phosphaborane was prepared previously by reaction of $B_{10}H_{14}$ and CH_3PCl_2 in the presence of a base.[3] The ^{11}B NMR and IR spectra of the methylation product were identical with those of the previously prepared compound.

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Supplementary Material Available: Tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and intramolecular angles (15 pages). Ordering information is given on any current masthead page.

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Steric Effects in Polypyrazolylborate Ligands. Poly(3-isopropylpyrazolyl)borates: Ligands of Intermediate Steric Requirements

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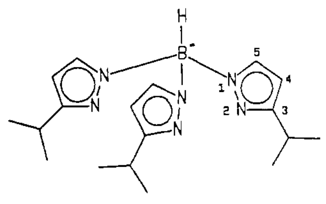
The synthesis, structures, and coordination chemistry of a series of polypyrazolylborate ligands, $[H_nB(3\text{-isopropylpyrazol-1-yl})_{4-n}]^-$ and $[HB(3\text{-isopropyl-4-bromopyrazol-1-yl})_3]^-$, are presented. These ligands are made by the reaction of tetrahydroborate ion with the appropriate pyrazole. A series of metal complexes was prepared and characterized by analytical and spectroscopic data. In addition, four complexes were characterized by means of X-ray diffraction techniques. The complex $Co(HB(3\text{-isopropyl-4-bromopyrazol-1-yl})_3)(NCS)$ crystallizes in the tetragonal space group $P\bar{4}2_1m$ with four molecules per unit cell of dimensions a = 17.450 (3) Å and c = 9.025 (1) Å at −70 °C. Least-squares refinement of 160 variables led to a value of the conventional R index (on F) of 0.042 and of R_w of 0.033 for 879 reflections with $I > 3.0\sigma(I)$. The geometry about the Co(II) ion, which is coordinated to three pyrazolyl nitrogen atoms and the nitrogen atom of the thiocyanate group, is tetrahedral. The isopropyl group and the bromine atom are in the 3- and 4-positions of the pyrazolyl ring, respectively. The complex $Co(B(3\text{-isopropylpyrazol-1-yl})_4)_2$ crystallizes in the monoclinic space group $C2/c$ with four molecules in a unit cell of dimensions a = 15.276 (3) Å, b = 19.856 (5) Å, c = 19.274 (3) Å, and β = 109.37 (1)° at −70 °C. Least-squares refinement of 309 variables led to a value of the conventional R index of 0.057 and of R_w of 0.050 for 2800 reflections with $I > 3.0\sigma(I)$. The geometry about the Co(II) ion, which is coordinated to four pyrazolyl nitrogen atoms from two ligands, is tetrahedral. The isopropyl group is in the 3-position of each pyrazolyl ring. The complex $Co(HB(3\text{-isopropylpyrazol-1-yl})_2(5\text{-isopropylpyrazol-1-yl}))_2$ crystallizes in the triclinic space group $P\bar{1}$ with one molecule in a unit cell of dimensions a = 9.076 (2) Å, b = 10.784 (2) Å, c = 11.079 (1) Å, α = 108.66 (1)°, β = 93.35 (1)°, and γ = 100.12 (1)° at −70 °C. Least-squares refinement of 232 parameters led to a value of the conventional R index of 0.037 and of R_w of 0.045 for 3581 reflections with $I > 3.0\sigma(I)$. The geometry about the Co(II) ion, which is coordinated to six pyrazolyl nitrogen atoms from two ligands, is octahedral. The isopropyl group is in the 3-position for two rings, whereas for the third, this group is in the 5-position. The complex $Co(HB(3\text{-isopropyl-4-bromopyrazol-1-yl})_2(5\text{-isopropyl-4-bromopyrazol-1-yl}))_2$ crystallizes in the triclinic space group $P\bar{1}$ with one molecule per unit cell of dimensions a = 10.164 (1) Å, b = 10.236 (2) Å, c = 12.938 (2) Å, α = 111.08 (1)°, β = 99.26 (1)°, and γ = 106.28 (1)° at −70 °C. Least-squares refinement of 259 variables led to a value of the conventional R index of 0.037 and of R_w of 0.032 for 2950 reflections with $I > 3.0\sigma(I)$. The geometry about the Co(II) ion and ring substitution patterns are the same as those for the octahedral complex described above, with the addition of a bromine atom in the 4-position of each ring. These last two structural studies reveal a unique feature of these new ligands: rearrangement of the mode of coordination by a pyrazolyl group in octahedral complexes to relieve steric crowding. The results presented here indicated that these ligands have properties that are unique and transitional from those of the previously reported, relatively unhindered ligands such as $[H_nB(\text{pyrazolyl-1-yl})_{4-n}]^-$ to the sterically bulky ligands $[H_nB(3\text{-R-pyrazol-1-yl})_{4-n}]^-$, where R = *tert*-butyl and phenyl groups.

Introduction

In this contribution, we present the synthesis and coordination chemistry of a new generation of polypyrazolylborate ligands that have properties lying between those of the parent $[H_{4-n}B(pz)_n]^-$ ligands[1] (pz = pyrazolyl) and those of the more recently reported derivatives $[H_{4-n}B(3\text{-Rpz})_n]^-$, where R = *tert*-butyl and phenyl groups.[2,3] The parent ligands, in particular the derivatives with $n = 3$, have been extensively used in inorganic and bioinorganic chemistry. However, the chemistry is severely limited because of the tendency of the first-row transition-metal ions to form the bisligand complex (i.e., $M(HB(pz)_3)_2$). On the other hand, the bulky groups of the 3-R derivatives[2,3] prevent formation of this type of complex. The 3-*tert*-butyl ligand allows no further access to the metal ion and is a "tetrahedral enforcer", whereas the 3-phenyl derivative accommodates five-coordination with a trigonal-bipyramidal geometry. Although bisligand complex formation is prevented, the metal ion is not readily accessible to other molecules because of the steric bulk of the 3-substituents. The new ligands reported here, with a 3-isopropyl group (**1**), show characteristics of both of these ligands: limited formation of the $M(HB(3\text{-Rpz})_3)_2$ complexes and accessibility of the metal ion. In addition the synthesis and coordination chemistry of another new derivative, $[HB(3\text{-}i\text{-Pr-4-Br-pz})_3]^-$, with a bromine atom in the 4-position of the pyrazolyl ring, are presented. The importance of electronic effects in the coordination chemistry of this growing family of ligands is demonstrated for the first time.



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Experimental Section

General Methods. All chemicals were reagent grade and were used as received. Elemental analyses were performed by Micro-Analysis, Inc., Wilmington, DE. Infrared spectra were obtained as Nujol mulls with a Perkin-Elmer 283-B infrared spectrophotometer. ^1H NMR spectra were obtained with a Nicolet NT360WB spectrometer. Diamagnetic compounds were studied with typical conditions of 16K data points, a spectral 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

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Table I. Properties of Complexes with the $[H_2B(3\text{-}i\text{-}Prpz)_2]^-$ Ligand (L)

		anal.,[a] %				
complex	color	C	H	N	mp, °C	IR data, cm^{-1}
CoL_2	violet	55.3 (54.9)	7.68 (7.86)	21.5 (21.5)	207–209	2420, 2380, 2340, 2290, 2280
NiL_2	orange	55.8 (55.5)	7.68 (7.86)	21.5 (21.2)	210–212	2440, 2370, 2350, 2280, 2265
CuL_2	pale lilac	54.8 (54.8)	7.61 (7.41)	21.3 (21.1)	161–163	2430, 2415, 2350, 2320, 2255, 2200
ZnL_2	white	54.6 (54.5)	7.59 (7.68)	21.3 (21.1)	225–227	2420, 2380, 2340, 2290, 2280

[a] Values determined are given in parentheses.

spectral width of 100 kHz, 45° pulse angles, and a recycle time of 1.2 s. 2-D COSY spectra of the paramagnetic compounds were observed at 60 °C for optimum cross-peak sensitivity. 512 t1 slices of 512 (complex) points were acquired and processed with a sine-bell window Fourier transform and magnitude calculation to give a final 2D spectrum of 512 × 512 real points.

Preparation of 3(5)-Isopropylpyrazole. To a suspension of dry sodium methoxide (108 g, 2.0 mol) stirred in 1 L of toluene was added in one portion a mixture of isopropyl methyl ketone (172 g, 2.0 mol) and ethyl formate (200 mL). A vigorous, but controlled, reaction took place. The resulting murky yellow solution was stirred for 0.5 h. Ice-cold water (1 L) was then added. The yellow color went into the aqueous layer, which was separated and then added to a stirred solution of hydrazine hydrochloride (134 g, 2.0 mol) in water (1 L). After 15 min, KOH pellets were added to yield a basic solution, followed by ice. An amber oil separated and was extracted with diethyl ether (400 mL). After removal of diethyl ether, the reaction mixture was heated under vacuum to remove all volatile materials. The product (108 g, 49% yield) was distilled in vacuo (bp 68–72 °C (0.3 mm), in agreement with the literature value[4]). ^1H NMR (ppm):[4] 13.4 (s, 1 H), 7.56 (d, 1 H), 6.12 (d, 1 H), 3.08 (septet, 1 H), 1.30 (d, 6 H).

3(5)-Isopropyl-4-bromopyrazole. Bromine (176 g, 1.1 mol) was added dropwise to a rapidly stirred suspension of 3(5)-isopropylpyrazole (122 g, 1.1 mol) in 1.5 L of water. The bromine color was rapidly discharged, and the solution became acidic. After complete addition, the solution was first cooled by adding ice and then neutralized with sodium hydroxide. A heavy oil separated, which was then extracted with dichloromethane. The solvent was stripped from the extracts and the product distilled in vacuo (bp 111–114 °C (0.6 Torr); yield 172 g, 82% yield). *Caution!* 3(5)-Isopropyl-4-bromopyrazole decomposes violently when overheated, unlike 3(5)-isopropylpyrazole, which can be refluxed at atmospheric pressure. ^1H NMR (ppm): 12.9 (s, 1 H), 7.40 (s, 1 H) 3.10 (septet, 1 H), 1.30 (d, 6 H). Anal. Calcd for $C_6H_9BrN_2$: C, 38.1; H, 4.76; N, 14.8. Found: C, 38.1; H, 4.82; N, 15.0.

Preparation of Potassium Dihydrobis(3-isopropylpyrazol-1-yl)borate, $KH_2B(3\text{-}i\text{-}Prpz)_2$. A mixture of potassium tetrahydroborate (5.40 g, 0.1 mol) and 3(5)-isopropylpyrazole (26.5 g, 0.22 mol) was heated in 250 mL of *N,N*-dimethylacetamide (DMAC) with the emanating gases passing through a −80 °C trap to a wet-test meter. After 5.0 L of hydrogen was evolved, the flask contents were distilled at 0.2 mmHg and an oil bath temperature of 130–140 °C to remove DMAC and residual starting pyrazole. The residue was cooled under nitrogen and dissolved in tetrahydrofuran (THF) to 500 mL, and the mixture was filtered through Celite to yield a 0.2 M solution of the ligand, which was used directly to make metal complexes.

Preparation of Potassium Hydrotris(3-isopropylpyrazol-1-yl)borate, $KHB(3\text{-}i\text{-}Prpz)_3$. A mixture of potassium tetrahydroborate (18 g, 0.33 mol) and 3(5)-isopropylpyrazole (212 g, 1.76 mol) was heated gradually with stirring until 28.5 L of hydrogen was evolved, as measured with the wet-test meter described above. The flask was then heated in an oil bath at 150–170 °C and 0.2 mmHg to distill the starting pyrazole (ca. 80 g). The residue was cooled under nitrogen and dissolved in 350 mL THF; this solution was then diluted with 300 mL of heptane. The volume was reduced to approximately 300 mL. To the cooled, stirred solution was added 300 mL of hexane and 200 mL of petroleum ether to precipitate a solid, which was collected by filtration to yield 60 g (46% yield) of product. Further concentration of the filtrate followed by dilution with hexane gave an additional 10 g (8% yield) of a second crop (total yield 54%). This solid still contained some starting pyrazole, but was used to make metal complexes described below.

Preparation of Potassium Tetrakis(3-isopropylpyrazol-1-yl)borate, $KB(3\text{-}i\text{-}Prpz)_4$. A mixture of 3(5)-isopropylpyrazole (110 g, 1.0 mol) and potassium tetrahydroborate (10.8 g, 0.2 mol) was heated gradually with stirring to 220 °C until hydrogen evolution stopped. The clear melt was cooled partially under nitrogen and poured into stirred heptane (500 mL). A solid precipitated on cooling, was collected by suction filtration, and was washed with heptane. This product (60 g, 62% yield) still contains some of the starting pyrazole but was used to make metal complexes described below.

Preparation of Potassium Hydrotris(3-isopropyl-4-bromopyrazol-1-yl)borate, $KHB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3$. Potassium tetrahydroborate (15.2 g, 0.28 mol) and 3(5)-isopropyl-4-bromopyrazole (270 g, 1.43 mol) were heated and stirred until the borohydride dissolved and 22.3 L of hydrogen was evolved, as measured with the wet-test meter. The residual pyrazole was then distilled out of the reaction mixture at 185–190 °C and 0.3 Torr; 85 g of the starting pyrazole was recovered. The remaining material was stirred with 400 mL of hexane until the solid was well dispersed. The solid was collected by filtration and washed with hexane to yield a white material (116 g, 67% yield), which was used for the preparation of metal complexes described below.

Preparation of ML_2 Complexes ($L = [H_2B(3\text{-}i\text{-}Prpz)_2]^-, [HB(3\text{-}i\text{-}Prpz)_3]^-, [B(3\text{-}i\text{-}Prpz)_4]^-$). To 2 equiv of KL (as 0.2 M THF solutions) was added with stirring 1 equiv of aqueous metal nitrate, followed after 5 min by twice the total volume of water. The product was extracted with dichloromethane. The extracts were washed several times with water to remove most of the THF and then were chromatographed on alumina. The eluate was evaporated; the resulting residue was washed with methanol to remove starting pyrazole and metal complexes of this pyrazole. After drying, ML_2 compounds were obtained in 60–80% yield. The complexes $M(H_2B(3\text{-}i\text{-}Prpz)_2)_2$ with M = Co(II) and Zn(II) are quite soluble in methanol; residues obtained from evaporation of dichloromethane were washed with only a very small amount of solvent, but even then solubility losses were substantial.

Properties of these complexes are listed in Tables I–III.

Preparation of $M(HB(3\text{-}i\text{-}Prpz)_3)(X)$ Complexes (M = Co(II), Ni(II), Zn(II); X = NCO, NCS, N_3, NO_3). A THF solution of $KHB(3\text{-}i\text{-}Prpz)_3$ was added to a vigorously stirred solution of excess metal nitrate (a 0.5 M solution was used) and 4 equiv of KX; an equal volume of methanol was then added. After 5 min, the mixture was diluted with water and extracted with dichloromethane. The combined extracts were washed with several portions of water and then chromatographed on alumina, dichloromethane being used for packing and eluting. The eluate was evaporated under reduced pressure; the resulting solid was stirred with hot hexane (or with methanol for M = Zn(II)), collected by filtration, and recrystallized from heptane. The properties of these compounds are listed in Table II.

Preparation of $Mo(HB(3\text{-}i\text{-}Prpz)_3)(\eta^3\text{-}CH_2C(CH_3)CH_2)(CO)_2$. Equimolar amounts of $KHB(3\text{-}i\text{-}Prpz)_3$ and $Mo(\eta^3\text{-}CH_2C(CH_3)CH_2)Cl(CH_3CN)_2(CO)_2$[5] were stirred in dichloromethane for 0.5 h. Following the addition of water and separation of layers, the organic phase was chromatographed on alumina. Evaporating the yellow eluate, washing with methanol, and drying yielded the compound in 59% yield. Its properties are listed in Table II.

Preparation of $MoL(NO)(CO)_2$ Compounds ($L = [HB(3\text{-}i\text{-}Prpz)_3]^-, [B(3\text{-}i\text{-}Prpz)_4]^-$). Equimolar amounts of KL and $Mo(CO)_6$ were refluxed in THF until the theoretical amount of carbon monoxide was evolved, as measured with the wet-test meter described above. The orange solution was cooled under nitrogen, and a slight excess of butyl nitrite or nitrosyl chloride was added. Heating was resumed until another 1 equiv of carbon monoxide was evolved. The solution was then poured into a large excess of water and the product extracted into dichloromethane. The extracts were chromatographed on alumina. Evaporating solvent from the orange eluate, stirring with methanol, filtering, and drying gave a yellow-orange solid, whose properties are listed in Tables II and III.

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Table II. Properties of Complexes with the $[NB(3\text{-}i\text{-}Prpz)_3]^-$ Ligand (L)

complex	color	anal.,[a] %			mp, °C	IR data, cm^{-1}
		C	H	N		
FeL_2[b]	pale green	58.9 (58.7)	7.63 (7.49)	22.9 (22.7)	209–211	2480, 2450
CoL_2[b]	pale yellow	58.6 (58.8)	7.60 (7.66)	22.8 (22.6)	226–228	2480, 2450
CoL(NCO)	blue	51.8 (51.8)	6.36 (6.49)	22.3 (22.2)	136–137	2524, 2230
CoL(NCS)	violet	50.0 (50.4)	6.14 (6.10)	21.5 (20.8)	159–161	2495, 2480, 2125
NiL_2[b]	pale lilac	58.6 (58.6)	7.60 (7.68)	22.8 (23.0)	263–265	2480, 2450
NiL(NCO)	lime	51.8 (52.2)	6.36 (6.48)	22.3 (22.5)	141–142	2505, 2250, 2215
NiL(NCS)	green	50.0 (49.8)	6.14 (6.28)	21.5 (21.3)	227–230	2480, 2150
CuL_2[c]	blue	58.3 (58.6)	7.56 (7.62)	22.7 (22.5)	129–131 239–240	2495, 2410 2508, 2480
ZnL_2[c]	white	58.1 (57.7)	7.54 (7.52)	22.6 (22.7)	156–158 244–246	2480, 2450 2500–2480
ZnL(NCO)	white	51.1 (50.8)	6.28 (6.30)	22.0 (21.9)	138–139	2520, 2230
ZnL(NCS)	white	49.3 (49.2)	6.06 (6.17)	21.2 (20.8)	145–146	2512, 2100
$ZnL(N_3)$	white	48.4 (48.4)	6.28 (6.27)	28.3 (28.3)	131–132	2510, 2095
$ZnL(NO_3)$	white	46.5 (46.7)	5.98 (6.25)	20.9 (20.8)	161–163	2520
$MoL(NO)(CO)_2$	orange	46.1 (46.2)	5.37 (5.22)	18.8 (18.5)	227–229	2510, 2005, 1910, 1650
$MoL(\eta^3\text{-}CH_2C(CH_3)CH_2)(CO)_2$	yellow	52.8 (53.0)	6.41 (6.40)	15.4 (15.1)	173–174	2460, 1982, 1940, 1828
$[N(C_2H_5)_4][MoL(CO)_3]$	cream	53.6 (53.6)	7.40 (7.60)	15.1 (15.3)	272–274	1880, 1755, 1735

[a] Values determined are given in parentheses. [b] L = $[HB(3\text{-}i\text{-}Prpz)_2(5\text{-}i\text{-}Prpz)]^-$. [c] Two forms isolated, one of which contains rearranged ligand.[b]

Table III. Properties of Complexes with the $[B(3\text{-}i\text{-}Prpz)_4]^-$ Ligand (L)

complex	color	anal.,[a] %			mp, °C	IR data, cm^{-1}
		C	H	N		
FeL_2	pale green	60.6 (61.0)	7.58 (7.52)	23.6 (23.9)	245–247	
CoL_2	purple	60.4 (60.6)	7.56 (7.68)	23.5 (23.7)	264–266	
NiL_2	reddish purple	60.4 (60.4)	7.56 (7.39)	23.5 (23.6)	258–260	
CuL_2	brown	60.2 (60.4)	7.52 (7.57)	23.4 (23.3)	198–200	
ZnL_2	white	60.0 (60.4)	7.50 (7.52)	23.4 (22.9)	254–256	
$MoL(NO)(CO)_2$	orange	49.6 (50.0)	5.72 (5.84)	20.0 (19.9)	210–211	2010, 2000, 1948, 1935, 1920, 1660
$[N(C_2H_5)_4][MoL(CO)_3]$	pale beige	55.5 (55.7)	7.40 (7.62)	16.6 (16.8)	240–243	1888, 1760, 1745

[a] Values determined are given in parentheses.

$Mo(B(3\text{-}i\text{-}Prpz)_4)(NO)(CO)_2$ could also be prepared in 81% yield by stirring overnight at room temperature $[N(C_2H_5)_4][Mo(B(3\text{-}i\text{-}Prpz)_4)(CO)_3]$ (vide infra) in acetonitrile with excess butyl nitrite, adding water, and working up the product as described above.

Preparation of $[N(C_2H_5)_4][Mo(B(3\text{-}i\text{-}Prpz)_4)(CO)_3]$. A mixture of 100 mL of 0.2 M $KB(3\text{-}i\text{-}Prpz)_4$ in THF and $Mo(CO)_6$ (5.3 g, 0.20 mol) was refluxed with stirring until 1.5 L of carbon monoxide was evolved, as measured with the wet-test meter described above. The orange solution was cooled and then poured into a stirred solution of excess tetraethylammonium bromide. The resulting slurry was diluted with additional water and extracted with dichloromethane. The extracts were washed several times with water and then chromatographed on alumina as described above. The dark yellow eluate was evaporated, and the residue was stirred with methanol and collected by filtration. After thorough washing with methanol (which removes a brown impurity) and drying, a pale creamy solid was obtained in 52% yield (7.9 g). The properties are listed in Table III.

Preparation of Thallium Hydrotris(3-isopropyl-4-bromopyrazol-1-yl)borate, $TlHB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3$. Equimolar amounts of $KHB(3\text{-}i\text{-}Pr\text{-}4\text{-}Brpz)_3$ in THF and $TlNO_3$ in water were mixed. Twice the total volume of water was then added. The product was extracted into dichloromethane. The extracts were chromatographed on alumina. A white solid was obtained on evaporation of solvent and recrystallization from toluene/heptane. Properties of this salt are shown in Table IV.

Preparation of $M(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)(X)$ Complexes (M = Co(II), Ni(II), Zn(II); X = Cl, NCO, NCS). To 100 mL of 0.5 M metal nitrate containing 4 equiv of KX was added an equal volume of methanol, followed by 100 mL of 0.2 M $KHB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3$ in THF. The slurry was diluted with water to twice its original volume and then filtered. The solid was dried until all traces of solvent were removed (the Co(II) and Ni(II) complexes are first isolated as solvates) and then recrystallized from toluene/heptane. The properties of these solids are listed in Table IV.

Preparation of $M(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_2(5\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz))_2$ Complexes (M = Fe(II), Co(II), Ni(II)). A mixture of 1 equiv of anhydrous MCl_2 and 2 equiv of $TlHB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3$ was refluxed in toluene, until precipitation of TlCl was complete. The slurry, which was the color of the octahedral metal complex, was filtered hot through a bed of Celite. Evaporation of solvent and recrystallization of the residue from toluene/heptane yielded the compounds listed in Table IV.

Table IV. Properties of Complexes with the [HB(3-*i*-Pr-4-Br-pz)$_3$]$^-$ Ligand (L)

complex	color	anal.,[a] % C	H	N	mp, °C	IR data, cm^{-1}
KL	white	35.1	4.07	13.7	104–106	2120–2320 (7 peaks)
		(34.3)	(4.61)	(13.7)		
TlL	white	27.7	3.21	10.8	187–189	2448
		(27.6)	(3.25)	(10.8)		
FeL$_2$[b]	pale green	35.8	4.14	13.9	>300	
		(35.6)	(4.53)	(13.7)		
CoL$_2$[b]	pale yellow	35.7	4.13	13.9	>300	2520, 2500, 2480
		(34.9)	(4.41)	(13.6)		
CoLCl	blue	32.2	3.73	12.5	>300	2520
		(32.5)	(3.70)	(12.7)		
CoL(NCO)	blue	33.7	3.69	14.5	296–298	2550, 2245
		(34.2)	(3.77)	(14.6)		
CoL(NCS)	blue	32.9	3.61	14.1	250 dec	2550, 2070
		(32.7)	(4.05)	(13.8)		
NiL$_2$[b]	pale lilac	35.7	4.13	13.9	>300	
		(34.9)	(4.25)	(13.8)		
NiLCl	red	32.2	3.73	12.5	291 dec	2530
		(32.5)	(3.70)	(12.7)		
NiL(NCO)	red	33.7	3.69	14.5	269–270	2560, 2230
		(34.0)	(3.62)	(14.4)		
NiL(NCS)	green	32.9	3.61	14.1	>260 (red), 277–280	
		(32.6)	(3.82)	(13.8)		
ZnLCl	white	32.0	3.70	12.4	300	2510
		(32.3)	(3.72)	(12.6)		
ZnL(NCO)	white	33.4	3.66	14.4	309–312	2550, 2260
		(33.4)	(3.81)	(14.7)		
ZnL(NCS)	white	32.6	3.58	14.0	270–272	2550, 2090
		(32.6)	(3.66)	(13.8)		
ZnL(N$_3$)	white	31.6	3.66	18.45	>295	2550, 2110
		(31.4)	(3.79)	(18.2)		
MoL(NO)(CO)$_2$	orange	31.7	3.30	12.9	255–268 dec	2500, 2025, 1920, 1870, 1670
		(31.5)	(3.29)	(13.0)		
MoL(η^3-CH$_2$C(CH$_3$)CH$_2$)(CO)$_2$	yellow	36.8	4.09	10.7	204–205	2480, 1930, 1840
		(37.0)	(4.02)	(11.0)		

[a] Values determined are given in parentheses. [b] L = [HB(3-*i*-Pr-4-Br-pz)$_2$(5-*i*-Pr-4-Br-pz)]$^-$.

Table V. Crystal Data for Co(HB(3-*i*-Pr-4-Br-pz)$_3$)(NCS) (I), Co(B(3-*i*-Prpz)$_4$)$_2$ (II), Co(HB(3-*i*-Prpz)$_2$(5-*i*-Prpz))$_2$ (III), and Co(HB(3-*i*-Pr-4-Br-pz)$_2$(5-*i*-Pr-4-Br-pz))$_2$ (IV)

	I	II	III	IV
mol formula	$C_{19}H_{25}BBr_3CoN_7S$	$C_{48}H_{72}B_2CoN_{16}$	$C_{36}H_{56}B_2CoN_{12}$	$C_{36}H_{50}B_2Br_6CoN_{12}$
M_r	692.99	953.77	737.48	1210.88
a, Å	17.450 (3)	15.276 (3)	9.076 (2)	10.164 (1)
b, Å	17.450 (3)	19.856 (5)	10.784 (2)	10.236 (2)
c, Å	9.025 (1)	19.274 (3)	11.079 (1)	12.938 (2)
α, deg	90	90	108.66 (1)	111.08 (1)
β, deg	90	109.37 (1)	93.35 (1)	99.26 (1)
γ, deg	90	90	100.12 (1)	106.28 (1)
V, Å^3	2750.8	5515.3	1003.7	1153.0
Z	4	4	1	1
space group	$P\bar{4}2_1m$	$C2/c$	$P\bar{1}$	$P\bar{1}$
radiation (λ, Å)	MoKα (0.71069) from graphite monochromator			
2θ limits, deg	2.3–55.0	2.2–55.0	5.7–55.0	4.4–55.0
temp, °C	−70	−70	−70	−70
abs coeff, cm^{-1}	50.33	3.54	4.65	55.61
no. of unique data used ($I > 3\sigma(I)$)	879	2800	3581	2950
no. of variables	160	309	232	259
R	0.042	0.057	0.037	0.037
R_w	0.033	0.050	0.045	0.032

Preparation of Mo(HB(3-*i*-Pr-4-Br-pz)$_3$)(NO)(CO)$_2$ and Mo(HB(3-*i*-Pr-4-Br-pz)$_3$)(η^3-CH$_2$C(CH$_3$)CH$_2$)(CO)$_2$. These compounds were prepared in a manner analogous to that with [HB(3-*i*-Prpz)$_3$]$^-$ described above. DMAC was used as solvent.

X-ray Data Collection and Structure Solution and Refinement. Co(HB(3-*i*-Pr-4-Br-pz)$_3$)(NCS) (I). Crystals suitable for diffraction studies were obtained by vapor diffusion of petroleum ether into a dichloromethane solution of the complex under an inert atmosphere. The crystal was encapsulated in a glass capillary, then was placed on an 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. 0.16° ω 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 V. 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.[6] Data were adjusted for a 5% decrease in intensity. The structure was solved by automated Patterson analysis (PHASE), using the space group $P2_12_12$, which was then transformed to the correct tetragonal group. The function minimized is given elsewhere.[6] Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[7] Hydrogen atom positions were calculated with C–H and B–H distances of 0.95 Å. The boron atom was refined isotropically because

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

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

Table VI. Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters for Co(HB(3-*i*-Pr-4-Br-pz)$_3$)(NCS) (I)

atom	x	y	z	B_{eq},^{a} Å^2
Br(1)	4237 (1)	763	9409 (2)	6.6 (1)
Br(2)	5020.9 (8)	3879.1 (5)	1165.2 (10)	3.6 (1)
Co(1)	2456 (1)	2544	4830 (2)	2.5 (1)
S(1)	763 (2)	4237	7098 (8)	7.7 (2)
N(1)	1746 (5)	3254	5713 (15)	3.7 (3)
N(11)	3583 (5)	1417	5358 (13)	2.4 (2)
N(12)	3120 (5)	1880	6174 (15)	3.3 (2)
N(21)	3765 (4)	2253 (4)	3109 (9)	2.4 (2)
N(22)	3325 (4)	2881 (4)	3510 (9)	2.3 (2)
C(1)	1331 (7)	3669	6335 (21)	3.4 (3)
C(13)	3252 (6)	1748	7626 (16)	2.5 (3)
C(14)	3819 (6)	1181	7701 (18)	3.5 (3)
C(15)	4007 (6)	993	6283 (19)	3.4 (3)
C(16)	2868 (7)	2132	8872 (19)	3.9 (3)
C(17)	2021 (8)	1969 (8)	8835 (14)	6.5 (4)
C(23)	3648 (5)	3506 (5)	2904 (10)	2.2 (3)
C(24)	4308 (6)	3259 (5)	2163 (10)	2.4 (3)
C(25)	4361 (5)	2500 (6)	2307 (10)	2.3 (3)
C(26)	3341 (6)	4288 (6)	3038 (12)	3.5 (3)
C(27)	3381 (9)	4570 (7)	4604 (14)	6.7 (5)
C(28)	2534 (8)	4358 (6)	2465 (14)	5.1 (4)
B(1)	3552 (7)	1448	3659 (21)	2.1 (4)*

[a] $B_{eq} = {}^4/_3\sum_i\sum_j\beta_{ij}a_i{\cdot}a_j$. The value with an asterisk is a B_{iso} value for the atom refined isotropically.

the temperature factor for this atom could not be refined anisotropically, presumably owing to the low data/parameter ratio. Least-squares refinement converged to $R = 0.042$ and $R_w = 0.043$ (R_w and w are described elsewhere[3]). All peaks in the final difference Fourier map were less than or equal to 0.05 e/Å^3.

The final positional parameters of the refined atoms appear in Table VI. Tables of general temperature factors, calculated hydrogen atom positions, and structure factor amplitudes and a complete listing of bond distances and angles are available.[8]

Co(B(3-*i*-Prpz)$_4$)$_2$ (II). Crystals suitable for diffraction studies were obtained by vapor diffusion of petroleum ether into a dichloromethane 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° 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 V. Intensity data collection, intensity measurements of standard reflections, and data processing were performed as described above. No absorption correction was done.

The structure solution and refinement were performed as described above. One of the isopropyl groups was disordered and was refined isotropically in three separate orientations with multiplicities of 0.5, 0.25, and 0.25. Least-squares refinement converged to values of $R = 0.057$ and $R_w = 0.050$. All peaks in the final difference map were less than or equal to 0.16 e/Å^3, with the largest residual density near N(32).

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 and a complete listing of bond distances and angles are available.[8]

Co(HB(3-*i*-Prpz)$_2$(5-*i*-Prpz))$_2$ (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 0.17° ω at −70 °C. The cell parameters, refined as described above, and other crystallographic data are summarized in Table V. Intensity data collection and data processing were performed as described above. Two standard reflections were collected 38 times throughout the data collection. No absorption correction was done.

The structure solution and refinement were done as described above. Least-squares refinement converged to values of $R = 0.037$ and $R_w = 0.045$. All peaks in the final difference map were less than or equal to 0.26 e/Å^3, with the largest residual density near N(21).

The final positional parameters for the non-hydrogen atoms appear in Table VIII. Tables of general temperature factors, calculated hydrogen atom positions, and structure factor amplitudes and a complete listing of bond distances and angles are available.[8]

Table VII. Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters for Co(B(3-*i*-Prpz)$_4$)$_2$ (II)

atom	x	y	z	B_{eq},^{a} Å^2
Co(1)	5000.0	3699.6 (4)	2500.0	2.9 (1)
N(11)	5549 (2)	4346 (2)	3958 (2)	3.3 (1)
N(12)	4872 (2)	4295 (1)	3285 (2)	3.2 (1)
N(21)	6660 (2)	3453 (2)	3764 (2)	3.6 (1)
N(22)	6165 (2)	3242 (2)	3058 (2)	3.4 (1)
N(31)	6987 (2)	4023 (2)	4963 (2)	4.0 (1)
N(32)	7538 (3)	4539 (2)	4890 (2)	5.6 (1)
N(41)	5672 (2)	3207 (2)	4535 (2)	3.6 (1)
N(42)	5092 (2)	3366 (2)	4921 (2)	4.3 (1)
C(13)	4315 (3)	4834 (2)	3207 (2)	3.8 (1)
C(14)	4626 (3)	5220 (2)	3843 (2)	4.5 (2)
C(15)	5388 (3)	4908 (2)	4290 (2)	4.3 (2)
C(16)	3499 (3)	4938 (2)	2515 (2)	4.9 (2)
C(17)	3493 (4)	5643 (3)	2225 (3)	9.0 (2)
C(18)	2602 (4)	4787 (3)	2636 (3)	9.0 (3)
C(23)	6759 (3)	2905 (2)	2806 (2)	4.1 (1)
C(24)	7634 (3)	2893 (2)	3344 (2)	5.2 (2)
C(25)	7541 (3)	3239 (2)	3931 (3)	4.9 (2)
C(26)	6441 (3)	2605 (2)	2052 (2)	4.6 (2)
C(27)	7170 (4)	2662 (4)	1695 (3)	10.2 (3)
C(28)	6188 (5)	1872 (3)	2090 (3)	10.1 (3)
C(33)	8234 (3)	4578 (2)	5532 (3)	5.4 (2)
C(34)	8132 (3)	4084 (3)	6017 (2)	5.2 (2)
C(35)	7339 (3)	3747 (2)	5642 (2)	4.3 (1)
C(36)	8982 (4)	5117 (4)	5623 (3)	8.8 (3)
C(37)	8787 (9)	5732 (7)	6097 (8)	9.1 (3)*
C(37′)	8659 (13)	5707 (11)	5426 (12)	5.4 (4)*
C(37″)	8820 (12)	5515 (9)	4968 (10)	4.4 (4)*
C(38)	9941 (10)	4880 (7)	6011 (8)	9.0 (4)*
C(38′)	9754 (16)	4916 (12)	6453 (13)	5.7 (5)*
C(38″)	9431 (26)	5280 (19)	6434 (19)	11.3 (10)*
C(43)	4820 (3)	2777 (2)	5115 (2)	4.3 (2)
C(44)	5213 (3)	2238 (2)	4856 (3)	4.6 (2)
C(45)	5751 (3)	2527 (2)	4499 (2)	4.1 (1)
C(46)	4158 (3)	2742 (3)	5551 (3)	6.0 (2)
C(47)	3484 (4)	3309 (3)	5396 (3)	7.1 (2)
C(48)	4694 (4)	2662 (4)	6361 (3)	10.0 (3)
B(1)	6199 (3)	3767 (3)	4303 (2)	3.6 (1)

[a] B_{eq} defined in Table VI.

Table VIII. Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters for Co(HB(3-*i*-Prpz)$_2$(5-*i*-Prpz))$_2$ (III)

atom	x	y	z	B_{eq},^{a} Å^2
Co(1)	5000	5000	5000	1.8 (1)
N(11)	3311 (2)	7126 (2)	6223 (1)	1.9 (1)
N(12)	3212 (2)	6112 (2)	5083 (1)	1.9 (1)
N(21)	4118 (2)	5889 (2)	7660 (1)	2.0 (1)
N(22)	4246 (2)	4728 (2)	6733 (2)	2.0 (1)
N(31)	6006 (2)	7629 (2)	7194 (1)	1.9 (1)
N(32)	6465 (2)	6781 (2)	6149 (1)	2.0 (1)
C(13)	2187 (2)	6298 (2)	4261 (2)	2.1 (1)
C(14)	1663 (2)	7458 (2)	4874 (2)	2.6 (1)
C(15)	2394 (2)	7940 (2)	6106 (2)	2.4 (1)
C(16)	1605 (2)	5279 (2)	2955 (2)	2.6 (1)
C(17)	−39 (3)	4634 (2)	2962 (2)	3.6 (1)
C(18)	1702 (3)	5842 (3)	1860 (2)	4.6 (1)
C(23)	3933 (2)	3744 (2)	7241 (2)	2.4 (1)
C(24)	3618 (3)	4281 (2)	8497 (2)	3.1 (1)
C(25)	3748 (2)	5622 (2)	8722 (2)	2.7 (1)
C(26)	3807 (3)	2291 (2)	6477 (2)	2.9 (1)
C(27)	2203 (3)	1527 (2)	6415 (3)	4.0 (1)
C(28)	4925 (3)	1620 (2)	6988 (3)	3.7 (1)
C(33)	7899 (2)	7318 (2)	6130 (2)	2.4 (1)
C(34)	8380 (2)	8499 (2)	7148 (2)	2.7 (1)
C(35)	7147 (2)	8672 (2)	7814 (2)	2.2 (1)
C(36)	7004 (2)	9723 (2)	9055 (2)	2.8 (1)
C(37)	7090 (3)	9164 (3)	10152 (2)	3.9 (1)
C(38)	8189 (3)	10993 (2)	9322 (3)	4.4 (1)
B(1)	4356 (2)	7240 (2)	7428 (2)	2.0 (1)

[a] B_{eq} defined in Table VI.

Co(HB(3-*i*-Pr-4-Br-pz)$_2$(5-*i*-Pr-4-Br-pz))$_2$ (IV). Crystals suitable for diffraction were obtained by vapor diffusion of petroleum ether into a THF solution of the complex. The crystal was handled as described

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(8) See paragraph at end of the paper regarding supplementary material.

Table IX. Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters for $\text{Co}(\text{HB}(3\text{-}i\text{-Pr-4-Br-pz})_2(5\text{-}i\text{-Pr-4-Br-pz}))_2$ (IV)

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Br(1)	−338.5 (5)	6591.7 (6)	3931.6 (5)	3.7 (1)
Br(2)	3598.3 (5)	2885.3 (6)	8786.9 (4)	3.3 (1)
Br(3)	9829.3 (5)	10843.5 (5)	8012.7 (5)	3.7 (1)
Co(1)	5000	5000	5000	1.5 (1)
N(11)	3182 (3)	6695 (3)	5922 (3)	1.8 (1)
N(12)	3221 (3)	5738 (4)	4880 (3)	1.9 (1)
N(21)	4169 (3)	5641 (3)	7216 (3)	1.6 (1)
N(22)	4301 (3)	4449 (3)	6372 (3)	1.6 (1)
N(31)	5774 (3)	7923 (3)	7118 (3)	1.7 (1)
N(32)	6243 (3)	7187 (4)	6233 (3)	1.9 (1)
C(13)	2095 (4)	5542 (4)	4049 (4)	2.1 (1)
C(14)	1352 (4)	6417 (5)	4606 (4)	2.3 (2)
C(15)	2058 (4)	7117 (4)	5767 (4)	2.2 (1)
C(16)	1766 (4)	4492 (5)	2801 (4)	2.6 (2)
C(17)	304 (5)	3231 (5)	2377 (4)	3.5 (2)
C(18)	1818 (5)	5282 (6)	1989 (4)	4.2 (2)
C(23)	4134 (4)	3354 (4)	6737 (3)	1.8 (1)
C(24)	3909 (4)	3877 (4)	7830 (3)	2.0 (1)
C(25)	3935 (4)	5295 (4)	8094 (3)	2.1 (1)
C(26)	4034 (4)	1809 (5)	5967 (4)	2.5 (2)
C(27)	2492 (5)	674 (5)	5614 (4)	3.1 (2)
C(28)	5086 (5)	1236 (6)	6495 (4)	3.7 (2)
C(33)	7582 (4)	8058 (5)	6426 (3)	2.1 (1)
C(34)	7991 (4)	9354 (5)	7426 (3)	2.2 (1)
C(35)	6831 (4)	9258 (4)	7870 (3)	1.9 (1)
C(36)	6636 (4)	10214 (5)	8981 (4)	2.9 (2)
C(37)	7015 (7)	9693 (6)	9896 (5)	5.0 (2)
C(38)	7457 (5)	11899 (5)	9419 (4)	3.8 (2)
B(1)	4230 (5)	7088 (5)	7086 (4)	1.8 (1)

[a] B_{eq} defined in Table VI.

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 ca. 0.23° ω at −70 °C. The cell parameters were refined on the basis of 23 reflections chosen from diverse regions of reciprocal space. These parameters and other crystallographic data are summarized in Table V. Intensity data and data processing were performed as described above. An empirical absorption correction was carried out, but the data suffer a severe absorption not completely correctable with the DIFABS routine.

The structure solution and refinement were carried out as described above. Least-squares refinement converged to $R = 0.037$ and to $R_w = 0.032$. All peaks in the final difference map were less than or equal to 0.61 e/Å^3, with the largest residual density near Br(1).

The final positional parameters for the non-hydrogen atoms appear in Table IX. Tables of general temperature factors, calculated hydrogen atom positions, and structure factor amplitudes and a complete listing of bond distances and angles are available.[8]

Results

Synthesis of Ligands and Metal Derivatives. The syntheses of the new polypyrazolylborate ligands described here are essentially the same as those used to prepare the parent ligands $[\text{H}_n\text{B}(\text{pz})_{4-n}]^-$[1,9,10] and the derivatives with substituents in the 3-position of the pyrazolyl ring $[\text{H}_n\text{B}(3\text{-Rpz})_{4-n}]^-$, where R is a *tert*-butyl or phenyl group:[2,3] heating potassium tetrahydroborate with an excess of the appropriate pyrazole. The bidentate ligand $[\text{H}_2\text{B}(3\text{-}i\text{-Prpz})_2]^-$, prepared in DMAC, was not isolated as a solid but used as a THF solution to prepare metal complexes. The ligand $[\text{B}(3\text{-}i\text{-Prpz})_4]^-$ could be obtained as the crystalline potassium salt. Unlike the previously reported ligands, their Tl(I) salts could not be isolated and were unsuitable for their characterization. The tris(pyrazole)borate derivative $[\text{HB}(3\text{-}i\text{-Prpz})_3]^-$ was obtained as a solid from the melt reaction of KBH_4 with 3(5)-isopropylpyrazole. It is very soluble in organic solvents but insoluble in alkanes.

A fourth ligand synthesized in this series was $[\text{HB}(3\text{-}i\text{-Pr-4-Br-pz})_3]^-$, easily prepared from 3(5)-isopropyl-4-bromopyrazole and KBH_4 in a melt reaction. The melt temperature must be carefully controlled because of the violent decomposition of the pyrazole when it is overheated. The ligand was obtained practically without contamination by the starting pyrazole, after washing with heptane, and could also be obtained as a crystalline Tl(I) salt (Table IV). These properties are in marked contrast to those of the 4-H derivative.

Metal complexes were prepared by mixing the ligand with the appropriate metal salt. With $[\text{H}_2\text{B}(3\text{-}i\text{-Prpz})_2]^-$, THF solutions of the ligand were added to aqueous solutions of metal nitrates to yield $\text{M}(\text{H}_2\text{B}(3\text{-}i\text{-Prpz})_2)_2$ complexes. Of these derivatives, the square-planar Cu(II) and Ni(II) derivatives were easily crystallized, whereas the tetrahedral Co(II) and Zn(II) derivatives were extremely soluble in hydrocarbon solvents and methanol and were thus difficult to crystallize. All compounds could be sublimed under vacuum and show the expected B–H stretching frequencies in the 2500–2200-cm^{-1} region. The sharp NMR spectrum of the Zn(II) complex shows only one type of pyrazolyl group, indicating rapid inversion of the coordinated $[\text{H}_2\text{B}(3\text{-}i\text{-Prpz})_2]^-$ ligand. In contrast, the proton NMR spectrum of the Ni(II) complex indicates a rigid structure with two types of isopropyl methyl groups.

The coordination chemistry of $[\text{B}(3\text{-}i\text{-Prpz})_4]^-$ is similar to that of $[\text{H}_2\text{B}(3\text{-}i\text{-Prpz})_2]^-$ described above. Organic-solvent-soluble $\text{M}(\text{B}(3\text{-}i\text{-Prpz})_4)_2$ complexes are readily formed with Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) salts. The infrared spectra of all of these complexes are essentially superimposable, suggesting identical structures. Surprisingly, the colors of the violet Co(II) complex, the reddish purple Ni(II) complex, and the red-brown Cu(II) complex are characteristic of tetrahedral, not planar or octahedral, geometries. The crystal structure determination of $\text{Co}(\text{B}(3\text{-}i\text{-Prpz})_4)_2$ confirmed the tetrahedral geometry about the metal ion (vide infra). The NMR spectra of the Zn(II) and Co(II) derivatives are also consistent with this structural assignment. This structure has not been observed with other tetrakis(pyrazolyl)borate ligands. In all other cases, these ligands coordinate as tridentate ligands, with one uncoordinated pyrazolyl group.

The coordination chemistry of $[\text{B}(3\text{-}i\text{-Prpz})_4]^-$ with molybdenum complexes is clearly different from that with first-row transition-metal and Zn(II) ions and similar to that of other tetrakis(pyrazolyl)borate ligands. In the complex $[\text{Mo}(\text{B}(3\text{-}i\text{-Prpz})_4)(\text{CO})_3]^-$ (prepared from $\text{Mo}(\text{CO})_6$ and isolated as the tetraethylammonium salt), the $[\text{B}(3\text{-}i\text{-Prpz})_4]^-$ ligand is clearly tridentate. The sharp NMR spectrum of $\text{Mo}(\text{B}(3\text{-}i\text{-Prpz})_4)(\text{NO})(\text{CO})_2$ shows three types of 3-isopropylpyrazolyl groups in a 1:2:1 ratio, consistent with tridentate coordination; rotation about the Mo–B axis is restricted, even for other tris(pyrazolyl)borate complexes, which show 2:1 pyrazolyl group patterns.[11]

Reactions of $[\text{HB}(3\text{-}i\text{-Prpz})_3]^-$ with first-row transition-metal ions analogous to those with $[\text{H}_2\text{B}(3\text{-}i\text{-Prpz})_2]^-$ and $[\text{B}(3\text{-}i\text{-Prpz})_4]^-$ yield two different types of compounds. Adding the ligand to iron(II), cobalt(II), and nickel(II) nitrates produced bisligand complexes that have relatively high melting points, are sublimable, and are soluble in organic solvents. The colors of these compounds suggest formation of octahedral compounds (Table II). On the other hand, the initial Cu(II) product from these reactions was a low-melting blue solid with an infrared spectrum showing two widely separated B–H stretching frequencies (2495, 2410 cm^{-1}), which differ significantly from the overlapping bands (2480, 2450 cm^{-1}) seen with the other complexes produced in this manner. When this product was heated under vacuum at 245 °C, a dark blue Cu(II) complex sublimed. This material has a relatively high melting point (239–240 °C), shows overlapping B–H stretching frequencies (2508, 2480 cm^{-1}), and has an EPR spectrum and elemental analyses identical with those of the initial low-melting derivative. Although the high-melting Cu(II) derivative appears to be isostructural with the other bisligand complexes, the differences between the low- and high-melting forms are not obvious. The high-melting form most likely contains the rearranged ligand

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Table X. Calculated Isotropic and Observed Shifts for Co(HB(3-*i*-Prpz)$_2$(5-*i*-Prpz))$_2$

calcd isotropic shift, ppm	obsd total shift, ppm	assignt
−122	−108	3-*i*-Pr H
+50	+55	5-*i*-Pr H
−32	−27, −35	3-*i*-Pr Me group H
+10	+18	5-*i*-Pr Me group H

described below, whereas the low-melting form contains the starting ligand [HB(3-*i*-Prpz)$_3$]$^-$ coordinated to the Cu(II) ion in a bidentate or unsymmetrical tridentate mode.

The reaction of zinc nitrate with [HB(3-*i*-Prpz)$_3$]$^-$ yields a mixture of products. The less soluble, and easier to isolate, product is Zn(HB(3-*i*-Prpz)$_3$)NO$_3$, which can be prepared in good yield by the slow addition of the potassium salt of the ligand to excess aqueous zinc nitrate. The second product from this reaction is a bisligand complex, very soluble in most organic solvents, difficult to isolate in pure form, and best obtained by using zinc perchlorate rather than the nitrate, followed by recrystallization from hexane (with considerable solubility losses). This material has a relatively low melting point (140 °C) and an IR spectrum similar to those of the Fe(II), Ni(II), and Co(II) analogues, presumably indicating an octahedral geometry. However, the observed NMR spectrum was not the expected one: the 5-H, 4-H, and isopropyl protons are in a 2:1 pattern, while the isopropyl methyl group protons are in a 6:6:6 ratio, with two of the peaks close together. These spectral features are in strong contrast to the NMR spectra of Zn(HB(3-*i*-Prpz)$_3$)(X) complexes, with only one type of pyrazolyl group because of the C_{3v} symmetry, or Zn(HB(pz)$_3$)$_2$ and Zn(B(pz)$_4$)$_2$, which show only one type of pyrazolyl group because of rapid exchange of coordinated and uncoordinated pyrazolyl groups.[12]

Sublimation of this low-melting Zn(II) complex under high vacuum at 250 °C yields a new product, which now has a relatively high melting point (244–246 °C) and an infrared spectrum showing a shift of the pair of B–H stretching frequencies from 2480, 2450 cm^{-1} to 2500, 2480 cm^{-1}. The NMR spectrum retains the 2:1 pattern for the 5-H, 4-H, and isopropyl group protons and the 6:6:6 methyl ratio, but their intensity patterns are reversed.

More insight into the structure of the bisligand complexes was gained from the NMR spectrum of the paramagnetic Co(II) complex, in which the peaks ranged from +93 to −108 ppm and were very clearly separated. The 5-H, 4-H, and isopropyl group proton peaks were in the 2:1 pattern, and the peaks for the isopropyl methyl groups appeared in a 6:6:6 ratio. Because the difference in the chemical shifts of the isopropyl group was too substantial to be accounted for by, e.g., the presence of two rotamers, we were forced to consider the possibility of a rearrangement of the ligand, with one of the pyrazolyl groups becoming bonded to the boron atom as a 5-isopropylpyrazolyl group.

The octahedral complex Co(HB(pz)$_3$)$_2$ is one of the best documented examples of quantitative calculation of paramagnetic shifts.[13] The sensitivity of the paramagnetic shifts results from the strong angular and distance dependence of the function (3 cos^2 θ − 1/3R^3), coupled with an unusually large magnetic susceptibility anisotropy ($\Delta\|\chi$ = 1.66 × 10^{-27} cm^3). These combine to produce a highly sensitive probe of the position of the protons relative to the metal through the dominance of the pseudocontact contribution to the proton chemical shifts.

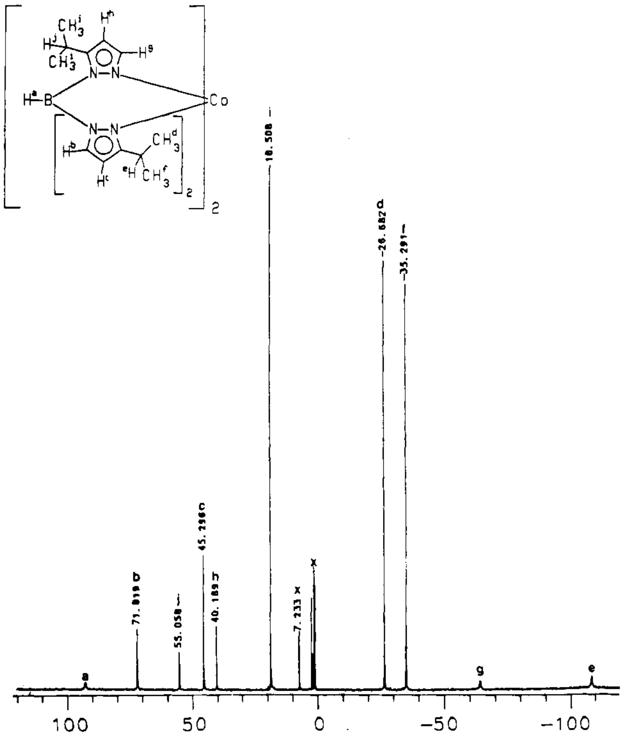

Figure 1. NMR spectrum of Co(HB(3-*i*-Prpz)$_2$(5-*i*-Prpz))$_2$ (III). Solvent and free ligand resonances are marked with an X.

Using the well-known geometry of this complex, we calculated the expected isotropic shifts for the isopropyl tertiary hydrogen atom of a 3-isopropyl and 5-isopropyl group and for the corresponding methyl groups. In each case, it was assumed that the isopropyl group was in the least hindered rotamer, with the methyl groups pointing toward the 4-proton of the pyrazolyl group and the tertiary hydrogens toward the Co and B atoms. The values shown in Table X were obtained. Alternative configurations produced considerably worse agreement. Given the approximations of geometry, neglect of contact contributions to the shift, and comparison with total shift uncorrected for coordination, the fit is remarkable.[13f] Additionally, the assignment clarifies an earlier vexing problem of a 2-D COSY cross-peak between the +55 ppm H atom and the +18 ppm methyl group. The peak represents J coupling between the 5-isopropyl methyl and tertiary protons that are now further removed from the metal center and have sufficiently sharp lines (long T_2) to allow coherence transfer to develop. Cross-peaks are not observed with the corresponding 3-isopropyl groups because of short T_2 values of the tertiary protons. An additional strong cross-peak is observed between two 3-isopropyl methyl resonances, indicating that the two methyl groups of a single isopropyl group have different chemical shifts.

The remainder of the peak assignments are shown in Figure 1. These data clearly show that the ligand in this complex has become [HB(3-*i*-Prpz)$_2$(5-*i*-Prpz)]$^-$, which was also confirmed by the subsequent X-ray diffraction study (vide infra). Such an assignment is consistent with the 2:1 patterns for the pyrazolyl protons and also predicts a 6:6:6 pattern for the isopropyl methyl groups, corresponding to the unique 5-isopropyl group and the outer and inner methyl groups of the equivalent 3-isopropyl groups.

Complexes of the form M(HB(3-*i*-Prpz)$_3$)(X) were synthesized by the slow addition of the ligand to excess aqueous MX$_2$. Unlike the 3-*tert*-butyl analogue,[2,3] this ligand is not a "tetrahedral enforcer"; formation of the bisligand complex is a competing reaction. The easiest derivatives to prepare are Zn(HB(3-*i*-Prpz)$_3$)(X) (X = NCO, NCS, N$_3$, NO$_3$) because of the strong tendency of Zn(II) ions to form tetrahedral complexes. The NMR spectra of these complexes are consistent with the expected C_{3v} symmetry and are, in fact, a very convenient way to check the

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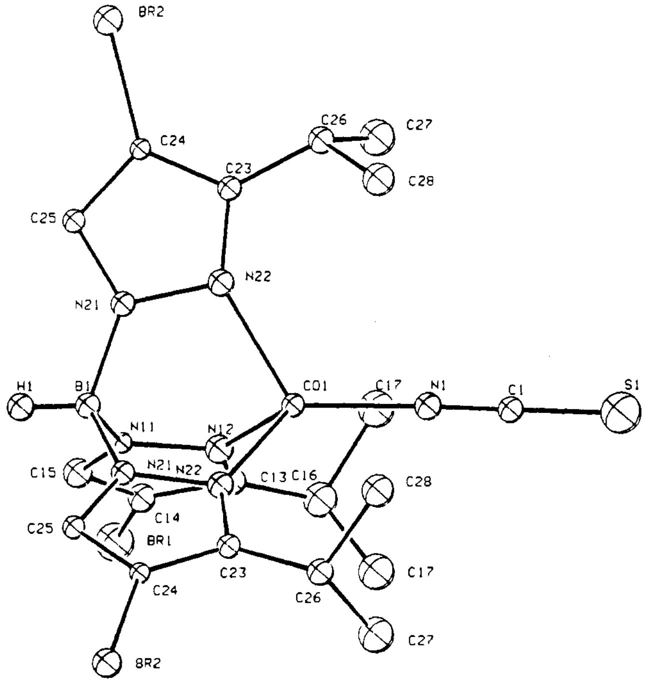

Figure 2. View of Co(HB(3-*i*-Pr-4-Br-pz)$_3$)(NCS) (I). The vibrational ellipsoids are drawn at the 50% level in this and the other figures.

purity of the ligand. The IR spectra show a single, sharp band for the B–H stretch in the 2510–2520-cm^{-1} region, which is noticably different from the asymmetric, overlapping doublet of the bisligand complexes.

The Co(HB(3-*i*-Prpz)$_3$)(X) complexes (X = NCO, NCS) show a somewhat different coordination chemistry. The complex with X = NCO is deep blue and is assigned a tetrahedral, monomeric structure. Deep blue solutions are formed on dissolution in noncoordinating solvents (hydrocarbons, dichloromethane, acetone, isopropyl alcohol), but pink to wine red solutions result in more coordinating solvents (acetonitrile, DMAC, methanol). The solvents in the second group thus are able to coordinate to the metal ion, as in the case of the 3-phenyl analogue Co(HB(3-Phpz)$_3$)(NCS)(THF).[2,3] These solvent molecules are only weakly coordinated, because evaporation of solvent yields the original blue Co(II) complex. The deep violet Co(HB(3-*i*-Prpz)$_3$)(NCS) complex behaves in a similar manner in the solvents indicated above, but on crystallization from the blue solution or blue melt, the original violet solid was obtained, suggesting formation of a five-coordinated dimeric structure. The green Ni(II) complexes Ni(HB(3-*i*-Prpz)$_3$)(X) (X = NCO, NCS) behave similarly.

The coordination chemistry of [HB(3-*i*-Prpz)$_3$]$^-$ with molybdenum compounds is similar to that of other polypyrazolylborate ligands.[1-3,14,15] Reaction of the potassium salt with Mo(CO)$_3$ produced the [Mo(HB(3-*i*-Prpz)$_3$)(CO)$_3$]$^-$ anion, which was isolated as a stable tetraethylammonium salt. The nitrosyl derivative Mo(HB(3-*i*-Prpz)$_3$)(NO)(CO)$_2$ was produced from this anion and showed a 2:1 pattern of the pyrazolyl protons. The yellow π-allyl complex Mo(HB(3-*i*-Prpz)$_3$)(η^3-CH$_2$C(CH$_3$)-CH$_2$)(CO)$_2$ was also prepared and shows a sharp proton NMR spectrum, indicating a rigid structure.

Preparation of metal complexes with [HB(3-*i*-Pr-4-Br-pz)$_3$]$^-$ was done in a manner similar to that described above for [HB-(3-*i*-Prpz)$_3$]$^-$. Complexes of the form M(HB(3-*i*-Pr-4-Br-pz)$_3$)(X) were formed readily on addition of the potassium salt to aqueous MX$_2$ solutions. Initially, a solvated complex was obtained, but on air drying, solvent was lost and four-coordinate complexes were obtained, with M = Co(II) and Ni(II). With zinc salts, tetrahedral complexes were obtained directly. The loss of solvent from the Co(II) and Ni(II) compounds was easy to observe because the Co(II) complexes changed from a salmon color to deep blue, whereas the Ni(II) complexes changed from green to light red. The NCO and NCS complexes are similar to those with [HB-(3-*i*-Prpz)$_3$]$^-$.

Table XI. Selected Bond Distances (Å) and Angles (deg) for Co(HB(3-*i*-Pr-4-Br-pz)$_3$)(NCS) (I)

Co–N(1)	1.927 (12)	N(11)–B	1.536 (21)
Co–N(12)	2.038 (12)	C(15)–C(14)	1.361 (21)
Co–N(22)	2.016 (8)	C(13)–C(14)	1.403 (19)
Co–N(22)a	2.017 (8)	C(13)–C(16)	1.470 (21)
S–C(1)	1.562 (18)	C(16)–C(17)	1.506 (15)
N(1)–C(1)	1.168 (18)	C(16)–C(17)a	1.507 (15)
N(11)–N(12)	1.359 (15)	C(14)–Br(1)	1.855 (15)
N(11)–C(15)	1.340 (16)		

N(1)–Co–N(12)	119.0 (5)	N(12)–C(13)–C(16)	126 (1)
N(1)–Co–N(22)	122.7 (3)	N(11)–C(15)–C(14)	109 (1)
N(1)–Co–N(22)a	122.8 (3)	C(14)–C(13)–C(16)	127 (1)
N(12)–Co–N(22)	95.2 (3)	C(13)–C(14)–C(15)	107 (1)
N(12)–Co–N(22)	95.1 (3)	C(13)–C(16)–C(17)	110 (1)
N(22)–Co–N(22)a	95.2 (4)	C(13)–C(16)–C(17)a	110 (1)
Co–N(12)–N(11)	111 (1)	C(17)–C(16)–C(17)a	112 (2)
S–C(1)–N(1)	177 (2)	C(13)–C(14)–Br(1)	127 (1)
N(12)–C(13)–C(14)	107 (1)	C(15)–C(14)–Br(1)	126 (1)

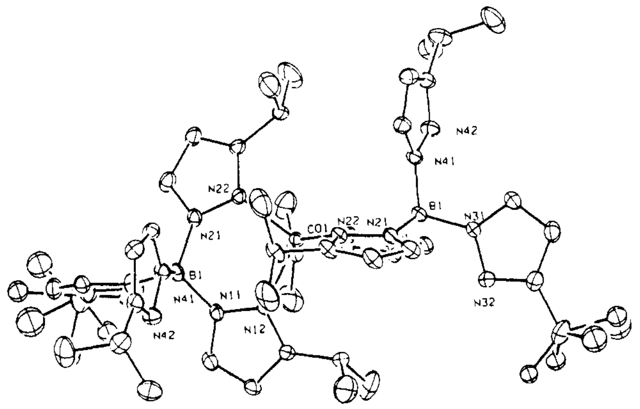

Figure 3. View of Co(B(3-*i*-Prpz)$_4$)$_2$ (II).

Bisligand complexes with [HB(3-*i*-Pr-4-Br-pz)$_3$]$^-$ were more difficult to form than those with the [HB(3-*i*-Prpz)$_3$]$^-$ ligand. These complexes with the 4-bromo analogue could only be formed under forcing conditions: reacting anhydrous MCl$_2$ with the thallium salt of the ligand in refluxing toluene. On the other hand, formation of the bisligand complex is unavoidable in reactions of the 4-H derivative. The reduced nucleophilicity of the [HB-(3-*i*-Pr-4-Br-pz)$_3$]$^-$ ligand is also evident in the higher temperature necessary for the reaction with Mo(CO)$_6$ to yield [Mo(HB(3-*i*-Pr-4-Br-pz)$_3$)(CO)$_3$]$^-$.

Description of the Structure of Co(HB(3-*i*-Pr-4-Br-pz)$_3$)(NCS) (I). The overall structure of this Co(II) compound is apparent in the drawing of the molecule (Figure 2) and consists of well-separated neutral monomeric Co(HB(3-*i*-Pr-4-Br-pz)$_3$)(NCS) molecules. The ligand coordinates to the Co(II) ion through the nitrogen atom in the 2-position of each of the pyrazolyl rings, in a manner analogous to that for other polypyrazolylborate ligands.[2,3,6,15-17] The thiocyanate group is coordinated to the Co(II) ion through the nitrogen atom to form a four-coordinate complex. In Figure 2 it can be seen that all of the isopropyl groups are in the 3-position of the pyrazolyl group and that all of its methyl groups are turned toward the NCS group and away from the bromine atom. This orientation thus closely resembles that ob-

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Table XII. Selected Bond Distances (Å) and Angles (deg) for $Co(B(3\text{-}i\text{-}Pr)_4)_2$ (II)

Co–N(12)	1.980 (3)	C(13)–C(14)	1.388 (5)
Co–N(22)	1.970 (3)	C(13)–C(16)	1.507 (5)
N(11)–N(12)	1.370 (4)	C(14)–C(15)	1.348 (5)
N(11)–C(15)	1.348 (5)	C(16)–C(17)	1.507 (7)
N(12)–C(13)	1.345 (4)	C(16)–C(18)	1.496 (7)
N(11)–B(1)	1.520 (5)		
N(12)–Co–N(22)	99.1 (1)	N(12)–C(13)–C(14)	108.8 (4)
N(12)–Co–N(12)a	106.6 (2)	N(12)–C(13)–C(16)	120.9 (4)
N(12)–Co–N(22)a	113.1 (1)	N(11)–C(15)–C(14)	109.3 (4)
Co–N(12)–N(11)	122.2 (2)	C(14)–C(13)–C(16)	130.3 (4)
Co–N(12)–C(13)	127.6 (3)	C(13)–C(14)–C(15)	106.4 (4)
N(12)–N(11)–C(15)	108.2 (3)	C(13)–C(16)–C(18)	111.5 (4)
C(15)–N(11)–B(1)	127.8 (3)	C(17)–C(16)–C(18)	110.5 (5)
N(11)–B(1)–N(21)	112.6 (3)		

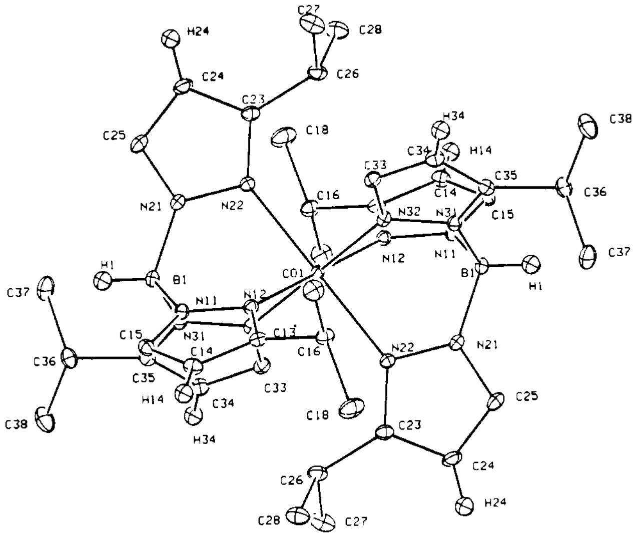

Figure 4. View of $Co(HB(3\text{-}i\text{-}Prpz)(5\text{-}i\text{-}Prpz))_2$ (III).

served for the *tert*-butyl groups in $Co(HB(3\text{-}t\text{-}Bupz)_3)(NCS)$.[2,3]

Selected bond distances and angles are presented in Table XI. The Co–N bond distances and angles are nearly identical with those observed in the structure of the 3-*tert*-butyl derivative,[2,3] with all distances and angles within 4ω. The geometry of the Co(II) inner coordination sphere may be described as trigonally distorted tetrahedral and is very nearly C_{3v}.

Description of the Structure of $Co(B(3\text{-}i\text{-}Prpz)_4)_2$ (II). The overall structure of this Co(II) complex is apparent in the drawing of the molecule (Figure 3) and consists of well-separated neutral, monomeric $Co(B(3\text{-}i\text{-}Prpz)_4)_2$ molecules. The ligands coordinate to the Co(II) ion through the nitrogen atom in the 2-position of two of the 3-isopropylpyrazolyl rings, with the two additional rings of the ligand not coordinated to, and well-displaced from, the metal ion. In Figure 3 it can also be seen that all of the isopropyl groups are in the 3-position of the pyrazolyl ring and that the metal-coordinating rings have their isopropyl groups bisecting the ring and the C–H bond oriented toward the metal ion, approaching within 2.8 Å, whereas the isopropyl groups of the uncoordinated groups are in an intermediate position.

Selected bond distances and angles are presented in Table XII. Co–N(pyrazolyl) distances and bond angles are nearly identical with those observed for $Co(H_2B(pz)_2)_2$, which also has a Co(II) ion coordinated to four pyrazolyl groups from two ligands.[16] These bond distances are also typical of Co^{II}–N distances in polypyrazolylborate complexes in general.[2,3,15-17] The geometry about the Co inner coordination sphere may be described as a flattened tetrahedron.

Description of the Structure of $Co(HB(3\text{-}i\text{-}Prpz)_2(5\text{-}i\text{-}Prpz))_2$ (III). The overall structure of the molecule is apparent in the drawing of the molecule (Figure 4) and consists of well-separated neutral, monomeric $Co(HB(3\text{-}i\text{-}Prpz)_2(5\text{-}i\text{-}Prpz))_2$ molecules. The ligands coordinate to the metal ion through the nitrogen atoms in the 2-position of the pyrazolyl rings of each of the two ligands.

Table XIII. Selected Bond Distances (Å) and Angles (deg) for $Co(HB(3\text{-}i\text{-}Prpz)_2(5\text{-}i\text{-}Prpz))_2$ (III)

Co–N(12)	2.170 (2)	N(12)–C(13)	1.348 (2)
Co–N(22)	2.164 (2)	C(13)–C(14)	1.398 (3)
Co–N(32)	2.102 (2)	C(13)–C(16)	1.506 (3)
N(11)–N(12)	1.366 (2)	C(14)–C(15)	1.376 (3)
N(11)–C(15)	1.340 (2)	C(16)–C(17)	1.533 (3)
N(11)–B	1.550 (3)	C(16)–C(18)	1.521 (3)
N(12)–Co–N(22)	84.45 (6)	N(11)–C(15)–C(14)	108.6 (2)
N(12)–Co–N(32)	88.77 (6)	C(14)–C(13)–C(16)	127.5 (2)
N(22)–Co–N(32)	88.58 (6)	C(13)–C(14)–C(15)	105.4 (2)
Co–N(12)–N(11)	113.4 (1)	C(13)–C(16)–C(17)	108.8 (2)
Co–N(12)–C(13)	138.2 (1)	C(13)–C(16)–C(18)	114.2 (2)
N(12)–N(11)–C(15)	109.8 (2)	C(17)–C(16)–C(18)	109.3 (2)
N(12)–N(11)–B	122.2 (1)	N(11)–B–N(21)	110.1 (2)
C(15)–N(11)–B	128.0 (2)	N(11)–B–N(31)	108.3 (2)
N(12)–C(13)–C(14)	109.5 (2)	N(21)–B–N(31)	109.2 (2)
N(12)–C(13)–C(16)	122.6 (2)		

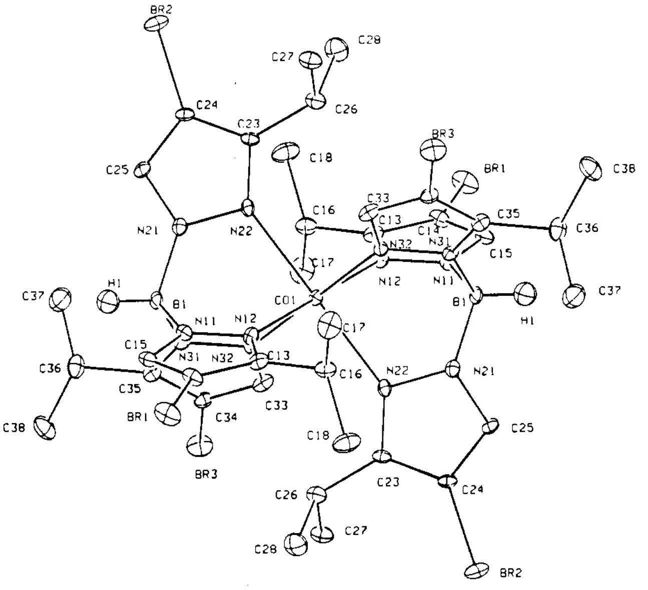

Figure 5. View of $Co(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}i\text{-}pz)_2(5\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz))_2$ (IV).

In Figure 4 it can be seen that, for two of the rings of each ligand, the isopropyl group is in the 3-position, whereas for the third ring the isopropyl group is in the 5-position. It can also be seen that these groups are oriented such that two of them bisect the pyrazolyl ring, whereas the third ring (with the 5-isopropyl group) has an intermediate arrangement. The C–C–H dihedral angles for rings 1, 2, and 3 are 8.2, 4.3, and 42.3°.

Selected bond distances and angles are presented in Table XIII. The Co–N distances and angles are typical of Co–N bonds in polypyrazolylborate complexes, particularly $Co(HB(pz)_3)_2$, and of Co–N bonds in general.[2,3,15-17] There are no unusual features in the structure.

Description of the Structure of $Co(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_2(5\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz))_2$ (IV). The overall structure of the molecule is apparent in the drawing of the molecule (Figure 5) and consists of well-separated neutral, monomeric $Co(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_2(5\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz))_2$ molecules. The overall features of this structure are identical with those for III described above. Again, the ligand has undergone a rearrangement, with one of the pyrazolyl groups having a 5-isopropyl rather than a 3-isopropyl group. The arrangement of the isopropyl groups is the same as that for III; two isopropyl groups bisect the pyrazolyl plane, whereas for the unique pyrazolyl ring, the isopropyl group is in an intermediate orientation. The C–C–H dihedral angles for rings 1, 2, and 3 are 2.1, 6.4, and 33.4°.

Selected bond distances and angles are presented in Table XIV. The Co–N bond distances and angles are nearly identical with those for III. The bromine atoms appear to have no effect on the ligand coordination to the cobalt ion. There are no other unusual features.

Table XIV. Selected Bond Distances (Å) and Angles (deg) for Co(HB(3-*i*-Pr-4-Br-pz)$_2$(5-*i*-Pr-4-Br-pz))$_2$ (IV)

Co–N(12)	2.151 (3)	C(13)–C(16)	1.500 (6)
Co–N(22)	2.207 (3)	C(14)–C(15)	1.369 (6)
Co–N(32)	2.086 (3)	C(16)–C(17)	1.526 (6)
N(11)–N(12)	1.367 (4)	C(16)–C(18)	1.538 (6)
N(11)–C(15)	1.341 (5)	Br(1)–C(14)	1.883 (4)
N(12)–C(13)	1.351 (5)	Br(2)–C(24)	1.875 (4)
N(11)–B	1.540 (6)	Br(3)–C(34)	1.872 (4)
C(13)–C(14)	1.407 (5)		

N(12)–Co–N(22)	84.8 (1)	N(12)–C(13)–C(16)	122.3 (3)
N(12)–Co–N(32)	87.3 (1)	N(11)–C(15)–C(14)	107.5 (3)
N(22)–Co–N(32)	89.6 (1)	C(14)–C(13)–C(16)	130.7 (4)
Co–N(12)–N(11)	113.8 (2)	C(13)–C(14)–C(15)	107.6 (3)
Co–N(12)–C(13)	138.2 (2)	C(13)–C(16)–C(17)	111.1 (3)
N(12)–N(11)–C(15)	109.9 (3)	C(13)–C(16)–C(18)	113.6 (4)
N(12)–N(11)–B	123.1 (3)	C(17)–C(16)–C(18)	109.0 (4)
C(15)–N(11)–B	126.9 (3)	N(11)–B–N(21)	109.9 (3)
N(11)–N(12)–C(13)	108.0 (3)	N(11)–B–N(31)	109.3 (3)
C(13)–C(14)–Br	127.8 (3)	N(21)–B–N(31)	108.7 (3)
N(12)–C(13)–C(14)	107.0 (4)		

Discussion

The preparations presented above yield new polypyrazolylborate ligands with properties different from either the parent ligands such as [H$_n$B(pz)$_{4-n}$]$^-$ and [H$_n$B(3,5-Me$_2$pz)$_{4-n}$]$^-$ or the more recently reported ligands [H$_n$B(3-Rpz)$_{4-n}$]$^-$ (R = *tert*-butyl, phenyl). The basic synthetic scheme is the same for all of these ligands: heating sodium or potassium tetrahydroborate with an excess of the appropriate pyrazole.[1-3,8,9] Hydrogen gas is evolved during the reaction and is used to measure its progress. The detailed synthesis is analogous to that for the 3-*tert*-butyl and 3-phenyl derivatives. Although it is difficult in some cases to obtain ligands free of starting pyrazole, the materials from these preparations are suitable for the synthesis of metal complexes (Tables I–IV).

The differences between these new ligands and those reported previously are evident in the reactions with transition-metal and zinc ions. The parent ligands lead to M(HB(pz)$_3$)$_2$ or M(HB(3,5-Me$_2$pz)$_3$)$_2$ complexes on reaction with MX$_2$ compounds. On the other hand, only M(HB(3-Rpz)$_3$)(X) and M(HB(3-Phpz)$_3$)(X)(solvent) complexes were isolated with R = *tert*-butyl and phenyl groups, respectively. With the [HB(3-*i*-Prpz)$_3$]$^-$ and [HB(3-*i*-Pr-4-Br-pz)$_3$]$^-$ ligands both types of complexes can be isolated, with the appropriate choice of reaction conditions. These new ligands are thus transitional in coordination properties to first-row metal ions between the sterically nondemanding ligands and those with bulky groups in the 3-position of the pyrazolyl ring.

In their coordination chemistry, the two ligands [HB(3-*i*-Prpz)$_3$]$^-$ and [HB(3-*i*-Pr-4-Br-pz)$_3$]$^-$ show many similarities, but also some significant differences, the major being the preference for the type of complex formed with MX$_2$ compounds. With the 4-H derivative, the bisligand complexes form very readily, whereas complexes of the form M(HB(3-*i*-Prpz)$_3$)(X) are more difficult to prepare. This coordination chemistry is thus somewhat similar to that of the parent ligands [HB(pz)$_3$]$^-$ and [HB(3,5-Me$_2$pz)$_3$]$^-$. On the other hand, M(HB(3-*i*-Pr-4-Br-pz)$_3$)(X) or M(HB(3-*i*-Pr-4-Br-pz)$_3$)(X)(solvent) complexes are easily prepared, whereas preparation of the bisligand complexes requires more forcing conditions. The properties of this ligand thus resemble those of the [HB(3-Rpz)$_3$]$^-$ ligands with bulky groups in the 3-position, which cannot form bisligand complexes.[2,3]

The spectroscopic and X-ray diffraction studies reveal a unique feature of these new ligands: rearrangement of the mode of coordination by the pyrazolyl group to relieve steric crowding. The crystal structure determinations of Co(HB(3-*i*-Pr-4-Br-pz)$_3$)(NCS) (I) and Co(B(3-*i*-Prpz)$_4$)$_2$ (II) unequivocally establish that the synthetic procedures yield ligands with the bulky substituent in the 3-position of the pyrazolyl ring and thus away from the boron atom. This result is consistent with our recently reported study of the [H$_n$B(3-*t*-Bupz)$_{4-n}$]$^-$ and [H$_n$B(3-Phpz)$_{4-n}$]$^-$ ligands, which established that the reaction between [BH$_4$]$^-$ and 3-R-pyrazoles is regiospecific.[2,3] However, the structural studies of the complexes Co(HB(3-*i*-Prpz)$_2$(5-*i*-Prpz))$_2$ (III) and Co(HB(3-*i*-Pr-4-Br-pz)$_2$(5-*i*-Pr-4-Br-pz))$_2$ (IV) show that the ligands have undergone a rearrangement, with one of the rings substituted in the 5- rather than 3-position. In several cases, addition of the potassium salt to a MX$_2$ compound yielded two types of bisligand complexes; these compounds differed in their IR spectral properties and melting points but not in their elemental analyses. Sublimation and/or recrystallization of the derivative with the lower melting point produces a sample with a relatively high melting point. IR spectra of all of the high-melting derivatives are nearly identical with those of the structurally characterized Co(II) compounds III and IV, suggesting that all of these compounds have similar structures.

Why does this surprising rearrangement take place and what prevents the existence of octahedral M(HB(3-*i*-Prpz)$_3$)$_2$ compounds and the 4-Br analogues? Molecular models show that such a structure, with all the isopropyl groups in the least hindered conformation with regard to the metal ion (i.e., straddling the pyrazolyl plane), is characterized by an equatorial belt (along the B–metal–B axis) of six isopropyl groups, with severe nonbonding interactions between the twelve methyl groups. Reversal of one pyrazolyl group to a 5-isopropyl group relieves this strain and makes the octahedral structure possible. This rearrangement most likely occurs unimolecularly through a 1,2-shift of the B–N bond of one of the pyrazolyl groups. Such rearrangement is, presumably, impossible in the case of the [B(3-*i*-Prpz)$_4$]$^-$ ligand because of steric interactions of 5-isopropyl groups with the fourth pyrazolyl substituent. These steric interactions make octahedral M(B(3-*i*-Pr)$_4$)$_2$ structures impossible and lead to tetrahedral coordination.

Conclusion

The polypyrazolylborate ligand [HB(3-Rpz)$_3$]$^-$ containing a 3-isopropyl group can be regarded as a transitional ligand in its reactions with first-row transition-metal ions, with properties lying between those of the 3-methyl and the 3-*tert*-butyl analogues. This ligand resembles the 3-methyl analogue in forming octahedral bisligand complexes. Yet simple bisligand complexes such as M(HB(pz)$_3$)$_2$ are not formed with this new ligand; rather, the ligand undergoes a 1,2-borotropic shift to yield a B–(5-isopropylpyrazolyl) bond. On the other hand, the 3-isopropyl derivatives also resemble the 3-*tert*-butyl derivatives in forming M(HB(3-Rpz)$_3$)X complexes. Yet the 3-isopropyl complexes offer greater accessibility of the metal to nucleophilic reagents. Subtle, though significant, modifications of reactivity with retention of the steric features are achieved through replacement of the 4-H atom of the pyrazolyl ring with a bromine atom. The coordination chemistry of the [B(3-*i*-Prpz)$_4$]$^-$ ligand is unique and different from that of the other tetrakis(pyrazolyl)borate derivatives. This ligand coordinates to first-row metal ions to form exclusively tetrahedral M(B(3-*i*-Prpz)$_4$)$_2$ complexes. All other ligands of this type coordinate as tridentate ligands with one, rather than two, uncoordinated pyrazolyl groups.

Registry No. I, 119010-22-9; II, 119038-48-1; III, 119010-10-5; IV, 119010-32-1; KH$_2$B(3-*i*-Prpz)$_2$, 119009-95-9; KHB(3-*i*-Prpz)$_3$, 119009-96-0; KB(3-*i*-Prpz)$_4$, 119009-97-1; KHB(3-*i*-Pr-4-Br-pz)$_3$, 119009-98-2; Co[H$_2$B(3-*i*-Prpz)$_2$]$_2$, 119009-99-3; Ni[H$_2$B(3-*i*-Prpz)$_2$]$_2$, 119010-00-3; Cu[H$_2$B(3-*i*-Prpz)$_2$]$_2$, 119010-01-4; Zn[H$_2$B(3-*i*-Prpz)$_2$]$_2$, 119010-02-5; Fe[HB(3-*i*-Prpz)$_2$(5-*i*-Prpz)]$_2$, 119010-09-2; Co[HB(3-*i*-Prpz)$_3$](NCO), 119010-03-6; Co[HB(3-*i*-Prpz)$_3$](NCS), 119010-04-7; Ni[HB(3-*i*-Prpz)$_2$(5-*i*-Prpz)]$_2$, 119010-11-6; Ni[HB(3-*i*-Prpz)$_3$](NCO), 119010-05-8; Ni[HB(3-*i*-Prpz)$_3$](NCS), 119010-06-9; Cu[HB(3-*i*-Prpz)$_2$(5-*i*-Prpz)]$_2$, 119010-12-7; Zn[HB(3-*i*-Prpz)$_2$(5-*i*-Prpz)]$_2$, 119010-13-8; Zn[HB(3-*i*-Prpz)$_3$](NCO), 119010-07-0; Zn[HB(3-*i*-Prpz)$_3$](NCS), 119010-08-1; Fe[B(3-*i*-Prpz)$_4$]$_2$, 119038-47-0; Ni[B(3-*i*-Prpz)$_4$]$_2$, 119038-49-2; Cu[B(3-*i*-Prpz)$_4$]$_2$, 119010-14-9; Zn[B(3-*i*-Prpz)$_4$]$_2$, 119010-15-0; Co[HB(3-*i*-Pr-4-Br-pz)$_3$]Cl, 119010-20-7; Mo[B(3-*i*-Prpz)$_4$](NO)(CO)$_2$, 119010-16-1; [N(C$_2$H$_5$)$_4$][Mo{B(3-*i*-Prpz)$_4$}(CO)$_3$], 119010-18-3; Tl[HB(3-*i*-Pr-4-Br-pz)$_3$], 119010-19-4; Fe[HB(3-*i*-Pr-4-Br-pz)$_2$(5-*i*-Pr-4-Br-pz)]$_2$, 119038-50-5; Co[HB(3-*i*-Pr-4-Br-pz)$_3$](NCO), 119010-21-8; Ni[HB(3-*i*-Pr-4-Br-pz)$_2$(5-*i*-Pr-4-Br-pz)]$_2$, 119010-33-2; Ni[HB(3-*i*-Pr-4-Br-pz)$_3$]Cl, 119010-23-0; Ni[HB(3-*i*-Pr-4-Br-pz)$_3$](NCO), 119010-24-1; Ni[HB(3-*i*-Pr-4-pz)$_3$](NCS), 119010-25-2; Zn[HB(3-*i*-Pr-4-Br-pz)$_3$]Cl, 119010-26-3; Zn[HB(3-*i*-Pr-4-Br-pz)$_3$](NCO), 119010-27-4; Zn[HB(3-*i*-Pr-4-Br-pz)$_3$](NCS), 119010-

28-5; $Zn[HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3]N_3$, 119010-29-6; $Mo[HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3](NO)(CO)_2$, 119010-31-0; $Mo[HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3](\eta^3\text{-}CH_2C(CH_3)CH_2)(CO)_2$, 119010-30-9; 3(5)-isopropylpyrazole, 49633-25-2; isopropyl methyl ketone, 563-80-4; ethyl formate, 109-94-4; hydrazine chloride, 2644-70-4; 3(5)-isopropyl-4-bromopyrazole, 60061-60-1; potassium tetrahydroborate, 13762-51-1.

Supplementary Material Available: Listings of thermal parameters (Tables S1, S5, S9, and S13), hydrogen atom positions (Tables S2, S6, S10, and S14), and all bond distances and angles (Tables S4, S8, S12, and S16) (13 pages); listings of observed and calculated structure factors (Tables S3, S7, S11, and S15) (10 pages). Ordering information is given on any current masthead page.

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Reactions of the Polyhydrides $Re_2H_8(PPh_3)_4$ and $ReH_7(PPh_3)_2$ with Acetic Acid/Acetic Anhydride. Isolation and Characterization of the Rhenium(I) Carbonyl Complexes $Re(O_2CCH_3)(CO)_{1+x}(PPh_3)_{3-x}$ (x = 0, 1) and the Homoleptic Dirhenium(III) Carboxylate Complex $Re_2(\mu\text{-}O_2CCH_3)_4(O_2CCH_3)_2$

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The dirhenium octahydride $Re_2H_8(PPh_3)_4$ reacts with acetic acid/acetic anhydride mixtures in dichlorobenzene to give the homoleptic acetate complex $Re_2(\mu\text{-}O_2CCH_3)_4(O_2CCH_3)_2$ as the major product together with small quantities of the carbonyl complex $Re(O_2CCH_3)(CO)_2(PPh_3)_2$. The related reaction with propionic acid/propionic anhydride gives only $Re(O_2CC_2H_5)(CO)_2(PPh_3)_2$ in very low yield. Treatment of $ReH_7(PPh_3)_2$ with these same acid/anhydride mixtures in THF, in the presence of PPh_3, affords yellow $Re(O_2CR)(CO)(PPh_3)_3$ (R = CH_3, C_2H_5) in high yield. Solutions of these complexes in 0.1 M $n\text{-}Bu_4NPF_6/CH_2Cl_2$ show a reversible couple in their cyclic voltammograms associated with a one-electron oxidation to their 17-electron cations. Chemical oxidation of $Re(O_2CR)(CO)(PPh_3)_3$ to the paramagnetic, orange salts $[Re(O_2CR)(CO)(PPh_3)_3]PF_6$ has been accomplished by using $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ in acetone. The acetate complex $[Re(O_2CCH_3)(CO)(PPh_3)_3]PF_6\cdot THF$ has been characterized structurally by X-ray crystallography. Crystal data at 20 °C: space group *Pnma*, $a = 15.785\ (4)$ Å, $b = 22.577\ (3)$ Å, $c = 23.824\ (3)$ Å, $V = 5656\ (5)$ Å^3, and $Z = 4$. The structure was refined to $R = 0.033$ and $R_w = 0.040$ for 2600 data with $F^2 > 3.0\sigma(F^2)$.

Introduction

The reversible protonation reactions (using $HBF_4\cdot Et_2O$) of rhenium polyhydride complexes of the types $Re_2H_8(PR_3)_4$, $Re(\eta^2\text{-}H_2)H_5(PR_3)_2$, and $ReH_5(PR_3)_3$ have recently been examined[1-3] and extended to include the analogous auration reactions with $[Au(PR_3)]^+$.[2,4] These protonation reactions are important from the point of view of activating these relatively stable molecules and for an understanding of the interconversion between isomeric dihydrido and η^2-dihydrogen ligands.[5] Since rhenium polyhydrides rank second to none among the transition elements in the variety of species that can be stabilized,[6] we are currently examining their reactivities toward a selection of other acids. In the present report we describe the products that are obtained from the reactions of $ReH_7(PPh_3)_3$ and $Re_2H_8(PPh_3)_4$ with acetic acid/acetic anhydride mixtures and the related propionic acid/propionic anhydride mixtures.

Experimental Section

Starting Materials. The polyhydride complexes $Re_2H_8(PPh_3)_4$, $ReH_7(PPh_3)_2$, and $ReH_5(PPh_3)_3$ were prepared by standard literature methods.[7] Other reagents and solvents were obtained from commercial sources. Solvents were deoxygenated prior to use. All reactions were carried out under an atmosphere of nitrogen at a pressure provided by bubbling the outlet nitrogen through a column of mercury approximately 8 cm in depth or with the use of a mineral oil bubbler.

A. Reactions of $Re_2H_8(PPh_3)_4$ with $RCO_2H/(RCO)_2O$ (R = CH_3, C_2H_5). (i) $Re_2(\mu\text{-}O_2CCH_3)_4(O_2CCH_3)_2$. A mixture of glacial acetic acid and acetic anhydride (10:1 by volume) (3.0 mL) was added to a solution of $Re_2H_8(PPh_3)_4$ (0.570 g, 0.400 mmol) in 100 mL of 1,2-dichlorobenzene. The mixture was refluxed for 4 h. The cooled reaction mixture was filtered under nitrogen, and the resulting light brown precipitate was washed with diethyl ether (20 mL); yield 0.153 g (53%). Anal. Calcd for $C_{12}H_{18}O_{12}Re_2$: C, 19.83; H, 2.50. Found: C, 19.19; H, 2.58. It is insoluble in THF, diethyl ether, acetone, dichloromethane, and ethanol and only slightly soluble in methanol, which turns it green. Its IR spectrum (Nujol mull) shows the following characteristic bands (cm^{-1}): 1554 (s, br), ≃1450 (vs, br), ≃1040 (sh), 1028 (m), 682 (s), 644 (w), 624 (w), 607 (w), 465 (m), 365 (ms), 340 (ms), ≃230 (ms).

This product is readily converted into $Re_2(O_2CCH_3)_4Cl_2$ upon reaction with hydrogen chloride. A slurry of $Re_2(O_2CCH_3)_6$ (0.065 g, 0.090 mmol) in ethanol (5 mL) was stirred under $N_2(g)$ at 0 °C (ice bath), while HCl gas was bubbled through the solution for 3 min. During this time the suspension turned from brown to orange, while the solution acquired a green coloration. The orange solid was filtered off and dried; yield 0.050 g (82%). The identity of this product was established on the basis of its IR and electronic absorption spectral properties.[8,9]

(ii) $Re(O_2CCH_3)(CO)_2(PPh_3)_2$ (1). Diethyl ether (50 mL) was added to the dark green filtrate from part A(i), and the resulting solution was slowly evaporated under a gentle stream of nitrogen until the volume was approximately 5 mL. The solution was then refrigerated for about 2 weeks. A small crop of yellow crystals was filtered off, washed with diethyl ether, and dried under vacuum; yield 0.020 g (3%). Anal. Calcd for $C_{40}H_{33}O_4P_2Re$: C, 58.18; H, 4.03. Found: C, 58.20; H, 4.32.

(iii) $Re(O_2CC_2H_5)(CO)_2(PPh_3)_2$ (2). A procedure similar to that described in part A(i) was used. A mixture of propionic acid and propionic anhydride (10:1 by volume) was reacted with $Re_2H_8(PPh_3)_4$ in 1,2-dichlorobenzene. The reaction was stopped after a 6-h reflux but did not afford any insoluble $Re_2(\mu\text{-}O_2CC_2H_5)_4(O_2CC_2H_5)_2$. The solution was treated as described in part A(ii). A few yellow crystals were filtered off, washed with diethyl ether, and dried under vacuum; yield ca. 2%.

B. Reactions of $ReH_7(PPh_3)_2$ with $RCO_2H/(RCO)_2O$ (R = CH_3, C_2H_5). (i) $Re(O_2CCH_3)(CO)(PPh_3)_3$ (3). A mixture of glacial acetic

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