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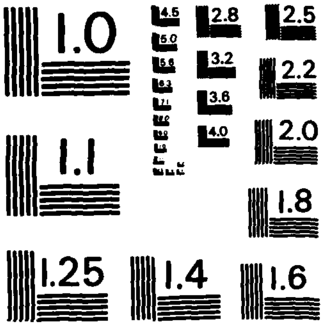

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Polynuclear Pyrazolyl-Bridged Spiro Species Containing Boron and Metal Centers

by

J. Bielawski, T. G. Hodgkins, W. J. Layton, K. Niedenzu, P. M. Niedenzu, and S. Trofimenko

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University of Kentucky
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A series of chain-type polynuclear pyrazolyl-bridged spiro species containing boron and metal centers has been prepared. Reaction of the tetrakis(1-pyrazolyl)borate ion, $[B(pz)_4]^{(-)}$ (Hpz = pyrazole), with one molar equivalent of a metal halide species LMX (L = nonreactive ligand(s); M = metal, e.g., Pd; X = halogen) yielded covalent compounds of the type $(pz)_2B(\mu\text{-}pz)_2ML$; and with two molar equivalents of LMX, trinuclear cationic species of the type $[LM(\mu\text{-}pz)_2B(\overset{mu}{\mu}\text{-}pz)_2ML]^+$ were obtained. Corresponding reactions using B-di(1-pyrazolyl)ovrazaboles gave the trinculear $[R_2B(\overset{mu}{\mu}\text{-}pz)_2B(\overset{mu}{\mu}\text{-}pz)_2ML]^{(+)}$ (R = non-coordinating

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substituent) and tetranuclear $[LM(\mu\text{-}pz)_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2ML]^{2+}$ ions, respectively. Reaction 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 $Cl_2ZnB(\mu\text{-}pz)_2B(\mu\text{-}pz)_2Zn(\mu\text{-}pz)_2B(\mu\text{-}pz)_2ZnCl_2$ was obtained from $Zn[B(pz)_4]$ and $ZnCl_2$. Originator supplied keywords include

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

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A series of chain-type polynuclear pyrazolyl-bridged spiro species containing boron and metal centers has been prepared. Reaction of the tetrakis(1-pyrazolyl)borate ion, $[B(pz)_4]^-$ (Hpz = pyrazole), with one molar equivalent of a metal halide species LMX (L = nonreactive ligand(s); M = metal, e.g., Pd; X = halogen) yielded covalent compounds of the type $(pz)_2B(\mu\text{-}pz)_2ML$; and with two molar equivalents of LMX, trinuclear cationic species of the type $[LM(\mu\text{-}pz)_2B(\mu\text{-}pz)_2ML]^+$ were obtained. Corresponding reactions using B-di(1-pyrazolyl)pyrazaboles gave the trinuclear $[R_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2ML]^+$ (R = non-coordinating substituent) and tetranuclear $[LM(\mu\text{-}pz)_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2ML]^{2+}$ ions, respectively. Reaction 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 $Cl_2ZnB(\mu\text{-pz})_2B(\mu\text{-pz})_2Zn(\mu\text{-pz})_2B(\mu\text{-pz})_2ZnCl_2$ 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 been described. Usually, they were accidentally obtained and, in most cases, scantly characterized, their suggested structures being based primarily on the results of elemental analyses and/or limited spectroscopic data.

In an extension of previous investigations of polyboron spiro species based on bridging polypyrazolylboron groups[7] we have now studied the specific preparation and characterization of complexes in which the cited groups bridge between two and more boron and/or metal centers. Such species were obtained by converting terminal di(1-pyrazolyl)boryl moieties, $B(pz)_2$, of either a tetrakis(1-pyrazolyl)borate or a B,B-di(1-pyrazolyl)pyrazabole into bridging units, i.e., $B(\mu\text{-pz})_2M$. The products include the first species containing three metal and two boron atoms in a pentanuclear chain.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. 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 downfield from the reference (internal Me_4Si for ^1H and ^{13}C, external Et_2OBF_3 for ^{11}B); s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, m = unresolved multiplet and an asterisk denotes a broad signal. Coupling constants J are given in Hz. Infrared spectra (frequencies in cm^{-1}) were recorded on a PE Model 621 spectrometer under standard operating conditions; s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad.

$\underline{(pz)_2B(\mu\text{-}pz)_2Pd(\eta^3\text{-}CH_2CCH_3CH_2)}$. A mixture of 3.2 g $K[B(pz)_4]$[8] and 2.0 g η^3-2-methylallylpalladium chloride dimer[9] (both 10 mmol) was stirred in 25 mL DMF until a clear solution was obtained. The solution was poured into water and the desired colorless product was extracted with methylene chloride and purified by chromatography on alumina. It was obtained in 4.2 g (95%) yield and was recrystallized from toluene/heptane; mp 162-164 °C. Anal. Calcd for $C_{16}H_{19}BN_8Pd$ (mol wt 440.6): C, 43.62; H, 4.33; B, 2.45; N, 25.44. Found: C, 43.58; H, 4.36; B, 2.39; N, 25.29.

NMR data (solution in $CDCl_3$): $\delta(^1H)$, +22 °C = 7.66 (4 H, d, J = 1.2), 7.03* (4 H, unresolved), 6.25 (4 H, t, J = 2.2), 3.55 (2 H, s), 2.79 (2 H, s), 1.77 (3 H, s); solution in CD_3CN: $\delta(^1H)$, +22 °C = 7.68 (4 H, d, J = 1.3), 6.94 (4 H, d, J = 2.2), 6.27 (4 H, t, J = 2.1), 3.65 (2 H, s), 2.83 (2 H, s), 1.80 (3 H, s); $\delta(^{11}B)$ = +1.3 (s, $h_{1/2}$ = 15 Hz); $\delta(^1H)$, -38 °C = 7.72* (4 H), ca. 6.9* (4 H), 6.29* (4 H), 3.65 (2 H, s), 2.84 (2 H, s), 1.75 (3 H, s).

$\underline{(pz)_2B(\mu\text{-}pz)_2Pd(\eta^3\text{-}CH_2CC_6H_5CH_2)}$. This colorless compound was prepared from 3.2 g $K[B(pz)_4]$ and 2.6 g η^3-2-phenylallylpalladium chloride dimer (both 10 mmol) and was obtained in 4.7 g (94%) yield. After recrystallization from toluene/heptane it had a mp 176-178 °C (decomp).

NMR data (solution in CD_3CN): $\delta(^1H)$ = 7.68 (4 H, d, J = 1.3), ca. 7.3 (5 H, unresolved m), 6.87 (4 H, d, J = 2.3), 6.23 (4 H, t, J = 2.1), 4.09 (2 H, s), 3.16 (2 H, s); $\delta(^{11}B)$ = +1.3 (s, $h_{1/2}$ = 15 Hz).

$[(\eta^3\text{-}CH_2CCH_3CH_2)Pd(\mu\text{-}pz)_2B(\mu\text{-}pz)_2Pd(\eta^3\text{-}CH_2CCH_3CH_2)]PF_6$. A mixture of 0.8 g (2.5 mmol) of $K[B(pz)_4]$, 1 g (5.0 mmol) η^3-methylallylpalladium chloride dimer and 10 mL dimethylformamide was stirred with heating for 30 min and 20 mL water was added. The colorless solution was poured into an excess of cold aqueous solution of ammonium hexafluorophosphate to yield a colorless precipitate which was collected, washed with water and dried under vacuum; yield: 1.6 g (86%). The compound decomposes near 230 °C (after recrystallization from acetonitrile). Anal. Calcd for $C_{20}H_{26}BF_6N_8PPd_2$ (mol wt 747.1): C, 32.15; H, 3.51; B, 1.45; F, 15.26; N, 15.00; P, 4.15. Found: C, 31.92; H, 3.47; B, 1.32; F, 15.31; N, 14.97; P, 4.13.

NMR data (solution in CD_3CN): $\delta(^1H)$, −38 °C = 8.05 (1 H, d, J = 1.7), 7.86 (1 H, d, J ca 2.8), 7.84 (1 H, unresolved), 6.91 (1 H, d, J = 2.7), 6.66 (1 H, unresolved t), 6.40 (1 H, unresolved t), 3.88 (2 H, d, J = 23, of d, J ca 2.9), 3.14 (2 H, d, J = 19), 2.01 (3 H, s) (as based on selective decoupling experiments, the signal sets 8.05/7.86/6.66 and 8.84/6.91/6.40 belong to individual pz groups); +23 °C = 7.99*, 7.83*, 7.75*, 6.99*, 6.61*, 6.42*, 3.88*, 3.11*, 2.04; +61 °C = 7.89*, ca 7.3*, 6.50*, 3.88, 3.10, 20.5; +78 °C = 7.83 (2 H, d, J = 1.9), 7.28 (2 H, d, J = 2.5), 6.44 (2 H, t, J = 2.2), 3.81 (2 H, s), 3.02 (2 H, s), 1.98 (3 H, s). $\delta(^{11}B)$ = +0.9 (s, $h_{1/2}$ = 20 Hz).

$[(\eta^3\text{-}CH_2CC_6H_5CH_2)Pd(\mu\text{-}pz)_2B(\mu\text{-}pz)_2Pd(\eta^3\text{-}CH_2CC_6H_5CH_2)]PF_6$. In analogous fashion, a reaction employing 2.59 g (10 mmol) of η^3-2-phenylallylpalladium chloride dimer and 1.6 g (5 mmol) of $K[B(pz)_4]$ was run. The product, after filtration, was extracted with methylene chloride. Extracts were dried, filtered and stripped. A solid colorless material remained in 3.5 g (81%) yield, which begins to darken at 202 °C and decomposes at 216-218 °C.

NMR data (solution in DMSO-d_6): $\delta(^1H)$ = 7.8* (2 H), 7.35 (5 H, s), 6.6* (2 H), 4.30 (2 H, s), 3.27 (2 H, s); $\delta(^{11}B)$ = +0.5 (s, $h_{1/2}$ = 20 Hz).

$[(\eta^3\text{-}CH_2CHCH_2)Pd(\mu\text{-}pz)_2B(\mu\text{-}pz)_2Pd(\eta^3\text{-}CH_2CHCH_2)]PF_6$. The reaction was run as described above but using η^3-allylpalladium chloride dimer. The colorless product was obtained in 76% yield. It was rather insoluble but could be recrystallized from acetonitrile.

NMR data (solution in DMSO-d_6): $\delta(^1H)$ = 8.08 (2 H, unresolved), ca 7.4* (2 H), 6.61 (2 H, unresolved), 5.80 (1 H, septet), 4.25 (2 H, d, J = 7), 3.26 (2 H, d, J = 12); $\delta(^{11}B)$ = +0.5 (s, $h_{1/2}$ = 25 Hz).

$(C_2H_5)_2B(\mu\text{-}pz)_2B(pz)_2$.[10] NMR data (solution in CD_3CN): $\delta(^1H)$ = 7.93 (1 H, d, J = 2.3), 7.61 (1 H, d, J = 1.3), 7.45 (1 H, d, J = 2.3), 6.97 (1 H, d, J = 2.3), 6.61 (1 H, t, J = 2.5), 6.26 (1 H, unsym t = 2 overlapping d, J ca 2.3), 0.4* (5 H, unresolved m) (as based on selective decoupling, the signal sets 7.93/7.45/6.61 and 7.61/6.97/6.26 belong to the individual types of pz groups); $\delta(^{11}B)$ = +3.9* (1 B, $h_{1/2}$ ca 350 Hz), +0.3 (1 B, s, $h_{1/2}$ = 50 Hz). Data in $CDCl_3$ solution have previously been reported.[11]

$[(C_2H_5)_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2Pd(\eta^3\text{-}CH_2CCH_3CH_2)]PF_6$. A mixture of 0.70 g (2 mmol) of 4,4-diethyl-8,8-di(1-pyrazolyl)pyrazabole[10] and 0.40 g (1 mmol) of η^3-2-methylallylpalladium chloride dimer was stirred in 5 mL dimethylformamide and ca 5 mL of water was added. When a colorless solution resulted, a large excess of aqueous ammonium hexafluorophosphate was added. The resulting colorless precipitate was collected and washed with water. A total of 1.1 g (78%) of the desired material was obtained, mp (after recrystallization from acetonitrile) 217-218 °C.

NMR data (solution in CD_3CN): $\delta(^1H)$, -44 °C = 8.44 (1 H, d, J = 2.6), 8.39 (1 H, d, J = 2.8), 8.25 (1 H, d, J = 2.0), 8.07 (1 H, d, J = 2.2), 8.02 (2 H, d, J = 1.7), 7.11 (2 H, d, J = 2.7), 6.96 (1 H, t, J = 2.5), 6.78 (1 H, t, J = 2.5), 6.49 (2 H, unsym t = 2 overlapping d, J ca 2.3), 4.14 (2 H, s), 3.38 (2 H, s), 2.28 (3 H, s), ca 0.66 (4 H, unresolved q), 0.44 (6 H, t, J ca 7.3) (as based on selective decoupling, the signals 8.39, 8.08 and 6.78 belong to the same pyrazolyl group); +24.5 °C = 8.37* (2 H), 8.13* (2 H), 7.99 (2 H, d, J = 1.7), 7.06 (2 H, d, J = 2.7), 6.85* (2 H), 6.47 (2 H, unsym t = 2 overlapping d, J ca 2.3), 4.13 (2 H, s), 3.38 (2 H, s), 2.29 (3 H, s), ca 0.66 (4 H, unresolved q), 0.47 (6 H, t); +60 °C = 8.33 (2 H, d), 8.11 (2 H, unresolved), 7.97 (2 H, d), 7.05 (2 H, d), 6.82 (2 H, unresolved), 6.47 (2 H, unsym t), 4.12 (2 H, s), 3.38 (2 H, s), 2.29 (3 H, s), ca 0.69 (4 H, unresolved q), 0.49 (6 H, t). $\delta(^{11}B)$, +24.5 °C = +5.0* (1 B, s, $h_{1/2}$ = 275 Hz), 0.4 (1 B, s, $h_{1/2}$ = 15 Hz).

$\underline{[(C_2H_5)_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2Pd(\eta^3\text{-}CH_2CC_6H_5CH_2)]PF_6}$. The colorless complex was obtained in 75% yield by the above procedure using η^3-2-phenylallylpalladium chloride dimer. It was purified by recrystallization from acetonitrile. It begins to decompose near 160 °C and gives a clear melt near 200 °C.

NMR data (solution in CD_3CN): $\delta(^1H)$, -38 °C = 8.38 (1 H, d, J = 2.5), 8.24 (1 H, d, J = 2.5), 8.09 (2 H, d, J = 1.7), 8.04 (1 H, d, J = 2.4), 7.95 (1 H, d, J = 2.0), 7.73-7.49 (5 H, phenyl m), 7.08 (2 H, d, J = 2.6), 6.98 (1 H, t, J = 2.5), 6.50 (2 H, t, J ca 2.4), 6.25 (1 H, t), 4.68 (2 H, s), 3.63

(2 H, s), ca 0.43 (4 H, unresolved), 0.43 (6 H, t, J ca 7) (as based on selective decoupling the signal sets 8.09/7.08/6.50 and 8.04/7.95/6.25 as well as 8.38/8.24/6.98 belong to individual pyrazolyl groups); +23 °C = ca 8.1*, 8.06, 7.72-7.48, 7.04, ca 6.9*, 6.48 ca 6.3*, 4.65, 3.62, 0.67, 0.43; +75 °C = 8.15* (2 H, unresolved), 8.05* (4 H, unresolved), 7.03 (2 H, d, J = 2.5), 6.60* (2 H), 6.47 (2 H, t, J = 2.4), 4.63 (2 H, s), 3.62 (2 H, s), ca 0.7 (4 H, unresolved q), 0.46 (6 H, t, J ca 7). $\delta(^{11}B)$, +23 °C = +5.0* (s, $h_{1/2}$ = 300 Hz), -0.6 (s, $h_{1/2}$ = 25 Hz).

$\underline{[(\eta^3\text{-}CH_2CCH_3CH_2)Pd(\mu\text{-}pz)_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2Pd(\eta^3\text{-}CH_2CCH_3CH_2)][PF_6]_2}$. A mixture of 4,4,8,8-tetrakis(1-pyrazolyl)pyrazabole[12] (1.06 g) and 1.0 g η^3-2-methylallylpalladium chloride dimer in 5 mL DMF was stirred for a few min and then water was added (ca 8 mL) until a colorless solution resulted. An aqueous solution of ammonium hexafluorophosphate was added and the resulting precipitate was collected, washed with water and dried to give 2.5 g product (99% yield). It was purified by dissolving in hot acetonitrile and diluting the concentrated solution with ethyl acetate. Colorless crystals formed which were dried at 110 °C/2 torr. The colorless material decomposes near 240 °C. Anal. Calcd for $C_{26}H_{32}B_2F_{12}N_{12}P_2Pd_2$ (mol wt 1037): C, 30.11; H, 3.11; B, 2.08; F, 21.98; N, 16.21; P, 5.97. Found: C, 30.11; H, 3.19; B, 1.95; F, 21.39; N, 16.34; P, 5.86.

NMR data (solution in CD_3CN): $\delta(^1H)$ = 8.59 (2 H, d, J = 2.8), 8.00 (2 H, d, J = 2.1), 7.02 (1 H, t, J = 2.7), 6.83 (2 H, d, J = 2.9), 6.83 (2 H, t, J = 2.5), 4.16 (2 H, s), 3.40 (2 H, s), 2.31 (3 H, s) (as based on selective decoupling experiments, the sets 8.59/7.02 and 8.00/6.83/6.38 belong to individual pz groups); $\delta(^{11}B)$ = -0.4 (s, $h_{1/2}$ = 30 Hz).

$[(\eta^3\text{-}CH_2CC_6H_5CH_2)Pd(\mu\text{-}pz)_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2Pd(\eta^3\text{-}CH_2CC_6H_5CH_2)][PF_6]_2$. This compound was obtained in 89% yield by the above procedure using η^3-2-phenylallylpalladium chloride dimer. The colorless compound was purified by recrystallization from acetonitrile, mp 266-268 °C.

NMR data (solution in CD_3CN): $\delta(^1H)$ = 8.3* (1 H?), 8.07 (2-3 H?), 7.73-7.49 (5 H, m), 6.76 (2 H), 6.39 (2 H?, unresolved t), 4.66 (2 H, s), 3.65 (2 H, s); $\delta(^{11}B)$ = -0.4 (s, $h_{1/2}$ = 35 Hz).

$H_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2ZnCl_2$. A solution of 0.68 g (5 mmol) of anhydrous $ZnCl_2$ in 25 mL of dry tetrahydrofuran was added to a solution of 1.61 g (5.5 mmol) of 4,4-di(1-pyrazolyl)pyrazabole[13] in 25 mL THF and the mixture was stirred at ambient temperature for several h. The volume was reduced to about one third under vacuum and the resultant precipitate was collected, washed with hot benzene and dried under vacuum to yield 1.53 g (67%) of the desired colorless compound, mp 232-233 °C. An analytical sample, mp 235-237 °C, was recrystallized from chloroform/heptane. Anal. Calcd for $C_{12}H_{14}B_2Cl_2N_8Zn$ (mol wt 428.2): C, 33.66; H, 3.30; Cl, 16.56; N, 26.15. Found: C, 33.66; H, 3.36; Cl, 16.27; N, 26.09.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 8.17 (1 H, d, J = 2.0), 8.01 (1 H, d, J = 2.2), 7.94 (1 H, d, J = 2.0), 7.10 (1 H, d, J = 2.5), 6.68 (1 H, t, J = 2.5), 6.51 (1 H, t, J ca 2.4), 3.7* (1 H, $h_{1/2}$ ca 200 Hz); $\delta(^{11}B)$ = -0.1 (1 B, s, $h_{1/2}$ = 60 Hz), -8.6* (1 B, s, $h_{1/2}$ = 420 Hz (proton decoupled), 680 Hz (proton coupled)); $\delta(^{13}C)$ (proton decoupled) = 145.2, 138.6, 138.1, 136.6, 109.1, 108.3. Solution in CD_3CN: $\delta(^1H)$ = 8.08* (2 H, unsym s), 7.96 (1 H, d, J = 2.4), 7.31 (1 H, d, J = 2.6), 6.66 (1 H, t, J = 2.5), 6.55 (1 H, t, J = 2.4), 3.7* (1 H, $h_{1/2}$ ca 300 Hz); $\delta(^{11}B)$ = +5.3 (1 B, s, $h_{1/2}$ = 25 Hz), -3.2*

(1 B, $h_{1/2}$ = 125 Hz (proton decoupled); ill-resolved t, J ca 105 Hz (proton coupled)); $\delta(^{13}C)$ (proton decoupled) = 145.6, 140.2, 139.3, 138.7, 109.8, 108.9.

Infrared spectrum (KBr pellet); 3210 (m), 2475 (m), 2415 (m), 2360 (vw), 2340 (sh), 2250 (vw), 1805 (vw, br), 1780 (vw, br), 1560 (vw, br), 1540 (sh), 1521 (sh), 1509 (m), 1500 (sh), 1450 (sh), 1427 (s), 1420 (sh), 1392 (s), 1375 (vw), 1334 (sh), 1322 (s), 1292 (s), 1248 (s), 1232 (s), 1220 (s), 1215 (sh), 1192 (s), 1180 (sh), 1155 (ms), 1143 (s), 1133 (ms), 1114 (s), 1106 (w), 1099 (s), 1086 (vs), 1072 (vs), 1024 (wm), 1017 (w), 985 (w), 933 (w), 920 (m), 908 (sh), 892 (w, br), 887 (m), 877 (sh), 870 (sh), 866 (m), 862 (sh), 828 (vs), 807 (s), 780 (vs, br), 719 (vw), 707 (w), 672 (m), 661 (w).

$\underline{Cl_2Zn(\mu\text{-}pz)_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2ZnCl_2}$. A solution of 2.12 g (5 mmol) of $(pz)_2B(\mu\text{-}pz)_2B(pz)_2$ in 50 mL methylene chloride was added to a solution of 1.36 g (10 mmol) of anhydrous $ZnCl_2$ in 150 mL of dry diethyl ether. The mixture was stirred at ambient temperature for 12 h. The precipitate was collected, washed with diethyl ether and then methylene chloride and dried under vacuum to give 2.99 g (86%) of the desired colorless compound, mp 364-367 °C.

NMR data (solution in CD_3CN): $\delta(^1H)$ = 8.72 (2 H, d, J = 2.9), 8.14 (2 H, d, J = 1.6), 7.00 (1 H, t, J = 2.5), 6.97 (2 H, d, J = 2.7), 6.51 (2 H, unsym t, J ca 2.1); $\delta(^{11}B)$ = -0.4 (s, $h_{1/2}$ = 25 Hz); $\delta(^{13}C)$ (proton decoupled) = 143.6, 141.1, 134.9, 109.5, 107.0. - As based on selective decoupling experiments, the signals $\delta(^1H)$ = 8.14/6.97/6.51 belong to one specific type of pyrazolyl group, and the set 8.72/7.00 to the other (= central bridging).

Infrared spectrum (KBr pellet): 3155 (w), 3115 (m), 3035 (vw), 2970 (vw), 1800 (vw,br), 1538 (sh), 1520 (m), 1509 (sh), 1454 (ms), 1430 (ms), 1417 (ms), 1398 (vs), 1322 (s), 1303 (vs), 1257 (s), 1240 (s), 1226 (ms), 1215 (ms), 1199 (ms), 1186 (w), 1152 (ms), 1110 (s), 1098 (vs), 1076 (vs), 1033 (m), 982 (w), 947 (w), 940 (m), 920 (w), 889 (m), 879 (w), 847 (m), 832 (s), 815 (s), 796 (s), 774 (s), 758 (s), 669 (vw), 611 (sh), 607 (m).

$Cl_2Pd(\mu\text{-}pz)_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2PdCl_2$. A mixture of 1.0 g (5.5 mmol) of $PdCl_2$, 1.18 g (2.8 mmol) $(pz)_2B(\mu\text{-}pz)_2B(pz)_2$ and 40 mL benzonitrile was refluxed with stirring for 5 h. After cooling to room temperature, the green-yellow precipitate was collected, washed with diethyl ether and dried in vacuum to yield 1.9 g (87%) of the desired pale olive compound, which decomposes at 395-398 ^{o}C. Anal. Calcd for $C_{18}H_{18}B_2Cl_4N_{12}Pd_2$: C, 27.76; H, 2.49; B, 3.32; Cl, 18.21; N, 21.59. Found: C, 28.06; H, 2.49; B, 3.32; Cl, 17.97; N, 21.31.

In a similar procedure, the corresponding $PtCl_2$ derivative was prepared in essentially quantitative yield as an intractable gray material, which does not melt and/or decompose up to 400 ^{o}C.

$Zn[B(pz)_4]_2$.[8] NMR data (solution in $CDCl_3$): $\delta(^{1}H) = 7.74$ (1 H, d, J = 2.0), 7.38 (1 H, unresolved), 6.25 (1 H, unsymm t, J = 2.0); $\delta(^{11}B) = -0.4$ (s, $h_{1/2} = 25$ Hz); $\delta(^{13}C) = 140.7$ (d, J = 182), 134.7 (d, J = 185), 104.9 (d, J = 177, of t, J = 11). Only three ^{1}H signals were previously observed for the compound but no numerical data were presented.[14]

$Cl_2Zn(\mu\text{-}pz)_2B(\mu\text{-}pz)_2Zn(\mu\text{-}pz)_2B(\mu\text{-}pz)_2ZnCl_2$. A mixture of 3.12 g (5 mmol) of $Zn[B(pz)_4]_2$, 11.5 mL of a 0.872 M solution of $ZnCl_2$ in diethyl ether (10 mmol) and 50 mL dry ether was stirred at room temperature for 15 h. Insolubles were collected, washed with dry ether and dried under vacuum for 6 h at 70 ^{o}C to give 4.24 g (95%) of the desired colorless compound, decomp near

260 °C. Anal. Calcd for $C_{24}H_{24}B_2Cl_4N_{16}Zn_2$ (mol wt 830.8): C, 34.70; H, 2.91; B, 2.60; Cl, 17.07; N, 26.97. Found: C, 34.68; H, 2.93; B, 2.49; Cl, 16.99; N, 26.96.

NMR data (solution in CD_3CN): $\delta(^1H)$ = 7.59* (1 H), 7.42* (1 H, unresolved d), 6.58* (1 H, unresolved unsym t); $\delta(^{11}B)$ = +0.5 (s, $h_{1/2}$ = 15 Hz).

Results and Discussion

The tetrakis(1-pyrazolyl)borate ion, $[B(pz)_4]^-$ (Hpz = pyrazole), reacts with one half molar equivalent of η^3-allylpalladium chloride dimer or its 2-substituted analogs, $[(\eta^3\text{-}CH_2CRCH_2)PdCl]_2$, to yield the neutral species $(pz)_2B(\mu\text{-}pz)_2Pd(\eta^3\text{-}CH_2CRCH_2)$ (R = CH_3, C_6H_5). This process is analogous to that previously reported for similar complexes derived from either the $[B(pz)_4]^-$ or the $[RB(pz)_3]^-$ ion (R = non-coordinating substituent).[15]

The room temperature ^1H NMR spectra of the two compounds cited above exhibit only three signals for all pz groups, thus implying their spectroscopic identity. This observation is common for some poly(1-pyrazolyl)borate complexes and has been ascribed to an exchange process of bridging and terminal pz groups which is fast on the NMR time scale. Frequently, this fluxional behavior is slowed down on lowering the temperature. Indeed, at -40 °C, the ^1H NMR signals of the pz groups of the species are considerably broadened whereas those of the η^3-allyl group are not affected by the change in temperature. Despite the exchange of pz groups, Pd is four-coordinate and two pz groups are available for further coordination, the molecule being a bidentate ligand. Thus, reaction of $[B(pz)_4]^-$ with one molar equivalent of η^3-allylpalladium chloride dimer produces the cations $[(\eta^3\text{-}CH_2CRCH_2)Pd(\mu\text{-}pz)_2B(\mu\text{-}pz)_2Pd(\eta^3\text{-}CH_2CRCH_2)]^+$ (R = H, CH_3, C_6H_5), which were isolated as the hexafluorophosphate salts. At -38 °C, the ^1H NMR spectrum of the compound with R = CH_3 exhibits two distinct sets of pz signals of equal abundance. As based on selective decoupling experiments, the signals $\delta(^1H)$ = 8.84, 6.91 and 6.40 ppm represent one type of pz group, the signals at 8.05, 7.86 and 6.66 ppm the other. At room temperature, all signals are broadened considerably; and at +61 °C, only one set of pz ^1H NMR signals, which are sharp at +78 °C, is observed.

The observation of two sets of ^1H NMR signals for the pz groups at lower temperatures suggests the existence of puckered $B(\mu\text{-}pz)_2Pd$ rings in boat form. Their rate of inversion increases with the temperature and, ultimately, becomes sufficiently rapid to make all pz groups equivalent on the NMR time scale. The ΔG and E_a for this process are 15.5 and 14.3 kcal, respectively.[2]

A different NMR behavior is observed for the cation $[(C_2H_5)_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2Pd(\eta^3\text{-}CH_2CRCH_2)]^+$, which can be obtained in two ways, i.e., from the reaction of 4,4-diethyl-8,8-di(1-pyrazolyl)pyrazabole with η^3-allylpalladium chloride dimer, or from $(pz)_2B(\mu\text{-}pz)_2Pd(\eta^3\text{-}CH_2CRCH_2)$ and diethylboryl tosylate. The low-temperature ^1H NMR spectrum shows the presence of three types of pz groups in 1:1:2 ratio, while at high temperature the peaks with intensity 2 remains unchanged, but the others coalesce into a second set of intensity 2. This is illustrated in Figure 1. The findings are reconcilable with a structure where one ring is essentially planar (or else undergoing rapid inversion even at low temperature) and the other is puckered in a boat conformation. Presumably, the planar system is the pyrazabole $B(\mu\text{-}pz)_2B$ ring: It is likely to be less strained and a planar $B(\mu\text{-}pz)_2B$ ring has been shown to exist in several pyrazaboles.[16,17] Structure <u>A</u> illustrates this situation.

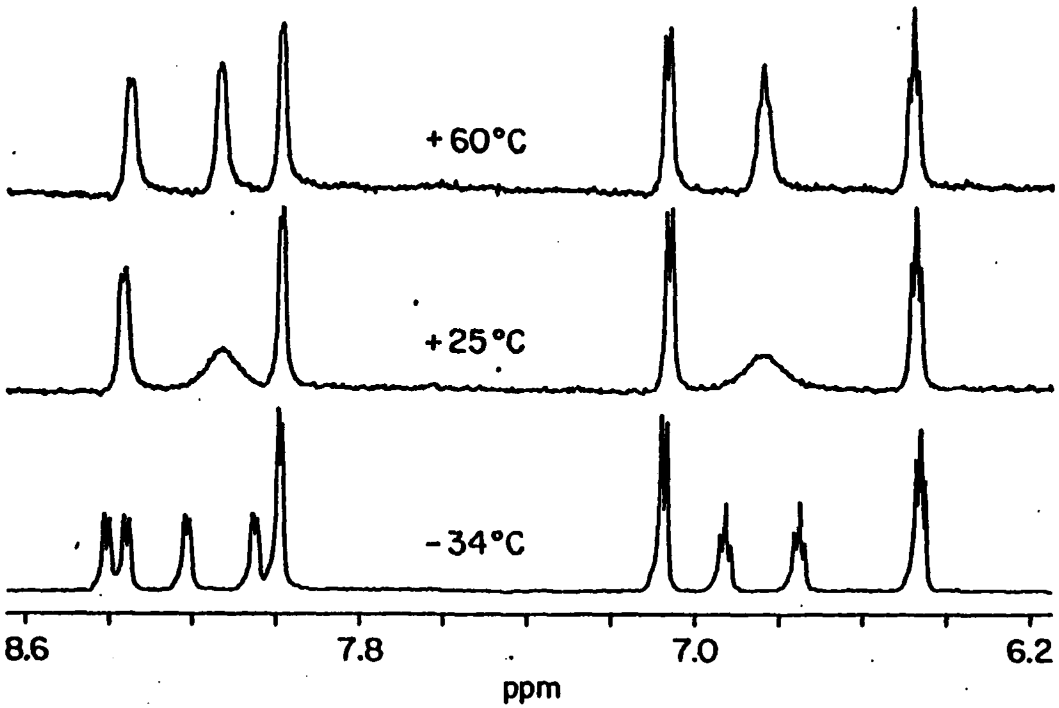
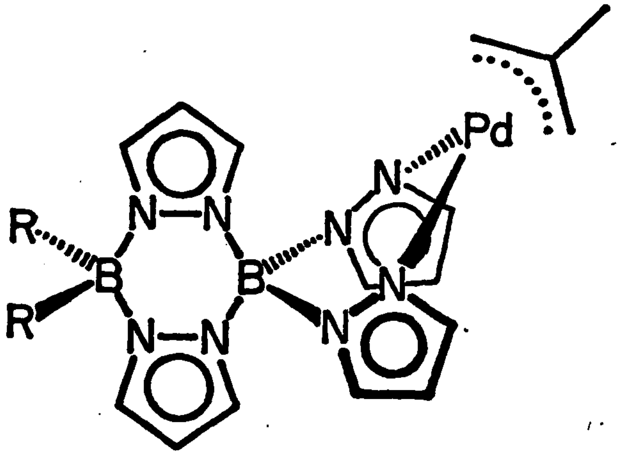


Figure 1. The ^1H NMR spectrum (pyrazole region only) of $[(C_2H_5)_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2Pd(\eta^3\text{-}CH_2CCH_3CH_2)]^+$ at various temperatures.



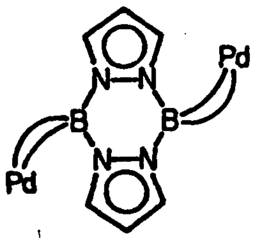
A

Both pz groups in the puckered B(μ-pz)$_2$Pd ring remain in identical magnetic environment, but they obviously affect the two pz groups in the planar B(μ-pz)$_2$B ring differently, until inversion of the B(μ-pz)$_2$Pd ring becomes rapid on the NMR time scale and the cation assumes C_{2v} symmetry. Based on the above structure A, the specific peaks can be assigned as follows:

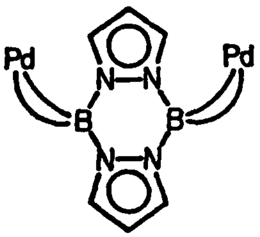
At -44 °C, the three peaks of intensity 2 at 8.02, 7.11 and 6.49 ppm belong to the 5H, 3H and 4H protons, respectively, of the Pd-bonded pz groups. By selective decoupling experiments, two sets of protons belonging to the non-*identical pyrazabole-type pz groups* have been established, i.e., 8.44/8.25/6.96 and 8.39/8.08/6.96 ppm. On the premise that the 5H of the bottom pz group in A will be in a magnetic environment more similar to that of the 5H atoms of the Pd-bonded pz groups than the 5H of the top pz group, the 8.08 signal is assigned to it (since it is the closest to the 8.02 signal).

This automatically leads to assigning the 8.39 and 6.78 peaks to the bottom pz 3H and 4H, respectively, and the set 8.44/8.25/6.96 to the top 3H, 5H and 4H, respectively. Such assignment is also consistent with the greatest chemical shift disparity being for the $B(\mu\text{-pz})_2B$ ring 5H atoms (8.25-8.08) closest to Pd, and the least (8.44-8.39) for the 3H atoms most distant from Pd.

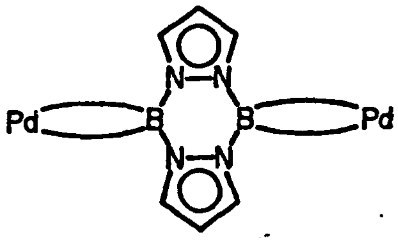
When 4,4,8,8-tetrakis(1-pyrazolyl)pyrazabole, $(pz)_2(B(\mu\text{-pz})_2B(pz)_2$, is reacted with one molar equivalent of η^3-allylpalladium chloride dimer, dications of the type $[(\eta^3\text{-}CH_2CRCH_2)Pd(\mu\text{-pz})_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2\text{-}Pd(\eta^3\text{-}CH_2CRCH_2)]^{2+}$ (R = CH_3, C_6H_5) are obtained. Surprisingly, their NMR spectra implied higher symmetry than would be anticipated on the basis of the expected boat conformation of the $B(\mu\text{-pz})_2Pd$ rings, since even with a planar conformation of the central pyrazabole ring, the two puckered $B(\mu\text{-pz})_2Pd$ rings - while having all the Pd-bonded pz groups in the same environment - would impart asymmetry to the central ring. In the schematic conformation C, each central pz ring would be different and four different protons should be ovserved in 2:1:2:1 ratio. Similarly, in B there should be three peaks in 2:2:2 ratio. Only a structure such as D can give the observed two peaks in 4:2 ratio.



B



C



D

Ignoring the possibility of planar $B(\mu\text{-pz})_2Pd$ rings, and assuming that the overall D_{2h} symmetry indicated by the NMR data is dynamic rather than static, it is still unclear why the inversion process of the puckered $B(\mu\text{-pz})_2Pd$ rings in this dication is so much more facile than with the related monocations. Surprisingly, this same type of NMR spectrum is also exhibited by the neutral complex $Cl_2Zn(\mu\text{-pz})_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2ZnCl_2$ (see below).

In another approach, B,B,-di(1-pyrazolyl)pyrazaboles were reacted with metal halides, MX_2, where M is favoring coordination number four. On reaction of equimolar quantities of the pyrazabole $H_2B(\mu\text{-pz})_2B(pz)_2$ and $ZnCl_2$, the complex $H_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2ZnCl_2$ was readily obtained. Similarly, $(pz)_2B(\mu\text{-pz})_2B(pz)_2$ reacted with an equimolar amount of $ZnCl_2$ to yield $(pz)_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2ZnCl_2$. However, a large excess of the pyrazabole is required in this reaction. Otherwise, substantial amounts of $Cl_2Zn(\mu\text{-pz})_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2ZnCl_2$ are formed as byproduct and the two complexes are difficult to separate. When the two cited reagents are combined in 2:1 molar ratio, the latter complex is the only product. (The corresponding $PdCl_2$ and $PtCl_2$ derivatives were prepared in analogous fashion. However, they are intractable materials and were identified by elemental analysis only.) The ^1H NMR spectrum of this latter zinc complex suggests a structure similar to the one of the corresponding dipalladium cation (i.e., where $[Pd(\eta^3\text{-}CH_2CRCH_2)]^+$ has replaced $ZnCl_2$) and is also indicated in another species: The two terminal $B(pz)_2$ groups of $Zn[B(pz)_4]_2$ = $(pz)_2B(\mu\text{-pz})_2Zn(\mu\text{-pz})_2B(pz)_2$ were found to react readily with $ZnCl_2$ to form the pentanuclear complex $Cl_2Zn(\mu\text{-pz})_2B(\mu\text{-pz})_2Zn(\mu\text{-pz})_2B(\mu\text{-pz})_2ZnCl_2$, where all bridging groups are of the type $B(\mu\text{-pz})_2Zn$. At room temperature, only three (though somewhat broadened) ^1H and one sharp ^{11}B NMR signal are observed for this species. The ^1H NMR spectral data clearly suggest that all pz groups are just about equivalent. This must be interpreted by a linear chain with essentially planar $B(\mu\text{-}pz)_2Zn$ rings or rapid inversion of the puckered ring system.

From a preparative point of view it is noteworthy that terminal halogen in a pyrazabole-type structure is readily replaced by pz groups.[18] Hence, the present study suggests that even longer chain-type structures containing spiro-boron and -metal atoms can be synthesized. Moreover, it may also be possible to build into such a polyspiro structure the same metal but in different oxidation states.

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