Polypyrazolylborates, a New Class of Ligands

SWIATOSLAW TROFIMENKO*

Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware   19898

Many of the upsurges in transition metal chemistry have resulted directly from the discovery of a new type of ligand, a particularly good example being that of the cyclopentadienide ion. Thus, when the polypyrazolylborate ion[1] was discovered, its outstanding chelating power and unusual structural features raised the possibility that this coordinating system, too, may eventually lead to a new subarea of coordination and organometallic chemistry.[2] Subsequent work was directed at establishing its scope and checking whether this new ligand system would prove itself in practice. While these studies were neither exhaustive nor complete, the presently available data warrant the conclusion that the new ligand has "passed the test," and the time is ripe for taking stock of what is known in this area and for considering its significance and the direction of future development.

The coordinating ability of a polypyrazolylborate ion, $[R_nB(pz)_{4-n}]^-$, is a consequence of favorable electronic and geometric factors. The dipyrazolylborate ion I is quite similar to a β-diketonate ion, II, and one would expect formation of chelates such as III

I   II

III
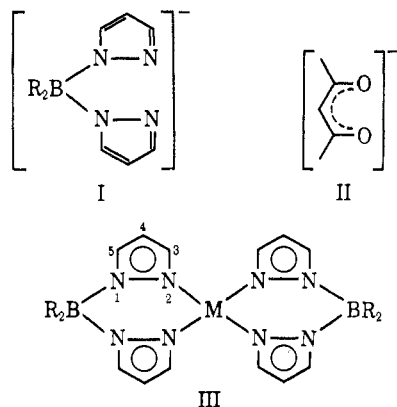
from the reaction of I with divalent transition metal ions. Such is indeed the case. However, the similarity of I and II notwithstanding, chelates III reflect some of the basic differences between ligands I and II. In III the nitrogens are unavailable for further coordination and the area around the metal is screened by substituents in the 3 position. Consequently, che-

lates III are always monomeric, in contrast to β-diketonates where various associative equilibria have been observed.[3] Also, neutral tris bidentate chelates analogous to $Fe(AcAc)_3$ have not been encountered. Furthermore, the B–N and N–M bond lengths and angles in the square-planar chelates III make these molecules puckered (although the four nitrogens bonded to the metal lie in a plane), with attendant nonequivalence of the R groups on boron (one "axial" and one "equatorial"). Models indicate that two conformations of III are possible; of these, the pseudochair conformation should be preferred since it entails much less nonbonding interactions between the hydrogens in position 3 than the pseudoboat conformation.

When one of the R groups in I is 1-pyrazolyl, it too can coordinate to a transition metal, and the resulting ion, IV, is the first known example of a uninegative

IV

V

VI
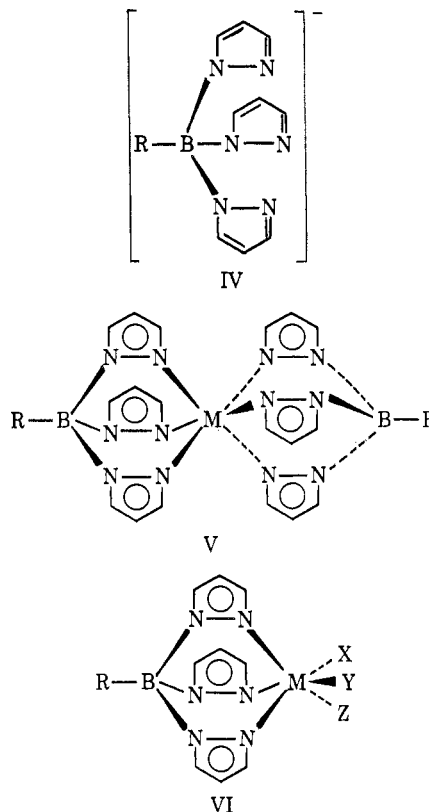
tridentate ligand of C_{3v} symmetry. This combination of properties is unique and poses a problem in finding known systems to compare it with. Neither the tetraarylborate ion nor the various known tridentate donor

---

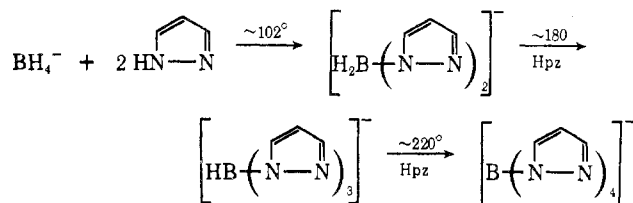(1) S. Trofimenko, *J. Amer. Chem. Soc.*, **88**, 1842 (1966).

(2) In the first paper and in some subsequent ones the area under investigation was referred to as "boron–pyrazole" chemistry. Such a definition, while accurate—insofar as all the compounds under study contained a boron–pyrazolyl bond—was not too informative. In particular, it failed to convey the fact that the greatest significance of the "boron–pyrazole" area lies in its contribution to coordination and organometallic chemistry, neither of which is apparent from the above name.

(3) See, for instance, F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **4**, 1145 (1965); G. J. Bullen, R. Mason, and P. Pauling, *ibid.*, **4**, 456 (1965), and references cited therein.

ligands of C_{3v} symmetry[4] are appropriate: the former lacks the symmetry and the tridentate coordinative ability; the latter ligands are all uncharged and thus cannot form neutral compounds such as V with divalent transition metals. The cyclopentadienide ion is also unsatisfactory: while it is uninegative and "tridentate" in the sense of supplying six electrons and occupying three coordination sites on the metal, it forms π- rather than σ-bonded complexes. Nevertheless, in terms of derivative chemistry it still provides the closest approximation to the behavior of IV in compounds such as L_2M, $LM(CO)_2Z$, etc. (vide infra), although derivatives based on IV are usually more stable.

Synthesis of Ligands

The parent ligands $H_2B(pz)_2^-$, $HB(pz)_3^-$, and $B(pz)_4^-$ (where pz = 1-pyrazolyl) are available by the reaction of pyrazole with an alkali metal borohydride salt, the extent of substitution being controlled by

$$BH_4^- + 2\,HN\text{---}N \xrightarrow{\sim102°} \left[H_2B\left(N\text{---}N\right)_2\right]^- \xrightarrow[\text{Hpz}]{\sim180}$$

$$\left[HB\left(N\text{---}N\right)_3\right]^- \xrightarrow[\text{Hpz}]{\sim220°} \left[B\left(N\text{---}N\right)_4\right]^-$$

adjusting the temperature.[5,6] These salts are remarkable in that, on acidification, they yield isolable and stable free acids (unlike any other BR_4^- species) which may be converted via neutralization with NR_4OH to quaternary ammonium salts, unavailable by the direct route.

Ligands containing C substituents are prepared by using an appropriately substituted pyrazole in the above scheme,[7] while B-substituted ligands are obtained by starting with a $[BR_nH_{4-n}]^-$ species instead of BH_4^-. The usual order of R replacement by a pyrazolyl group is halogen > H > alkyl > aryl. Steric effects play a definite role in these syntheses. For instance, the reaction of tetraalkylborate or tetraarylborate ion with pyrazole stops at the $R_2B(pz)_2^-$ stage. Compounds of the type $RB(pz)_3^-$ can be prepared, however, starting with an RBH_3^- or RBX_2 species. Similarly, the reaction of 3,5-dimethylpyrazole with BH_4^- stops completely at the trisubstitution stage as the boron in $HB(3,5-Me_2pz)_3^-$ is too crowded by the methyl groups to accommodate another large substituent.

Obvious physical properties such as volatility, solubility, chemical reactivity, etc., can be changed by changes in substituents. In the case of Fe(II) compounds dramatic changes in magnetic moments result (vide infra).

Bis Bidentate Chelates

The reaction of the parent bidentate ligand $H_2B(pz)_2^-$ with most first-row transition metal ions in the 2+ state gives rise to monomeric chelates $[H_2B(pz)_2]_2M$. They are organic-soluble, sublimable substances quite stable to air, except for the Mn(II) and Fe(II) derivatives.[5] The isomorphous Ni and Cu chelates are square planar, while chelates of Mn, Fe, Co, and Zn are tetrahedral. This was established from optical spectra as well as from magnetic and nmr data.[8] An X-ray structure determination[9] of $[H_2B(pz)_2]_2Co$ confirmed the above assignment.

Presence of alkyl substituents in the 3 position enhanced the stability of these chelates. Thus $[H_2B(3,5-(CH_3)_2pz)]_2M$ chelates (M = Mn, Fe) were stable to air, presumably as a result of screening of the metal by the 3-methyl groups.

Presence of alkyl groups on boron, as in $[(C_2H_5)_2B(pz)_2]_2Ni$, also results in some steric protection for the metal. This is manifested by failure of $[(C_2H_5)_2B(pz)_2]_2Ni$ to form octahedral complexes by coordinating with, e.g., pyridine ($[H_2B(pz)_2]_2Ni$ does this readily) and by a substantial nmr shift of the pseudoaxial methylene protons[7] toward lower field. Similar nmr shifts have been also noted[10] in other complexes containing protons in proximity of transition metals. The reason for just one methylene group showing this effect in planar $[R_2B(pz)_2]_2M$ compounds is that the chelate ring is puckered and hence only one methylene group can approach the metal as in VII.

VII

The nmr spectrum of $[Et_2B(pz)_2]_2Ni$ remained unchanged up to >150°, indicating lack of inversion (which would have made both ethyl groups spectroscopically equivalent).

Mono Bidentate Chelates

The stabilizing effect of alkyl substituents on carbon and boron in $R_2B(pz)_2^-$ ligand was utilized in the synthesis of a number of stable organometallic compounds with noninert gas configuration.[11,12] For instance, the reaction of $H_2B(3,5-(CH_3)_2pz)_2^-$ with $Mo(CO)_6$ gave

(4) See, for instance, H. A. Goodwin in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, p 143; also W. J. Kasowski and J. C. Bailar, Jr., J. Amer. Chem. Soc., 91, 3212 (1969).

(5) S. Trofimenko, ibid., 89, 3170 (1967).
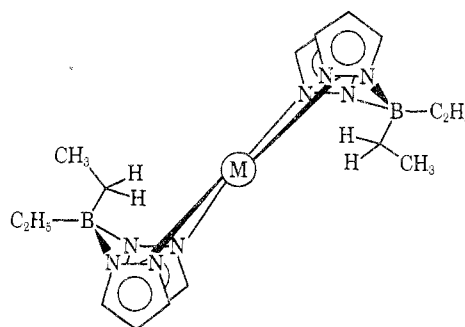
(6) S. Trofimenko, Inorg. Syn., 12, 99 (1970).

(7) S. Trofimenko, J. Amer. Chem. Soc., 89, 6288 (1967).

(8) J. P. Jesson, S. Trofimenko, and D. R. Eaton, ibid., 89, 3148 (1967).

(9) C. T. Prewitt, private communication.

(10) R. G. Miller, R. D. Stauffer, D. R. Fahey, and D. R. Parnell, J. Amer. Chem. Soc., 92, 1511 (1970).

(11) S. Trofimenko, ibid., 90, 4754 (1968).

(12) S. Trofimenko, Inorg. Chem., 9, 2493 (1970).

an air-sensitive tetracarbonyl anion, VIII, which upon reaction with allyl halides was readily converted to the π-allyl derivative IXa, possessing 16 electrons in the 4d, 5s, and 5p orbitals and thus two electrons short of the stable xenon configuration.[13] The same type of product was obtained from substituted allylic halides, from cyclic systems such as cyclohexenyl, as

a, R = H; R' = CH₃
b, R' = C₂H₅; R' = H

VIII

IXa, R = H; R' = CH₃; R'' = H
b, R = C₂H₅; R' = H; R'' = H
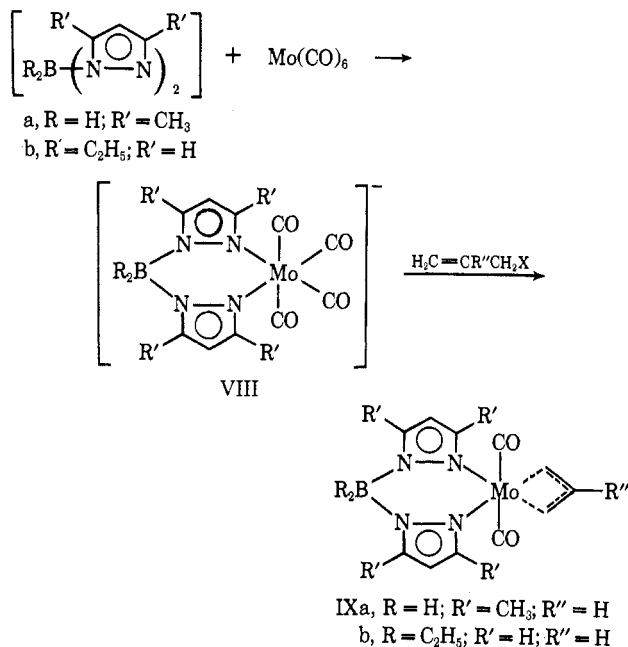
well as from ligands such as $H_2B(3,5-(C_2H_5)_2pz)_2^-$ and $H_2B(3,5-(C_6H_5)_2pz)_2^-$. These orange-red compounds displayed remarkable inertness toward nucleophiles and toward air, consistent with a sterically inaccessible Mo atom. Their nmr spectra indicated fluxional behavior[14] similar to that found in $RB(pz)_3Mo(CO)_2$-π-allyl compounds.[15]

The 16-electron structures IXb, obtained from B-substituted ligands, gave no indication of stereochemical nonrigidity; they were moderately air sensitive and readily added nucleophiles to form 18-electron structures. The nmr spectra of IXb showed one of two $B(C_2H_5)_2$ methylenes to be unique, the two hydrogens appearing in the τ 13-14 range. This shift, coupled with the presence of CH stretch bands of remarkably low frequency ($\sim$2700 cm⁻¹), was interpreted to imply significant interaction between Mo and the pseudoaxial methylene group. Why such an interaction gives rise to an upfield shift here but to a downfield shift in $[(C_2H_5)_2B(pz)_2]_2Ni$ remains unclear.

Bis Tridentate Chelates

Ligands of structure $RB(pz)_3^-$ form octahedral coordination compounds with divalent transition metals, while trivalent ions (e.g., Fe(III), Cr(III)) give rise to cationic species $[RB(pz)_3]_2M^+$. When the R group is another 1-pyrazolyl ring, the ligand remains tridentate but the complexes are soluble in acid because

of the available protonation site on the fourth pyrazolyl group. In some chelates, such as $Zn[B(pz)_4]_2$, the structure is ionic, or dynamic as judged by nmr equivalence of all four pyrazolyl groups. On the other hand, the isomorphous Co derivative has three of the pyrazolyl groups per ligand identical, but different from the fourth. This is seen particularly well because of the paramagnetic contact shifts which spread the spectrum over 200 ppm.

The simplest compounds involving a C_{3v} tridentate ligand are the parent $[HB(pz)_3]_2M$ derivatives. They are stable to light, air, water, dilute acids, and bases. They are soluble in organic solvents and can be sublimed in vacuo with ease. The overall D_{3d} symmetry for these compounds has been implicit from spectral and nmr data and has subsequently been confirmed by an X-ray crystal structure determination of [HB-(pz)₃]₂Co.[16]

The same general type of octahedral structure is present in compounds derived from symmetrically substituted derivatives, which usually are more thermally stable than the parent compounds. While the preparation of mixed ligands, e.g., $[HB(pz)_2pz']^-$, has not been studied, it is possible to prepare tridentate chelates with less than D_{3d} symmetry by the reaction of $[H_2B(pz)_2]_2M$ with a substituted pyrazole, Hpz'. The compound $[HB(pz)_2(4\text{-cyano-1-pyrazolyl})]_2Ni$ was prepared in this fashion[17] and was converted to the corresponding carboxylic acid via alkaline hydrolysis.

Mono Tridentate Chelates

The expectation that a $RB(pz)_3^-$ ligand will possess a derivative chemistry equalling or surpassing that of the cyclopentadienide ion received a particularly gratifying confirmation in the "half-sandwich" area, i.e., in monotridentate complexes corresponding to half-sandwiches based on $C_5H_5^-$. This is illustrated best by compounds derived from the group VIb hexacarbonyls, especially those of molybdenum. As can be seen from Scheme I a broad spectrum of derivatives can be obtained from the intermediate anion, X. Generally, these derivatives correspond to their C_5H_5 counterparts although some have been obtained only in the $RB(pz)_3$ system. On the whole, the $RB(pz)_3$ compounds exhibit greater thermal and chemical stability as a result of a combination of steric and electronic factors.

The anions, X, isolated best as the tetraethylammonium salts, are moderately air stable for R = H or pz; the presence of alkyl groups in the 3 position, as in $HB(3,5-(CH_3)_2pz)_3Mo(CO)_3^-$, makes these salts indefinitely air stable. This enhanced stability of the 3-methyl-substituted derivatives is encountered throughout the pyrazolylborate area. It is explained in terms of steric hindrance, i.e., inaccessibility of Mo to prospective attacking reagents. Protonation of the anions X yields the air-sensitive free acids containing
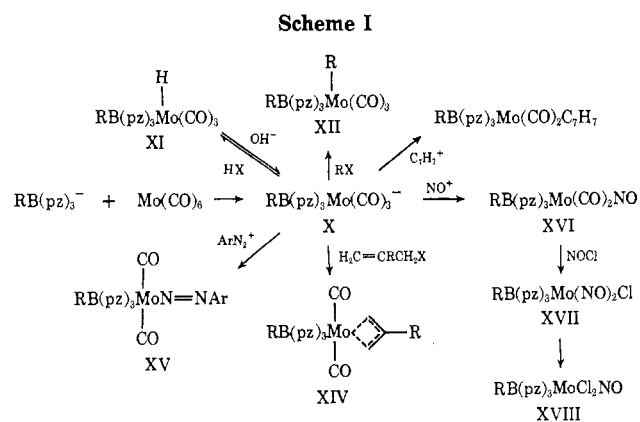
(13) For a discussion of the inert gas (18-electron) rule see D. P. Craig and R. S. Nyholm in ref 4, p 85.
(14) F. A. Cotton, Accounts Chem. Res., 1, 257 (1968).
(15) S. Trofimenko, J. Amer. Chem. Soc., 91, 3183 (1969).

(16) M. R. Churchill, K. Gold, and C. E. Maw, Jr., Inorg. Chem., 9, 1597 (1970).
(17) S. Trofimenko, unpublished work.

Scheme I

$$RB(pz)_3Mo(CO)_3 \xleftarrow{H} \quad \xrightarrow{R} RB(pz)_3Mo(CO)_3 \quad XII$$

$$RB(pz)_3Mo(CO)_3 \quad XI \qquad RB(pz)_3Mo(CO)_2C_7H_7$$

$$RB(pz)_3^- + Mo(CO)_6 \longrightarrow RB(pz)_3Mo(CO)_3^- \xrightarrow{NO^+} RB(pz)_3Mo(CO)_2NO \quad XVI$$
$$X$$

$$RB(pz)_3MoN{=}NAr \quad XV$$

$$RB(pz)_3Mo \diamond\!\!-R \quad XIV$$
$$CO$$

$$RB(pz)_3Mo(NO)_2Cl \quad XVII$$

$$RB(pz)_3MoCl_2NO \quad XVIII$$

a Mo–H bond which can be deprotonated with base, while the reaction with alkyl halides forms the seven-coordinate Mo–alkyl derivatives.

The reaction of X with allylic halides produces the π-allyl derivative XIV directly, without isolation of an intermediate σ-allyl species. This is in contrast to the $C_5H_5Mo(CO)_3^-$ ion where the σ-allyl derivative has to be irradiated to effect the σ-π conversion. The anion $HB(3,5\text{-}(CH_3)_2pz)_3Mo(CO)_3^-$, however, failed to react with allylic halides. This is interpreted in terms of its inability to accommodate a crowded SN2 transition state. The compound $HB(3,5\text{-}(CH_3)_2pz)_3Mo(CO)_2\text{-}\pi\text{-}C_3H_5$ can be prepared by an indirect route involving an SN1 transition state.[14] Many of these π-allyl derivatives are thermally stable beyond 250° and are thus the most thermally stable π-allyl compounds known.

The reaction of X with tropylium ion produced the C_7H_7 derivative XIII, thought to involve a dynamic *pentahapto*-C_7H_7 ring, although a 16-electron structure containing a *trihapto*-C_7H_7 moiety could not be excluded.

Nitrogen functional groups as represented by NO and N=NAr groups, could be readily attached to molybdenum by treating X with a source of NO^+ (nitrosyl chloride, nitrous acid, butyl nitrite) or with an aryldiazonium salt.[18] In this fashion the stable derivatives XVI and XV were produced. The nitrosation reaction proceeded equally well for the parent anions (X, R = H or pz) or for the sterically hindered species, $HB(3,5\text{-}(CH_3)_2pz)_3Mo(CO)_3^-$. On the other hand the reaction of $HB(3,5\text{-}(CH_3)_2pz)_3Mo(CO)_3^-$ with aryldiazonium salts formed blue compounds which were assigned the structure $HB(3,5\text{-}(CH_3)_2pz)_3Mo(CO)_3Ar$;[19] the reason for this difference in behavior is not entirely clear.

The mononitroso compound XVI reacts readily with further nitrosyl chloride to yield the emerald-green dinitroso monochloride XVII. The sterically hindered species $HB(3,5\text{-}(CH_3)_2pz)_3Mo(NO)_2Cl$ reacts cleanly with additional nitrosyl chloride to form the stable, monomeric mononitroso dichloride XVIII. While XVII differs from $C_5H_5Mo(NO)_2Cl$ in being indefinitely stable to storage, no counterpart is known for XVIII in the C_5H_5 system.

Another anomalous reaction was found to take place between the hindered anion $HB(3,5\text{-}(CH_3)_2pz)_3Mo(CO)_3^-$ and arylsulfonyl chlorides. Instead of the anticipated sulfones or sulfinates, arylmercapto derivatives (XIX) were obtained.[19] They were also obtained from ArSCl compounds. In contrast to the dimeric C_5H_5 analogs,[20–22] compounds XIX were all monomeric.
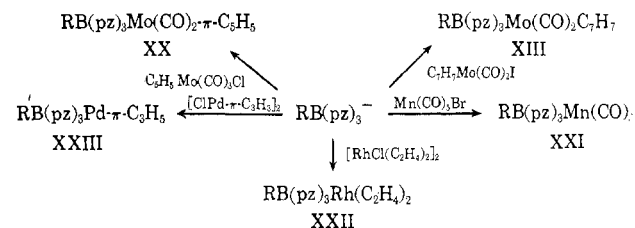
$$HB(3,5\text{-}(CH_3)_2pz)_3Mo(CO)_3^- + ArSO_2Cl \longrightarrow$$
$$(\text{or } ArSCl)$$
$$HB(3,5\text{-}(CH_3)_2pz)_3Mo(CO)_2SA$$
$$XIX$$
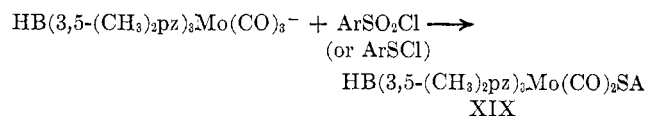
The reaction of $HB(3,5\text{-}(CH_3)_2pz)_3Mo(CO)_3^-$ with $SOCl_2$ gave the green compound $HB(3,5\text{-}(CH_3)_2pz)_3MoOCl_2$, also obtainable[19] from $HB(3,5\text{-}(CH_3)_2pz)_3^-$ and $MoOCl_3$.

In addition to a variety of derivatives, containing diverse ligands on Mo, available *via* the anion X, many well-defined, stable organometallic compounds were prepared by simple metathetical reactions of an organometallic halide with an $RB(pz)_3^-$ ligand. For instance the compound XIII was prepared more easily by the reaction of $RB(pz)_3^-$ with $C_7H_7Mo(CO)_2I$. Similarly, the reaction of $C_5H_5Mo(CO)_3Cl$ with $RB(pz)_3^-$ yielded $RB(pz)_3Mo(CO)_2\text{-}\pi\text{-}C_5H_5$ which contains both an $RB(pz)_3$ and a C_5H_5 ligand on the same metal.[23] Here, the structure probably contains a bidentate $RB(pz)_3$ ligand and *pentahapto*-C_5H_5.

Typical examples of organometallic compounds with metals other than the VIb group include the manganese carbonyl derivative XXI and the rhodium bisethylene complex XXII.

The π-allyl derivative of palladium, XXIII, was obtained by the reaction of $RB(pz)_3^-$ with $Pd\text{-}(\pi\text{-}allyl)$ chloride dimer. The nmr spectrum indicated a fluxional structure, *i.e.*, all three pz groups in XVIII and all four pz groups in $B(pz)_4Pd\text{-}\pi\text{-}C_3H_5$ were spec-

$$RB(pz)_3Mo(CO)_2\text{-}\pi\text{-}C_5H_5 \quad XX$$
$$C_5H_5Mo(CO)_3Cl$$
$$RB(pz)_3Pd\text{-}\pi\text{-}C_3H_5 \xleftarrow{[ClPd\text{-}\pi\text{-}C_3H_5]_2} RB(pz)_3^- \xrightarrow{Mn(CO)_5Br} RB(pz)_3Mn(CO)_3 \quad XXI$$
$$XXIII$$
$$RB(pz)_3Mo(CO)_2C_7H_7 \quad XIII$$
$$C_7H_7Mo(CO)_2I$$
$$[RhCl(C_2H_4)_2]_2$$
$$RB(pz)_3Rh(C_2H_4)_2 \quad XXII$$

troscopically identical at room temperature. On cooling to −40° this exchange slowed to the point that the two coordinated and the uncoordinated pyrazolyl groups became clearly discernible.

The reaction of $RB(pz)_3^-$ ligands with group VIII organometallic compounds has also been reported briefly. It was found that $RB(pz)_3^-$ is a powerful ligand which displaces $C_5H_5^-$ or phosphines.[24]

(18) S. Trofimenko, *Inorg. Chem.*, **8**, 2675 (1969).

(19) S. Trofimenko, *ibid.*, in press.

(20) P. M. Treichel, J. H. Morris, and F. G. A. Stone, *J. Chem. Soc.*, 720 (1963).

(21) P. M. Treichel and G. R. Wilkes, *Inorg. Chem.*, **5**, 1182 (1966)

(22) R. Havlin and G. R. Knox, *Z. Naturforsch. B*, **21**, 1108 (1966).

(23) Attempts to prepare a mixed sandwich $RB(pz)_3MC_5H_5$, *e.g.*, by the reaction of $C_5H_5Fe(CO)_2X$ with $RB(pz)_3^-$ led invariably to $[RB(pz)_3]_2Fe$ (S. Trofimenko, unpublished results).
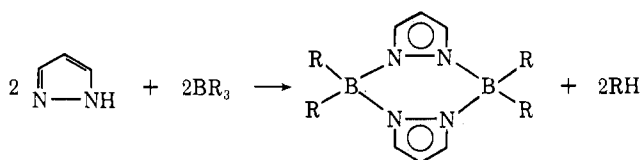
Pyrazaboles

Pyrazaboles are neutral and rather stable boron heterocycles of structure XXIV. The reason for their inclusion in this Account is that they may be formally regarded as boronium dipyrazolylborates, at least in

XXIV
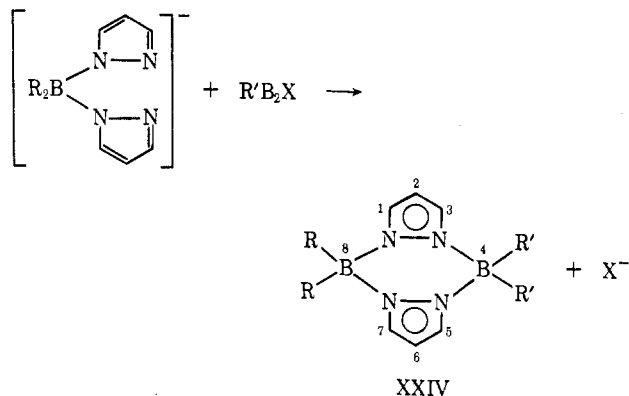
terms of synthesis from a polypyrazolylborate anion and a borane species containing a leaving group.[25] This is reminiscent of the various BR_2-bridged chelating systems.[26]

By a suitable choice of polypyrazolylborate and borane components, asymmetrically substituted pyrazaboles may be prepared. Pyrazaboles where R = R' are synthesized more conveniently from pyrazole and a borane.[27]

Diversely substituted symmetrical pyrazaboles have been synthesized by an appropriate choice of substituted pyrazole and borane components.[28] The pyrazabole ring system is remarkably stable: it has been possible to effect various transformations on functional groups attached to the 2,6 positions (e.g., C–Br → C–Li → C–CHO (or C–COOH); C–CN → C–COOH; C–NO_2 → C–NH_2 → C–NHCOR), maintaining the ring system intact. Also, 2,6-dinitration in high yield was effected by nitrating 4,4,8,8-tetrafluoropyrazabole with fuming nitric acid.[29] No further work has been reported in this area except for the formation of some pyrazabole polymers.[30] Clearly, much chemistry of this novel boron–nitrogen heterocycle of unusual stability still remains to be done, particularly with regard to electrophilic substitution.

Physical Studies

A number of spectral properties of polypyrazolyl-

borate complexes have been determined in the course of characterizing these compounds. The largest amount of optical data is in one of the earlier papers.[8]

Nmr studies were carried out (apart from simple structure determination) from several points of view. In conjunction with magnetic and Mössbauer data they were used to investigate the spin equilibria encountered in iron(II) polypyrazolylborates. The magnetic moments in these compounds were dependent on rather minor changes in substituents at the periphery of the molecule. Thus, while $[B(pz)_4]_2Fe$ is diamagnetic at room temperature, $[HB(3,5-(CH_3)_2pz)_3]_2Fe$ is fully paramagnetic (μ_{eff} ~5.2 BM) and $[HB(pz)_3]_2Fe$ has an intermediate value (2.7 BM). The last magnetic moment is strongly temperature dependent, and it was shown that here one deals with a spin equilibrium between the $^5A_{1g}$ and $^1A_{1g}$ states.[31] In addition to the above results obtained on solutions, similar behavior was found in the solid state[32,33] and was studied in detail by Mössbauer and magnetic susceptibility techniques down to a temperature of 4.2°K. In the solid state, the compound $[HB(pz)_3]_2Fe$ was diamagnetic at room temperature and below, although paramagnetism could be induced by raising the temperature above 300°K, while the compound $[C_6H_5B(pz)_3]_2Fe$ was diamagnetic even above room temperature. Compound $[HB(3,4,5-(CH_3)_3pz)_3]_2Fe$ was fully paramagnetic down to 4.2°K; on the other hand $[HB(3,5-(CH_3)_2-pz)_3]_2Fe$ is paramagnetic at room temperature but becomes fully diamagnetic at 147°K. In the intermediate temperature range, the Mössbauer transition for the high-spin and low-spin states may be clearly observed. Analysis of the Mössbauer and magnetic susceptibility data led to the conclusion that the orbital splitting of the high-spin ground state due to a trigonal component in the octahedral crystal field is ~1000 cm^{-1}, leaving an orbital singlet lowest. The separate Mössbauer transitions for the two electronic states could be observed because the thermal relaxation time between the singlet and quintet manifolds is anomalously long.

In the "half-sandwich" area the fluxional nature of compounds having the structure $RB(pz)_3Mo(CO)-\pi$-allyl was investigated.[14] The limiting high- and low-temperature spectra were interpreted in terms of a rotation of the $RB(pz)_3$ ligand around the C_3 axis. The rotational barrier is about 15 kcal/mole.[34] As could be expected, this barrier depends on steric factors such as the substituents on the 3 positions or on the π-allyl group. The π-cyclopentenyl derivative is stereochemically rigid in the available temperature range. It is interesting to note in this context that $RB(pz)_3Mo(CO)_2NO$ compounds are stereochemically rigid; this may be explained in terms of a nonlinear $MN=O$ sequence.

Nmr spectroscopy was also used to study the struc-

(24) M. I. Bruce, M. Z. Iqbal, D. N. Sharrocks, and F. G. A. Stone, Abstracts of the IVth International Symposium on Organometallic Chemistry, Bristol, 1969, Abstract S2.

(25) S. Trofimenko, *Inorg. Chem.*, **8**, 1714 (1969).

(26) See ref 27, and also R. Köster and G. W. Rotermund, *Justus Liebigs Ann. Chem.*, **689**, 40 (1965).

(27) S. Trofimenko, *J. Amer. Chem. Soc.*, **89**, 3165 (1967).

(28) S. Trofimenko, *ibid.*, **89**, 4948 (1967).

(29) C. W. Heitsch, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstract No. L109.

(30) S. Trofimenko, *J. Amer. Chem. Soc.*, **92**, 5118 (1970).

(31) J. P. Jesson, S. Trofimenko, and D. R. Eaton, *ibid.*, **89**, 3158 (1967).

(32) J. P. Jesson and J. F. Weiher, *J. Chem. Phys.*, **46**, 1995 (1967).

(33) J. P. Jesson, J. F. Weiher, and S. Trofimenko, *ibid.*, **48**, 2058 (1968).

(34) P. Meakin, private communication.

ture of a labile second sphere coordination complex[35] between [HB(pz)₃]₂Co and pyridine or aniline, using [HB(pz)₃]₂Zn as a diamagnetic reference. The effect of dipolar interactions, resulting from the magnetic anisotropy of the cobalt chelate, on the nmr spectra of the complexing molecules was used for this purpose. It was found that both aniline and pyridine show a preferred direction of approach perpendicular to the threefold symmetry axis of [HB(pz)₃]₂Co: aniline orients itself with the NH₂ group toward the cobalt complex, while pyridine does so with the γ-H. Enthalpies of −2.4 ± 0.2 kcal and −2.9 ± 0.3 kcal were obtained for these complexations.

A detailed study of optical and paramagnetic resonance data[36] of [HB(pz)₃]₂Co and of its carbon analog [HC(pz)₃]₂Co²⁺ yielded accurate g values for the lowest Kramers doublet in these complexes and approximate g values for the other levels in the ground-state manifold. The principal g tensor components showed a large axial anisotropy as established by single-crystal epr results at 4.2°K (e.g., for [HB(pz)₃]₂Co $g_\| = 8.534 \pm 0.005$ and $g_\perp = 0.807 \pm 0.005$).

From a combination of high-resolution nmr, epr, and optical data derived from several substituted [HB-(pz)₃]₂Co complexes a quantitative evaluation of the dipolar contribution to the proton resonance shifts in the ligands was carried out.[37] This made it possible to achieve an approximate separation of the dipolar and scalar contributions to the shifts; the scalar contributions were found to be similar to those in corresponding Ni(II) complexes.

An X-ray study of [HB(pz)₃]₂Co which crystallizes in the centrosymmetric monoclinic space group confirmed[16] the approximate (although not precise) D_{3d} symmetry of this molecule, the central cobalt atom being in a trigonally distorted octahedral environment. The distortion from D_{3d} symmetry entails slight rotations of the pyrazolyl rings about their appropriate N(1)–N(2) axes and is probably a result of *inter*molecular repulsions in the crystal. The average Co–N distance is 2.129 Å, while the other distances are: B–N = 1.544 Å, N–N = 1.364 Å, N–C = 1.335 Å, and C–C = 1.386 Å. From these data it follows that the cobalt atom is substantially, although not completely, screened by H-3 and, by extrapolation, that the metal would be completely screened by 3-methyl (or larger) groups.

The tetrahedral [H₂B(pz)₂]₂Co chelate was found to have shorter Co–N distances (1.99 Å) but longer B–N distances (1.58 Å).[9]

Conclusion and Perspectives

The poly(1-pyrazolyl)borate ligand system, despite its seemingly exotic nature, may now be regarded as a common and useful type of ligand. Both bidentate

and tridentate variants thereof assure the formation of monomeric bis chelates. This property is mandatory in a number of comparative physical studies where it is essential to have a constant environment around the metal, unperturbed by dissociation, dimerization, solvolysis, etc. A fine example of such a system is provided by the compact octahedral [RB(pz)₃]₂M compounds where the metal lies safely buried in the center of the molecule. Even more protection is accorded to the metal in the readily available [HB(3,5-(CH₃)₂-pz)₃]₂M compounds.

The RB(pz)₃⁻ ligand and its substituted analogs are useful as reagents for the isolation and identification of organometallic compounds. In this function they stabilize compounds that would be otherwise hard to isolate.

Some of the attractive features of this new ligand system are summarized below. (1) Stable alkali metal salts are readily available. They are indefinitely stable in air; some are quite stable in aqueous solution. (2) Stable free acids derived from the [RₙB(pz)₄₋ₙ]⁻ ligands may be prepared and used for synthesis of salts, unavailable by the direct route, such as quaternary ammonium salts which have good solubility in organic solvents. (3) The three hydrogens on pyrazolyl groups in the diamagnetic (and even in some paramagnetic) complexes can be used as a reference for proton count and also as a convenient nmr probe of molecular symmetry. (4) Diversely carbon- and boron-substituted ligands are readily prepared. This makes it possible to introduce up to ten substituents into the HB(pz)₃ ligand, thus altering the steric and electronic effects around the metal while leaving the original symmetry intact. (5) For each polypyrazolylborate ligand there exists an isosteric and isoelectronic but neutral polypyrazolylmethane counterpart which has the same coordinative behavior, but leads to complexes with a charge greater by 1+ per ligand.[30]

The greatest promise for polypyrazolylborates seems to lie in the "half-sandwich" area which has been only cursorily explored, in comparative physical studies on series of isostructural polypyrazolylborate compounds, and in the investigation of heavy metal derivatives. Another area of interest is the aromatic substitution on [HB(pz)₃]₂M systems akin to that done with metallocenes and the study of transformations of functional groups attached at various positions of a [HB(pz)₃]₂M cage, such a cage being treated as a basic molecular unit.

Lastly, in extending the isosteric and isoelectronic series of ligands RₙC(pz)₄₋ₙ and [RₙB(pz)₄₋ₙ]⁻ a very worthwhile goal would be the synthesis of beryllium analogs, [RₙBe(pz)₄₋ₙ]²⁻, which, in the case of Be-(pz)₄²⁻, have the potential to act as both bis uninegative bidentate or dinegative tridentate. The study of coordination chemistry based on these beryllium-derived ligands should prove to be extremely fruitful.

(35) D. R. Eaton, *Can. J. Chem.*, **47**, 2645 (1969).
(36) J. P. Jesson, *J. Chem. Phys.*, **45**, 1049 (1966).
(37) J. P. Jesson, *ibid.*, **47**, 582 (1967).