found in regular M(RB(pz)$_3$)$_2$ octahedral compounds. This arrangement, in turn, forces L into a deep boat conformation, which automatically curls the pseudoaxial BH in scorpioid fashion toward the metal, to a greater extent than it would occur in an unhindered ring arrangement.

Conclusion

The complexes M(HB(3-*i*-Pr-4-Br-pz)$_3$)Cl possess a favorable combination of steric protection around the metal and selective accessibility to other ligands. This combination makes them unique among the known polypyrazolylborate ligands, in being suitable for controlled preparation of mixed species ML*L. Such complexes are five-coordinate, when L is bidentate, and can become six-coordinate either through the reversible addition of an unhindered donor molecule or through the formation of an agostic B–H–M bond when L is [H$_2$B(pz*)$_2$]$^-$ and also when the third pz* cannot coordinate for steric reasons, as in [HB(3-Phpz)$_3$]$^-$. Octahedral complexes of C_{3v} symmetry are formed when L is [HB(pz)$_3$]$^-$ or [HB(3,5-Me$_2$pz)$_3$]$^-$. It should be possible to use a wide variety of ligands L in the reaction with ML*Cl to construct

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sequentially binuclear and even more complex molecular architecture by choosing a relatively unhindered, uninegative L, with donor atoms capable of displacing chloride ion.

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Supplementary Material Available: Listings of crystallographic data (Table S17), thermal parameters (Tables S1, S5, S9, and S13), hydrogen atom positions (Tables S2, S6, S10, and S14), and complete bond distances and angles (Tables S4, S8, S12, and S16) (19 pages); listings of observed and calculated structure factors (Tables S3, S7, S11, and S15) (35 pages). Ordering information is given on any current masthead page.

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Formation and Characterization of the Unsymmetrical Dirhenium Polyhydrides $Re_2H_6(PMe_3)_5$ and $Re_2H_6(SbPh_3)_5$ and Observations Concerning the Mechanism of the Conversion of $Re_2H_8(PMe_3)_4$ to $[Re_2H_5(PMe_3)_6]^+$

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The reaction of $Re_2H_8(PMe_3)_4$ with PMe_3 in methanol proceeds to give $[Re_2H_5(PMe_3)_6]^+$ via the intermediacy of $Re_2H_6(PMe_3)_5$ and $[Re_2H_7(PMe_3)_5]^+$, both of which have been isolated and characterized on the basis of their ^1H and ^{31}P NMR spectra and their electrochemical properties. Measurements of the ^1H NMR spectrum of $Re_2H_6(PMe_3)_5$ in C_7D_8 over the temperature range +50 to -100 °C show that this complex possesses the unsymmetrical structure $(Me_3P)_3HRe(\mu\text{-}H)_3ReH_2(PMe_3)_2$, at least at low temperatures. A similar type of structure has been found in the solid state for $Re_2H_6(SbPh_3)_5$, a complex that is formed by the reaction of $(n\text{-}Bu_4N)_2Re_2Cl_8$ with an excess of $SbPh_3$ and $NaBH_4$ in ethanol. A single-crystal X-ray structure determination on $Re_2H_6(SbPh_3)_5$ has been carried out with the data collected at -100 °C. Crystal data are as follows: monoclinic space group $P2_1/n$, $a = 13.287$ (5) Å, $b = 40.137$ (8) Å, $c = 14.392$ (5) Å, $\beta = 92.55$ (2)°, $V = 7667$ (7) Å^3, and $Z = 4$. The structure was refined to $R = 0.030$ ($R_w = 0.037$) for 7182 data with $I > 3.0\sigma(I)$. The Re-Re distance is 2.5340 (6) Å, and all six hydride ligands (three terminal, three bridging) have been located and refined.

Introduction

Dirhenium polyhydride complexes of stoichiometry $Re_2H_8(PR_3)_4$ (PR_3 represents a monodentate phosphine or half a bidentate phosphine ligand), whose syntheses,[1-10] structures,[8,9,11-13] redox behavior,[14] and chemical reactivities[14-20] have been of considerable recent interest, are potential starting materials for other neutral dirhenium polyhydrides of the types $Re_2H_6(PR_3)_5$ and $Re_2H_4(PR_3)_6$ through sequential reductive elimination of dihydrogen and the coordination of additional PR_3 ligands as shown in eq 1.

$$Re_2H_8(PR_3)_4 \xrightarrow[-H_2]{+PR_3} Re_2H_6(PR_3)_5 \xrightarrow[-H_2]{+PR_3} Re_2H_4(PR_3)_6 \quad (1)$$

Surprisingly, very few examples of these conversions have been reported, although the first step has been shown to occur when $PR_3 = PMe_2Ph$,[2] and the structure of the resulting complex has been determined.[2a] The second step has been encountered in the case of the reaction between $Re_2H_8(PMe_2Ph)_4$ and the phosphine ligand $P(OCH_2)_3CEt$, which gives $Re_2H_4(PMe_2Ph)_4[P(OCH_2)_3CEt]_2$,[21] while $Re_2H_8(dppe)_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) reacts with dppe in THF to give $Re_2H_4(dppe)_3$.[22] The latter two products are readily protonated by HBF_4 to give $[Re_2H_5(PMe_2Ph)_4[P(OCH_2)_3CEt]_2]BF_4$[21] and $[Re_2H_5(dppe)_3]BF_4$,[22] respectively. The cationic species contain a $[HRe(\mu\text{-}H)_3ReH]$ disposition of hydride ligands and resemble structurally the complex $[Re_2H_5(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]PF_6$.[14,17]

Recently, in the course of studying the reaction of $Re_2H_8(PMe_3)_4$ with PMe_3 in methanol, we were able to isolate the complex $[Re_2H_5(PMe_3)_6]PF_6$,[16] which we found has a structure closely akin to those of the aforementioned[14,17,21,22] dirhenium pentahydride cations, viz., $[(Me_3P)_3HRe(\mu\text{-}H)_3ReH(PMe_3)_3]^+$. In seeking to understand the mechanism of this reaction, in particular the role that methanol might play,[23] we have carried

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