Other authors have reported similar theoretical studies for related polyhedral systems. Kleier, McKee, and Lipscomb have found that the DSD mechanism for the rearrangement of tetrahedral B_4H_4 is blocked by a crossing of HOMO and LUMO.[24,25] The tetrahedral–square planar step involved here requires that two bonds be broken simultaneously, a more strenuous situation than is encountered in the trigonal bipyramid–square pyramid step of the $C_2B_3H_5$ rearrangement. Halgren, Pepperberg, and Lipscomb[26] have carried out PRDDO MO calculations to study possible mechanisms for the interconversion of the two isomers of $C_2B_4H_6$. Kleier, Dixon, and Lipscomb[27,28] have also shown on the basis of PRDDO MO calculations that DSD processes are allowed and are of low activation energy in structural rearrangements of $B_8H_8^{2-}$ and $B_{11}H_{11}^{2-}$ for which fluxional behavior has long been known experimentally.[29-31] Lipscomb has suggested that polyhedral rearrangements occurring at high temperatures might involve symmetry crossings of molecular orbitals.[32]

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Contribution from the Department of Chemistry,
University of Kentucky, Lexington, Kentucky 40506

Triply Bridged Diboron Species of the Pyrazabole Type[1]

J. Bielawski and K. Niedenzu*

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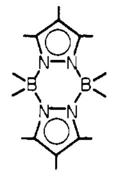
Tri-*B*-organylboroxins, $(\text{-BR-O-})_3$, react with pyrazole, Hpz, to yield pyrazaboles in which the two boron atoms are further bridged by an O–BR–O link, i.e., $RB(\mu\text{-pz})_2(\mu\text{-OBRO})BR$. The neutral species are structurally related to dibora cations of the type $[RB(\mu\text{-pz})_3BR]^+$. The preparation of the latter by reaction of either tris(1-pyrazolyl)borate(1−) ions, $[RB(pz)_3]^-$, or the pz^- ion with trigonal boranes containing two ready leaving groups, $R'BX_2$, has been studied, and the first unsymmetrical species of the type $[RB(\mu\text{-pz})_3BR']^+$ is described. In addition, some data on pyrazaboles of the type $R_2B(\mu\text{-pz})_2BR'_2$ (R = or ≠ R') are reported. They include the preparation and characterization of $(C_6H_5)_2B(\mu\text{-pz})_2B(C_2H_5)_2$, the first known pyrazabole containing different hydrocarbon substituents on the two boron atoms.

Introduction

The pyrazaboles (=dimeric (1-pyrazolyl)boranes (**1**)) are a chemically remarkably stable class of heterocyles containing four-coordinate boron.[2] Although various boron- and/or carbon-substituted derivatives are known, so far no species containing boron-bonded OH or alkoxy groups have been described. As a matter of fact, the only known pyrazaboles containing B–O bonds are one phenol[3] and two catechol[3,4] derivatives.



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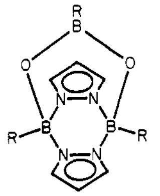
In our search for B–O derivatives of pyrazaboles, we have accidentally obtained a novel type of pyrazabole, in which the two pyrazabole boron atoms are also bridged by an O–BR–O group. Thus, the species contain not only two four-coordinate borons but an additional three-coordinate boron, as shown in **2**.

Dibora monocations of the type $[RB(\mu\text{-pz})_3BR]^+$, in which the boron atoms are bridged by three pyrazolyl groups, are structurally related to species of type **2**. Only two examples of the former have so far been described in the literature.[5,6] Within the framework of this investigation on diboron species containing the unit $B(\mu\text{-pz})_2B$, the specific preparation of $[RB(\mu\text{-pz})_3BR]^+$ ions has also been studied. Such species were obtained from either pz^- or $[RB(pz)_3]^-$ by reaction with trigonal boranes containing two readily leaving groups X, i.e., $R'BX_2$.



2

This investigation is supplemented by some studies on B- and/or C-substituted pyrazaboles. They include the preparation and characterization of $(C_2H_5)_2B(\mu\text{-pz})_2B(C_6H_5)_2$, the first known pyrazabole containing two different hydrocarbon substituents on the two boron atoms.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY; all compounds gave satisfactory data. Melting points (uncorrected) were determined on a Mel-Temp block. NMR spectra were recorded on a Varian XL-200 instrument. Chemical shift data are given in ppm with positive values indicating a downfield shift from the reference (internal Me_4Si for ^1H and ^{13}C; external

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$Et_2O{\cdot}BF_3$ for ^{11}B); s = singlet, d = doublet, t = triplet, q = quartet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling constants J are given in Hz. Infrared spectra were recorded on a Perkin-Elmer Model 621 instrument under standard operating conditions; w = weak, m = medium, s = strong, v = very, br = broad, sh = shoulder.

$C_2H_5B(\mu\text{-}pz)_2(\mu\text{-}OBC_2H_5O)BC_2H_5$ (2, R = C_2H_5). A mixture of 19.0 g (113 mmol) of tri-*B*-ethylboroxin and 23.15 g (340 mmol) of pyrazole was slowly warmed to give a clear solution that was refluxed for 6 h. After the mixture was cooled to room temperature, a pasty material remained, which was treated with 80 mL of water. The colorless insoluble material was collected and dried under vacuum over P_4O_{10} to give 25.8 g (90%) of crude product. The latter was recrystallized from cyclohexane to give 20.2 g of pure material, mp 126–128 °C.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 7.71 (4 H, d, J = 2.4), 6.28 (2 H, t, J = 2.4), 1.15–0.56 (15 H, m); $\delta(^{11}B)$ +31.5 (1 B, s, $h_{1/2}$ = 600 Hz), +1.8 (2 B, s, $h_{1/2}$ = 140 Hz); $\delta(^{13}C)$ (proton decoupled) 133.9, 104.7, 8.7, 8.5. (Note: The intensity of the last two signal is 2:1; the boron-bonded carbon atoms were not observed but were indicated by a very broad signal underneath those of the CH_3 groups.)

Infrared spectrum (KBr pellet): 3160 (sh, vw), 3130 (w), 2970 (s), 2900 (s), 2850 (w, sh), 1510 (m), 1455 (w–m, sh), 1418 (s), 1320 (vs, br), 1290 (s, sh), 1199 (vs, br), 1128 (w), 1070 (s, br), 1020 (m, br), 985 (w, sh), 875 (w, sh), 815 (m–s, br), 752 (s, br), 615 (m, vbr) cm^{-1}.

$C_6H_5B(\mu\text{-}pz)_2(\mu\text{-}OBC_6H_5O)BC_6H_5$ (2, R = C_6H_5). A solution of 6.2 g (20 mmol) of tri-*B*-phenylboroxin and 5.4 g (80 mmol) of pyrazole in 50 mL of bromoform was refluxed with stirring for 7 h. After the mixture was cooled to room temperature, a very small amount of insoluble material was filtered off, the clear solution was washed with 100 mL of water and dried, and the solvent was removed under vacuum to leave 7.1 g (83%) of crude product. The latter was purified by recrystallization from cyclohexane to give a pure compound, mp 202–204 °C.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 8.17 (2 H, m), 7.97 (4 H, m), 7.49 (m) + 7.36 (m) (13 H), 6.10 (2 H, t); $\delta(^{11}B)$ +28.7 (1 B, s, $h_{1/2}$ = 800 Hz), +1.5 (2 B, s, $h_{1/2}$ = 290 Hz).

$[C_2H_5B(\mu\text{-}pz)_3BC_2H_5]^+[PF_6]^-$. A slurry of 3.19 g (30 mmol) of potassium pyrazolide in a solution of 7.6 g (20 mmol) of ethylboryl ditosylate[5] in toluene was refluxed with stirring for several hours. After the mixture was cooled to room temperature, 40 mL of water was added and the mixture was stirred at ambient temperature for 1 h. The aqueous layer was separated, and 2.5 g (15 mmol) of ammonium hexafluorophosphate was added with stirring. The resultant insoluble material was collected, washed with water and then ether, and dried to give 0.95 g (22.3%) of crude material. An analytical sample, mp 298–302 °C (lit.[5] mp 299–301 °C), was obtained by dissolution of the compound in acetone, precipitation with diethyl ether, and subsequent recrystallization from acetonitrile.

NMR data: $\delta(^1H)$ (solution in $Me_2SO\text{-}d_6$) 8.51 (6 H, d, J = 2.5), 6.68 (3 H, t, J = 2.5), 1.65 (4 H, q, J = 7), 1.38 (6 H, t, J = 7); $\delta(^{11}B)$ (solution in Me_2SO) +0.2* ($h_{1/2}$ = 600 Hz); $\delta(^1H)$ (solution in CD_3CN) 8.13 (6 H, d, J = 2.5), 6.52 (3 H, t, J = 2.5), 1.69 (4 H, q, J = 7.5), 1.42 (6 H, t, J = 7.5); $\delta(^{11}B)$ (solution, in CD_3CN) +0.2 ($h_{1/2}$ = 100 Hz).

No effort was made to characterize the hygroscopic tosylate salt. The trifluoromethanesulfonate salt was obtained (in an analogous manner as described above but employing ethylboryl ditriflate[7]) as a precipitate from toluene. It was purified by dissolution of the crude product in methanol, precipitation with diethyl ether, and subsequent recrystallization from acetonitrile. The compound, mp 236–238 °C, was obtained in ca. 40% yield.

NMR data: $\delta(^1H)$ (solution in $(CD_3)_2CO$) 8.45 (6 H, d, J = 2.5), 6.66 (3 H, t, J = 2.5), 1.82 (4 H, q, J = 7.5), 1.49 (6 H, t, J = 7.5); $\delta(^1H)$ (solution in $Me_2SO\text{-}d_6$) 8.53, 6.70, 1.67, 1.40; $\delta(^1H)$ (solution in CD_3CN) 8.17 (6 H, d, J = 2.5), 6.54 (3 H, t, J = 2.5), 1.70 (4 H, q, J = 7.5), 1.41 (6 H, t, J = 7.5); $\delta(^{11}B)$ (solution in CD_3CN) +0.3 ($h_{1/2}$ = 100 Hz).

$[HB(\mu\text{-}pzMe)_3BC_2H_5]^+[PF_6]^-$. A slurry of 5.9 g (20 mmol) of potassium hydrotris(3-methyl-1-pyrazolyl)borate[8] in 100 mL of a 0.2 M solution of ethylboryl ditosylate[5] in toluene was refluxed with stirring for 3 h. After the mixture was cooled to room temperature, the solid material was collected and dissolved in 50 mL of water. A saturated aqueous solution containing 5.0 g (30 mmol) of ammonium hexafluorophosphate was added with stirring. The desired material precipitated and was collected and washed with water and ether to give 2.3 g (26.1%) of product. After additional washing with a small amount of tetrahydrofuran, it had a melting point of 225–230 °C.

NMR data (solution in CD_3CN): $\delta(^1H)$ 7.94 (3 H, d, J = 2.6), 6.30 (3 H, d, J = 2.6), 2.53 (9 H, s), 1.41 (2 H, ill-resolved q), 1.36 (3 H, ill-resolved t); $\delta(^{11}B)$ +0.2 (1 B, s, $h_{1/2}$ = 95 Hz), –8.4 (1 B, d, J = 127).

$[HB(\mu\text{-}pzMe_2)_3BH]^+[OTf]^-$. A solution of 5.1 g (15 mmol) of ethylboryl ditriflate[7] in 20 mL of toluene was added with stirring to a slurry of 5.05 g (15 mmol) of potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate[9] in 50 mL of toluene. The mixture was refluxed for 6 h. After the mixture was cooled to room temperature, the insoluble material was collected and washed with 50 mL of water and then with ether to give 3.6 g (52.4% yield) of the crude material. It was purified by dissolution in acetonitrile and precipitation with ethyl acetate; mp 294–298 °C dec.

NMR data (solution in CD_3CN): $\delta(^1H)$ 6.06 (3 H, s), 4.77* (ca. 2 H, s), 2.43 (18 H, s); $\delta(^{11}B)$ –4.1 (d, J = 127).

$(C_2H_5)_2B(\mu\text{-}pz)_2B(pz)_2$.[4] NMR data (solution in CD_3CN): $\delta(^1H)$ 7.93 (1 H, d, J = 2.2), 7.61 (1 H, d, J = 1.2), 7.44 (1 H, d, J = 2.6), 6.97 (1 H, d, J = 2.1), 6.61 (1 H, t, J = 2.5), 6.26 (1 H, two overlapping d, J = 2.3), 0.4 (5 H, unresolved m); $\delta(^{11}B)$ +3.9* (1 B), +0.3 (1 B). On the basis of selective decoupling experiments, the signals 7.61, 6.97, and 6.26 ppm belong to the terminal pyrazolyl groups. Previous NMR data have been reported for solutions in $CDCl_3$.[10]

$(pz)_2B(\mu\text{-}pz)_2B(pz)_2$.[3] NMR data (solution in CD_3CN): $\delta(^1H)$ 7.57 (2 H, d, J = 2.3), 7.51 (2 H, d, J = 1.5), 6.75 (2 H, d, J = 2.2), 6.65 (1 H, t, J = 2.4), 6.07 (2 H, t, J = 1.7); $\delta(^{11}B)$ +0.7 (s, $h_{1/2}$ = 35 Hz); $\delta(^{13}C)$ (proton decoupled) 143.6, 141.1, 134.9, 109.5, 107.0. Previous NMR data have been reported for solutions in $CDCl_3$.[10]

Infrared spectrum (KBr pellet): 3100 (sh), 3090 (w), 1770 (vw), 1721 (vw), 1507 (m), 1493 (sh), 1411 (s, br), 1382 (vs), 1342 (m), 1326 (ms), 1291 (vs, br), 1247 (sh), 1233 (s), 1219 (s), 1213 (s), 1202 (s), 1186 (m), 1143 (m), 1095 (s), 1082 (vs), 1060 (m), 1045 (m), 1037 (m), 1023 (m), 971 (vw), 946 (sh), 943 (m), 933 (vw), 918 (m), 889 (sh), 883 (sh), 873 (s), 859 (sh), 851 (sh), 838 (sh), 833 (vs), 816 (m), 811 (s), 756 (s), 782 (sh), 772 (s), 760 (sh), 755 (vs), 673 (sh), 668 (w), 658 (w), 650 (w) cm^{-1}.

$(C_2H_5)_2B(\mu\text{-}pz)_2B(C_6H_5)_2$. A solution of 4.4 g (20 mmol) of diethylboryl triflate[7] in 25 mL of toluene was added with stirring to a slurry of 6.8 g (20 mmol) of potassium diphenylbis(1-pyrazolyl)borate[11] in 50 mL of toluene. The reaction mixture was refluxed for 4 h. After cooling to room temperature, the mixture was filtered and toluene was evaporated from the clear filtrate to give 7.05 g (95.8%) of the crude product, mp 118–120 °C (after recrystallization from cyclohexane).

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 7.66 (i H, d, J = 2.4), 7.39 (2 H, d, J = 2.4), 7.20 (6 H, m), 6.94 (4 H, m), 6.40 (2 H, t, J = 2.4), 0.43 (10 H, s); $\delta(^{11}B)$ 1.7 ($h_{1/2}$ = 450 Hz).

Results and Discussion

The reaction of tri-*B*-organylboroxins, $(\text{–}BR\text{–}O\text{–})_3$ (R = C_2H_5, C_6H_5), with pyrazole, Hpz, did not yield the expected pyrazabole $(HO)RB(\mu\text{-}pz)_2BR(OH)$. Rather, the reaction stopped after attack of one of the B–O–B bonds of te boroxine ring to give pyrazaboles of type **2**, containing a bridging O–BR–O unit, in very good yield (as based on the employed boroxin).

The structure of the species was readily confirmed by NMR data: the ^{11}B NMR spectra clearly revealed the presence of one three-coordinate and two four-coordinate boron atoms,[12] and ^1H and ^{13}C NMR data also confirmed the suggested structure, i.e., the presence of hydrocarbon groups bonded to two types of boron atoms in different environments and also of symmetrically bridging pyrazolyl groups in the correct ratio. In addition, elemental analyses and molecular weight measurements by cryoscopy in benzene (R = C_2H_5, *m*/*e* 285.8 calcd, *m*/*e* 283 found; R = C_6H_5, *m*/*e* 429.0 calcd, *m*/*e* 431 found) confirmed the composition.

In contrast to all previously known pyrazaboles, which can be viewed as intermolecular adducts of two trigonal borane species, compounds of type **2** are formally diboryl oxide derivatives, i.e., $RB[OBR(pz)]_2$, but exist as intramolecular adducts. Remarkably, despite the presence of three-coordinate boron in the structures, the crystalline compounds of type **2** are not moisture-sensitive and are readily handled in air.

At considerably higher temperatures than employed in the above reaction, further interaction was found to occur but was accom-

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panied by extensive ligand rearrangements. This resulted in the formation of pyrazaboles of the type $R_2B(\mu\text{-pz})_2BR_2$ as the only isolated boron-containing species.

Triply bridged diboron units are also contained in dibora cations of the type $[RB(\mu\text{-pz})_3BR]^+$. Only two examples of such species have so far been described in the literature. The first one, $[C_2H_5B(\mu\text{-pz})_3BC_2H_5]^+$, was obtained as a minor product on interaction of ethylboryl ditosylate, $C_2H_5B(OTs)_2$ (OTs = $O_3SC_6H_4\text{-4-}CH_3$), with pz^- and was isolated as the hexafluorophosphate salt; no experimental details were given.[5] The structure of the species was, however, confirmed by ^{1}H NMR[5] and X-ray diffraction[13] data. The second example, $[HB(\mu\text{-pzMe}_2)_3BH]^+$ ($HpzMe_2$ = 3,5-dimethylpyrazole), was accidentally obtained in low yield when $K[HB(pzMe_2)_3]$ was reacted with MCl_5 (M = Nb, Ta). Although the process of formation of the cation is not well understood, its structure was again confirmed by NMR and X-ray crystallographic data.[6]

When potassium pyrazolide, Kpz, was reacted with $C_2H_5BX_2$ (X = OTs, O_3SCF_3(=OTf)) in 3:2 molar ratio, the desired cation $[C_2H_5B(\mu\text{-pz})_3BC_2H_5]^+$ was obtained in about 20% (X = OTs) or 40% (X = OTf) yield, respectively. The tosylate salt of the cited cation is extremely hygroscopic, and it is best to convert it immediately to the hexafluorophosphate salt. The triflate salt is only slightly soluble in water but readily dissolves in methanol or acetone. Remarkably, no defined boron-containing product could be obtained from $KpzMe_2$ and $C_2H_5BX_2$ under analogous reaction conditions.

In another set of experiments, $[RB(pz)_3]^-$ ions (R = H, pz) were reacted with $C_2H_5BX_2$. Both $[HB(pz)_3]^-$ and $[B(pz)_4]^-$ gave only the cation $[C_2H_5B(\mu\text{-pz})_3BC_2H_5]^+$, and no species with unsymmetrical substitution at the boron atoms could be obtained. In the reaction of $[HB(pz)_3]^-$, the yield of the cation was comparable to the one obtained in the preparation originating from the pz^- ion; for $[B(pz)_4]^-$, the yield was only about 5%. No other defined boron-containing products could be identified as products in these reactions. On the other hand, when stereochemically pure $[HB(pzMe)_3]^-$ (HpzMe = 3-methylpyrazole) was reacted with $C_2H_5BX_2$, the desired unsymmetrical cation $[HB(\mu\text{-pzMe})_3BC_2H_5]^+$ was obtained. NMR spectral data of the species clearly confirm its structure and also the formation of only one isomer. This latter observation tends to suggest that the ion $[HB(pzMe)_3]^-$ reacts as such and no intermediate cleavage of a boron–pyrazolyl bond is involved. Surprisingly, $[HB(pzMe_2)_3]^-$ reacted with $C_2H_5BX_2$ to form the species $[HB(\mu\text{-pzMe}_2)_3BH]^+$.

The foregoing observations suggest a directive influence of the pyrazole methyl groups with respect to the resulting product but do not explain the differing rearrangements of the boron substituents. Presumably, in the above case of reacting the $[HB(pz)_3]^-$ and $[B(pz)_4]^-$ ions, an unsymmetrically B-substituted ion, $[RB(\mu\text{-pz})_3BC_2H_5]^+$ (R = pz, H), is formed initially, but this is followed rapidly by displacement of the boron-bonded R by an ethyl group. On the other hand, the results of the reaction of $K[HB(pzMe_2)_3]$ with $C_2H_5BX_2$ illustrate that a reverse ligand exchange, i.e., displacement of ethyl by H, is also possible.

Unusual ligand redistribution reactions have also been observed in other instances. For example, the reaction of $K[(C_6H_5)_2B(pz)_2]$ with $(C_2H_5)_2BOTf$ readily gave the desired pyrazabole $(C_6H_5)_2B(\mu\text{-pz})_2B(C_2H_5)_2$. This reaction was found to proceed much more smoothly than the reaction of $[B(pz)_4]^-$ with $(C_2H_5)_2BOTs$ to yield the pyrazabole $(pz)_2B(\mu\text{-pz})_2B(C_2H_5)_2$.[4] As a matter of fact, this latter reaction is not easily duplicated but most often yields the symmetrical pyrazabole $R_2B(\mu\text{-pz})_2BR_2$ with R = C_2H_5 under apparently identical conditions. Thus, the present study illustrates that the ligand-exchange reactions are not yet well understood and often are unpredictable.

Finally, it is worth mentioning that a fairly strong solvent effect has been noticed not only for terminal but also for bridging pz groups of pyrazaboles when the ^{1}H NMR spectra are recorded. For example, the terminal-pz ^{1}H signals of $(pz)_2B(\mu\text{-pz})_2B(C_2H_5)_2$ were observed at δ 7.73/6.94/6.26 in $CDCl_3$[10] and at δ 7.61/6.97/6.26 in CD_3CN, and the bridging-pz ^{1}H signals were found at δ 7.76/7.46/6.52 in $CDCl_3$[10] but at δ 7.91/7.44/6.61 in CD_3CN. The corresponding values for $(pz)_2B(\mu\text{-pz})_2B(pz)_2$ are δ (in $CDCl_3$) 7.70/6.81/6.16 (terminal pz) and 7.67/6.70 (bridging pz)[10] but δ (in CD_3CN) 7.57/6.75/6.07 and 7.51/6.65, respectively. This may impair the assignments of ^{1}H NMR signals of pyrazaboles by correlation if different solvents are employed.

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Contribution from the Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506,
and Polymer Products Department, E. I. du Pont de Nemours & Company, Parkersburg, West Virginia 26101

Polynuclear Pyrazolyl-Bridged Spiro Species Containing Boron and Metal Centers[1]

J. Bielawski,[†] T. G. Hodgkins,[†] W. J. Layton,[†] K. Niedenzu,*[†] P. M. Niedenzu,[†] and S. Trofimenko[‡]

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A series of chain-type polynuclear pyrazolyl-bridged spiro species containing boron and metal centers have been prepared. Reaction of the tetrakis(1-pyrazolyl)borate ion, $[B(pz)_4]^-$ (Hpz = pyrazole), with 1 molar equiv of a metal halide species LMX (L = nonreactive ligand(s); M = metal, e.g., Pd; X = halogen) yielded covalent compounds of the type $(pz)_2B(\mu\text{-pz})_2ML$; with 2 molar equiv of LMX, trinuclear cationic species of the type $[LM(\mu\text{-pz})_2B(\mu\text{-pz})_2ML]^+$ were obtained. Corresponding reactions using *B,B*-bis(1-pyrazolyl)pyrazaboles gave the trinuclear $[R_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2ML]^+$ (R = noncoordinating substituent) and tetranuclear $[LM(\mu\text{-pz})_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2ML]^{2+}$ ions, respectively. Reactions of metal dihalides, MX_2 (e.g., M = Zn, Pd, Pt), with *B*-(1-pyrazolyl)pyrazaboles yielded species of the types $R_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2BMX_2$ and $X_2M(\mu\text{-pz})_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2MX_2$. In addition, the pentanuclear compound $Cl_2Zn(\mu\text{-pz})_2B(\mu\text{-pz})_2Zn(\mu\text{-pz})_2B(\mu\text{-pz})_2ZnCl_2$ was obtained from $Zn[B(pz)_4]$ and $ZnCl_2$.

Introduction

The complexes $[(\eta^3\text{-}CH_2CRCH_2)Pd(\mu\text{-pz})_2B(\mu\text{-pz})_2Pd(\eta^3\text{-}CH_2CRCH_2)]^+$ and $[(\eta^3\text{-}CH_2CRCH_2)Pd(\mu\text{-pz})_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2Pd(\eta^3\text{-}CH_2CRCH_2)]^{2+}$ (Hpz = pyrazole) were first mentioned in 1972, but only limited experimental data were presented.[2] Four additional species in which a tetrakis(1-pyrazolyl)borate unit bridges between two metal centers, i.e., $LM(\mu\text{-pz})_2B(\mu\text{-pz})_2ML'$ (L and L′ = various ligands; M = Ti,[3] Th,[4] Ru,[5] Pd[6]), have since

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[†] University of Kentucky.

[‡] E. I. du Pont de Nemours & Co.

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