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THE DIMETHYLAMINO-TRIS(1-PYRAZOLYL)BORATE(1-) ION A NEW
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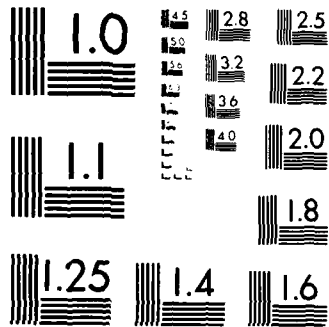
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The Dimethylamino-tris(1-pyrazolyl)borate(1-) Ion,
A New Hybrid Poly(1-pyrazolyl)borate Ligand

by

K. Niedenzu and S. Trofimenko

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University of Kentucky
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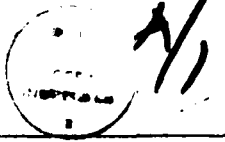
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Dimethylamine-tris(1-pyrazolyl)borane, $\text{Me}_2\text{HN-B}(\text{pz})_3$ (Me = CH_3), was found to react as the acid $\text{H}[\text{Me}_2\text{NB}(\text{pz})_3]$. The Li salt of this latter was obtained on interaction of the species with MeLi, and on interaction with $(\text{MeCN})_2\text{MoX}(\text{CO})_2(\eta^3\text{-CH}_2\text{CRCH}_2)$ (X = Cl, Br; R = H, CH_3) the complexes																							

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(pz)B(μ -pz)₂(μ -NMe₂)Mo(CO)₂(η^3 -CH₂CRCH₂) were obtained as yellow solids. The coordination of the NMe₂ rather than the third pz group from B to Mo was demonstrated by variable temperature ¹H NMR studies.

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The Dimethylamino-tris(1-pyrazolyl)borate(1-) Ion, A New Hybrid
Poly(1-pyrazolyl)borate Ligand

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Among the various poly(1-pyrazolyl)borate ligands only one example is known where, apart from the pz groups (Hpz = pyrazole), an additional coordination site is attached to boron. That ligand, $[\text{HB}(\text{pz}-3,5\text{-Me}_2)_2(\text{SAr})]^-$ (Me = CH₃, Ar = C₆H₄-4-CH₃), was synthesized from $\text{K}[\text{H}_2\text{B}(\text{pz}-3,5\text{-Me}_2)_2]$ and ArSH.¹

When tris(dimethylamino)borane, $\text{B}(\text{NMe}_2)_3$, was reacted with Hpz at room temperature, the dimethylamine adduct of tris(1-pyrazolyl)borane was obtained in essentially quantitative yield. As based on low-temperature ¹H NMR data, the species may be presented by the formula $\text{Me}_2\text{HN-B}(\text{pz})_3$. However, at room temperature the N-bonded proton undergoes site exchange and $\text{H}[\text{Me}_2\text{NB}(\text{pz})_3]$ may be a better illustration of the compound.²

In this context it was of interest to establish whether or not an ion $[\text{Me}_2\text{NB}(\text{pz})_3]^-$ ($= \text{L}^*$) exists and can act as chelating poly(1-pyrazolyl)borate ligand, and what type of denticity it would exhibit.

The lithium salt of L^* was easily prepared from HL^* by treatment with MeLi . The salt is soluble in DMSO and exhibits the expected ^1H and ^{11}B NMR spectra. However, even the acid HL^* was found to react readily with $(\text{MeCN})_2\text{Mo}(\text{CO})_2\text{X}(\eta^3\text{-CH}_2\text{CRCH}_2)$ ($\text{X} = \text{Cl}, \text{Br}; \text{R} = \text{H}, \text{CH}_3$) to form the complexes $\text{L}^*\text{Mo}(\text{CO})_2(\eta^3\text{-CH}_2\text{CRCH}_2)$ in good yield as yellow solids which are quite soluble in organic solvents.

An 18-electron configuration of Mo demands tridentate coordination of L^* in these complexes, which can be either of the type $\text{Me}_2\text{NB}(\mu\text{-pz})_3\text{Mo}$ or $(\text{pz})\text{B}(\mu\text{-pz})_2(\mu\text{-NMe}_2)\text{Mo}$. ^1H NMR data of the species indicate stereochemical nonrigidity, due to rotation of the $\text{Mo}(\text{CO})_2(\text{CH}_2\text{CRCH}_2)$ moiety around the B-Mo axis. The barrier to rotation is high for the case of $\text{R} = \text{H}$ (which is in consonance with earlier findings on related $\text{RB}(\text{pz})_3\text{Mo}(\eta^3\text{-CH}_2\text{CRCH}_2)$ compounds^{3,4}) and a variable-temperature study is depicted in Fig. 1.

As can be seen from Fig. 1, the high-temperature spectrum still shows two different types of pz groups in 2:1 ratio, consistent with a $(\text{pz})\text{B}(\mu\text{-pz})_2(\mu\text{-NMe}_2)\text{Mo}(\text{CO})_2(\eta^3\text{-CH}_2\text{CHCH}_2)$ structure, since analogous $\text{RB}(\text{pz})_3$ complexes show all pz groups to be identical at high temperatures. Furthermore, for $\text{RB}(\text{pz})_3$ complexes the η^3 -allyl part of the spectrum remains unchanged throughout the temperature range, while in the L^* complex the η^3 -allyl protons end up in a variety of environments at low temperature. In addition, one has to account for three types of Me groups and four different types of pz groups (evidenced best via the 4-H signals near 6.4 ppm) at low temperature.

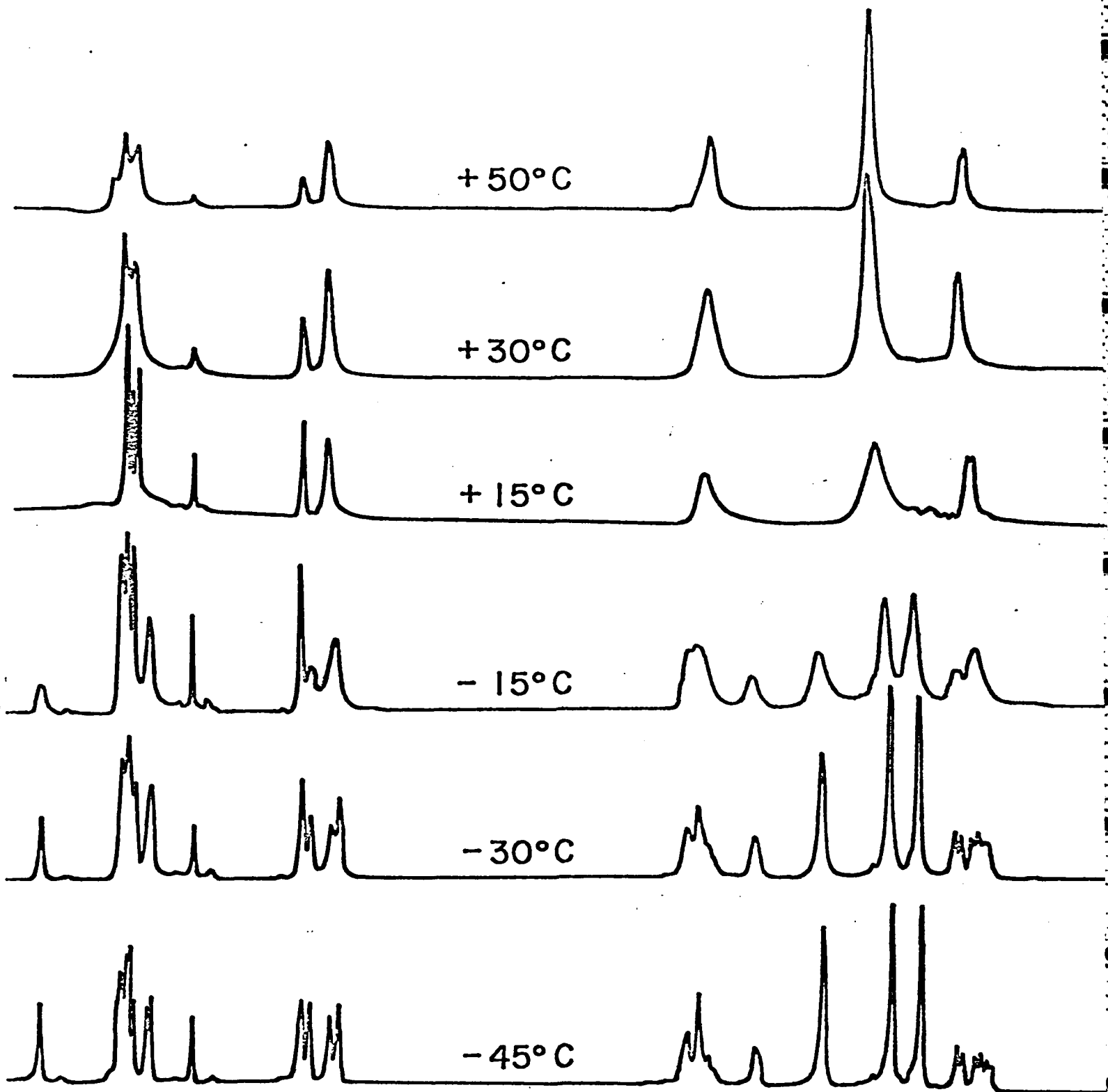
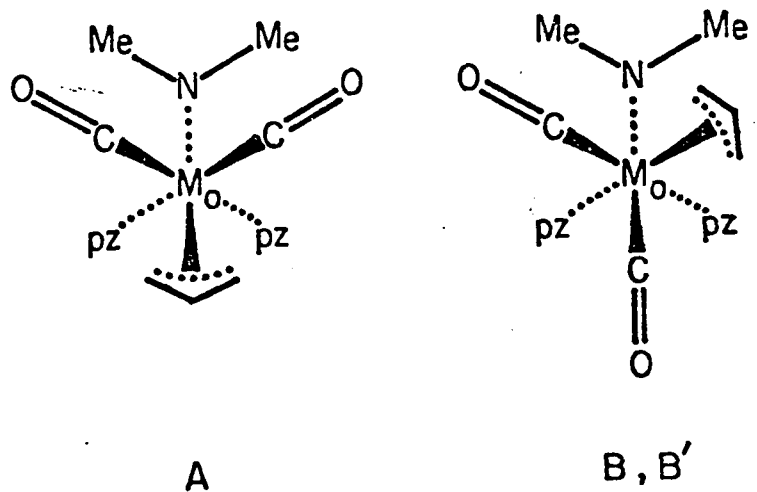


Figure 1. Variable temperature ^1H NMR spectrum of $(\text{pz})\text{B}(\mu\text{-pz})_2(\mu\text{-NMe}_2)\text{Mo}(\text{CO})_2(\eta^3\text{-CH}_2\text{CHCH}_2)$.

The $(pz)B(\mu-pz)_2(\mu-NMe_2)Mo(CO)_2(\eta^3-CH_2CHCH_2)$ formulation accounts for all these features as follows: Looking down the Mo-B axis, and disregarding the uncoordinated pz group, it is apparent that three rotamers should exist, i.e., A, B and its mirror image B' with identical chemical shifts.



Assuming statistical distribution of these rotamers at low temperature (1/3 A, 2/3 B + B') one should observe (a) three Me peaks of equal intensity; (b) four pz 4-H peaks in 1:2/3:2/3:2/3 ratio corresponding to the uncoordinated pz group, the two identical coordinated pz groups in rotamer A, and the two dissimilar coordinated pz groups in B and B'; and (c) three different environments for the syn- and anti-protons of the η^3 -allyl group. All these features are indeed observed in the low-temperature spectrum!

There are only very minor differences in the 1H NMR spectrum of $(pz)B(\mu-pz)_2(\mu-NMe_2)Mo(CO)_2(\eta^3-CH_2CCH_3CH_2)$ over the range +60 to -44°C. As based on selective decoupling experiments (and in agreement with the intensity measurements), the signals $\delta(^1H) = 7.88/7.76/6.46$ ppm are readily assigned to the lone terminal pz group.

The reason for L* coordinating as it does, instead of as $\text{Me}_2\text{NB}(\mu\text{-pz})_3$, resides probably in the stronger nucleophilicity of the NMe_2 group vs. pz (since the lone pair of the NMe_2 -nitrogen is not donating to boron); it may also be favored by the greater compactness of the of the molecule where the $\text{B}(\mu\text{-pz})_2$ ring is further bridged by a single atom. Similar single-atom bridging has been found in the anion $[\text{ONNi}(\mu\text{-pz})_2(\mu\text{-X})\text{NiNO}]^-$ (X = Cl, Br, I)⁵ and in $\text{MeGa}(\mu\text{-pz-3,5-Me}_2)_2(\mu\text{-OH})\text{M}(\text{CO})_2(\eta^3\text{-allyl})$ (M = Mo, W).⁶

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY; the 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 downfield from the reference (internal Me_4Si for ^1H , external Et_2OBF_3 for ^{11}B); s = singlet, d = doublet, t = triplet and an asterisk denotes a broad signal. Coupling constants J are given in Hz.

$\text{Li}[\text{Me}_2\text{NB}(\text{pz})_3]$. A solution of methyllithium in ether (10 mL of a 1.8 M solution) was added dropwise with stirring to a mixture of 2.5 g (9.7 mmol) of dimethylamine-tris(1-pyrazolyl)borane² and 20 mL of benzene. Gas evolution started immediately with slight warming of the reaction mixture. After complete addition, the mixture was stirred at ambient temperature for 3 h. The precipitate was collected, washed with benzene and hexane to yield 2.2 g (86%) of the desired compound; it began, on heating, to decompose near 130°C.

NMR data (solution in DMSO-d_6): $\delta(^1\text{H}) = 7.48$ (1 H, d, $J = 1.2$), 7.20 (1 H, d, $J = 1.9$), 6.10 (1 H, t, $J = 1.7$), 2.08 (2 H, s); $\delta(^{11}\text{B}) = +2.7$ ($h_{1/2} = 140$ Hz).

$\text{pzB}(\mu\text{-pz})_2(\mu\text{-NMe}_2)\text{Mo}(\text{CO})_2(\eta^3\text{-CH}_2\text{CCH}_3\text{CH}_2)$. A mixture of 2.56 g (10 mmol) of dimethylamine-tris(1-pyrazolyl)borane² and 3.25 g (10 mmol) of freshly prepared $(\text{MeCN})_2\text{Mo}(\text{CO})_2\text{Cl}(\eta^3\text{-CH}_2\text{CCH}_3\text{CH}_2)$ ⁷ was stirred overnight in 50 mL of methylene chloride. The solution was shaken with water and the organic layer was chromatographed on alumina packing and eluted with cyclohexane. Evaporation of the solvent gave 3.4 g (74%) of a yellow residue, which was recrystallized from heptane, mp 141-142°C.

NMR data (solution in CD_3CN): $\delta(^1\text{H}) = 7.96$ (2 H, d, $J = 1.9$), 7.90 (2 H, d, $J = 1.9$), 7.88 (1 H, d, J ca. 1.5), 7.76 (1 H, d, J ca. 1.5), 6.46 (1 H, unsym t = two overlapping d, J ca. 1.3), 6.31 (2 H, t, $J = 2.2$), 3.50 (2 H, s), 2.48^* (6 H, s), 1.83 (3 H, s), 1.14 (2 H, 2); $\delta(^{11}\text{B}) = +2.4$ (s, $h_{1/2} = 25$ Hz). At 60°C: $\delta(^1\text{H}) = 7.94$ (2 H, d), 7.87 (3 H, 2 overlapping d), 7.74 (1 H, d), 6.45 (1 H, unsym t = 2 overlapping d), 6.30 (2 H, t), 3.49 (2 H, s), 2.50^* (s, 6 H), 1.84 (3 H, s), 1.14 (2 H, s). At -44°C: $\delta(^1\text{H}) = 7.98$ (2 H, d), 7.95 (2 H, d), 7.91 (1 H, d), 7.79 (1 H, d), 6.48 (1 H, unsym t = two overlapping d), 6.34 (2 H, t), 3.51 (2 H, s), 2.49 (small s) + 2.43 (s) (6 H), 1.81 (3 H, s), 1.14 (2 H, s), 1.14 (2 H, s).

$\text{pzB}(\mu\text{-pz})_2(\mu\text{-NMe}_2)\text{Mo}(\text{CO})_2(\eta^3\text{-CH}_2\text{CHCH}_2)$ was prepared in analogous fashion as described for the preceding compound using $(\text{MeCN})_2\text{MoBr}(\text{CO})_2(\eta^3\text{-CH}_2\text{CHCH}_2)$.⁷ The desired compound was obtained in 67% yield, mp (after recrystallization from heptane) 122-123°C.

NMR data (solution in CDCl_3 ; 25°C): $\delta(^1\text{H}) = \text{ca. } 8.0\text{-}7.5$ (1 H, very very broad), 7.85 (2 H, d, $J = 2.3$), 7.80 (1 H, d, $J = 1.5$), 7.75 (2 H, d, $J = 2.2$), 6.44 (1 H, t, $J = 2.1$), 6.25 (2 H, unresolved t), 3.41^* (3 H, very broad unresolved m), 2.18^* (6 H, very broad s), 1.39 (2 H, d, J ca. 8); $\delta(^{11}\text{B}) = +2.7$ ($h_{1/2} = 30$ Hz). Additional ^1H NMR data see Fig. 1.

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