toluene at reflux give the desired product. In particular, oxidation of the neutral and anionic carbonyl complexes of rhodium in the following reactions by complexes **4** and **5** occurs:

$$Pt(bzta)_2(PPh_3)_2 + [RhCl(CO)_2]_2 \rightarrow (Ph_3P)Pt(\mu\text{-bzta})_2RhCl(CO)$$

$$Pt(bzta)_2(PPh_3)_2 + [RhCl_2(CO)_2]NBu_4 \rightarrow (Ph_3P)Pt(\mu\text{-bzta})_2RhCl(CO)$$

$$PtH(bzta)(PPh_3)_2 + [RhCl(CO)(PPh_3)]_2 \rightarrow (Ph_3P)Pt(\mu\text{-bzta})_2RhCl(CO)$$

Nevertheless mixtures of compounds result, from which the isolated yield of compound **2** is similar or even smaller than in the full described preparation.

In conclusion, we describe here the synthesis and characterization of the first two heterobinuclear complexes with just two short-bite bridging anionic ligands in which they adopt a relative trans disposition. Acting in this way, they bridge a short metal–metal bond as can be anticipated by steric arguments.

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Supplementary Material Available: Tables of thermal parameters (Table S1), positional parameters for hydrogen atoms (Table S2), and full details of crystal data and data collection (Table S3) and listings of bond lengths and bond angles, least-squares planes, and interatomic contacts (17 pages); a listing of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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1,5-Cyclooctanediylbis(pyrazol-1-yl)borate: A Ligand with Enhanced Agostic Interaction

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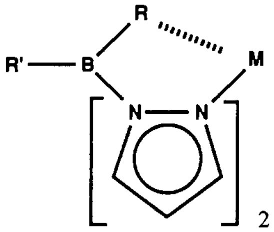
1,5-Cyclooctanediylbis(pyrazol-1-yl)borate (=L*) is a new type of $[R_2B(pz)_2]^-$ ligand in which the R_2 groups form part of a rigid bicyclic system and in the complexes of which the pseudoaxial bridgehead hydrogen is forced into close proximity to the metal. The complexes ML^*_2 (M = Co, Ni, Zn), $ML^*(\eta^3\text{-}CH_2CRCH_2)(CO)_2$ (M = Mo, W; R = H, Me, Ph), and $PdL^*(\eta^3\text{-}CH_2CRCH_2)$ (R = H, Me, Ph) were synthesized. The agostic interaction was confirmed in $ML^*(\eta^3\text{-}CH_2CRCH_2)(CO)_2$ complexes by IR and NMR spectroscopy and by an X-ray structure determination of CoL^*_2. There was no agostic interaction in the mixed complex $CoL^*(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)$, the bridgehead hydrogen being 2.62 Å from the Co atom. The complex $Co(L^*)_2$ crystallizes in the space group $P\bar{1}$ with 1 molecule per unit cell of dimensions $a = 7.665$ (1) Å, $b = 9.301$ (2) Å, $c = 10.551$ (3) Å, $\alpha = 88.56$ (2)°, $\beta = 80.27$ (2)°, $\gamma = 66.26$ (2)° at −70 °C. Least-squares refinement of 178 variables led to a value of the conventional R index (on F) of 0.046 and $R_w = 0.066$ for reflections with $I > 3.0\sigma(I)$. The geometry about the Co(II) ion, which is coordinated to four pyrazolyl nitrogen atoms from two L* ligands and two H atoms from the borabicyclononane ring systems, is pseudooctahedral with the pyrazolyl nitrogen atoms in a planar arrangement and the agostic hydrogen atoms in axial positions. The complex $CoL^*(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)$ crystallizes in the space group $P\bar{1}$ with 4 molecules per unit cell of dimensions $a = 10.075$ (2) Å, $b = 20.640$ (10) Å, $c = 20.700$ (10) Å, $\alpha = 99.09$ (4)°, $\beta = 102.91$°, and $\gamma = 97.98$ (2)° at −70 °C. Least-squares refinement of 917 variables led to a value of the conventional R index (on F) of 0.055 and $R_w = 0.057$ for reflections with $I > 3.0\sigma(I)$. The geometry about the Co(II) ion, which is coordinated to five pyrazolyl nitrogen atoms from two different polypyrazolylborate ligands, is square pyramidal.

Introduction

Over the years since their introduction, the polypyrazolylborates[1] have been viewed in a dichotomous way: either as tridentate ligands (when $[RB(pz^*)_3]^-$) analogous to the cyclopentadienyl anion or as bidentate ligands (when $[R_2B(pz^*)_2]^-$) similar to β-diketonates. As the area was explored more thoroughly, it became more and more apparent that the two structures mentioned above are in reality members of a continuum within one family, since instances are known where $[RB(pz^*)_3]^-$ functions as a bidentate ligand and, conversely, $[R_2B(pz^*)_2]^-$ may coordinate in a tridentate fashion.

The unifying feature in all polypyrazolylborate complexes is the six-membered ring $M(RR'B(\mu\text{-}pz^*)_2)$, where M may contain additional ligands and where R, R′ can be H, alkyl, aryl, NR_2, ArS, or pz* (pz* = 1-pyrazolyl or substituted 1-pyrazolyl). Because of the bond angles and distances involved, this ring has almost always a boat structure of varying depth. In such a structure the pseudoaxial group R is curled toward the metal and may bond to or interact with it.[2]



We can distinguish two categories of polypyrazolylborate ligands: those where the pseudoaxial R = pz* and those where the coordinating pseudoaxial R is anything but pz*; it can, however,

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(1) Trofimenko S. *J. Am. Chem.* **1966**, *88*, 1842–1844.

(2) On the basis of their structural features and coordinative behavior it is very tempting to call the geminal polypyrazolyl ligands, and polypyrazolylborates in particular, "scorpionates", as the scorpion is the only species whose prey-attacking behavior resembles that of polypyrazolylborate coordination to metal ions. The two identical pz* groups, symmetrically coordinated to the metal are the "claws", while the pseudoaxial substituent R, arching toward the metal ion, is the "sting". While the "claws" always grab the metal ion, an attack by the sting is an option, which may or may not be exercized, depending on a variety of factors pertaining to the structural features of the ligand and the metal.

be a differently substituted pz group. The first category contains the most common polypyrazolylborates of local C_{3v} symmetry, including inter alia the frequently used $[HB(pz)_3]^-$, $[B(pz)_4]^-$, and $[HB(3,5\text{-}Me_2pz)_3]^-$ ligands. At the same time it should be noted that there are situations where the pseudoaxial pz group does not coordinate and the $[RB(pz)_3]^-$ ligand is bidentate, as for instance in $Mo(RB(pz)_3)(\eta^5\text{-}C_5H_5)(CO)_2$[3] or in square planar $Pd(RB(pz)_3)(\eta^3\text{-allyl})$ complexes.[4] In the latter compounds, there is a rapid exchange of the coordinated and uncoordinated pyrazolyl groups on the NMR time scale, so that the stereochemically rigid bidentate species can only be seen at low temperatures.

While tris(pyrazolyl)borates have, by definition, a two-atom bridge (the -N-N- sequence of pz*) in their tricoordinated complexes, the bis(pyrazolyl)borates may have either a two-atom or a one-atom bridge, depending on the nature of R. There are only two examples where a non-pyrazolyl *heteroatom* fulfills the bridging function. The ligand $[Me_2NB(pz)_3]^-$ coordinates with the dimethylamino, rather than pyrazolyl, group,[5] and in $[HB(3,5\text{-}Me_2pz)_2(SAr)]^-$ the bonding occurs through the sulfur atom of the arylthio group.[6] A fairly large group of polypyrazolylborates containing the ligand $[H_2B(pz^*)_2]^-$ have a pseudoaxial B-H which often bridges to the metal. The first complex where such a structure was established is $Mo(H_2B(3,5\text{-}Me_2pz)_2)(\eta^3\text{-allyl})(CO)_2$.[7] Some of the other examples are $Mo(H_2B(3,5\text{-}Me_2pz)_2)(\eta^3\text{-}C_7H_7)(CO)_2$,[8] $Ta(H_2B(3,5\text{-}Me_2pz)_2)(Me)_3Cl$,[9] $Pt(H_2B(3,5\text{-}Me_2pz)_2)(Me)_3$,[10] $Y(H_2B(pz)_2)_3$,[11] $Zr(H_2B(pz)_2)(C_5H_5)Cl_2$,[12] and $Co(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)(H_2B(3\text{-}Phpz)_2)$.[13] An unusual case, where the bonding is carried out by B-H, rather than by an available B-pz*, is $Co(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)(HB(3\text{-}Phpz)_3)$,[13] where steric hindrance in the equatorial belt of the octahedral structure can accommodate only two of the three 3-phenylpyrazolyl groups and the sixth coordination site accrues by default to the B-H agostic bond.

Even pseudoaxial alkyl groups can bond to the coordinated metal through a C-H-M interaction, as was found some time ago in the case of $Mo(Et_2B(pz)_2)(\pi\text{-allyl})(CO)_2$ complexes.[14] However, since the C-H-M interactions in $[Et_2B(pz)_2]^-$ complexes are complicated by the extensive degrees of freedom of the B-bonded ethyl groups and the relative ease of inversion of the $B(\mu\text{-}pz)_2M$ ring,[14d] we synthesized a $[R_2B(pz)_2]^-$ ligand where the agostic C-H would be part of a rigid cage system with a unique CH directed at the metal. Such a ligand, cyclooctane-1,5-diylbis(pyrazol-1-yl)borate (=L*) was prepared from 9-borabicyclo[3.3.1]nonane (=BBN), pyrazolide ion, and pyrazole as shown in eq 1. The ligand L* was found to yield more stable MoL*$(\eta^3\text{-allyl})(CO)_2$ complexes than those derived from $[Et_2B(pz)_2]^-$. Surprisingly, it also provided the first example of a CoL^*_2 complex with *two* agostic C-H-M interactions, as reported in a preliminary communication[15] and in detail here. This structure gives rise to unusual spectroscopic properties, as detailed elsewhere.[16]

$$\text{9-BBN} + \text{Hpz} + \text{Kpz} \rightarrow \text{KBBN(pz)}_2 + H_2\uparrow \qquad (1)$$

Experimental Section

General Methods. All the chemicals were reagent grade and were used as received. Elemental analyses were done by Microanalysis, Inc., of Wilmington, DE. Infrared spectra were obtained as Nujol mulls with a Perkin-Elmer 283B infrared spectrophotometer. Proton NMR spectra were obtained with a Nicolet NT360WB spectrometer. Diamagnetic compounds were studied with typical conditions of 16K data points, a sweep width of 3000-4000 Hz, 90° pulse angles, and a recycle time of 4-5 s. Paramagnetic compounds were studied with 64K data points, a sweep width of 100 kHz, 45° pulse angles, and a recycle time of 1.2 s.

Potassium Cyclooctane-1,5-diylbis(pyrazol-1-yl)borate (=KL*). A mixture of 30.4 g (0.44 mol) of pyrazole, 450 mL of toluene, and 11.2 g (0.2 mol) of dry KOH pellets was stirred and refluxed in a 1-L flask, removing water by means of a Dean-Stark trap. When all the water was removed, 400 mL of a 0.5 M solution of 9-borabicyclo[3.3.1]nonane in tetrahydrofuran (THF) was added dropwise at such a rate that THF distilled slowly, and evolution of hydrogen was followed by means of a wet-test meter. When about 5 L of hydrogen was evolved and the addition was completed, the slurry was concentrated down to about 400 mL, then cooled partly, and diluted with hexane to 1 L. It was filtered hot, and the product was then washed with hexane and air-dried. There was obtained 54 g (93%) of a white solid, which was used for the preparation of complexes without further purification.

TlL* and ML*$_2$ Complexes. These compounds were prepared by mixing an aqueous solution of the appropriate metal nitrate with a methanolic solution of KL*. The precipitated products were isolated by filtration, washed with water and then with methanol, and air-dried. Final purification was by recrystallization from toluene.

TlL*: white crystals, mp 273-276 °C dec, with prior very gradual darkening from 220 °C on. NMR: d 7.60, d 7.30, t 6.12, m 1.1-2.4 (with sharp spike at 1.75) ppm (ratio 2:2:2:14). Anal. Calc for $C_{14}H_{20}BN_4Tl$: C, 36.2; H, 5.39; N, 12.1. Found: C, 36.3; H, 5.43; N, 12.0.

CoL^*_2: salmon crystals, mp 191-192 °C, turning purple. Anal. Calc for $C_{28}H_{40}BCoN_8$: C, 59.1; H, 7.10; N, 19.9. Found: C, 59.7, H, 7.07; N, 19.9.

NiL^*_2: orange crystals, mp none up to 300 °C. Anal. Calc for $C_{28}H_{40}BN_8Ni$: C, 59.1; H, 7.10; N, 19.9. Found: C, 59.4; H, 7.12; N, 19.6.

ZnL^*_2: white crystals, mp 192-193 °C. Anal. Calc for $C_{28}H_{40}BN_8Zn$: C, 58.4; H, 6.96; N, 19.5. Found: C, 58.7; H, 7.08; N, 19.7.

Co[hydrotris(3-isopropyl-4-bromopyrazol-1-yl)borato]L*, Co(HB(3-*i*-Pr-4-Br-pz)$_3$)L* (II). An equimolar mixture of L*Tl and $Co(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)Cl$[17] was stirred in dichloromethane at room temperature for 2 h, during which time the color of the slurry changed from blue to wine red. The slurry was filtered through a layer of Celite to remove TlCl, and the filtrate was evaporated. The residue was stirred with methanol, yielding the mixed-ligand complex, which was purified by recrystallization from toluene; mp 203-205 °C. Anal. Calc for $C_{32}H_{45}B_2Br_3CoN_{10}$: C, 43.2; H, 5.06; N, 15.7. Found: C, 43.3; H, 5.24; N, 15.6.

PdL*(η^3-CH$_2$CRCH$_2$) Complexes (R = H, Me, Ph). These complexes were prepared by stirring for 1 h at room temperature an equimolar mixture of TlL* and $Pd(\eta^3\text{-}CH_2CRCH_2)Cl$ dimer in methylene chloride. Filtration of the slurry through a bed of Celite and alumina to remove TlCl and evaporation of the filtrate gave the crude product, which was purified by recrystallization from a toluene/heptane mixture.

R = H: white crystals, mp 179-180 °C. NMR: d 7.63, d (7.42 + 7.20), t 6.07, m 5.57, d (3.92 + 3.83), d (3.04 + 2.94), m 0.8-2.4 ppm (ratio 2:(2):2:1:(2):(2):14). Anal. Calc for $C_{17}H_{25}BN_4Pd$: C, 50.2; H, 6.26; N, 13.9. Found: C, 49.9; H, 6.35; N, 14.0.

R = Me: white crystals, mp 129-130 °C. NMR: d 7.66, d (7.43 + 7.26), overlapping t 6.10, s (3.69 + 3.61), s (2.90 + 2.82), m 2.3-2.6, s (2.18 + 2.10), m 0.9-2.3 ppm (ratio 2:(2):2:(2):(2):1:(3):13). Anal. Calc for $C_{18}H_{27}BN_4Pd$: C, 51.9; H, 6.49; N, 13.5. Found: C, 52.2; H, 6.58; N, 13.3.

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Table I. Crystal Data for Co(L*)$_2$ (I) and CoL*(HB(3-*i*-Pr-4-Br-pz)$_3$) (II)

	I	II
mol formula	$C_{28}H_{40}B_2CoN_8$	$C_{35.5}H_{49}B_2Br_3CoN_{10}$
M_r	569.23	936.13
a, Å	7.665 (1)	10.075 (2)
b, Å	9.301 (2)	20.640 (10)
c, Å	10.551 (3)	20.700 (10)
α, deg	88.56 (2)	99.09 (4)
β, deg	80.27 (2)	102.91 (7)
γ, deg	66.26 (2)	97.98 (2)
V, Å^3	667.9	4074.7
Z	1	2
space group	$P\bar{1}$	$P\bar{1}$
radiation (λ, Å)	Mo Kα (0.710 69) from graphite monochromator	
temp, °C	−70	−70
abs coeff, cm^{-1}	6.63	33.72
R	0.046	0.055
R_w	0.066	0.057

R = Ph: white crystals, mp 139–140 °C. NMR: d 7.58, d 7.45, m 7.28, t 6.06, s (4.08 + 3.98), s (3.10 + 3.05), m 0.6–2.5 ppm (ratio 2:2:5:2:(2):(2):14). Anal. Calc for $C_{22}H_{29}BN_4Pd$: C, 56.7; H, 6.22; N, 12.0. Found: C, 56.9; H, 6.38; N, 11.9.

M(CO)$_2$L*(η^3-CH$_2$CRCH$_2$) Complexes (M = Mo, W; R = H, Me, Ph). The compounds were prepared by the same method, exemplified for M = Mo, R = H. A mixture of 5.9 g of KL* (an equivalent amount of TlL* may also be used) and 5.3 g of Mo(CO)$_6$ (both 0.02 mol) was stirred and heated in 100 mL of DMAC until 1.0 L of CO was evolved, as measured by a wet-test meter. The yellow solution was cooled under nitrogen with an ice bath. Allyl bromide (3 g; 0.025 mol) was added, and the solution was allowed to warm and was heated until another 1.0 L of CO was evolved. The orange solution was poured into 800 mL of ice-cold water and was extracted with three 150-mL portions of methylene chloride, and the extracts were washed four times with 500-mL portions of water to remove most of the DMAC. Chromatography on alumina yielded an orange band, which was collected, and the solvent was removed. Stirring of the residue with a small amount of methanol and filtration produced 5.8 g (65%) of an orange solid, which was recrystallized from heptane. Properties of this material and of its analogues are shown below.

M = Mo, R = H: orange solid, mp 133–134 °C. IR: 2590–2710 (b), 1965, 1945, 1877, 1850 cm^{-1}. NMR: d 8.00, d 7.38, t 6.14, m 3.95, m 0.8–2.1, m −5.22 ppm (ratio 2:2:2:1:2:15:1). Anal. Calc for $C_{19}H_{25}BMoN_4O_2$: C, 50.9; H, 5.58; N, 12.5. Found: C, 50.9; H, 5.86; N, 12.9.

M = Mo, R = Me: orange solid, mp 133–134 °C (same as for R = H). IR: 2560–2640 (b), 1940 (b), 1865 (b) cm^{-1}. NMR: d 8.01, d 7.45, t 6.16, s 3.52, m 0.8–2.1 (with s 2.02 and s 1.57), m −4.50 ppm (ratio 2:2:2:2:18:1). Anal. Calc for $C_{20}H_{27}BMoN_4O_2$: C, 52.0; H, 5.84; N, 12.1. Found: C, 52.2; H, 5.78; N, 12.1.

M = Mo, R = Ph: orange solid, mp 157–159 °C dec. IR: 2500–2650 (b), 1945, 1932 sh, 1868, 1857 sh, 1845 cm^{-1}. NMR: d 8.08, m 7.34, m 7.06, t 6.14, s 4.09, m 1.4–1.9 (with s 1.65), m 0.8–1.3, t (b) 0.0–0.5, m −5.18 ppm (ratio 2:4:3:2:2:7(2):6:2:1). Anal. Calc for $C_{25}H_{29}BMoN_4O_2$: C, 57.3; H, 5.53; N, 10.7. Found: C, 57.4; H, 5.73; N, 11.0.

M = W, R = Me: orange solid, mp 141–143 °C. IR: 2480–2620 (b), 1952 sh, 1940 sh, 1932, 1860 sh, 1850, 1845 sh cm^{-1}. NMR: d 8.03, s 7.48, t 6.13, s 3.38, m (with s 2.17, 1.95) 0.8–2.2, m −4.06 ppm (ratio 2:2:2:2:18(with 3, 2):1). Anal. Calc for $C_{20}H_{27}BN_4O_2W$: C, 43.6; H, 4.91; N, 10.2. Found: C, 44.0; H, 5.12; N, 10.3.

M = W, R = H: orange solid, mp 138–140 °C dec. IR: 2540–2720 (b), 1955, 1940, 1855, 1840, 1835 cm^{-1}. NMR: s (b) 8.00, d 7.42, s (b) 6.10, d + m 2.9–3.6, m 0.9–2.3, m −4.60 ppm (ratio 2:2:2:2+1:15:1). Anal. Calc for $C_{19}H_{25}BN_4O_2W$: C, 42.5; H, 4.66; N, 10.5. Found: C, 42.2; H, 4.58; N, 10.3.

X-ray Data Collection and Structure Solution and Refinement. Co(BBN(pz)$_2$)$_2$ (I). Crystals suitable for diffraction were obtained by evaporation of solvent from a benzene solution of the compound. The crystal was encapsulated in a glass capillary that was then placed on the Enraf-Nonius CAD4 diffractometer. The crystal was shown to be suitable for diffraction on the basis of ω-scans, which showed the peak width at half-height to be ca. 0.23° 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 I. 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.[18]

Table II. Fractional Coordinates (×10^4) and Isotropic Thermal Parameters for Co(BBN(pz)$_2$)$_2$ (I)

atom	*x*	*y*	*z*	B_{eq},^{a} Å^2
Co(1)	5000	5000	5000	1.3 (1)
N(11)	2503 (5)	3522 (4)	6104 (3)	1.6 (1)
N(12)	3300 (5)	3941 (4)	4990 (3)	1.6 (1)
N(21)	7423 (5)	4411 (4)	2534 (3)	1.6 (1)
N(22)	6640 (5)	3740 (4)	3502 (3)	1.5 (1)
C(13)	2538 (6)	3606 (5)	4047 (4)	1.9 (1)
C(14)	1240 (6)	2971 (5)	4532 (4)	2.3 (1)
C(15)	1228 (6)	2962 (5)	5848 (4)	2.0 (1)
C(23)	7456 (4)	2182 (5)	3251 (4)	2.0 (1)
C(24)	8795 (6)	1824 (5)	2120 (4)	2.1 (1)
C(25)	8733 (6)	3254 (5)	1710 (4)	1.9 (1)
C(31)	4448 (6)	7146 (5)	2865 (4)	1.7 (1)
C(32)	3899 (7)	8899 (5)	3218 (4)	2.6 (1)
C(33)	4817 (8)	9675 (5)	2085 (5)	3.1 (2)
C(34)	6957 (7)	8719 (6)	1578 (4)	2.6 (2)
C(35)	7554 (6)	6940 (5)	1367 (4)	1.9 (1)
C(36)	6775 (7)	6583 (5)	206 (4)	2.3 (1)
C(37)	4580 (7)	7119 (5)	394 (4)	2.4 (1)
C(38)	3666 (6)	6782 (5)	1704 (4)	2.3 (1)
B(1)	6764 (7)	6240 (5)	2641 (5)	1.7 (1)

^{a} $B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$.

The structure was solved by automated Patterson analysis (PHASE). The function minimized is given elsewhere,[18] Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[19] Hydrogen atom positions were calculated with C–H and B–H distances of 0.95 Å. Least-squares refinement converged to $R = 0.046$ and $R_w = 0.066$ (R_w and *w* are described elsewhere[18]). All peaks in the final difference Fourier map were less than or equal to 0.48 e/Å^3.

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

[Co(HB(3-*i*-Pr-4-Br-pz)$_3$)(BBN(pz)$_2$)](toluene)$_{0.5}$ (II). Crystals suitable for diffraction were obtained by evaporation of solvent from a toluene solution of the compound. The crystal was encapsulated in a glass capillary that was then placed on the Enraf-Nonius CAD4 diffractometer. The crystal was shown to be suitable for diffraction on the basis of ω-scans, which showed the peak width at half-height to be ca. 0.15° at −70 °C. The cell parameters were then refined on the basis of 23 reflections chosen from diverse regions of reciprocal space. These parameters and other crystallographic data are summarized in Table I. 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.[18]

The structure was solved by direct methods (Multan). The function minimized is given elsewhere.[18] Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[19] Hydrogen atom positions were calculated with C–H and B–H distances of 0.95 Å. The disordered molecule of toluene was modeled with two orientations of half-weighted carbon atoms. Least-squares refinement converged to $R = 0.055$ with $R_w = 0.057$ (R_w and *w* are described elsewhere[18]). All peaks in the final difference Fourier map were less than or equal to 0.77 e/Å^3.

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

Results and Discussion

Synthesis and Spectroscopic Characterization. The new ligand L* was prepared in good yield by the reaction of 9-BBN with an equivalent amount of pyrazolide ion in excess pyrazole and was characterized as the Tl(I) salt. Its salts exhibit stability superior to those of the [Et$_2$B(pz)$_2$]$^-$ ligand. L* formed readily derivatives similar to those obtained from [Et$_2$B(pz)$_2$]$^-$, such as ML*$_2$ (M = Ni, Co, Cu, Zn) and ML*(η^3-allyl)(CO)$_2$.

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

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

Table III. Fractional Coordinates (×10^4) and Isotropic Thermal Parameters for CoL*(HB(3-*i*-Pr-4-Br-pz)$_3$)(toluene)$_{0.5}$ (II)

atom	*x*	*y*	*z*	B_{eq},[a] Å^2	atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Br(1)	6510.4 (9)	4078.3 (5)	4900.1 (5)	4.4 (1)	C(34′)	10097 (7)	7288 (3)	1835 (4)	2.1 (2)
Br(1′)	16343.0 (11)	8079.1 (6)	4735.7 (5)	5.9 (1)	C(35)	2931 (8)	6549 (4)	3701 (4)	2.4 (2)
Br(2)	4957.5 (10)	5558.7 (5)	725.4 (5)	4.1 (1)	C(35′)	10197 (7)	7710 (4)	2430 (4)	2.1 (2)
Br(2′)	10976.9 (12)	11239.4 (5)	2851.2 (7)	6.7 (1)	C(36)	−441 (7)	5479 (4)	3508 (4)	2.4 (2)
Br(3)	904.3 (11)	7183.8 (5)	4208.3 (6)	5.3 (1)	C(36′)	11688 (7)	7251 (4)	1003 (4)	2.4 (2)
Br(3′)	8657.1 (9)	6567.2 (4)	1443.3 (5)	4.2 (1)	C(37)	−477 (8)	5403 (4)	4230 (4)	3.7 (3)
Co(1)	1802.7 (9)	4518.6 (5)	2678.1 (5)	1.6 (1)	C(37′)	12127 (9)	6590 (4)	1087 (5)	4.2 (3)
Co(1′)	13608.5 (9)	8842.3 (5)	2053.4 (5)	1.8 (1)	C(38)	−1638 (9)	5790 (5)	3185 (4)	4.0 (3)
N(11)	4539 (5)	5091 (3)	3613 (3)	1.8 (2)	C(38′)	10660 (9)	7185 (4)	322 (4)	3.8 (3)
N(11′)	13379 (6)	8679 (3)	3454 (3)	1.9 (2)	C(43)	2531 (7)	3223 (4)	2014 (4)	2.3 (2)
N(12)	3547 (5)	4534 (3)	3464 (3)	1.8 (2)	C(43′)	16158 (8)	9939 (4)	2593 (4)	2.7 (2)
N(12′)	14309 (6)	8642 (3)	3070 (3)	1.9 (2)	C(44)	1904 (8)	2651 (4)	1555 (4)	2.9 (3)
N(21)	4167 (6)	5475 (3)	2511 (3)	1.9 (2)	C(44′)	17084 (9)	10328 (4)	2362 (5)	3.9 (3)
N(21′)	11910 (6)	9432 (3)	2924 (3)	2.2 (2)	C(45)	540 (8)	2602 (4)	1515 (4)	2.9 (3)
N(22)	3138 (5)	4964 (3)	2139 (3)	1.6 (2)	C(45′)	16938 (8)	10031 (4)	1710 (5)	3.4 (3)
N(22′)	12571 (5)	9579 (3)	2439 (3)	2.0 (2)	C(53)	−442 (7)	5006 (3)	1732 (4)	2.3 (2)
N(31)	3058 (6)	5946 (3)	3391 (3)	1.8 (2)	C(53′)	11780 (7)	8951 (4)	685 (4)	2.8 (3)
N(31′)	11285 (6)	8191 (3)	2539 (3)	1.8 (2)	C(54)	−1659 (8)	4770 (4)	1237 (4)	3.1 (3)
N(32)	1841 (6)	5507 (3)	3262 (3)	1.7 (2)	C(54′)	11867 (8)	9121 (4)	78 (4)	3.2 (3)
N(32′)	11912 (6)	8087 (3)	2020 (3)	1.8 (2)	C(55)	−2021 (8)	4123 (4)	1295 (4)	2.9 (2)
N(41)	336 (6)	3116 (3)	1938 (3)	1.9 (2)	C(55′)	13214 (9)	9128 (4)	73 (4)	2.9 (3)
N(41′)	15975 (6)	9481 (3)	1555 (3)	2.0 (2)	C(61)	−854 (7)	3479 (4)	2914 (4)	2.4 (2)
N(42)	1586 (5)	3515 (3)	2248 (3)	1.7 (2)	C(61′)	15612 (7)	8198 (4)	1116 (4)	2.1 (2)
N(42′)	15472 (6)	9420 (3)	2104 (3)	2.0 (2)	C(62)	−650 (8)	2839 (4)	3183 (4)	3.3 (3)
N(51)	−1109 (6)	3979 (3)	1805 (3)	2.1 (2)	C(62′)	17149 (8)	8216 (4)	1459 (4)	3.1 (3)
N(51′)	13893 (6)	8959 (3)	629 (3)	2.1 (2)	C(63)	−1773 (8)	2234 (4)	2844 (5)	3.8 (3)
N(52)	−102 (6)	4531 (3)	2074 (3)	1.9 (2)	C(63′)	18164 (8)	8395 (4)	1039 (4)	3.6 (3)
N(52′)	12989 (6)	8849 (3)	1025 (3)	2.1 (2)	C(64)	−2183 (8)	2128 (4)	2081 (4)	3.4 (3)
C(13)	4009 (7)	4112 (4)	3866 (3)	2.0 (2)	C(64′)	17866 (8)	8949 (4)	649 (4)	3.4 (3)
C(13′)	15403 (7)	8443 (3)	3420 (4)	2.0 (2)	C(65)	−2385 (7)	2761 (4)	1800 (4)	2.5 (2)
C(14)	5339 (7)	4421 (4)	4259 (3)	2.3 (2)	C(65′)	16353 (8)	8964 (4)	348 (4)	2.6 (2)
C(14′)	15180 (7)	8358 (4)	4035 (4)	2.4 (2)	C(66)	−3663 (8)	3017 (4)	1964 (5)	3.6 (3)
C(15)	5623 (7)	5022 (4)	4095 (3)	1.9 (2)	C(66′)	15743 (8)	8372 (5)	−260 (4)	3.6 (3)
C(15′)	13919 (8)	8505 (4)	4045 (4)	2.4 (2)	C(67)	−3494 (9)	3352 (5)	2675 (5)	5.1 (4)
C(16)	3121 (7)	3467 (4)	3860 (4)	2.5 (2)	C(67′)	15625 (9)	7687 (4)	−95 (4)	3.6 (3)
C(16′)	16560 (7)	8294 (4)	3103 (4)	2.3 (2)	C(68)	−2128 (8)	3749 (4)	3057 (4)	3.6 (3)
C(17)	2676 (9)	3500 (4)	4521 (4)	3.7 (3)	C(68′)	15019 (8)	7629 (4)	513 (4)	3.2 (3)
C(17′)	16590 (9)	7548 (4)	3001 (5)	4.0 (3)	C(70)	9445 (24)	1389 (11)	4549 (11)	6.1 (5)*
C(18)	3808 (9)	2862 (4)	3723 (4)	3.9 (3)	C(70′)	9005 (33)	564 (15)	4801 (16)	10.6 (9)*
C(18′)	17948 (8)	8712 (4)	3495 (5)	3.9 (3)	C(71)	8200 (24)	1139 (11)	4477 (10)	4.1 (5)*
C(23)	3228 (7)	4899 (3)	1498 (3)	1.7 (2)	C(72)	7742 (24)	688 (14)	4534 (11)	4.8 (5)*
C(23′)	12369 (7)	10187 (4)	2333 (4)	2.5 (2)	C(72′)	7489 (30)	362 (14)	4632 (11)	5.0 (5)*
C(24)	4325 (7)	5373 (3)	1471 (3)	1.8 (2)	C(73)	6560 (28)	197 (9)	4545 (10)	3.2 (4)*
C(24′)	11590 (8)	10425 (4)	2759 (4)	3.0 (3)	C(73′)	5919 (31)	293 (11)	4393 (12)	4.3 (5)*
C(25)	4896 (7)	5728 (3)	2112 (4)	1.9 (2)	C(74)	5141 (24)	416 (12)	4241 (11)	3.7 (4)*
C(25′)	11310 (8)	9939 (4)	3109 (4)	3.1 (3)	C(74′)	5175 (24)	730 (17)	4121 (12)	5.0 (5)*
C(26)	2280 (7)	4367 (3)	940 (3)	1.9 (2)	C(75)	5327 (26)	1099 (14)	4033 (11)	4.4 (5)*
C(26′)	12915 (8)	10511 (4)	1820 (4)	2.8 (3)	C(75′)	6129 (35)	1354 (12)	4075 (11)	5.3 (5)*
C(27)	3134 (8)	3908 (4)	620 (4)	2.8 (2)	C(76)	7001 (25)	1461 (9)	4182 (9)	2.7 (3)*
C(27′)	11738 (10)	10625 (4)	1267 (5)	4.2 (3)	C(76′)	7519 (28)	1243 (12)	4311 (11)	4.1 (5)*
C(28)	1411 (8)	4667 (4)	414 (4)	2.9 (2)	B(1)	−1026 (8)	3326 (4)	2107 (4)	2.1 (3)
C(28′)	13940 (9)	11154 (4)	2140 (5)	3.7 (3)	B(1′)	15470 (8)	8907 (4)	901 (4)	2.1 (3)
C(33)	950 (7)	5842 (4)	3502 (3)	2.0 (2)	B(2)	4351 (8)	5690 (4)	3278 (4)	2.2 (3)
C(33′)	11195 (7)	7534 (3)	1584 (3)	1.7 (2)	B(2′)	11899 (9)	8767 (4)	3155 (4)	2.4 (3)
C(34)	1616 (8)	6499 (4)	3775 (4)	2.4 (2)					

[a] B_{eq} is defined as in Table II. A value with an asterisk is a B_{iso} value for the atom refined isotropically.

The agostic interaction of the bridgehead proton with the coordinated metal was indicated by a strong and sharp band present in IR spectrum of the Tl(I) salt at 2766 cm^{-1}, and also in those of the ML*$_2$ complexes, of which the Co(II) complex had the lowest frequency (2690 cm^{-1}), as compared with the Cu(II) complex (2780 cm^{-1}), the Ni(II) complex (2800 cm^{-1}), and the Zn(II) complex (2820 cm^{-1}), which seemed to indicate the highest degree of agostic bonding. The correlation between the agostic M–H distance and the C–H frequency in the IR spectrum is supported by the finding that in the complex CoL*(HB(3-*i*-Pr-4-Br-pz)$_3$), where the steric hindrance of the 3-isopropyl groups precludes close approach of the agostic C–H (Co–H distance 2.61 vs 2.16 Å in CoL*$_2$), the tertiary CH spike of L* shifts from 2690 to 2770 cm^{-1}.

In the η^3-allyl complexes, the C–H–M interaction was indicated by broad low-frequency C–H stretch bands in the 2500–2700-cm^{-1} region and by a well-resolved room-temperature NMR signal from the unique bridging proton, located at higher fields than the averaged signal for the two exchanging methylene protons in the $[Et_2B(pz)_2]^-$ analogues, although not quite as high as the signal of the single coordinated proton of $[Et_2B(pz)_2]^-$ analogues at −60 °C. The upfield shift, which may be a function of the proximity of the bridgehead proton to the metal, is dependent both on the nature of R in the η^3-allyl substituent and on the nature of the metal ion. The shift increases as a function of the η^3-allyl substituent R in Mo complexes in the order R = H (−5.22 ppm) > Ph (−5.18 ppm) > Me (−4.50 ppm) and is greater for the Mo complex than for the identical W complex. Thus, in the W complexes the lesser shifts for R = H and R = Me (−4.60 and −4.06 ppm, respectively) presumably reflect a larger agostic C–H–W bond distance, due to a longer N–W bond. In agreement with this, the pyrazolyl peaks and the η^3-allyl proton peaks for the W derivatives are considerably broadened, indicating incipient exchange, while these same peaks are sharp for the Mo derivatives.

Although the upfield shifts of the unique protons in ML*-(η^3-allyl)(CO)$_2$ complexes were well-defined, and generally similar

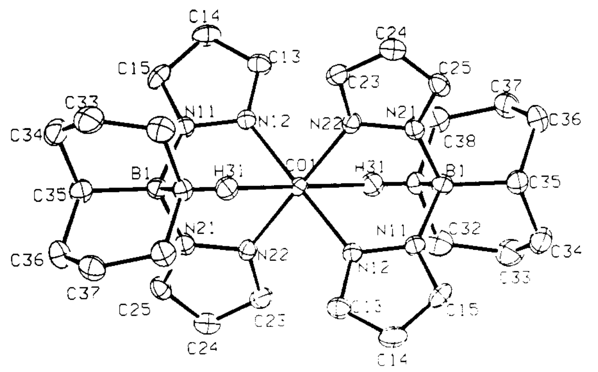

Figure 1. View of $Co(BBN(pz)_2)_2$ (I).

to those for the corresponding $[Et_2B(pz)_2]^-$ compounds, the corresponding downfield-shifted signals for $NiL^*{}_2$, which for $Ni(Et_2B(pz)_2)_2$ and its butyl analogue appear at 3.6 ppm, were not observed, being hidden among the peaks of the other 1,5-cyclooctanediyl protons in the 1.0–2.3 ppm range.

$PdL^*(\eta^3\text{-}CH_2CRCH_2)$ complexes with R = H, Me, and Ph were readily prepared by the reaction of TlL* with the $Pd(\eta^3\text{-}CH_2CRCH_2)Cl$ dimer. The NMR spectra of these compounds indicated the presence of isomers, by showing two well-separated signals for the pyrazole 3-H protons, slightly separated signals for the 4-H, and a single signal for the remote 5-H. Two signals were also present for the η^3-allyl syn and anti protons and for the R group. This indicated the presence of two isomers arising from two possible conformations of the η^3-allyl ligand. When R was H, the two isomers were present in almost equal amounts. When R was methyl or phenyl, they were in a ratio of about 2:1, with presumably the less sterically hindered isomer predominating. The presence of some agostic interaction in the methallyl derivative was suggested by a separate broad peak for one proton at 2.3–2.6 ppm.

It was found recently[13] that formation of mixed polypyrazolylborate complexes, where one of the ligands is $[HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3]^-$ (L**), yields useful information on the steric requirements of the other polypyrazolylborate ligand. Reaction of KL* with $Co(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)Cl$ produced the mixed-ligand complex $Co(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)L^*$, which was pale wine red and which proved to be five-coordinate, by means of an X-ray crystallographic structure determination. In this compound, the Co(II) ion is shielded by the three isopropyl groups and the C–H–Co interaction cannot occur. The agostic H is 2.62 Å away from Co(II) ion, and the $Co(NN)_2$ array is almost planar.

L* exhibits considerable flexibility, as can be seen from the nonbonding B–Co distances in $CoL^*{}_2$ and in CoL**L*. In the former, because of the agostic B–H–Co bond, the B–Co distance is a quite short 3.054 Å, whereas in the mixed-ligand complex the B–Co distance for L* is a much longer 3.347 Å. The other B–Co distance (in the L** portion of the molecule) is 3.143 Å, similar to that found in $Co(HB(pz)_3)_2$ (3.195 Å).[20]

Description of the Structure of $Co(BBN(pz)_2)_2$ (I). The overall structure of this Co(II) complex is apparent in the drawing of the molecule (Figure 1) and consists of the well-separated neutral monomeric complexes $Co(BBN(pz)_2)_2$. This structure establishes the overall octahedral structure of the complex and the existence of two C–H···Co bonds. This geometry is consistent with the sharp IR band at 2690 cm^{-1} and the pink color of the compound. The Co–H distance of 2.2 Å is consistent with the formation of an agostic hydrogen bond. The square planar arrangement of the four pyrazolyl nitrogen atoms is very unusual for a bis(pyrazolyl)borate complex. $Co((CH_3CH_2)_2B(pz)_2)_2$ has a tetrahedral geometry, with no agostic interaction.

Selected bond distances and angles are presented in Table IV. The Co–N distances and angles are typical of complexes of first-row transition metal ions with this ligand. There are no unusual features in this regard.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $Co(BBN(pz)_2)_2$ (I)

Co(1)–N(12)	1.925 (3)	N(12)–C(13)	1.337 (5)
Co(1)–N(22)	1.920 (3)	N(21)–C(25)	1.343 (5)
N(11)–N(12)	1.354 (4)	N(22)–C(23)	1.340 (5)
N(21)–N(22)	1.362 (4)	N(11)–B(1)[a]	1.576 (6)
N(11)–C(15)	1.344 (5)	N(21)–B(1)	1.569 (6)
N(12)–Co(1)–N(12)[a]	180 (8)	Co(1)–N(12)–C(13)	131.9 (3)
N(12)–Co(1)–N(22)[a]	90.6 (1)	Co(1)–N(22)–C(23)	131.9 (3)
N(12)–Co(1)–N(22)	89.4 (1)	N(12)–N(11)–C(15)	108.7 (3)
N(22)–Co(1)–N(22)[a]	180 (11)	N(11)–N(12)–C(13)	107.2 (3)
Co(1)–N(12)–N(11)	120.6 (2)	N(22)–N(21)–C(25)	108.0 (3)
Co(1)–N(22)–N(21)	119.8 (2)	N(21)–N(22)–C(23)	107.6 (3)
B(1)–N(21)–N(22)	117.4 (3)	B(1)[a]–N(11)–N(12)	116.5 (3)
B(1)–N(21)–C(25)	134.5 (3)	B(1)[a]–N(11)–C(15)	134.7 (3)

[a] Symmetry operation: 1 − *x*, 1 − *y*, 1 − *z*.

Table V. Selected Bond Distances (Å) and Angles (deg) for $Co(BBN(pz)_2)(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)(toluene)_{0.5}$ (II)

Co(1)–N(12)	2.103 (6)	Co(1′)–N(12′)	2.189 (6)
Co(1)–N(22)	2.134 (6)	Co(1′)–N(22′)	2.114 (6)
Co(1)–N(32)	2.192 (5)	Co(1′)–N(32′)	2.127 (6)
Co(1)–N(42)	2.082 (6)	Co(1′)–N(42′)	2.051 (6)
Co(1)–N(52)	2.049 (6)	Co(1′)–N(52′)	2.082 (6)
N(11)–N(12)	1.359 (7)	N(11′)–N(12′)	1.358 (7)
N(21)–N(22)	1.365 (7)	N(21′)–N(22′)	1.370 (8)
N(31)–N(32)	1.365 (7)	N(31′)–N(32′)	1.367 (7)
N(41)–N(42)	1.364 (7)	N(41′)–N(42′)	1.359 (8)
N(51)–N(52)	1.364 (7)	N(51′)–N(52′)	1.374 (7)
N(12)–Co(1)–N(52)	167.9 (2)	N(12′)–Co(1′)–N(52′)	169.2 (2)
N(12)–Co(1)–N(42)	95.6 (2)	N(12′)–Co(1′)–N(42′)	93.2 (2)
N(12)–Co(1)–N(32)	82.7 (2)	N(12′)–Co(1′)–N(32′)	81.7 (2)
N(12)–Co(1)–N(22)	89.1 (2)	N(12′)–Co(1′)–N(22′)	89.7 (2)
N(22)–Co(1)–N(52)	101.0 (2)	N(22′)–Co(1′)–N(52′)	100.1 (2)
N(22)–Co(1)–N(42)	100.5 (2)	N(22′)–Co(1′)–N(42′)	100.3 (2)
N(22)–Co(1)–N(32)	89.7 (2)	N(22′)–Co(1′)–N(32′)	90.0 (2)
N(32)–Co(1)–N(52)	90.8 (2)	N(32′)–Co(1′)–N(52′)	93.7 (2)
N(32)–Co(1)–N(42)	169.7 (2)	N(32′)–Co(1′)–N(42′)	168.5 (2)
N(42)–Co(1)–N(52)	88.9 (2)	N(42′)–Co(1′)–N(52′)	89.6 (2)

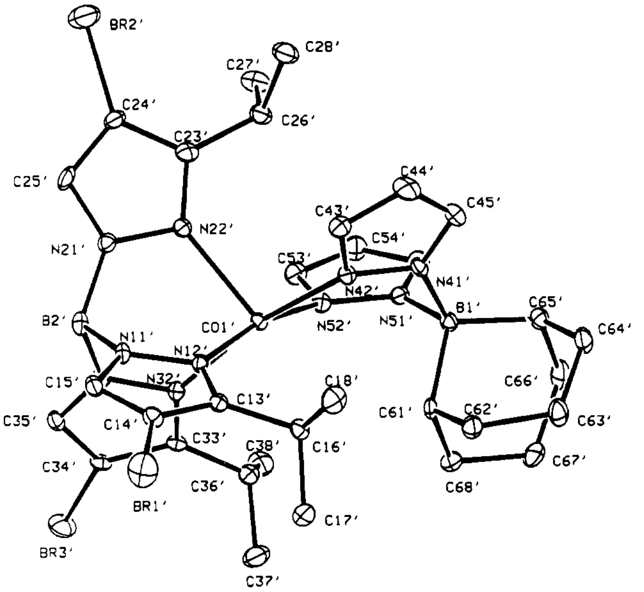

Figure 2. View of $Co(BBN(pz)_2)(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)$ (II).

Description of the Structure of $[Co(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)(BBN(pz)_2)](toluene)_{0.5}$ (II). The overall structure of this Co(II) complex is apparent in the drawing of the molecule (Figure 2) and consists of the well-separated neutral monomeric complexes $Co(HB(3\text{-}i\text{-}Pr\text{-}4\text{-}Br\text{-}pz)_3)(BBN(pz)_2)$ and one-half solvent molecule. This structure establishes the formation of a mixed-ligand complex containing two different polypyrazolylborate ligands and a first-row transition metal ion.

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(20) Churchill, M. R.; Gold, K.; Maw, C. E. *Inorg. Chem.* **1970**, *9*, 1597–1604.

Selected bond distances and angles are presented in Table V. The Co–N distances and angles are typical of complexes of first-row transition metal ions with this ligand. There are no unusual features in this regard.

Summary

The 1,5-cyclooctanediylbis(pyrazol-1-yl)borate ligand is in many ways preferable to the other known dialkylbis(pyrazol-1-yl)borates for the study of C–H–M interactions, as it has a single bridgehead hydrogen well-directed at the coordinated metal. Not only is the ligand readily prepared from convenient starting materials, but its salts and complexes are more stable to storage and have better crystallinity. L* is quite flexible and adapts itself through distortion of other ligands present on the metal. This flexibility suggests the use of L* in situations where it may act as a temporary blocker of a coordination site on the metal, which can be unblocked later under appropriate conditions.

Supplementary Material Available: Listings of crystal data (Table S1), thermal parameters (Tables S2 and S6), hydrogen atom positions (Tables S3 and S7), and all bond distances and angles (Tables S4 and S8) (11 pages); listings of observed and calculated structure factors (Tables S5 and S9) (29 pages). Ordering information is given on any current masthead page.

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Synthesis and Chemistry of $B_{11}H_{11}Sn^{2-}$ and Its Germanium and Lead Analogues. Crystal Structure of $[B_{11}H_{11}SnCH_3]PPh_3CH_3 \cdot CH_2Cl_2$

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The heteroborane dianions $B_{11}H_{11}E^{2-}$ (E = Ge, Sn) have been prepared in good yield starting with the $B_{11}H_{14}^-$ ion, ECl_2, and *n*-butyllithium. The $B_{11}H_{11}Pb^{2-}$ ion was made from $B_{11}H_{14}^-$ and $PbCl_2$ in aqueous sodium hydroxide solution. Methylation of the respective heteroborane dianion formed the $B_{11}H_{11}GeCH_3^-$ and $B_{11}H_{11}SnCH_3^-$ ions in good yield. The compound [1-CH_3-1-$SnB_{11}H_{11}$]$PPh_3CH_3 \cdot CH_2Cl_2$ has been characterized by a single-crystal X-ray structure determination (space group $P\bar{1}$, a = 11.659 (3) Å, b = 13.580 (3) Å, c = 9.980 (2) Å, α = 109.65 (1)°, β = 94.91 (1)°, γ = 99.83 (1)°, Z = 2).

Introduction

In the 1970's, Union Carbide developed a synthesis of $B_{11}H_{14}^-$ which gave the anion in 63% isolated yield as an alkyl ammonium salt. With sodium borohydride as the starting material, the overall chemical reaction of this process is as follows:[1,2]

$$17NaBH_4 + 20BF_3 \cdot O(C_2H_5)_2 \xrightarrow[105\ ^\circ C]{\text{diglyme solvent}} 15NaBF_4 + 2NaB_{11}H_{14} + 20H_2 + 20O(C_2H_5)_2$$

It has been demonstrated that this product can be made safely in pilot plant quantities using simple equipment. Thus, the $B_{11}H_{14}^-$ ion has become an attractive starting material for the production of higher boron hydride derivatives because it is accessible from $NaBH_4$ by a safe procedure using general laboratory glassware.

We have previously investigated the syntheses of several icosahedral heteroboranes of the type $B_{11}H_{11}E$ using $B_{11}H_{14}^-$ as the starting reagent. Thus, reaction of $NaB_{11}H_{14}$ with excess $NaHSeO_3$ or solid TeO_2 in a water/heptane mixture at room temperature over 24 h formed $B_{11}H_{11}Se$ or $B_{11}H_{11}Te$ in 18% and 25% yield, respectively.[3] More recently we have found that $HNEt_3[B_{11}H_{14}]$ will react with KOH/As_2O_3 in water to form the $B_{11}H_{11}As^-$ ion in 48% yield.[4] An anhydrous protocol was employed to form the $B_{11}H_{11}Sb^-$ and $B_{11}H_{11}Bi^-$ ions. Treatment of $Me_3NH[B_{11}H_{14}]$ with excess butyllithium followed by $SbCl_3$ or $BiCl_3$ formed $B_{11}H_{11}Sb^-$ and $B_{11}H_{11}Bi^-$ in 13% and 25% yields, respectively.[5,6] Similar results for the syntheses of the $B_{11}H_{11}E^-$ (E = As, Sb, Bi) ions were recently reported by Frange and co-workers.[7]

There have been many examples of the incorporation of Ge, Sn, and Pb atoms into carborane structures.[8] For example, reaction of $1,2\text{-}C_2B_9H_{11}^{2-}$ with the element dihalides EX_2 (E = Sn, Ge, Pb) formed the icosahedra $1,2,3\text{-}(CH)_2EB_9H_9$.[9] A similar series of smaller carborane derivatives such as $(CH)_2EB_4H_4$ (E = Ge, Sn, Pb)[10] and the trimethylsilyl-containing compounds $1\text{-}E\text{-}2\text{-}[Si(CH_3)_3]\text{-}2,3\text{-}C_2B_4H_5$ (E = Si, Ge, Sn) have been reported.[11-14] For most of the compounds reported, the group 14 element is in the +2 oxidation state. More recently, the first fully cage-incorporated silacarborane derivatives have been reported.[15,16] For most of these compounds, the silicon atom is in the +4 oxidation state.

The incorporation of group 14 elements into boron hydride cage structures has not been investigated as extensively. Bridge-substituted compounds having the general formula $R_3MB_5H_8$ (M = Si, Ge, Sn, Pb) were formed in the low-temperature reaction of LiB_5H_8 with R_3MX (X = Cl, Br, I). In the presence of a Lewis base, these compounds isomerized to $2\text{-}R_3MB_5H_8$ compounds in

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