

Figure 4. Proposed structural analogy between compound **8** and the triiridatritriacyclohexane crown-like compound $\text{Ir}_3(\mu\text{-S-}t\text{-Bu})_3(\text{CO})_6(\mu\text{-}\eta^1\text{-(CH}_3\text{COOC)}_2)_2$.

equivalent phosphorus nuclei in both cases [**5** $\delta(^{31}\text{P})$ 139.0 (d) ($J_{\text{P-Rh}} = 238$ Hz) and **6** $\delta(^{31}\text{P})$ 37.95 (d) ($J_{\text{P-Rh}} = 153$ Hz) in CD_2Cl_2], indicate molecular structures in which phosphorus ligands occupy a regular disposition according to a molecular structure of C_3 symmetry.

$\text{Rh}_3(\text{CH}_3\text{C}(\text{CH}_2\text{S})_3)(\text{P}(\text{OMe})_3)_6$ (**7**) has been quantitatively obtained by reaction of $\text{Rh}_2\text{Cl}_2(\text{P}(\text{OMe})_3)_4$, prepared in situ by addition of 4 equiv of trimethyl phosphite to a toluene solution of $\text{Rh}_2\text{Cl}_2(\text{C}_8\text{H}_{12})_2$, with $\text{CH}_3\text{C}(\text{CH}_2\text{SLi})_3$, added in a 3:2 molar ratio. **7** crystallizes from toluene/hexane solutions, upon cooling, as an air-sensitive red-orange solid.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **7** in CD_2Cl_2 , which exhibits a single doublet centered at 143.8 ppm ($J_{\text{P-Rh}} = 262$ Hz), reveals a molecular structure of C_{3v} symmetry.

Reaction of 4 with Dimethyl Acetylenedicarboxylate. **4** reacts quantitatively at room temperature with stoichiometric amounts of dimethyl acetylenedicarboxylate to yield a 1:1 adduct, **8**. During the reaction, the three typical $\nu(\text{CO})$ bands of the highly symmetrical starting material, **4**, disappear and six new $\nu(\text{CO})$ bands appear at 2094 (s), 2076 (vs), 2059 (vs), 2044 (s), 2030 (m), and 2000 (vs) cm^{-1} for the adduct **8** (IR spectrum in hexane). As far

as the number and the intensities of the $\nu(\text{CO})$ bands are concerned, the IR spectrum of **8** is remarkably similar to that observed, and previously reported,^{8a} for $\text{Ir}_3(\mu\text{-S-}t\text{-Bu})_3(\text{CO})_6(\mu\text{-}\eta^1\text{-(CH}_3\text{COOC)}_2)_2$, i.e. 2084 (s), 2066 (vs), 2042 (vs), 2033 (s), 2011 (m), and 1977 (vs) cm^{-1} . As in the latter complex, whose crystal structure has been previously described, we assumed the added alkene in **8** to be $\mu\text{-}\eta^1$ bonded to two of the three iridium atoms, leading to a molecular structure of C_3 symmetry, with the two bridged metallic centers mutually bonding (Figure 4).

To our knowledge, the ability of trifunctional ligands to bind together three metallic centers has been recognized so far in cases of ligands with tertiary phosphine or arsine functionalities.²⁶⁻²⁹

The above results clearly show that 1,1,1-tris(sulfidomethyl)ethane can serve as a 12-electron-donor ligand to complex three nonbonded metal atoms, leading to triple-square-planar rhodium(I) and iridium(I) species. Our preliminary observations on the reactivity of these new trimetallic complexes toward electrophilic substrates also indicate that the bridging tripod 1,1,1-tris(sulfidomethyl)ethane is flexible enough to support the geometric deformations induced by the formation of a metal-metal bond.

Supplementary Material Available: Tables SI-SIII, listing final anisotropic thermal parameters for non-hydrogen atoms, hydrogen positional and thermal parameters, and least-squares planes and dihedral angles for **4** (6 pages); tables of calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

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Novel Polypyrazolylborate Ligands: Coordination Control through 3-Substituents of the Pyrazole Ring

Swiatoslaw Trofimenko, Joseph C. Calabrese, and Jeffery S. Thompson*

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The synthesis, structures and coordination chemistry of a series of polypyrazolylborate ligands, $[\text{H}_n\text{B}(\text{3-Rpz})_{4-n}]^-$, are presented, where R is a *tert*-butyl or phenyl group. These ligands are made by the reaction of tetrahydridoborate ion with the appropriate pyrazole. A series of transition-metal complexes were prepared and characterized by analytical and spectroscopic data. In addition two complexes were characterized by means of X-ray diffraction techniques. The complex $\text{Co}(\text{HB}(\text{3-}t\text{-butylpyrazol-1-yl})_3)(\text{NCS})$ crystallizes in the monoclinic space group $P2_1/n$ with 4 molecules per unit cell of dimensions $a = 16.466$ (4) Å, $b = 16.884$ (2) Å, $c = 9.635$ (2) Å, and $\beta = 95.04$ (2)°, at -75 °C. Least-squares refinement of 289 variables led to a value of the conventional R index (on F) of 0.043 and of R_w of 0.042 for 3401 reflections having $I > 3.0\sigma(I)$. 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 *tert*-butyl group is in the 3-position of the pyrazolyl group. The complex $\text{Co}(\text{HB}(\text{3-phenylpyrazol-1-yl})_3)(\text{NCS})(\text{tetrahydrofuran})$ crystallizes in the monoclinic space group $P2_1/n$ with 4 molecules per unit cell of dimensions $a = 18.530$ (2) Å, $b = 14.177$ (2) Å, $c = 11.733$ (2) Å, and $\beta = 100.34$ (1)° at -100 °C. Least-squares refinement of 388 variables led to a value of the conventional R index (on F) of 0.045 and of R_w of 0.043 for 3094 reflections with $I > 3.0\sigma(I)$. The geometry about the Co(II) ion, which is coordinated to three pyrazolyl nitrogen atoms, the nitrogen from the NCS group, and the oxygen atom of a tetrahydrofuran molecule, is trigonal bipyramidal. The phenyl group is in the 3-position of the pyrazolyl ring. The results presented here indicate that appropriate selection of the 3-R group in the $[\text{HB}(\text{3-Rpz})_3]^-$ ligand will permit the construction of custom-sized pockets around metal ions, allowing access only to molecules of predetermined size and/or shape.

In this contribution, we present the synthesis and coordination chemistry of a new series of polypyrazolylborate ligands with bulky

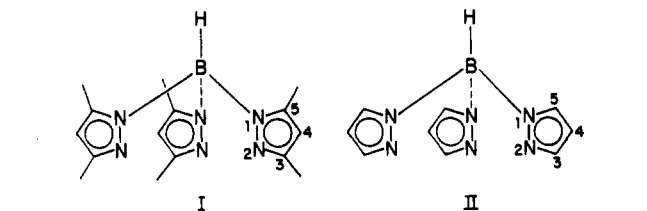
alkyl and phenyl groups in the 3-position of the pyrazole ring. The polypyrazolylborate ligands have been widely used in inorganic,

Table I. Properties of Complexes with $[\text{H}_2\text{B}(3\text{-Rpz})_2]^-$ Ligands (L^*)

complex	color	anal., %			mp, °C	IR data, cm^{-1}
		C	H	N		
R = <i>tert</i> -Butyl						
TiL*	white	36.3 (36.4)	5.18 (5.15)	12.1 (12.1)	194–195	2410, 2355, 2290, 2275, 2218, 2178
R = Phenyl						
TiL*	white	43.0 (42.8)	3.18 (3.27)	11.1 (10.9)	235–237 ^b	2460, 2300, 2240
CoL* ₂	violet	65.8 (66.1)	4.87 (4.98)	17.1 (17.3)	168–169	2450, 2430, 2295
NiL* ₂	yellow-orange	65.8 (65.6)	4.87 (4.83)	17.1 (17.4)	229–230	2424
ZnL* ₂	white	65.1 (65.5)	4.83 (4.85)	16.9 (16.8)	213–214	2460, 2470, 2425, 2315
MoL*(CO) ₂ ($\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2$)	orange	56.9 (57.0)	4.55 (4.45)	11.1 (11.0)	171–172	2478, 2060, 1970, 1950, 1852
MoL*(CO) ₂ ($\eta^3\text{-C}_3\text{H}_5$)	orange	56.1 (55.9)	4.27 (4.34)	11.4 (11.5)	185 ^b	2480, 2030, 1950, 1855

^a Values determined are given in parentheses. ^b Decomposition temperature.

bioinorganic, and organometallic chemistry.¹ Although a large number of ligands of the form $[\text{R}_n\text{B}(\text{pz})_{4-n}]^-$ have been prepared,^{1,2} where R = H, alkyl, or aryl groups and pz = pyrazole or substituted pyrazoles, the ligands $[\text{HB}(3,5\text{-Me}_2\text{pz})_3]^-$ (I) and $[\text{HB}(\text{pz})_3]^-$ (II) are the most extensively used. It is clear from the many studies in the literature that the chemistry of these ligands with first-row transition-metal ions is dominated by the formation of ML_2 complexes. $\text{ML}(\text{X})$ complexes are in general unstable to ligand-exchange reactions to form ML_2 and MX_2 compounds.^{3,4}



We report here the synthesis, structures, and coordination chemistry of several polypyrazolylborate ligands with phenyl or *tert*-butyl groups in the 3-position of the pyrazole ring, which makes the formation of ML_2 complexes impossible. The ligands $[\text{H}_n\text{B}(3\text{-Rpz})_{4-n}]^-$, with $n = 0\text{--}2$, and their coordination chemistry with a variety of MX_2 compounds are presented. These ligands allow the synthesis of stable (to ligand exchange), monomeric $\text{ML}(\text{X})$ species with varying degrees of access to the transition-metal ion. The chemistry of this new group of ligands is otherwise similar to the parent ligands I and II. Initial results from this study have appeared.⁵

Experimental Section

General Methods. All chemicals were reagent grade and used as received unless otherwise noted. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, and MicroAnalysis, Inc., Wilmington, DE. Infrared spectra were obtained as Nujol mulls with a Perkin-Elmer 283-B infrared spectrophotometer. NMR spectra were obtained with a Perkin-Elmer EM-390 spectrometer.

Preparation of 3(5)-*tert*-Butylpyrazole.⁶ To a slurry of dry sodium methoxide (140 g, 2.60 mol) in 800 mL of toluene was added with rapid stirring a mixture of pinacolone (270 g, 2.70 mol) and ethyl formate (222 g, 3 mol). An exothermic, but well-contained, reaction ensued. When

the bubbling stopped (approximately 0.25 h) low-boiling materials (250 mL) were distilled off under aspirator vacuum. Ice-cold water (1 L) was added. The resulting two-phase system was stirred, during which time the color of the reaction mixture passed into the aqueous phase, which was then separated and added to a solution of hydrazine monohydrochloride (2.6 mol) in 800 mL water. An oil separated from the aqueous phase and was extracted with dichloromethane. The 3-*tert*-butylpyrazole was obtained in 185 g yield (58%) by distillation and collection of the fraction with a boiling point of 76–80 °C at 0.3 mmHg. NMR (ppm): 12.35 (s, 1 H), 7.44 (d, 1 H), 6.03 (d, 1 H), 1.32 (s, 9 H).

Preparation of 3(5)-Phenylpyrazole.⁷ Acetophenone (240 g, 2.00 mol) and ethyl formate (222 g, 3.00 mol) were added in one portion with rapid stirring to a slurry of sodium methoxide (108 g, 2.00 mol) in 1.5 L of toluene in a 4-L beaker. A vigorous reaction took place, and a large amount of solid precipitated from the reaction mixture. The thick slurry was stirred for 1 h and then filtered. The solid was washed with hot toluene and then with hexane, air-dried, and then slurried in 1 L of methanol. To this methanol slurry was added hydrazine monohydrochloride (137 g, 2.00 mol) in 1 L of water. The product was extracted with 1 L of dichloromethane. The solvent was stripped from the extracts and the product distilled in vacuo (bp 139 °C (0.9 mm)). 3-Phenylpyrazole was obtained in 184 g yield (64%) with a melting point of 83 °C by differential scanning calorimetry (DSC). NMR (ppm): 13.13 (s, 1 H), 7.8–7.6 (m, 2 H), 7.45 (d, 1 H), 7.4–7.2 (m, 3 H), 6.50 (d, 1 H).

Preparation of Potassium Dihydrobis(3-phenylpyrazol-1-yl)borate, $\text{KH}_2\text{B}(3\text{-Phpz})_2$. A mixture of potassium tetrahydridoborate (5.4 g, 0.10 mol) and 3(5)-phenylpyrazole (31.7 g, 0.22 mol) was stirred and heated in anhydrous *N,N*-dimethylacetamide (DMAC). Hydrogen gas evolved during this reaction was conducted through a water-cooled condenser and a –80 °C trap to a wet-test meter; the cold trap condensed small amounts of dimethylamine evolved during the reaction. Hydrogen gas evolution stopped after approximately 5 L, at which point heating was discontinued. The reaction mixture was then heated under vacuum at 130–135 °C to remove all volatile materials. The cool reaction mixture was dissolved in 500 mL of tetrahydrofuran (THF), stirred with Celite, and filtered to yield a clear solution that is 0.2 M in the ligand. This solution was used for the preparation of derivatives.

Preparation of Metal Complexes with Dihydrobis(3-phenylpyrazol-1-yl)borate. To an aliquot of the 0.2 M THF solution of the ligand described above was added an appropriate amount of an aqueous solution of metal nitrate (Co(II), Ni(II), Zn(II), or Ti(II)). The reaction mixture was then extracted with methylene chloride. The extracts were combined, washed with water, and chromatographed on a short alumina column. Evaporation of solvent and recrystallization from toluene–heptane yielded $\text{M}(\text{H}_2\text{B}(3\text{-Phpz})_2)_2$ ($\text{M} = \text{Co}(\text{II}), \text{Zn}(\text{II})$ or $\text{Ti}(\text{H}_2\text{B}(3\text{-Phpz})_2)_2$). The very insoluble complex $\text{Ni}(\text{H}_2\text{B}(3\text{-Phpz})_2)_2$ was obtained by extensive washing of the solid obtained from the above reaction with water and methanol, followed by recrystallization from toluene. Complexes of the form $\text{Mo}(\text{H}_2\text{B}(3\text{-Phpz})_2)(\eta^3\text{-CH}_2\text{CRCH}_2)(\text{CO})_2$ were prepared by the method described previously.^{2d} Properties of the various compounds are listed in Table I.

Preparation of Potassium Dihydrobis(3-*tert*-butylpyrazol-1-yl)borate, $\text{KH}_2\text{B}(3\text{-}t\text{-Bupz})_2$. This compound was prepared and isolated as a 0.2 M THF solution by the method described above for $\text{KH}_2\text{B}(3\text{-Phpz})_2$. The Ti(I) salt was prepared in the manner described above for the 3-phenyl analogue. Properties of this ligand are described in Table I.

Preparation of Potassium Hydrotris(3-phenylpyrazol-1-yl)borate, $\text{KHB}(3\text{-Phpz})_3$. The ligand $\text{KH}_2\text{B}(3\text{-Phpz})_2$ was prepared as described above. The solid material generated after heating the crude reaction mixture in vacuo at 130–135 °C was used here; the material was not

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Table II. Properties of Complexes with $[\text{HB}(3\text{-Rpz})_3]^-$ Ligands (L^*)

complex	color	anal., ^a %			mp, °C	IR data, cm^{-1}
		C	H	N		
R = <i>tert</i> -Butyl						
TiL*	white	50.2 (50.2)	3.43 (3.66)	13.0 (13.1)	191 ^b	2438, 2418
CoL*Cl	blue	53.0 (53.0)	7.16 (7.17)	17.7 (17.7)	245–246	2540
CoL*(NO ₃)	blue-violet	50.2 (50.4)	6.77 (6.70)	19.5 (19.3)	191–193	2490, 2450
CoL*(NCS)	blue	53.0 (52.7)	6.88 (6.87)	19.7 (19.6)	276 ^b	2534, 2082
CoL*(NCO)	blue	54.8 (54.9)	7.05 (7.15)	20.3 (20.0)	290 ^b	2515, 2234
CoL*(N ₃)	blue	52.3 (52.0)	7.05 (7.05)	26.1 (26.3)	275 ^c	2505, 2091
NiL*Cl	purple	53.0 (53.0)	7.16 (7.20)	17.7 (17.4)	222–224	2525
NiL*(NCS)	purple	53.0 (52.9)	6.88 (6.97)	19.7 (19.7)	226 ^c	2527, 2070
NiL*(NCO)	purple	54.8 (55.1)	7.05 (7.17)	20.3 (20.1)	259–261	2515, 2222
NiL*(N ₃)	purple	52.3 (52.3)	7.05 (7.14)	26.1 (25.8)	200 ^c	2515, 2100
CuL*Cl	brown	52.5 (52.5)	7.08 (6.84)	17.5 (17.3)	153–155	2512
CuL*(NO ₃)	green	49.8 (49.9)	6.72 (6.71)	19.3 (19.1)	160–163	2508
CuL*(NCO)	brown	54.3 (54.2)	6.99 (6.99)	20.1 (19.9)	145–147	2510, 2230
ZnL*(NO ₃)	white	49.6 (49.5)	6.69 (6.65)	19.3 (19.0)	202–203	2510
ZnL*(NCS)	white	52.3 (52.2)	6.74 (6.58)	19.4 (19.4)	283	2529, 2087
ZnL*(NCO)	white	54.0 (53.8)	6.96 (6.82)	20.1 (19.9)	232	2510, 2244
ZnL*(N ₃)	white	51.6 (51.7)	6.96 (7.01)	25.8 (25.5)	242	2502, 2108
MoL*(CO) ₂ NO	yellow-orange	49.0 (49.1)	6.04 (6.12)	17.4 (17.1)	174–176	2505, 2000, 1908, 1885, 1655
PdL*($\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2$)	white	55.4 (55.7)	7.56 (7.52)	15.5 (15.4)	134–136 ^c	2398
R = Phenyl						
KL*	white	67.5 (67.8)	4.58 (4.59)	17.5 (17.3)	267–270	2415
TiL*	white	50.2 (50.2)	3.43 (3.66)	13.0 (13.1)	185–187	2420
CoL*(NCS)	blue	60.2 (60.5)	3.94 (3.99)	17.6 (17.3)	223–224	2510, 2077
CoL*(NCO)	blue	62.0 (62.2)	4.06 (4.08)	18.1 (18.0)	223–224	2510, 2220
CoL*(N ₃)	blue	59.8 (60.1)	4.06 (4.01)	23.3 (23.1)	222–223	2504, 2078
NiL*(NCS)	brown	60.2 (59.9)	3.94 (3.73)	17.6 (17.5)	242–244	2510, 2070
ZnL*(NCS)	white	59.5 (59.4)	3.90 (4.04)	17.4 (17.2)	261–263	2508, 2092
ZnL*(NCO)	white	61.3 (61.1)	4.01 (4.07)	17.9 (17.7)	248–250	2510, 2238
ZnL*(N ₃)	white	59.1 (58.9)	4.01 (4.08)	23.0 (22.8)	239–241	2505, 2100
CoL*(NCS)·THF	burgundy	61.0 (60.8)	4.80 (4.78)	15.6 (15.6)	196–200	2515, 2080
MoL*(CO) ₂ NO	yellow-orange	55.9 (55.8)	3.53 (3.66)	15.7 (15.4)	298–301 ^c	2518, 2000, 1910, 1660
MoL*(CO) ₂ ($\eta^3\text{-CH}_2\text{CHCH}_2$)	yellow	60.6 (60.6)	4.26 (4.28)	13.2 (13.0)	204–206	2475, 1929, 1842
MoL*(CO) ₂ ($\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2$)	yellow	61.1 (60.9)	4.48 (4.49)	13.0 (12.8)	243	2505, 2495, 1932, 1835
PdL*($\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2$)	white	61.8 (61.7)	4.82 (4.72)	14.0 (14.0)	169–172 ^c	2414
PdL*($\eta^3\text{-CH}_2\text{C}(\text{C}_6\text{H}_5)\text{CH}_2$)	white	65.1 (64.7)	4.67 (4.71)	12.6 (12.6)	169–171	2443

^a Values determined are given in parentheses. ^b Melting point determined by DSC. ^c Decomposition temperature.

dissolved in THF for further purification. 3(5)-Phenylpyrazole (16.0 g, 0.11 mol) and 250 mL of anisole were added. This mixture was refluxed with vigorous stirring for 6–8 h. During this heating period, hydrogen was evolved and fine needles precipitated from the solution. At the end of the heating time, a thick slurry resulted. The mixture was cooled, and the precipitate was collected by filtration, washed with hot toluene and then hexane, and air-dried. This material (23 g, 48% yield) is suitable for the preparations described below but can be purified by dissolving in THF, stirring with Celite, filtering, and removing solvent.

Preparation of Potassium Hydrotris(3-*tert*-butylpyrazol-1-yl)borate, KHB(3-*t*-Bupz)₃. Potassium tetrahydridoborate (16.2 g, 0.30 mol) and 3(5)-*tert*-butylpyrazole (82.0 g, 0.66 mol) were refluxed in 500 mL of anhydrous DMAC, with the emanating gases being conducted through a water-cooled condenser and a –80 °C trap to a wet-test meter. After evolution of 15 L of hydrogen, the flask was heated in an oil bath at 135 °C under vacuum to remove volatile materials. To the cooled reaction mixture was added 3(5)-*tert*-butylpyrazole (41 g, 0.33 mol) and 500 mL of anisole. This mixture was refluxed overnight and produced approximately 7.5 L of hydrogen. Volatile materials (including excess starting pyrazole) were removed with heating under vacuum at 165–170 °C. The glassy residue was stirred with 500 mL of heptane; the separated solid was collected by filtration and washed with hexane to yield crude KHB(3-*t*-Bupz)₃ (47 g, 37% yield). The filtrate from this filtration was evaporated to a syrup, dissolved in 300 mL methanol, and stirred with 600 mL of a 0.35 M aqueous thallium nitrate solution. This mixture was extracted with dichloromethane. The extracts were chromatographed on a short alumina column. Evaporation of solvent yielded a solid that was then stirred with 500 mL of methanol. The insoluble material was collected by filtration and washed thoroughly with methanol and dried to yield a white solid (42 g, 23%). This Ti(I) salt was recrystallized from toluene; its properties are shown in Table II. The overall yield for potassium and thallium salts is 60%. In another preparation, the residue from the final stripping of the anisole solution described above was dissolved in THF to a total volume of 1.5 L, stirred with Celite, and filtered. Treatment of this solution with excess aqueous thallium nitrate followed by the workup given above yielded the thallium salt in 61% yield.

Preparation of M(HB(3-*t*-Bupz)₃)X Complexes. The preparations of Co(HB(3-*t*-Bupz)₃)(NCS) and the Ni(II) analogue are presented as representative examples of this type of complex. The properties of these compounds are presented in Table II.

A. Preparation of Co(HB(3-*t*-Bupz)₃)(NCS). A mixture of Co(NCS)₂ (2.1 g, 12 mmol) and 50 mL of the THF solution (0.2 M) of the crude potassium salt of [HB(3-*t*-Bupz)₃][–] was stirred for 1 h to yield a deep blue solution. Dichloromethane (50 mL) and water (300 mL) were added; the deep blue organic layer was separated and chromatographed on alumina and eluted with dichloromethane. The residue obtained from solvent evaporation was stirred with methanol and filtered to yield blue crystals (2.9 g, 58% yield), which were purified further by recrystallization from toluene–heptane.

B. Preparation of Ni(HB(3-*t*-Bupz)₃)(NCS). Potassium thiocyanate (2.4 g, 25 mmol) and 25 mL of methanol were added to 25 mL of 0.5 M nickel nitrate (8 mmol). To this stirred solution was added all at once 40 mL of the 0.2 M THF solution of the crude ligand described above. The solution became deep purple in color, with separation of some purple solid material. Water (0.1 L) and additional methanol were added to yield a purple precipitate, which was collected by filtration and washed thoroughly with hot water and then with methanol. The purple solid (2.4 g, 60% yield) was recrystallized from toluene–heptane.

Other M(HB(3-*t*-Bupz)₃)X complexes were prepared similarly and in comparable yields by substituting other M(NO₃)₂ solutions (M = Co(II), Cu(II), and Zn(II) ions) and other pseudohalide salts (NaN₃, KNCO). For X = Cl and NO₃, aqueous solutions of these salts were used directly. The products were recrystallized from toluene–heptane. Generally, M(HB(3-*t*-Bupz)₃)X complexes of the Co(II) and Zn(II) ions could be easily purified by chromatography, whereas those of the Ni(II) and Cu(II) ions could be purified only by flash chromatography, as significant decomposition was observed on prolonged contact with alumina.

Preparation of M(HB(3-Phpz)₃)X Complexes. These compounds were generally prepared by method B given above and were recrystallized from toluene or xylene. The properties of compounds in this class are shown in Table II. In some cases, prolonged boiling in toluene or xylene was necessary to remove coordinated solvent molecules.

Table III. Properties of Complexes with $[B(3-Rpz)_4]^-$ Ligands (L^*)

complex	color	anal., %			mp, °C	IR data, cm^{-1}
		C	H	N		
R = <i>tert</i> -Butyl						
TiL*	white	47.5 (47.7)	6.22 (6.08)	15.8 (15.7)	146	
CoL*(NCS)	blue	56.1 (56.0)	7.10 (6.94)	20.3 (20.0)	359–361	2076
CoL*(NCO)	blue	57.6 (58.0)	7.28 (7.43)	20.8 (20.3)	242–244	2240
ZnL*(NCS)	white	55.6 (56.0)	7.02 (7.10)	20.1 (19.8)	264	2088
ZnL*(NCO)	white	57.1 (57.5)	7.21 (7.14)	20.6 (20.2)	253–255	2250
ZnL*(N ₃)	white	55.1 (55.5)	7.21 (7.31)	25.2 (24.6)	252–254	2110
PdL*(η^3 -CH ₂ C(CH ₃)CH ₂)	white	57.8 (58.0)	7.68 (7.45)	16.9 (17.0)	277	...
MoL*(CO) ₂ NO	orange	52.6 (52.6)	6.42 (6.14)	18.4 (18.1)	193–195	2030, 1926, 1670
R = Phenyl						
TiL*	white	54.9 (55.3)	3.56 (3.65)	14.2 (14.5)	215–216	...
MoL*(CO) ₂ NO	orange	59.6 (59.9)	3.66 (3.95)	16.5 (16.4)	283	2020, 1945, 1670
MoL*(CO) ₂ (η^3 -CH ₂ CHCH ₂)	yellow	63.4 (62.6)	4.25 (4.60)	14.4 (14.1)	197–199	1940, 1850
PdL*(η^3 -CH ₂ C(CH ₃)CH ₂)	white	64.5 (64.7)	4.70 (4.72)	15.0 (14.7)	266	...

^a Values determined are given in parentheses.

Preparation of Co(HB(3-Phpz)₃)(NCS)·THF. This compound was prepared by procedure A given above using KHB(3-Phpz)₃. During chromatography of the deep blue dichloromethane solution of the Co(II) complex, the product changed color on the column to wine red. Evaporation of the eluent produced a burgundy solid. Recrystallization from THF–hexane produced burgundy crystals.

Preparation of Potassium Tetrakis(3-*tert*-butylpyrazol-1-yl)borate, KB(3-*t*-Bupz)₄. A mixture of 3(5)-*tert*-butylpyrazole (124 g, 1.0 mol) and potassium tetrahydridoborate (6.75 g, 0.125 mol) was heated with stirring in a dry 250-mL round-bottom flask until 12.5 L of hydrogen was evolved. The flask was then placed in an oil bath, and excess 3(5)-*tert*-butylpyrazole was distilled at a bath temperature of 150–155 °C (1 Torr). The white solid residue was boiled in 300 mL of heptane, filtered hot, washed with heptane, and dried to yield 56.2 g (82.7% yield) of the potassium salt of the ligand suitable for preparation of complexes.

Preparation of Sodium Tetrakis(3-phenylpyrazol-1-yl)borate, NaB(3-Phpz)₄. A mixture of 3(5)-phenylpyrazole (272 g, 1.9 mol) and sodium tetrahydridoborate (7.2 g, 0.19 mol) was heated with stirring until 19 L of hydrogen was evolved and further gas evolution stopped. The hot melt was poured into 500 mL of stirred toluene. The resulting slurry was filtered hot. The solids were washed with hot dimethylcyclohexane and air-dried to yield 75 g (66% yield) of material suitable for the preparation of metal complexes.

Preparation of MoL*(η^3 -CH₂CRCH₂)(CO)₂ Complexes (L^* = [HB(3-Phpz)₃]⁻, [B(3-Phpz)₄]⁻). Equimolar quantities of KL* or TiL* and Mo(η^3 -CH₂CRCH₂)X(CH₃CN)₂(CO)₂, prepared by the literature method,⁸ were stirred at room temperature in a 50/50 mixture of DMAC and dichloromethane. After 5 min, the slurry was poured into a 10-fold volume of cold water and the layers then were separated. The dichloromethane layer was washed several times with water to remove the DMAC and was then chromatographed on alumina. The yellow band was collected and solvent evaporated by heating until precipitation began, at which point methanol was added. Heating was continued to remove all of the dichloromethane. The cooled slurry was filtered, and the yellow product, obtained in 50–60% yield, was recrystallized from toluene–heptane.

Preparation of PdL*(η^3 -CH₂CRCH₂) (L^* = [HB(3-*t*-Bupz)₃]⁻, [B(3-*t*-Bupz)₄]⁻, [HB(3-Phpz)₃]⁻, [B(3-Phpz)₄]⁻). These compounds were prepared as described above, starting with [Pd(η^3 -CH₂CRCH₂)Cl]₂, which was prepared by the literature procedure.⁹ After chromatography on alumina, the eluent was concentrated at reduced pressure and at 50–60 °C to a thick slurry, which was then stirred with methanol and cooled. The white product (60–70% yield) was collected by filtration.

Preparation of MoL*(NO)(CO)₂ Complexes (L^* = [HB(3-*t*-Bupz)₃]⁻, [HB(3-Phpz)₃]⁻, [B(3-*t*-Bupz)₄]⁻, [B(3-Phpz)₄]⁻). To 100 mL of 0.2 M THF solution of KL* (0.02 mol) was added Mo(CO)₆ (5.3 g, 0.02 mol). The mixture was refluxed with stirring until 1.5 L of CO, measured with a wet-test meter, was evolved. The yellow solution was cooled under nitrogen to room temperature. Butyl nitrite (3.1 g, 0.03 mol) was added, and the resulting solution was stirred and heated gently until 0.5 L of CO was evolved. The reaction mixture was then poured into 500 mL of cold water, and the product was extracted with dichloromethane. The extracts were concentrated and chromatographed on alumina. The yellow–orange band, which was eluted with dichloromethane, was collected and concentrated until solids started to appear. Methanol (500 mL) was added,

Table IV. Crystal Data for Co(HB(3-*t*-Bupz)₃)(NCS) (III) and Co(HB(3-Phpz)₃)(NCS)(THF) (IV)

	III	IV
mol formula	C ₂₂ H ₃₄ BCoN ₇ S	C ₃₂ H ₃₀ BCoN ₇ OS
M_r	498.37	630.44
a , Å	16.466 (4)	18.530 (2)
b , Å	16.884 (2)	14.177 (2)
c , Å	9.635 (2)	11.733 (2)
β , deg	95.04 (2)	100.34 (1)
V , Å ³	2668.3	3032.2
Z	4	4
space group	$P2_1/n$	$P2_1/n$
radiation (λ , Å)	Mo K α (0.710 69) from graphite monochromator	Mo K α (0.710 69) from graphite monochromator
2θ limits, deg	4.2–55.0	4.5–53.0
temp, °C	-75	-100
abs coeff, cm^{-1}	7.37	6.66
no. of unique data used ($I > 3\sigma(I)$)	3401	3094
no. of variables	289	388
R	0.043	0.045
R_w	0.042	0.043

and the remaining dichloromethane was removed by gentle heating to yield an orange slurry. The product was collected by filtration (40–60% yield) and recrystallized from toluene–heptane.

An equivalent amount of nitrosyl chloride can be used in place of butyl nitrite.

X-ray Data Collection and Structure Solution and Refinement. Co(HB(3-*t*-Bupz)₃)(NCS). Crystals suitable for diffraction studies were obtained by vapor diffusion of petroleum ether into a THF solution of the complex under an inert atmosphere. The crystal was handled in the manner described elsewhere,¹⁰ was placed on an Enraf-Nonius CAD-4 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 at -100 °C. The cell parameters were then refined on the basis of 20 reflections chosen from diverse regions of reciprocal space. These parameters and other crystallographic data are summarized in Table IV. Intensity data collection by the ω -scan technique, intensity measurement of standard reflections, empirical corrections for absorption, and data processing were performed as described elsewhere.¹⁰ The solution and refinement of the structure were carried out on a Digital Equipment VAX 11/780 computer with a system of programs developed by J.C.C. The cobalt atom was located by the heavy-atom Patterson method. The positions of the remaining non-hydrogen atoms were obtained by the usual combination of structure factor and Fourier synthesis calculations and full-matrix least-squares refinement. The function minimized in these refinements is given elsewhere.¹⁰ Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.¹¹ Hydrogen atom positions were calculated with a C–H distance of 0.95 Å. Least-squares refinement converged to $R = 0.043$ and $R_w = 0.042$, where

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

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

(8) Hayter, R. G. *J. Organomet. Chem.* **1968**, *13*, P1–P3.

(9) Dent, W. T.; Long, R.; Wilkinson, A. J. *J. Chem. Soc.* **1964**, 1585–1588.

Table V. Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters for $\text{Co}(\text{HB}(3-t\text{-Bupz})_3)(\text{SCN})$

atom	x	y	z	$B_{\text{eq}}^a, \text{\AA}^2$
Co(1)	2298.5 (3)	2363.3 (3)	2021.8 (4)	2.2 (1)
S(1)	272.7 (7)	691.8 (6)	3447.7 (14)	5.0 (1)
N(1)	1453 (2)	1653 (2)	2452 (3)	3.5 (1)
N(11)	3493 (2)	3452 (2)	3055 (3)	2.4 (1)
N(12)	2954 (2)	2934 (2)	3587 (3)	2.3 (1)
N(21)	2757 (2)	3766 (2)	730 (3)	2.4 (1)
N(22)	2061 (2)	3329 (2)	808 (3)	2.3 (1)
N(31)	3787 (2)	2662 (2)	949 (3)	2.3 (1)
N(32)	3276 (2)	2020 (2)	1057 (3)	2.3 (1)
C(1)	953 (2)	1250 (2)	2859 (4)	2.9 (1)
C(11)	3907 (2)	3843 (2)	4099 (4)	2.9 (1)
C(12)	3637 (2)	3580 (2)	5340 (4)	2.9 (1)
C(13)	3046 (2)	3011 (2)	4988 (3)	2.4 (1)
C(14)	2558 (2)	2513 (2)	5917 (3)	2.7 (1)
C(15)	1647 (2)	2689 (2)	5631 (4)	3.5 (1)
C(16)	2826 (3)	2710 (3)	7449 (4)	4.2 (1)
C(17)	2712 (2)	1634 (2)	5672 (4)	3.3 (1)
C(21)	2582 (2)	4411 (2)	-42 (4)	3.2 (1)
C(22)	1767 (3)	4404 (2)	-478 (4)	3.6 (1)
C(23)	1459 (2)	3717 (2)	60 (3)	2.8 (1)
C(24)	603 (2)	3394 (2)	-85 (4)	3.4 (1)
C(25)	251 (2)	3398 (3)	1352 (4)	5.1 (1)
C(26)	586 (2)	2559 (3)	-653 (4)	4.4 (1)
C(27)	56 (3)	3911 (3)	-1088 (5)	5.5 (1)
C(31)	4430 (2)	2426 (2)	296 (3)	2.9 (1)
C(32)	4358 (2)	1634 (2)	-9 (4)	3.2 (1)
C(33)	3620 (2)	1396 (2)	480 (3)	2.6 (1)
C(34)	3212 (3)	598 (2)	378 (4)	3.8 (1)
C(35)	2380 (3)	659 (3)	-419 (5)	5.8 (2)
C(36)	3108 (3)	268 (2)	1827 (5)	5.1 (1)
C(37)	3728 (4)	28 (3)	-384 (8)	10.4 (3)
B(1)	3582 (2)	3493 (2)	1465 (4)	2.6 (1)

$$^a B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i a_j$$

$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ with w proportional to $[\sigma^2(I) + 0.0009I]^{-1/2}$. The final difference map shows electron density near the Co(II) atom ($0.32e/\text{\AA}^3$).

The final positional parameters of the refined atoms appear in Table V. Tables of general temperature factors, calculated hydrogen atom positions, and structure factor amplitudes and a complete listing of bond distances and angles are available.¹²

Co(HB(3-Phpz)₃)(NCS)(THF). Crystals suitable for diffraction studies were obtained by vapor diffusion of petroleum ether into a THF solution of the compound. The crystal was handled in the manner described above, placed on a Syntex R3 diffractometer, and shown to be suitable for diffraction studies of ω scans, which showed the peak width at half-height to be 0.26 at -100°C . The cell parameters were refined on the basis of 24 reflections chosen from diverse regions of reciprocal space. These parameters and other crystallographic data are summarized in Table IV. Intensity data collection, intensity measurements of standard reflections, empirical corrections for absorption, and data processing were performed as described above.

The cobalt atom was located by the heavy-atom Patterson method. The structure solution and refinement were performed as described above. Least-squares refinement converged to values of $R = 0.045$ and $R_w = 0.043$. All peaks in the final difference Fourier map were less than $0.33 e/\text{\AA}^3$.

The final positional parameters for the non-hydrogen 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.¹²

Results

Synthesis of Ligands and Metal Derivatives. The syntheses of the new polypyrazolylborate ligands described here are essentially the same as that used to prepare the parent ligands $[\text{H}_n\text{B}(\text{pz})_{4-n}]^-$: heating sodium or potassium tetrahydridoborate with an excess of the appropriate pyrazole.^{1,2,13} Hydrogen gas is evolved during the reaction and is used to measure its progress. The $[\text{H}_2\text{B}(3\text{-Rpz})_2]^-$ and $[\text{B}(3\text{-Rpz})_4]^-$ derivatives were prepared in a manner analogous to the preparations of the parent ligands. The crude

Table VI. Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters for $\text{Co}(\text{HB}(3\text{-Phpz})_3)(\text{SCN})(\text{THF})$

atom	x	y	z	$B_{\text{eq}}^a, \text{\AA}^2$
C(1)	1451.7 (4)	1674.2 (5)	3345.1 (6)	1.5 (1)
S(1)	-925 (1)	1241 (1)	1195 (1)	2.9 (1)
O(1)	1464 (2)	2812 (2)	2146 (3)	2.1 (1)
N(1)	494 (2)	1284 (3)	2489 (4)	2.3 (1)
N(11)	2952 (2)	1481 (3)	4636 (3)	1.9 (1)
N(12)	2566 (2)	1496 (3)	3516 (3)	1.8 (1)
N(21)	2000 (2)	667 (3)	5562 (3)	1.8 (1)
N(22)	1535 (2)	484 (3)	4539 (3)	1.7 (1)
N(31)	2111 (2)	2429 (3)	5620 (3)	1.7 (1)
N(32)	1537 (2)	2602 (3)	4735 (3)	1.6 (1)
C(1)	-99 (3)	1258 (3)	1950 (4)	1.8 (1)
C(2)	1990 (3)	3581 (3)	2290 (5)	2.6 (2)
C(3)	1962 (4)	3979 (4)	1112 (6)	4.0 (2)
C(4)	1183 (5)	3813 (5)	531 (6)	6.2 (3)
C(5)	945 (3)	2957 (4)	1076 (5)	3.1 (2)
C(11)	3673 (3)	1467 (4)	4614 (4)	2.5 (1)
C(12)	3770 (3)	1479 (4)	3484 (4)	2.4 (1)
C(13)	3070 (3)	1487 (3)	2817 (4)	1.9 (1)
C(14)	2848 (3)	1479 (3)	1552 (4)	2.0 (1)
C(15)	3258 (3)	1965 (3)	863 (5)	2.5 (1)
C(16)	3047 (4)	1980 (4)	-337 (5)	3.5 (2)
C(17)	2419 (4)	1506 (4)	-847 (5)	3.4 (2)
C(18)	2003 (3)	1007 (4)	-187 (5)	3.1 (2)
C(19)	2229 (3)	998 (3)	1011 (4)	2.3 (1)
C(21)	1906 (3)	36 (4)	6367 (4)	2.3 (1)
C(22)	1368 (3)	-585 (4)	5886 (4)	2.3 (1)
C(23)	1152 (3)	-295 (3)	4735 (4)	1.6 (1)
C(24)	641 (3)	-780 (3)	3829 (4)	1.7 (1)
C(25)	30 (3)	-1242 (4)	4110 (4)	2.2 (1)
C(26)	-431 (3)	-1764 (4)	3279 (5)	2.8 (2)
C(27)	-303 (3)	-1815 (4)	2156 (5)	2.9 (2)
C(28)	303 (3)	-1357 (3)	1876 (4)	2.4 (1)
C(29)	768 (3)	-853 (3)	2695 (4)	2.1 (1)
C(31)	2230 (2)	3190 (4)	6310 (4)	2.2 (1)
C(32)	1726 (3)	3872 (4)	5891 (5)	2.3 (1)
C(33)	1296 (2)	3482 (3)	4911 (4)	1.8 (1)
C(34)	655 (3)	3889 (3)	4146 (4)	1.8 (1)
C(35)	76 (2)	3330 (4)	3623 (4)	2.0 (1)
C(36)	-516 (3)	3727 (4)	2894 (5)	2.9 (2)
C(37)	-556 (3)	4683 (4)	2716 (5)	3.1 (2)
C(38)	2 (3)	5253 (4)	3265 (5)	3.3 (2)
C(39)	610 (3)	4869 (4)	3970 (5)	2.7 (2)
B(1)	2542 (3)	1503 (4)	5664 (5)	1.8 (1)

^a B_{eq} defined in Table V.

sodium or potassium salts produced are suitable for the preparation of derivatives. The $[\text{HB}(3\text{-Rpz})_3]^-$ derivatives were prepared in a somewhat different manner. The $[\text{H}_2\text{B}(3\text{-Rpz})_2]^-$ salt was prepared first and was then mixed with additional 3(5)-R-pyrazole and refluxed in anisole until the compound precipitated from solution, or until the appropriate amount of hydrogen was evolved. The parent ligands I and II were prepared in one step from the pyrazole and sodium or potassium tetrahydridoborate; this reaction is done in a melt, without added solvent. When this procedure was tried with 3(5)-phenylpyrazole, $\text{KHB}(3\text{-Phpz})_3$ precipitated from solution partway through the reaction while KBH_4 was still present. Purification of the ligand was tedious. The melt reaction of KBH_4 with $\text{H}(3-t\text{-Bupz})$ was difficult to control. On the other hand, preparation of $\text{KH}_2\text{B}(3-t\text{-Bupz})_2$ first, followed by reaction with 1 equiv of 3(5)-*tert*-butylpyrazole, was a convenient way to prepare crude ligands, suitable for reaction with transition-metal ions. In both cases, analytically pure ligands were easily obtained as their TI salts.

Metal complexes were prepared by mixing the ligand with the appropriate metal salt. With the $[\text{HB}(3\text{-Rpz})_3]^-$ ligands, only $\text{M}(\text{HB}(3\text{-Rpz})_3)(\text{X})$ and $\text{M}(\text{HB}(3\text{-Rpz})_3)(\text{X})(\text{solvent})$ compounds (Table II) were obtained because of the steric bulk of the substituents in the 3-position of the pyrazole ring. This coordination chemistry is very different from that of the parent ligands I and II, which readily form ML_2 or rarely form dimeric $\text{ML}(\text{X})$ complexes. A similar coordination chemistry is observed with the $[\text{B}(3\text{-Rpz})_4]^-$ ligands (Table III), whereas the ligand $[\text{H}_2\text{B}(3-$

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

(13) Trofimenko, S. *Inorg. Synth.* 1970, 12, 99-109.

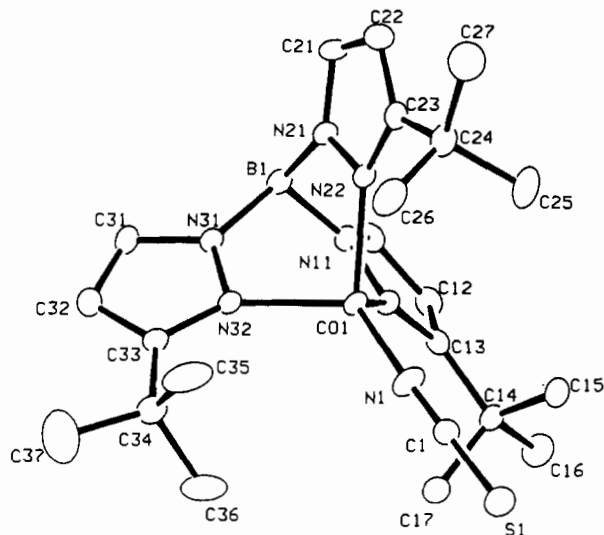


Figure 1. View of $\text{Co}(\text{HB}(3-t\text{-Bupz})_3)(\text{NCS})$. The vibrational ellipsoids are drawn at the 50% level in this and the other figure. Atom labels are included.

$\text{Phpz}_2\text{]}^-$ forms complexes analogous to those of the less sterically crowded ligands $[\text{H}_2\text{B}(\text{pz})_2\text{]}^-$ and $[\text{H}_2\text{B}(3,5\text{-Me}_2\text{pz})_2\text{]}^-$ (Table I).

The ligand with the $R = \textit{tert}$ -butyl group has the greatest steric bulk of the ligands reported to date and forms $\text{M}(\text{HB}(3-t\text{-Bupz})_3)(\text{X})$ complexes exclusively with divalent first-row transition-metal ions (Mn, Fe, Co, Ni, Cu, and Zn). They were obtained as crystalline solids, insoluble in water and methanol but very soluble in dichloromethane and other organic solvents, and were purified by crystallization from toluene or by sublimation in vacuo. Acceptable analytical results were obtained. These complexes all show a B-H stretch at approximately 2500 cm^{-1} in the infrared spectrum. For pseudohalide complexes, typical stretches¹⁴ were observed (NCS, $2070\text{--}2090\text{ cm}^{-1}$; NCO, $2220\text{--}2240\text{ cm}^{-1}$; N_3 , $2090\text{--}2110\text{ cm}^{-1}$). Spectra of the various metal complexes were essentially superimposable for any given X and ligand, implying isostructural tetrahedral complexes.

Other types of complexes can be synthesized with $\text{HB}(3-t\text{-Bupz})_3^-$ and the proper choice of metal complex. An octahedral molybdenum(0) complex was prepared by the reaction of the potassium salt of the ligand with $\text{Mo}(\text{CO})_6$ to yield $[\text{Mo}(\text{HB}(3-t\text{-Bupz})_3)(\text{CO})_3\text{]}^-$; addition of nitrosyl chloride yields the orange, crystalline material $\text{Mo}(\text{HB}(3-t\text{-Bupz})_3)(\text{NO})(\text{CO})_2$. A different type of coordination is observed for this ligand when the potassium salt is added to π -methallylpalladium chloride dimer. The product from this reaction has a very complicated NMR spectrum, which is consistent with a bidentate coordination of the ligand to form a square-planar coordination (both pyrazole 4-H and the *tert*-butyl groups were observed in a 2:1 pattern). These results are different from those with the parent ligands $[\text{HB}(\text{pz})_3\text{]}^-$ and $[\text{B}(\text{pz})_4\text{]}^-$, which show only one type of pyrazole group, indicating rapid exchange of the coordinated and uncoordinated pyrazole groups.

The coordination chemistry of the ligand $[\text{HB}(3\text{-Phpz})_3\text{]}^-$ is similar to that of the *tert*-butyl analogue in that ML_2 complexes are not formed with first-row transition-metal ions, but it does permit greater access to the metal ion than this other ligand. This property can be illustrated in the reactions of $\text{K}(\text{HB}(3\text{-Phpz})_3)$ with $\text{Co}(\text{NCS})_2$. Mixing of these components in dichloromethane yields a deep blue solution, analogous to $\text{Co}(\text{HB}(3-t\text{-Bupz})_3)(\text{NCS})$. During chromatography on alumina, the color changes to wine red. Recrystallization from THF yields a material with the same color, which was shown by X-ray diffraction techniques to have a coordinated solvent molecule (Figure 2). This change in color, indicating a change of coordination between tetrahedral and trigonal bipyramidal geometries, is reversible. Recrystallizing the wine red material from xylene or toluene or heating in vacuo

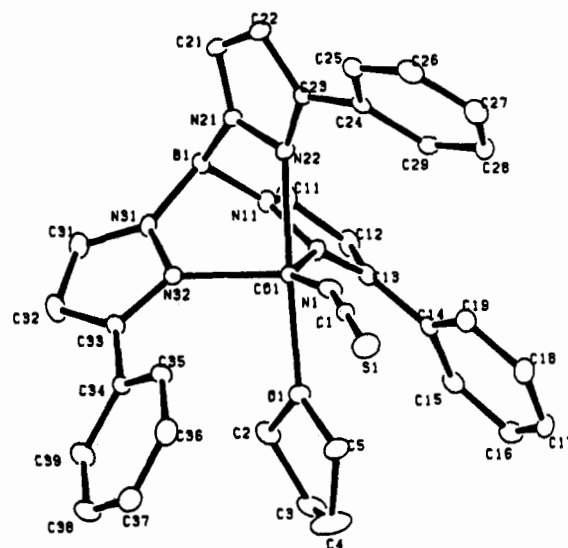


Figure 2. View of $\text{Co}(\text{HB}(3\text{-Phpz})_3)(\text{NCS})(\text{THF})$.

yields the blue tetrahedral complex.

Other types of compounds can be prepared from this ligand with the proper choice of metal complex. Adding $\text{KHB}(3\text{-Phpz})_3$ to $\text{Mo}(\text{CO})_6$ followed by addition of butyl nitrite yields $\text{Mo}(\text{HB}(3\text{-Phpz})_3)(\text{NO})(\text{CO})_2$, analogous to the compound with $[\text{HB}(3-t\text{-Bupz})_3\text{]}^-$. The π -allyl complex $\text{Mo}(\text{HB}(3\text{-Phpz})_3)(\eta^3\text{-CH}_2\text{CRCH}_2)(\text{CO})_2$ ($R = \text{H}, \text{CH}_3$) was prepared, as was the Pd(II) complex $\text{Pd}(\text{HB}(3\text{-Phpz})_3)(\eta^3\text{-CH}_2\text{CRCH}_2)$, with $R = \text{H}$ and CH_3 ; the NMR spectra of these complexes showed the presence of only one type of pyrazolyl group, indicating rapid exchange of the coordinated and uncoordinated pyrazolyl groups. This rapid interconversion of coordinated and uncoordinated pyrazolyl groups is observed with other polypyrazolylborate derivatives, but is not seen with the *tert*-butyl derivative (vide supra).

The coordination chemistry of the tetrapyrazolylborate ligands $[\text{B}(3\text{-Rpz})_4\text{]}^-$ is similar to that of $[\text{HB}(3\text{-Rpz})_3\text{]}^-$. The same types of $\text{ML}(\text{X})$ compounds are formed, but there are subtle differences that can be attributed to the presence of the fourth pyrazolyl group. The thallium(I) salts are soluble in methanol, whereas the tripyrazolyl analogues are not. The NMR spectra of $\text{Zn}(\text{B}(3-t\text{-Bupz})_4)(\text{X})$ complexes indicate exchange of the pyrazolyl groups. For $\text{X} = \text{NCS}^-$, only one type of pyrazolyl group is observed; with $\text{X} = \text{NCO}^-$ and N_3^- , a 3:1 pattern is observed for the ligand resonances, but the peaks are broad. On the other hand, the resonances in the NMR spectrum of $\text{Pd}(\text{B}(3-t\text{-Bupz})_4)(\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2)$ are sharp; the 2:1:1 pattern of the pyrazolyl resonances suggests noninterchangeable axial and equatorial (3-*t*-Bupz) groups. The same pattern is observed with $\text{Mo}(\text{B}(3-t\text{-Bupz})_4)(\text{NO})(\text{CO})_2$, resulting from a static, octahedral structure. Similar results are obtained with $[\text{B}(3\text{-Phpz})_4\text{]}^-$.

The chemistry of the dipyrazolyl ligand $[\text{H}_2\text{B}(3\text{-Phpz})_2\text{]}^-$ is analogous to that of the parent ligands and $[\text{H}_2\text{B}(3,5\text{-Ph}_2\text{pz})_2\text{]}^-$.^{1,2,13} Tetrahedral complexes of the form $\text{M}(\text{H}_2\text{B}(3\text{-Phpz})_2)_2$ were formed with Co(II) and Zn(II) ions, whereas a square-planar complex was obtained with Ni(II) ions. The properties of these complexes are shown in Table III.

The coordination chemistry of $[\text{H}_2\text{B}(3-t\text{-Bupz})_2\text{]}^-$ is very different from that of the phenyl analogue. Addition of the ligand to Ni(II) or Co(II) ions led to a fleeting formation of a species with the correct color for a ML_2 complex, followed by rapid evolution of hydrogen and apparent decomposition of the ligand. No reduction of the metal was observed. To date, only the potassium and thallium(I) salts of this ligand have been isolated and characterized.

Description of the Structure of $\text{Co}(\text{HB}(3-t\text{-Bupz})_3)(\text{NCS})$. The overall structure of this Co(II) compound is apparent in the drawing of the molecule (Figure 1) and consists of well-separated neutral monomeric $\text{Co}(\text{HB}(3-t\text{-Bupz})_3)(\text{NCS})$ molecules. The ligand coordinates to the Co ion through the nitrogen atom in the

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Table VII. Selected Bond Distances (Å) and Angles (deg) for Co(HB(3-*t*-Bupz)₃)(NCS)

Co-N(1)	1.911 (3)	N(11)-B	1.554 (5)
Co-N(12)	2.020 (3)	C(11)-C(12)	1.386 (5)
Co-N(22)	2.024 (3)	C(12)-C(13)	1.387 (5)
Co-N(32)	2.013 (3)	C(13)-C(14)	1.509 (4)
S-C(1)	1.605 (4)	C(14)-C(15)	1.531 (5)
N(1)-C(1)	1.162 (4)	C(14)-C(16)	1.540 (5)
N(11)-N(12)	1.376 (3)	C(14)-C(17)	1.528 (5)
N(11)-C(11)	1.338 (4)		
N(1)-Co-N(12)	119.3 (1)	C(11)-C(12)-C(13)	106.4 (3)
N(1)-Co-N(22)	121.6 (1)	C(12)-C(13)-C(14)	129.7 (3)
N(1)-Co-N(32)	123.2 (1)	C(13)-C(14)-C(15)	110.4 (3)
N(1)-C(1)-S	178.9 (4)	C(13)-C(14)-C(16)	109.0 (3)
N(12)-Co-N(22)	96.3 (1)	C(13)-C(14)-C(17)	110.2 (3)
N(12)-Co-N(32)	94.9 (1)	C(15)-C(14)-C(16)	108.9 (3)
N(22)-Co-N(32)	95.0 (1)	C(15)-C(14)-C(17)	109.5 (3)
Co-N(12)-N(11)	110.2 (2)	C(16)-C(14)-C(17)	108.7 (3)
N(12)-N(11)-B	121.0 (3)	N(11)-B-N(21)	108.0 (3)
N(22)-N(21)-B	121.3 (3)	N(11)-B-N(31)	108.7 (3)
N(32)-N(31)-B	122.6 (2)	N(21)-B-N(31)	109.5 (3)
C(11)-N(11)-B	129.3 (3)	N(11)-C(11)-C(12)	108.0 (3)

2-position of each ring of the 3-*tert*-butylpyrazolyl ring, in a manner analogous to complexation with the parent ligand. The thiocyanate group is coordinated to the Co ion through the nitrogen atom to form a four-coordinate complex. In Figure 1 it can be seen that the Co ion is in a pocket formed by the *tert*-butyl groups. Presumably in this way dimerization and ML₂ formation are prevented. This structure confirms that the *tert*-butyl substituents are in the 3-position of the pyrazolyl ring.

Selected bond distances and angles are presented in Table VII. The Co-N distances are typical of both Co-N distances in polypyrazolylborate complexes and Co-N distances in general.^{4,15} The geometry of the Co inner coordination sphere may be described as trigonally distorted tetrahedral and is very nearly C_{3v}, as evidenced by the N(pyrazolyl)-Co-N(NCS) bond angles of 119.3–123.2° and the N(pyrazolyl)-Co-N(pyrazolyl) bond angles of 94.9–96.3°.

Description of the Structure of Co(HB(3-Phpz)₃)(NCS)(THF). The overall structure of the molecule is apparent in the drawing of the molecule (Figure 2) and consists of well-separated neutral, monomeric Co(HB(3-Phpz)₃)(NCS)(THF) molecules. The ligand coordinates to the Co ion through the nitrogen atoms in the 2-position of the pyrazolyl rings. In addition, a nitrogen-bound thiocyanate ion and a THF molecule are present to produce a 5-coordinate Co(II) complex. In Figure 2 it can be seen that the phenyl groups form a pocket about the Co(II) ion, which presumably prevents formation of dimers and ML₂ compounds, but the pocket here is clearly larger than that with the 3-*tert*-butyl derivative. This structure confirms that the phenyl groups are in the 3-position of the pyrazolyl ring.

Selected bond distances and angles are presented in Table VIII. The Co-N(pyrazolyl) distances are nearly identical with those for the Co(HB(3-*tert*-Bupz)₃)(NCS) complex and typical of Co(II)-pyrazolyl distances in general.^{4,15} The overall geometry is trigonal bipyramidal. The average intramolecular nonbonding distance between the phenyl rings is 7.6 Å. These rings are rotated with respect to the pyrazolyl rings by 36.6, 36.2, and 32.3°.

Discussion

The preparations presented above yield polypyrazolylborate ligands with bulky alkyl or aryl groups in the 3-position of the pyrazolyl ring. The structures of Co(II) compounds with each of the [HB(3-Rpz)₃]⁻ ligands presented here confirm this assignment. These two ligands are prepared from the analogous [H₂B(3-Rpz)₂]⁻ ligand, which should thus have the same regiochemistry. Similarly, the [B(3-Rpz)₄]⁻ ligands are prepared from the simpler tripyrazolyl ligands. Previous work from these laboratories suggested a very crowded transition state for the reaction

Table VIII. Selected Bond Distances (Å) and Angles (deg) for Co(HB(3-Phpz)₃)(NCS)(THF)

Co-O	2.143 (3)	N(12)-C(13)	1.348 (5)
Co-N(1)	1.955 (4)	C(11)-C(12)	1.370 (7)
Co-N(12)	2.054 (4)	C(12)-C(13)	1.388 (6)
Co-N(22)	2.180 (4)	C(13)-C(14)	1.467 (6)
Co-N(32)	2.079 (4)	C(14)-C(15)	1.387 (6)
S-C(1)	1.624 (5)	C(14)-C(19)	1.387 (6)
N(1)-C(1)	1.167 (6)	C(15)-C(16)	1.392 (7)
O-C(2)	1.451 (5)	C(16)-C(17)	1.383 (8)
C(2)-C(3)	1.486 (7)	C(17)-C(18)	1.382 (7)
C(3)-C(4)	1.501 (9)	C(18)-C(19)	1.393 (7)
C(4)-C(5)	1.476 (8)	B-N(11)	1.537 (6)
N(11)-N(12)	1.379 (5)	B-N(21)	1.544 (7)
N(11)-C(11)	1.342 (6)	B-N(31)	1.532 (6)
O-Co-N(1)	89.5 (1)	N(11)-C(11)-C(12)	108.8 (4)
O-Co-N(12)	91.6 (1)	N(12)-C(13)-C(12)	109.7 (4)
O-Co-N(22)	175.0 (1)	N(12)-C(13)-C(14)	121.0 (4)
O-Co-N(32)	91.7 (1)	C(11)-C(12)-C(13)	106.0 (4)
N(1)-Co-N(12)	144.9 (2)	C(12)-C(13)-C(14)	129.3 (4)
N(1)-Co-N(22)	93.7 (2)	C(13)-C(14)-C(15)	120.2 (4)
N(1)-Co-N(32)	121.1 (2)	C(13)-C(14)-C(19)	121.7 (4)
N(12)-Co-N(22)	83.6 (1)	C(15)-C(14)-C(19)	118.1 (5)
N(12)-Co-N(32)	93.9 (1)	C(14)-C(15)-C(16)	120.9 (5)
N(22)-Co-N(32)	90.0 (1)	C(15)-C(16)-C(17)	119.5 (5)
Co-N(1)-C(1)	165.4 (4)	C(16)-C(17)-C(18)	121.1 (5)
S-C(1)-N(1)	179.0 (5)	C(17)-C(18)-C(19)	118.2 (5)
O-C(2)-C(3)	105.5 (4)	C(14)-C(19)-C(18)	122.1 (5)
O-C(5)-C(4)	106.7 (5)	N(11)-B-N(21)	109.2 (4)
C(2)-C(3)-C(4)	103.5 (5)	N(11)-B-N(31)	108.7 (4)
C(3)-C(4)-C(5)	105.6 (5)	N(21)-B-N(31)	109.2 (4)
N(12)-N(11)-C(11)	109.3 (4)		

of tetrahydridoborate ion with pyrazole,² leading to the less sterically hindered product. Such products were observed with the derivatives prepared with 3(5)-methylpyrazole; only the less sterically hindered 3-methyl derivatives [H₂B(3-Mepz)₂]⁻ and [HB(3-Mepz)₃]⁻ were obtained.¹⁶ Additional ligands prepared in these laboratories confirm that such preparations yield the less-sterically hindered derivatives.¹⁷

The bulky substituents in the 3-position of the pyrazolyl ring do have a profound effect on the coordination chemistry of these ligands. Formation of ML₂ complexes with [HB(3-*t*-Bupz)₃]⁻ and [HB(3-Phpz)₃]⁻ does not appear to be possible with the first-row transition-metal ions. Addition of KL to M(X)₂ complexes yields simple ML(X) compounds. The coordination chemistry of all other tripyrazolylborate derivatives reported to date is dominated by the formation of ML₂ complexes. With first-row transition-metal ions, the ligand [HB(3-*t*-Bupz)₃]⁻ appears to be a tetrahedral enforcer, leading to complexes with C_{3v} symmetry.

This study also demonstrates that the accessibility to the metal ion can be controlled by changing the substituent in the 3-position of the pyrazolyl ring. With both of the tripyrazolylborate ligands reported here, only one ligand fits around a first-row transition metal. Yet the 3-phenyl derivative provides a more open cavity for the metal ion. This increased accessibility is clearly seen in Figures 1 and 2. A single complex was observed with [HB(3-*t*-Bupz)₃]⁻, whereas solvated and unsolvated derivatives can be isolated with the 3-phenyl derivative. Thus, appropriate choice of 3-R groups will permit the construction of custom-sized pockets around the metal ions, regulating the access to it by other ligands.

The structures and reactivity of M(HB(3-*t*-Bupz)₃)(X) complexes clearly demonstrate that this polypyrazolylborate ligand is sterically restrictive and limits the accessibility of the metal ion. One way to quantify accessibility is to determine the cone angle of a ligand. Cone angle values of 180 and 225° were reported for Mo(RB(pz)₃)(X)₃ and Fe(HB(3,5-Me₂pz)₃)(X)₃, respectively.¹⁸ Our calculations were based on the established di-

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mensions of the crystallographically characterized $\text{Co}(\text{HB}(3\text{-}t\text{-Bupz})_3)(\text{NCS})$ complex. Because the sharpness of the *tert*-butyl peak in the NMR spectrum of the analogous $\text{Zn}(\text{II})$ complex indicated free rotation of that group, we chose for calculations the cone angle of the conformation that brings one of the methyl hydrogen atoms closest to the Co atom. Then, the same calculations were repeated with a methyl group in place of the *tert*-butyl group, and finally with a hydrogen atom in place of the methyl group. Values of cone angles are 244, 224, and 184° for the *tert*-butyl group, the methyl group, and the hydrogen atom, respectively. Clearly, the *tert*-butyl group generates the largest cone angle known for polypyrazolylborate ligands.

Conclusion

The introduction of these new ligands broadens significantly

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the scope of polypyrazolylborate chemistry. The reaction between $[\text{BH}_4]^-$ and 3-R-pyrazole is regiospecific. This property allows the preparation of a wide variety of unsymmetrically substituted polypyrazolylborates. The bulky groups in the 3-position of the pyrazole ring prevent dimerization and bis-chelate formation, two properties that severely limit the usefulness of the parent ligands. This property coupled with the ability to construct custom-sized pockets around the metals ions, allowing access to molecules of predetermined size and/or shape, makes this new series of polypyrazolylborate ligands potentially very useful.

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Supplementary Material Available: Listings of thermal parameters (Tables S1 and S5), hydrogen atom positions (Tables S2 and S6), and complete bond distances and angles (Tables S4 and S8) (7 pages); listings of observed and calculated structure factors (Tables S3 and S7) (16 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843

Low-Valent Molybdenum Carbonyl Complexes as an Entry to Octahedral MoI_3L_3 Complexes. Synthesis and X-ray Molecular Structure of $\text{MoI}_3(\text{THF})_3$

F. Albert Cotton* and Rinaldo Poli

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$\text{MoI}_3(\text{THF})_3$ has been synthesized by iodination at room temperature of either $\text{Mo}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)$ or $\text{Mo}_2\text{I}_4(\text{CO})_8$ in tetrahydrofuran (THF) as solvent. Crystals are orthorhombic, space group *Pbcn*, with $a = 9.252(3) \text{ \AA}$, $b = 14.541(5) \text{ \AA}$, $c = 14.273(3) \text{ \AA}$, $V = 1920(2) \text{ \AA}^3$, $Z = 4$, $d_{\text{calcd}} = 2.397 \text{ g cm}^{-3}$, and $R = 0.0501$ for 926 data having $F_o^2 > 3\sigma(F_o^2)$. The molecule is octahedral, in the meridional configuration. Substitution reactions have been carried out with PR_3 ($R = \text{Me, Et}$) to produce $\text{MoI}_3(\text{PR}_3)_3$. The direct interaction between MoX_3 ($X = \text{Cl, I}$) and PR_3 ($R = \text{Me, Et}$) in toluene has been studied. Reduction competes with coordinative addition to produce mixtures of $\text{MoX}_3(\text{PR}_3)_3$ and $\text{Mo}_2\text{X}_4(\text{PR}_3)_3$ for $X = \text{Cl, I}$ and $R = \text{Me}$ and mixtures of $[\text{PHR}_3][\text{MoI}_4(\text{PR}_3)_2]$ and $\text{Mo}_2\text{X}_4(\text{PR}_3)_4$ for $X = \text{I}$ and $R = \text{Et}$. A possible mechanism for these reactions is discussed.

Introduction

In relation to our recent work on the synthesis of $\text{Mo}_2\text{I}_4\text{L}_4$ and $\text{Mo}_2\text{I}_4(\text{LL})_2$ ($L = \text{phosphine}$; $\text{LL} = \text{diphosphine}$) complexes by decarbonylation of molybdenum(II) carbonyl derivatives,¹⁻⁴ where molybdenum(III) iodide complexes were also sometimes obtained as a result of a competitive disproportionation reaction, we became interested in finding alternative and better routes to derivatives of molybdenum(III) iodide. This interest was reinforced upon realizing that such derivatives were not known, although the chemistry of the corresponding chlorides and bromides had been developed. The $[\text{MoX}_6]^{3-}$ and $[\text{Mo}_2\text{X}_9]^{3-}$ ($X = \text{Cl, Br}$)^{5,6} anions are well-known. MoX_3L_3 ($X = \text{Cl, Br}$) compounds with $L = \text{pyridine}$ were prepared for the first time⁷ by high-temperature reaction of MoX_3 and the ligand and later^{8,9} from $(\text{NH}_4)_2\text{MoX}_5 \cdot \text{H}_2\text{O}$. Compounds with other hard-donor-based ligands were obtained¹⁰ by disproportionation reactions from $\text{Mo}_2\text{X}_4(\text{CO})_8$; the unavailability of a good preparative method for

$\text{Mo}_2\text{I}_4(\text{CO})_8$ ^{11a} may have prevented such chemistry from being performed on the iodide system.^{11b} San Filippo and Schaefer King were able to prepare the $\text{MoX}_3(\text{py})_3$ ($X = \text{Cl, Br}$; $\text{py} = \text{pyridine}$) compounds by interaction of the $\text{Mo}_2\text{X}_4(\text{py})_4$ dimers of $\text{Mo}(\text{II})$ with pyridine at high temperatures.¹²

The cleanest route to MoX_3L_3 complexes, which also has the advantage of being applicable to the preparation of derivatives containing soft-donor-based ligands,¹³ seems to be the substitution reaction on preformed $\text{MoX}_3(\text{THF})_3$ ($\text{THF} = \text{tetrahydrofuran}$). Such a method has been applied so far only to the chloride system, the corresponding bromide and iodide being unknown. $\text{MoCl}_3(\text{THF})_3$ has been conveniently obtained by reduction of $\text{MoCl}_4(\text{THF})_2$ with zinc¹⁴ or tin¹⁵ or more recently via $\text{MoCl}_3(\text{MeCN})_3$, which in turn had been obtained from $\text{MoCl}_4(\text{MeCN})_2$.¹⁶ The

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