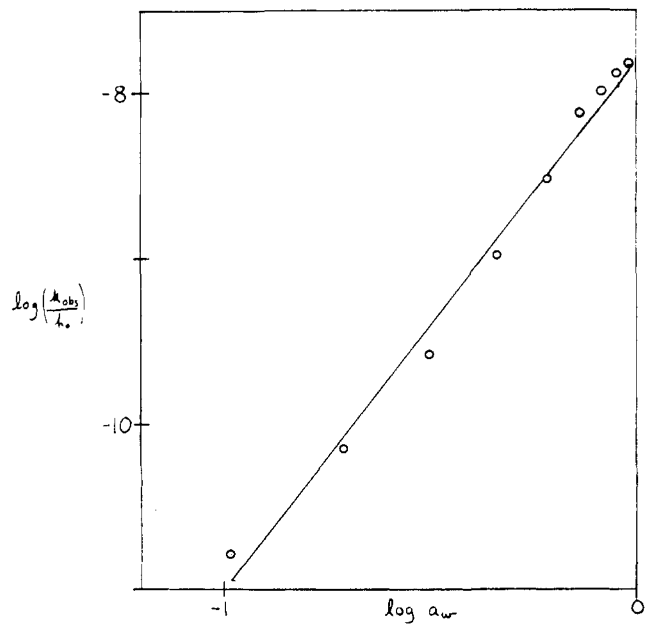

Figure 1. log (k_{obsd}/h_0) vs. log a_w (data for C_{HClO_4} = 1-9 mol L^{-1}). The line is given by the equation log (k_{obsd}/h_0) = -7.800 + 3.21 log a_w. (Values of a_w for 25 °C for perchloric acid solution containing no other electrolytes were used.)

evaluated by extrapolating from the studies carried out at higher temperatures[4]) is less than the experimental uncertainty at all acidities. The increase in reaction rate with increasing acidity is attributable to the rate law term $k_1[\text{CrF}^{2+}][\text{H}^+]$ detected by Swaddle and King in studies at lower acidity, constant ionic strength, and higher temperature.[4] In this study the problem of medium effects has not been suppressed by maintainance of constant ionic strength, and as in the study of azidochromium(III) ion, an appropriate handling of medium effects is a crucial aspect of correlating the data.

There are marked differences between aquation reactions of fluorochromium(III) ion and azidochromium(III) ion. Between 1 and 6 M perchloric acid, the value of k_1 increases by a factor of ~28 for the fluorochromium(III) ion but by a factor of ~185 for the azidochromium(III) ion. Over this same range of acidity, the corrected value of k_{obsd} divided by the product of the Hammett function h_0 and the activity of water decreases gradually by a factor of 6.8 for the fluorochromium(III) ion but is essentially constant for the azidochromium(III) ion. At still higher acidities, the first-order rate constant for aquation of azidochromium(III) displays a transition from $k \propto (h_0 a_w)^1$ to $k \propto (h_0 a_w)^0$ that allows estimation of the acid dissociation constant for the (hydrogen)-azidochromium(III) ion. The data for the present system are not amenable to a quantitative interpretation that yields the acid dissociation constant for (hydrogen)fluorochromium(III) ion. Rather, the gradual increase of k with increasing acidity suggests a dependence of k/h_0 upon a power of the activity of water greater than first, as shown in Figure 1. The data in Table I, excluding the value of k at C_{HClO_4} = 10 mol L^{-1}, are correlated with the equation

$$k_{\text{obsd}} = (1.59 \times 10^{-8}\ \text{s}^{-1}) h_0 a_w^{3.2}$$

The average difference between calculated and observed values of k_{obsd} is 19%. No other two-parameter equation correlates the data as well as this. The value of k_{obsd} at 10 M HClO$_4$ is ~3.7-fold larger than predicted by this equation; this deviation is in the opposite direction from that expected if the deviation were due to an appreciable fraction of fluorochromium(III) ion being converted to its protonated form. Thus in the context of this correlation, one concludes that $K_a((\text{H}_2\text{O})_5\text{CrFH}^{3+}) > \sim 10^6$. (This statement is based upon the assumed appropriateness of using h_0 as a measure of proton-donating ability of the solution toward the fluorochromium(III) ion and of correlating the data with the activity of water raised to a single power, rather than with more complex functions of this variable.) This sensitivity to the activity of water is reasonable for formation of an activated complex from which hydrofluoric acid is being produced and into which water is being incorporated.

Registry No. $\text{Cr(OH}_2)_5\text{F}^{2+}$, 19559-07-0.

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The (Dimethylamido)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, $[\text{HB(pz-3,5-Me}_2)_2(\text{SAr})]^-$ (Me = CH$_3$, Ar = C$_6$H$_4$-4-CH$_3$), was synthesized from K[H$_2$B(pz-3,5-Me$_2$)$_2$] and ArSH.[1]

When tris(dimethylamino)borane, B(NMe$_2$)$_3$, was reacted with Hpz at room temperature, the dimethylamine adduct of tris(1-pyrazolyl)borane was obtained in essentially quantitative yield. On the basis of low-temperature ^{1}H NMR data, the species may be presented by the formula Me$_2$HN·B(pz)$_3$. However, at room temperature the N-bonded proton undergoes site exchange, and H[Me$_2$NB(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 [Me$_2$NB(pz)$_3$]$^-$ (=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 Me$_2$SO and exhibits the expected ^{1}H and ^{11}B NMR spectra. However, even the acid HL* was found to react readily with (MeCN)$_2$Mo(CO)$_2$X(η^3-CH$_2$CRCH$_2$) (X = Cl, Br; R = H, CH$_3$) to form the complexes L*Mo(CO)$_2$(η^3-CH$_2$CRCH$_2$) in good yield as yellow solids that 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 Me$_2$NB(μ-pz)$_3$Mo or (pz)B(μ-pz)$_2$(μ-NMe$_2$)Mo. ^{1}H NMR data of the species indicate stereochemical nonrigidity, due to rotation of the Mo(CO)$_2$(CH$_2$CRCH$_2$) moiety around the B-Mo axis. The barrier to rotation is high for the case of R = H (which is in consonance with earlier findings on related RB(pz)$_3$Mo(η^3-CH$_2$CRCH$_2$) compounds[3,4]), and a variable-temperature study is depicted in Figure 1.

As can be seen from Figure 1, the high-temperature spectrum still shows two different types of pz groups in 2:1 ratio, consistent with a (pz)B(μ-pz)$_2$(μ-NMe$_2$)Mo(CO)$_2$(η^3-CH$_2$CHCH$_2$) structure, since analogous RB(pz)$_3$ complexes show all pz groups to be identical at high temperatures. Furthermore, for RB(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.

The (pz)B(μ-pz)$_2$(μ-NMe$_2$)Mo(CO)$_2$(η^3-CH$_2$CHCH$_2$) formulation accounts for all these features as follows: Looking down the Mo-B axis and disregarding the uncoordinated pz group, one

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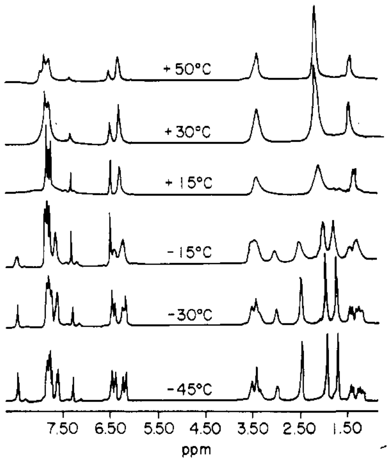
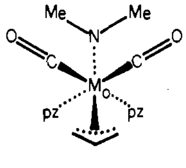
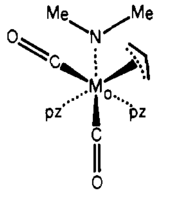


Figure 1. Variable-temperature ^{1}H NMR spectrum of (pz)B(μ-pz)$_2$(μ-NMe$_2$)Mo(CO)$_2$(η^3-CH$_2$CHCH$_2$).

can see that three rotamers should exist, i.e., A, B, and its mirror image B′, with B and B′ having 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′, (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, e.g., the three sharp Me signals near 2.6–2.2 ppm and the pz 4-H peaks in the 6.5–6.2 ppm range.



A



B , B′

There are only very minor differences in the ^{1}H NMR spectrum of (pz)B(μ-pz)$_2$(μ-NMe$_2$)Mo(CO)$_2$(η^3-CH$_2$CCH$_3$CH$_2$) over the range +60 to −44 °C. On the basis of selective-decoupling experiments (and in agreement with the intensity measurements), the signals δ(^{1}H) = 7.88/7.76/6.46 are readily assigned to the lone terminal pz group.

The reason for L* coordinating as it does, instead of as Me$_2$NB(μ-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 molecule where the B(μ-pz)$_2$Mo ring is further bridged by a single atom.

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 shifts from the reference (internal Me$_4$Si for ^{1}H; external Et$_2$O·BF$_3$ for ^{11}B); s = singlet, d = doublet, t = triplet, and an asterisk denotes a broad signal. Coupling constants J are given in Hz.

Li[Me$_2$NB(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)borane[2] 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 and 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 Me$_2$SO-d_6): δ(^{1}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); δ(^{11}B) = +2.7 ($h_{1/2}$ = 140 Hz).

pzB(μ-pz)$_2$(μ-NMe$_2$)Mo(CO)$_2$(η^3-CH$_2$CCH$_3$CH$_2$). A mixture of 2.56 g (10 mmol) of (dimethylamine)–tris(1-pyrazolyl)borane[2] and 3.25 g (10 mmol) of freshly prepared (MeCN)$_2$Mo(CO)$_2$Cl(η^3-CH$_2$CCH$_3$CH$_2$)[5] 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 are as follows. For solution in CD$_3$CN: δ(^{1}H) = 7.96 (2 H, d, J = 1.9), 7.90 (2 H, d, J = 1.9), 7.88 (1 H, d, $J \approx$ 1.5), 7.76 (1 H, d, $J \approx$ 1.5), 6.46 (1 H, unsym t = two overlapping d, $J \approx$ 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); δ(^{11}B) = +2.4 (s, $h_{1/2}$ = 25 Hz). At 60 °C: δ(^{1}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* (6 H, s), 1.84 (3 H, s), 1.14 (2 H, s). At −44 °C: δ(^{1}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 (6 H, s), 1.81 (3 H, s), 1.14 (2 H, s), 1.14 (2 H, s).

pzB(μ-pz)$_2$(μ-NMe$_2$)Mo(CO)$_2$(η^3-CH$_2$CHCH$_2$) was prepared in a fashion analogous to that described for the preceding compound using (MeCN)$_2$MoBr(CO)$_2$(η^3-CH$_2$CHCH$_2$).[5] The desired compound was obtained in 67% yield; mp (after recrystallization from heptane) 122–123 °C.

NMR data (solution in CDCl$_3$; 25 °C): δ(^{1}H) = ca. 8.0–7.5 (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, $J \approx$ 8); δ(^{11}B) = +2.7 ($h_{1/2}$ = 30 Hz). For additional ^{1}H NMR data see Figure 1.

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Registry No. Li[Me$_2$NB(pz)$_3$], 98839-65-7; pzB(μ-pz)$_2$(μ-NMe$_2$)Mo(CO)$_2$(η^3-CH$_2$CCH$_3$CH$_2$), 98839-66-8; pzB(μ-pz)$_2$(μ-NMe$_2$)Mo(CO)$_2$(η^3-CH$_2$CHCH$_2$), 98839-67-9; Me$_2$HN·B(pz)$_3$, 81004-03-7; (MeCN)$_2$Mo(CO)$_2$Cl(η^3-CH$_2$CCH$_3$CH$_2$), 97590-30-2; (MeCN)$_2$MoBr(CO)$_2$(η^3-CH$_2$CHCH$_2$), 33221-76-0.

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Phosphato Complexes of Pentaammineruthenium

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The (NH$_3$)$_5$Ru$^{II/III}$ moiety has been utilized recently to study molecules of biological interest. It was attached to several metalloproteins in order to study electron transfer to the metal centers of these molecules,[1,2] and to other proteins, as a probe of their structure and properties.[3,4] Attempts have also been made to

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