

Pyrolyses of the Triaminodioxyporphoranes XIII, XV, XVI, and XIX. The phosphoranes XIII, XV, XVI, and XIX were stable up to 140°. Decomposition was quite rapid in the temperature range of 155–160°. No volatile perfluoro ketones were evolved during the pyrolyses. The residues were analyzed by P^{31} nmr with the following conclusions: (1) pyrolysis of the hexafluoroacetone-pyrrolidino phospholane adduct, XIII, at 155°; no phosphoramidate, XVII, was produced. Two P^{31} nuclei were produced in a 1:1.6 ratio. The minor signal was a triplet, $\delta P^{31} = +16.6$, $J_{PF} = 954$ cps; the major signal was a quintuplet, $\delta P^{31} = +144.6$ ppm, $J_{PF} = 704$ cps. (2) With pyrolysis of hexafluoroacetone-dimethylaminophospholane, XV, at 160°, there were two nuclei in a 1:3 proportion. The minor signal was a triplet at $\delta P^{31} = +16.3$, $J_{PF} = 955$ cps. The major signal was a quintuplet at $\delta P^{31} = +144.4$ ppm, $J_{PF} = 713$ cps. (3) With pyrolysis of the trifluoroacetophenone-pyrrolidino phospholane adduct, XVI, at 155°, there were small amounts of amidate, XVII, at $\delta P^{31} = -23.8$ ppm. There was a triplet at $\delta P^{31} = +15.0$ ppm, $J_{PF} = 961$ cps. There was a very weak quintuplet, which was not calibrated. (4) With pyrolysis of the trifluoroacetophenone-dimethylaminophospholane adduct, XIX, at 158°; three nuclei were present in a 2.5:1:3.0 proportion respectively at $\delta P^{31} = -27.5$ ppm (amidate XX), a triplet at $\delta P^{31} = +15.2$ ppm, and a quintuplet at $\delta P^{31} = +144.5$ ppm.

Reaction of Fluorenone, XXII, with 2-N-Pyrrolidino-1,3-dimethyl-1,3,2-diazaphospholane, XII. A solution of the aminophosphine XII (4.2 g) in 5 ml of CH_2Cl_2 was added over a 5-min period to a stirred solution of fluorenone, XXII (8.5 g, 2 mole equiv), in 5 ml of CH_2Cl_2 at 0°. The solution changed immediately from yellow to orange, and within 10 min crystallization took place. The mixture was kept 24 hr at 20°, and the solvent was evaporated (20 mm). The yellow solid was triturated with five 100-ml portions of ether. The colorless solid, XXIII (3.26 g), had mp 140–142°, and was analyzed without further purification. It can be recrystallized from benzene-pentane.

Anal. Calcd for $C_{24}H_{24}O_2N_3P$: C, 74.6; H, 6.2; N, 7.7; P, 5.7. Found: C, 74.7; H, 6.4; N, 7.9; P, 5.3; $\delta P^{31} = +40.3$ ppm (CH_2Cl_2).

The H^1 nmr in $CDCl_3$ had 16 aromatic protons at τ 2.5 and 3.1, and 18 aliphatic protons which included a doublet at τ 7.46, $J_{HP} = 9.7$ cps (CH_3N), a multiplet centered at τ 6.7 ($\alpha-CH_2$), and a multiplet at τ 8.2 ($\beta-CH_2$).

The infrared spectrum in CH_2Cl_2 had bands (μ): 6.25 (w), 6.35 (w), 6.95 (m), 7.50 (m), 8.30 (s), 8.65 (s), 9.05 (m), 9.30 (m), 9.6 (s), 9.95 (s), 10.5 (s), and 10.75 (s).

The ether solution was evaporated giving 9 g of additional material; the spectral characteristics of the latter were very similar to those of pure adduct XXIII; total yield: 90%.

Thermal Decomposition of the Fluorenone-2-N-Pyrrolidino-1,3-dimethyl-1,3,2-diazaphospholane, XXIII. a. In Diglyme. A solution of the adduct (1.85 g, 3.4 mmoles) in 5 ml of diglyme was heated 30 min at 150°. The pale yellow solution became dark red. The P^{31} nmr spectrum contained only one signal for the amidate, XVII. The solution was passed through a column (12 × 1 in.) of neutral alumina. The column was eluted with C_6H_6 and the deep red fraction was collected. This solution was distilled first at 20° (20 mm) to remove benzene, then at 100° (0.1 mm) to remove the diglyme. The residue was sublimed at 150° (0.1 mm) to yield fluorenone (50% of the theoretical based on dissociation of the 2:1 adduct into the 1:1 adduct), identified by its infrared spectrum. No pure material could be obtained from the dark residue.

b. In Benzene. A benzene solution of the adduct XXIII was kept at reflux for 5 hr. The P^{31} nmr spectrum showed only traces of the amidate and unchanged adduct.

Reaction of Fluorenone, XXII, with Tris(dimethylamino)phosphine, V. The aminophosphine (2.66 g, 16.3 mmoles) was added to a solution of fluorenone (2.93 g, 16.3 mmoles) in 6.5 ml of methylene chloride (2.5 M) at 20°. The solution became deep red within 1–2 min. The infrared spectrum was examined at intervals. After 4 hr, the reaction was about 90% complete. The infrared band at 5.85 μ due to fluorenone had almost disappeared; the infrared band at 10.18 μ characteristic of hexamethylphosphoramide had appeared. The P^{31} nmr spectrum contained only a single peak at $\delta P^{31} = -23.9$ ppm due to the amidate. The solution was evaporated, and the residue was distilled at 0.1 mm and a bath temperature of 150° to recover the amidate (2.40 g, 82%). The solid residue was recrystallized from benzene to yield dibiphenyleneethylene, XXIV, in about 50% yield; it was identified by comparison of its infrared spectrum with an authentic sample. One recrystallization from ethanol gave deep red needles of XXIV, mp 183–185° (lit.¹³ mp 187°).

A series of reactions of fluorenone with tris(dimethylamino)phosphine was carried out in methylene chloride solution at 20° with the reagents in 2:1, 1:1, and 1:2 proportions. The course of the reactions was followed by infrared and P^{31} nmr spectrometry. When 1 mole of the aminophosphine was added to 2 moles of the fluorenone, 1 mole of the latter remained unchanged at the end of the reaction. When 2 moles of the aminophosphine was added to 1 mole of fluorenone, the latter was completely consumed, but 1 mole of the aminophosphine remained unchanged at the end of the reaction. In the equimolar reaction, both reactants were consumed; the amidate was isolated in 85% yield and the dibiphenyleneethylene was isolated in 50% yield; the latter was formed in excess of this amount.

Boron-Pyrazole Chemistry. IV. Carbon- and Boron-Substituted Poly(1-pyrazolyl)borates

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Abstract: Syntheses of bidentate and tridentate alkali metal poly(1-pyrazolyl)borates containing substituents on carbon or boron and of transition metal compounds derived therefrom are described. Their properties are discussed.

In one of the preceding papers of this series,¹ we reported the syntheses and properties of salts, free acids, and coordination compounds derived from uninegative ligands of the general formula² $[H_nB(pz)_{4-n}]^-$ where n was 0, 1, and 2. The above structures where

n is 2 and 1 are parent compounds, each representing a new class of coordinating ligands. The former is bidentate, resembling conventional chelating agents such as acetylacetonate ion; the latter is tridentate of C_{3v} symmetry and as such without precedent. Their optical, electronic, and nmr spectroscopic properties have been reported³ as has the intriguing case of spin

(1) S. Trofimenko, *J. Am. Chem. Soc.*, **89**, 3170 (1967).

(2) "pz" stands for the 1-pyrazolyl residue.

Table I. Compounds of Structure $M \left[\text{H}_2\text{B} \left(\text{N} \begin{array}{c} \text{Y} \\ \text{X} \quad \text{X} \end{array} \right)_2 \right]_2$

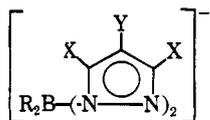
Color	M	X	Y	Mp, °C	Yield, %			Calcd, %			Found, %			Ultraviolet spectrum, $m\mu$ (ϵ)
					%	C	H	M	Z	C	H	N	M	
White	Mn	CH ₃	H	190–192	59	52.2	6.96	11.9	Mol wt 461	52.3	7.20	12.0	Mol wt 496 ^b	224 (26,500)
White (greenish tinge)	Fe	CH ₃	H	218–220	34 ^a	52.1	6.94	12.1	Mol wt 462	52.5	7.21	12.0	Mol wt 451 ^b	222 (21,800)
Purple-violet	Co	CH ₃	H	242–245	23 ^a	51.7	6.88	24.1	12.6	51.9	6.98	23.9	12.4	
Orange-red	Ni	CH ₃	H	245 dec	53	51.7	6.88	24.1	12.6	52.0	7.03	23.8	12.2	
Purple-violet	Co	CH ₃	CH ₃	282–283	65	55.3	7.68	21.5		55.6	7.45	22.3		
Orange-red	Ni	CH ₃	CH ₃	259–260 dec	57	55.3	7.68	21.5		55.5	7.26	22.0		

^a Yields of recrystallized material. ^b Ebullioscopic in ethylene chloride.

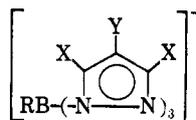
equilibrium⁴ found in Fe[HB(pz)₃]₂. A single-crystal epr study of Co[HB(pz)₃]₂ has also been published.⁵

In extending our work in the boron-pyrazole chemistry area, it was desirable to determine what effect the presence of diverse substituents on carbon or boron would have on the properties of transition metal poly-(1-pyrazolyl)borates and to devise synthetic approaches to such compounds. This paper reports some of the results of our studies from this point of view.

We shall consider, in turn, (A) bidentate ligands containing substituents on carbon (Ia) or boron (Ib) and the chelates derived therefrom, and (B) tridentate ligands with substituents on carbon (IIa) or boron (IIb) and their compounds with transition metals.



Ia, R = H; X and/or Y ≠ H
Ib, R ≠ H; X = Y = H



IIa, R = H; X and/or Y ≠ H
IIb, R ≠ H; X = Y = H

A special case of IIb, [B(pz)₄]⁻, has been discussed before.¹

Results and Discussion

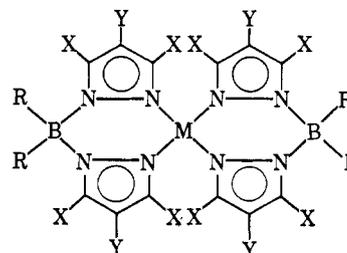
A. Bidentate Ligands. Bidentate ligands of structure Ia were prepared satisfactorily by the reaction of potassium borohydride with 3,5-dimethylpyrazole and 3,4,5-trimethylpyrazole in dimethylformamide or dimethylacetamide. The potassium salts were not isolated; the resulting solutions were used to prepare directly the first-row transition metal chelates of structure IIIa (X = CH₃, Y = H, and X = Y = CH₃), where M = Mn(II), Fe(II), Co(II), Ni(II), and Zn(II), which were obtained in fair yields (see Table I). The colors of these compounds were, essentially, the same as those of their C-unsubstituted analogs, M[H₂B(pz)₂]₂.

(3) J. P. Jesson, S. Trofimenko, and D. R. Eaton, *J. Am. Chem. Soc.*, **89**, 3148 (1967).

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

(5) J. P. Jesson, *J. Chem. Phys.*, **45**, 1049 (1966).

Again, the infrared spectra of compounds IIIa fell into two categories corresponding to the isomorphous square-planar (Ni, Cu) and tetrahedral (Mn, Fe, Co, Zn) chelates. It is noteworthy that the Mn and Fe chelates did not exhibit the extreme air sensitivity of Mn[H₂B(pz)₂]₂ and Fe[H₂B(pz)₂]₂ and were stable to storage. Such enhanced oxidative stability may be ascribed to the steric protection of the central metal by the methyl groups in tetrahedral chelates.



IIIa, R = H; X and/or Y ≠ H
IIIb, R ≠ H; X = Y = H

In the case of the square-planar chelates, where X = CH₃, only the chair form can be constructed from Stewart-Briegleb models, nonbonding interactions of the methyl groups precluding the construction of a boat form. By contrast, both chair and boat forms are unstrained in the parent system M[H₂B(pz)₂]₂. The BH₂ stretch region in the infrared was complex and consistent with an out-of-plane BH₂ group, as was also suggested by molecular models.

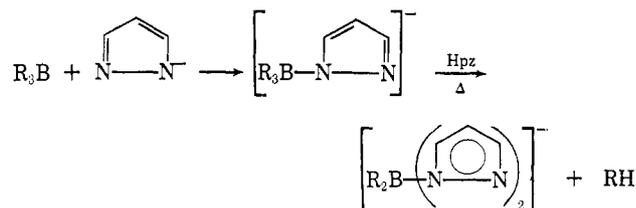
The above findings indicated that C-substituted pyrazoles behave much like pyrazole itself in forming the ligands of structure I. Hence, only pyrazole itself was used in synthesizing B-substituted bidentate ligands with the assumption that most substituted pyrazoles would be equally operable except, perhaps, those with very bulky 3,5 substituents.

Dialkylbis(1-pyrazolyl)borate ligands of structure Ib (R = Et or Bu) were prepared by the reaction of the appropriate trialkylborane with pyrazolide ion followed by heating with excess pyrazole.

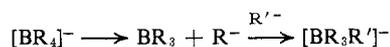
Table II. Compounds of Structure $M[R_2B-N(\text{pyrazolyl})_2]_2$

Color	M	R	Mp, °C	Yield, %	Calcd, %			Found, %			Nmr (mult, τ , J)	
					C	H	N	M	C	H		N
Purple	Co	C ₂ H ₅	103-104	47	51.6	6.88	24.1	51.5	6.98	24.3		
Orange	Ni	C ₂ H ₅	203-204	55	51.6	6.88	24.1	51.5	7.26	23.9		
Violet	Cu	C ₂ H ₅	200-201	49	51.1	6.82	23.9	50.9	6.68	24.4		
White	Zn	C ₂ H ₅	109-111	48	51.0	6.80		13.9	51.2	7.15	14.1	
Orange	Ni	<i>n</i> -C ₄ H ₉	185-186	49	58.2	8.32	19.4	10.2	57.9	8.23	19.8	d 2.49 (2.4), d 3.28 (2.2), t 4.03 (2.3), m 6.4, and two m, 8.5 and 9.0, in 1:1:1:1:8 ratio
Violet	Cu	<i>n</i> -C ₄ H ₉	168-170	39	57.7	8.25	19.3	58.0	8.78	18.9		
White	Zn	<i>n</i> -C ₄ H ₉	112-113	56	57.5	8.22	19.2	57.2	7.75	19.3	d 2.16 (2.3), d 2.55 (2.1), t 3.76 (2.2), m ~9, in 1:1:1:9 ratio	
Purple	Co	C ₆ H ₅	296-298	99	65.8	4.88		65.9	5.05			
Orange	Ni	C ₆ H ₅	~390 dec	73	65.8	4.88		66.0	4.85			
Pale violet	Cu	C ₆ H ₅	294-295	71	65.4	4.84		65.4	5.05			

It is noteworthy that despite extended heating the reaction stopped at the disubstitution stage. Since alkyltris(1-pyrazolyl)borates are stable compounds,



this result may be rationalized as follows: if one assumes that a direct SN₂-type substitution on tetrasubstituted anionic boron is not feasible for steric reasons



and that the reaction proceeds *via* an SN₁-like dissociation then it should be apparent that from R₂B(pz)⁻ a much better departing entity would be the resonance-stabilized pyrazolide ion than the CH₃CH₂⁻ ion. The only reaction that could occur then would be the reintroduction of pyrazolide ion with regeneration of R₂B(pz)₂⁻.

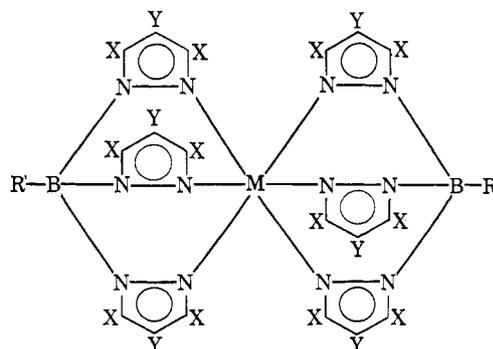
The crude sodium salts could be obtained as solids by removing all volatiles from the reaction mixture, but they were difficult to recrystallize. Hence, transition metal chelates of structure IIIb were prepared directly from the crude reaction mixture. Their properties are listed in Table II. Sodium diphenylbis(1-pyrazolyl)borate was prepared analogously from sodium tetraphenylborate and pyrazole. This salt was isolated and recrystallized from toluene.

Chelates of structure IIIb had the same colors as their B-unsubstituted counterparts. The presence of two alkyl groups on boron did not stabilize the tetrahedral Mn and Fe chelates (as did the presence of alkyl groups on carbon). These compounds were just as sensitive to air as Mn[H₂B(pz)₂]₂ and Fe[H₂B(pz)₂]₂. However, an interesting effect was observed in the square-planar compounds. For instance, Ni[Et₂B(pz)₂]₂ formed no complexes with pyridine, ammonia, or amines in contrast to the behavior of Ni[H₂B(pz)₂]₂. It was even recovered unchanged after prolonged reflux in boiling pyrazole under which

conditions Ni[H₂B(pz)₂]₂ is rapidly converted to Ni[HB(pz)₃]₂.

This inertness is ascribed to the screening of the nickel by one of the ethyl groups from each ligand (above and below the molecular plane). Support for this steric effect has been elicited from nmr. Thus while in 4,4,8,8-tetraethylpyrazole⁶ ten protons of the BEt₂ bridge appear as a fairly narrow pseudo-triplet at about τ 9, the nmr spectrum of Ni[Et₂B(pz)₂]₂ has only eight protons causing that signal. The remaining two are present as a complex multiplet at τ 6.3 (Figure 1). It is apparent from molecular models that only the methylene hydrogens of the "axial" ethyl group, which are positioned in close proximity to the metal, could experience a field effect sufficient to shift their resonance peak by 2.5 ppm. The "equatorial" methylene group experiences no such interaction and its resonance coincides with that of the methyl groups. A similar phenomenon was observed (Figure 2) in Ni[Bu₂B(pz)₂]₂: one methylene group per ligand was unique and was also shifted by about 2.5 ppm. Nevertheless Ni[Et₂B(pz)₂]₂ is hydrolyzed by boiling mineral acid just as readily as its B-unsubstituted analog. Apparently, the B-alkyl groups do not protect the nitrogen atoms from attack by protons.

B. Tridentate Ligands. Tridentate ligands containing C substituents were prepared by heating an alkali metal borohydride with an excess of appropri-



IVa, R = H; X and/or Y ≠ H
IVb, R ≠ H; X = Y = H

(6) S. Trofimenko, *J. Am. Chem. Soc.*, **89**, 3165 (1967).

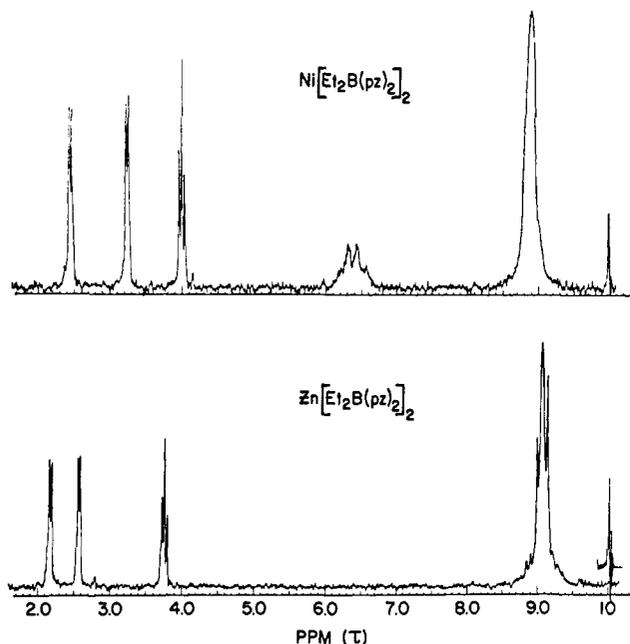


Figure 1. Nmr spectra of $\text{Ni}[\text{Et}_2\text{B}(\text{pz})_2]_2$ and $\text{Zn}[\text{Et}_2\text{B}(\text{pz})_2]_2$.

ately substituted pyrazole in the absence of solvent. The ligands of structure IIa prepared in this fashion include those where $\text{X} = \text{CH}_3$, $\text{Y} = \text{H}$; $\text{X} = \text{CH}_3$, $\text{Y} = \text{CH}_3$; $\text{X} = \text{CH}_3$, $\text{Y} = n\text{-C}_4\text{H}_9$; $\text{X} = \text{H}$, $\text{Y} = \text{Cl}$; and $\text{X} = \text{H}$, $\text{Y} = i\text{-C}_3\text{H}_7$. Some of the salts were isolated and purified as, for instance, the sublimable lithium and potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borates; others were not isolated but were converted directly to the transition metal compounds IVa.

The latter were all essentially octahedral, as judged by their electronic spectra, which were the same as in the corresponding $\text{M}[\text{HB}(\text{pz})_3]_2$ compounds, magnetic properties, and nmr studies.³ One notable exception was found in the case of octahedral iron(II) compounds having structure IVa ($\text{X} = \text{CH}_3$, $\text{Y} = \text{H}$, and $\text{X} = \text{Y} = \text{CH}_3$). These compounds were not magenta, like $\text{Fe}[\text{HB}(\text{pz})_3]_2$, but rather colorless with a faint greenish tinge. They were fully paramagnetic (μ_{eff} , room temperature, ~ 5.2 BM) in contrast to the "spin equilibrium" between high- and low-spin forms³ found in $\text{Fe}[\text{HB}(\text{pz})_3]_2$.

Molecular models show that substituents X and Y do not interfere with each other in essentially octahedral structures of D_{3d} symmetry such as IVa. The fact that salts of IIa where X is CH_3 require higher temperatures for their formation and that the reaction does not proceed to give, e.g., the tetrakis(3,5-dimethyl-1-pyrazolyl)borate ion may be rationalized in terms of steric crowding in the transition state.

Transition metal compounds of structure IVa containing large alkyl groups on carbon had enhanced solubility in organic solvents. The melting points and thermal stability of C-substituted compounds were substantially higher than those of the analogous $\text{M}[\text{HB}(\text{pz})_3]_2$ compounds. For instance, compounds IVa ($\text{X} = \text{H}$, $\text{Y} = \text{Cl}$) were stable in air above 400° (see Table III).

Tridentate ligands with substituents on boron were synthesized in two ways, exemplified by the specific cases shown in eq 1 and 2. In the former, phenyl-

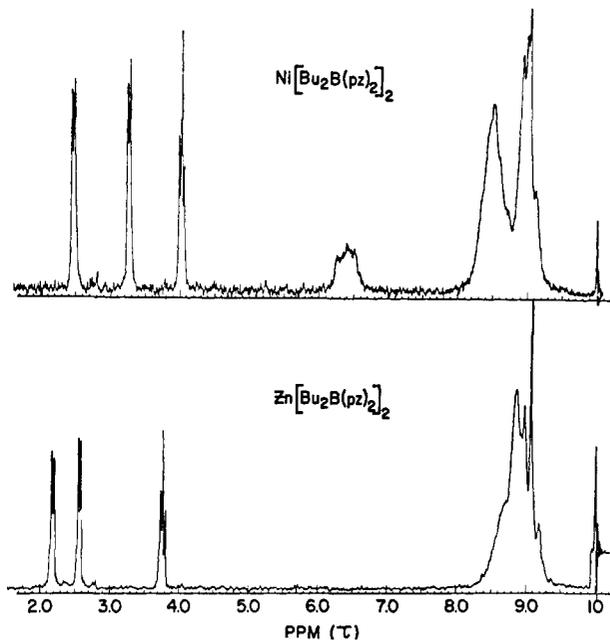
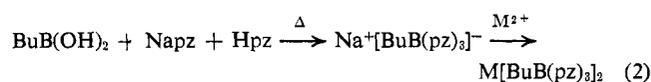
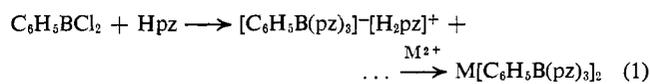


Figure 2. Nmr spectra of $\text{Ni}[\text{Bu}_2\text{B}(\text{pz})_2]_2$ and $\text{Zn}[\text{Bu}_2\text{B}(\text{pz})_2]_2$.

dichloroborane was added to excess pyrazole in ben-



zene. This reaction also gives rise to 4,8-diphenyl-4,8-bis(1-pyrazolyl)pyrazole.⁷ The two products are easy to separate, however, since one can extract the phenyltris(1-pyrazolyl)borate salt with water and prepare the transition metal compounds, IVb, directly from this solution. These compounds were similar to those derived from the $\text{B}(\text{pz})_4^-$ ion. Of course, lacking the uncoordinated pyrazole group, they were insoluble in acid.

The reaction of butylboronic acid with sodium pyrazolide and excess pyrazole gave, after distilling out water, crude sodium butyltris(1-pyrazolyl)borate, which was difficult to recrystallize. However it could be used directly to prepare compounds of type $\text{M}[\text{BuB}(\text{pz})_3]_2$. The properties of compounds $\text{M}[\text{C}_6\text{H}_5\text{B}(\text{pz})_3]_2$ and $\text{M}[\text{BuB}(\text{pz})_3]_2$ are summarized in Table IV.

The reaction of boron trifluoride etherate with 3,5-dimethylpyrazolide ion gave rise to the difluorobis(3,5-dimethyl-1-pyrazolyl)borate ion, isolated in the form of its cobalt and nickel chelates.

As can be seen from the foregoing examples, synthetic routes are available for the synthesis of bidentate and tridentate ligands with a wide variety of substituents on carbon or boron. The original symmetry of the parent ligand is maintained in most cases. Steric factors are of greater significance in the square-planar and tetrahedral chelates than in the octahedral transition metal compounds.

Experimental Section

Pyrazole, 3,5-dimethylpyrazole, triethylborane, tributylborane, phenyldichloroborane, butylboronic acid, and sodium tetra-

(7) S. Trofimenko, *J. Am. Chem. Soc.*, **89**, 4948 (1967).

Transition metal dihydrobis(3,4,5-trimethyl-1-pyrazole)borates were prepared as in the preceding experiment and are listed in Table I.

Transition Metal Diethylbis(1-pyrazolyl)borates. To a nitrogen-blanketed suspension of 14 g (0.33 mole) of 56% sodium hydride in 100 ml of tetrahydrofuran was added a solution of 20.4 g (0.3 mole) of pyrazole. When the theoretical amount of hydrogen had been evolved (7.5 l.), 42 ml (0.3 mole) of triethylborane was added slowly. The solution was refluxed briefly and then 68 g (1 mole) of pyrazole was added in portions. Tetrahydrofuran was distilled at atmospheric pressure. The residue was heated further by means of an oil bath. At about 160° ethane evolution commenced. The reaction mixture was heated overnight at 170° and then pyrazole was distilled out *in vacuo*. The residue was boiled in 1 l. of heptane, filtered, and dried. There was obtained 68 g (97%) of crude sodium diethylbis(1-pyrazolyl)borate as a light tan solid, which was used for subsequent reactions without further purification. In a typical reaction 50 ml of a 0.5 M solution of the appropriate cation was added to a solution of 10 g of the above crude sodium salt in 200 ml of water. The product was isolated by extraction with ether. After stripping the solvent, the residue was purified by recrystallization—the Ni and Cu chelates from xylene, the Zn chelate from hexane. Their properties are shown in Table II.

Transition Metal Dibutylbis(1-pyrazolyl)borates. To a solution of freshly prepared sodium pyrazolide (from 8.82 g of 55.6% NaH and 13.6 g of pyrazole, both 0.2 mole) in 150 ml of dry tetrahydrofuran was added slowly 50 ml (0.2 mole) of tributylborane. The reaction mixture was refluxed 15 min, then 40 g (0.59 mole) of pyrazole was added. Tetrahydrofuran was distilled out and then the reaction mixture was heated to the reflux temperature of pyrazole. About 3 l. of gas was evolved (0.12 mole) rapidly and no further evolution occurred on 48-hr reflux. The melt was cooled and dissolved in water. Aliquots of this solution were stirred with solutions of the appropriate metal ion. The products were extracted with methylene chloride. The extracts were dried, filtered, and stripped of solvent. The residues were stirred with methanol, filtered, and air dried. The crude products were purified by recrystallization from heptane. Their properties are shown in Table II.

Sodium Diphenylbis(1-pyrazolyl)borate. A mixture of 250 g (3.7 moles) of pyrazole and 100 g (0.29 mole) of sodium tetraphenylborate was stirred and heated so that benzene distilled out slowly through a Vigreux column. After 47 g (0.6 mole) of benzene had been collected, pyrazole was distilled at reduced pressure until the residue became a thick slurry. This was boiled in 800 ml of hexane and filtered. The solid was recrystallized from toluene and was obtained in two crops of 98 and 24 g. It still contained pyrazole. The analytical sample was recrystallized once more and dried at 160° (1 mm) overnight.

Anal. Calcd for $C_{18}H_{16}BN_4Na$: C, 67.2; H, 4.97; B, 3.36. Found: C, 67.2; H, 5.17; B, 3.42.

Transition Metal Diphenylbis(1-pyrazolyl)borates. To 200 ml of 0.1 M $Na(C_6H_5)_2B(pz)_2$ (made from the crude reaction product from the above experiment) was added 20 ml of 0.5 M solution of the appropriate metal ion followed by 100 ml of water. The precipitated product was filtered, washed with water, and air dried. It was purified by recrystallization from *o*-dichlorobenzene. The properties of the products are listed in Table II.

Potassium Hydrotris(3,5-dimethyl-1-pyrazolyl)borate. A mixture of 54 g (1 mole) of potassium borohydride and 480 g (5 moles) of 3,5-dimethylpyrazole was heated with stirring until 75 l. of hydrogen (3 moles) was evolved. The melt temperature was 238° and the evolution of hydrogen ceased at this point. The melt was cooled to 200° and poured into 2 l. of stirred toluene. The mixture was cooled to room temperature and the precipitate was filtered and air dried. There was obtained 114 g (34%) of white solid, indicating considerable solubility of this potassium salt in toluene. The product, purified by sublimation at 280° (1 mm), melts at 298–300° dec.

Anal. Calcd for $C_{15}H_{22}BKN_6$: C, 53.6; H, 6.55. Found: C, 53.7; H, 6.72.

Lithium Hydrotris(3,5-dimethyl-1-pyrazolyl)borate. A mixture of 4.6 g (0.2 mole) of lithium borohydride and 96 g (1.0 mole) of 3,5-dimethylpyrazole was heated under reflux until 0.6 mole of hydrogen was evolved. The melt was allowed to cool; it was crushed and heated overnight at 150° (1 mm) to sublime almost all excess 3,5-dimethylpyrazole. The residue was recrystallized from xylene and obtained in two crops, 24.2 and 6.0 g. An analytical sample was purified by sublimation. The pure product melts at 304–305°.

Anal. Calcd for $C_{15}H_{22}BLiN_6$: C, 59.2; H, 7.24; N, 27.6; Li, 2.3. Found: C, 59.3; H, 7.03; N, 27.7; Li, 2.2.

Transition metal hydrotris(3,5-dimethyl-1-pyrazolyl)borates were prepared by adding to a solution of the above potassium salt in 1:1 aqueous dimethylformamide a 10% excess of the appropriate transition metal ion. The resulting precipitates were filtered, washed with water, and air dried. They were purified further by recrystallization from toluene. Their properties are listed in Table III.

Potassium Hydrotris(3,4,5-trimethyl-1-pyrazolyl)borate. A mixture of 27 g (0.5 mole) of potassium borohydride and 275 g (2.5 moles) of 3,4,5-trimethylpyrazole was heated, ultimately at 220–230°, until about 38 l. of hydrogen was evolved. The melt was cooled, broken up, and heated to sublime unreacted 3,4,5-trimethylpyrazole which was recovered in 94 g (85%) yield. The residue was used directly in subsequent syntheses. The potassium salt sublimes at 280° (1 mm).

Anal. Calcd for $C_{18}H_{26}BKN_6$: N, 22.2. Found: N, 22.1.

Transition metal hydrotris(3,4,5-trimethyl-1-pyrazolyl)borates were prepared by adding to a solution of the above salt in 1:1 aqueous dimethylformamide a 10% excess of the appropriate transition metal ion. The products were filtered, washed with water, and air dried. They were purified further by recrystallization from cyclohexane. Their properties are listed in Table III.

3,5-Dimethyl-4-butylpyrazole. A solution of 33.2 g (0.212 mole) of 3-butyl-2,4-pentanedione¹⁰ in 50 ml of methanol was added slowly at 10° to 11.0 g (0.233 mole) of hydrazine hydrate in 100 ml of methanol. The solution was stripped and the residual oil was distilled to give 25 g (78%) of 3,5-dimethyl-4-butylpyrazole, bp 119–120° (1 mm), which solidified on standing, mp 44–45°.

Anal. Calcd for $C_9H_{16}N_2$: C, 71.0; H, 10.6; N, 18.4. Found: C, 71.1; H, 10.6; N, 18.5.

Transition Metal Hydrotris(3,5-dimethyl-4-butylpyrazolyl)borates. A mixture of 30 g (0.20 mole) of 3,5-dimethyl-4-butylpyrazole and 3.6 g (0.066 mole) of potassium borohydride was heated slowly to 290° with stirring, until 4.6 l. of hydrogen was evolved. The melt was cooled and dissolved in 260 ml of dimethylformamide. Aliquots of this solution were stirred with solutions of the appropriate transition metal ion. The products were isolated by filtration and purified by recrystallization from xylene. Their properties are listed in Table III.

Transition Metal Hydrotris(4-chloro-1-pyrazolyl)borates. A mixture of 148 g (1.4 moles) of 4-chloropyrazole and 19 g (0.35 mole) of potassium borohydride was heated until 27.4 l. of hydrogen was evolved, at which point the reaction stopped. The melt was cooled and dissolved in 1 l. of water. Aliquots of this solution were stirred with solutions of the appropriate cation. The precipitated products were isolated by filtration. They were washed with water, then methanol, and were air dried. Further purification was effected by recrystallization from *o*-dichlorobenzene. The properties of the products are listed in Table III.

Transition Metal Hydrotris(4-isopropyl-1-pyrazolyl)borates. A mixture of 1.3 g (0.013 mole) of 4-isopropylpyrazole¹¹ and 0.23 g (0.004 mole) of potassium borohydride was heated in a test tube with a Bunsen flame until the reaction mixture reached a temperature of 210°. It was then cooled to 170° and poured on ice. The product was dissolved by dropwise addition of 20% hydrochloric acid. The solution was stirred with 20 ml of a 0.5 M solution of the approximate transition metal ion. The precipitated solid was extracted with methylene chloride; the extracts were dried, filtered, and stripped. The residue was purified by recrystallization from toluene. Properties of the products are listed in Table III.

Transition Metal Butyltris(1-pyrazolyl)borates. To 1 mole of sodium pyrazolide (prepared from sodium hydride and pyrazole) in 800 ml of tetrahydrofuran was added 280 g (4 moles) of pyrazole and 102 g (1 mole) of *n*-butylboronic acid. The resulting solution was stirred and heated until tetrahydrofuran, water, and pyrazole distilled, in that order, at atmospheric pressure. After about 50 ml of pyrazole (bp 185°) had distilled, heating was stopped. The melt was cooled and dissolved in 3 l. of water. The solution was stirred with decolorizing carbon and filtered and a small amount of mineral oil (from sodium hydride suspension) was removed mechanically. Aliquots of the resulting solution were stirred with solutions of the appropriate metal ion. The precipitated products

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were extracted with methylene chloride. The extracts were dried, filtered, and stripped. The residues were stirred with methanol and the mixtures were filtered. Further purification was effected by recrystallization from heptane. Properties of the products are listed in Table IV.

Transition Metal Phenyltris(1-pyrazolyl)borates. To 100 g (1.46 moles) of pyrazole stirred in 240 ml of toluene was added over 2 hr a solution of 20 g (0.12 mole) of phenyldichloroborane in 35 ml of toluene. The reaction was exothermic, the temperature of the solution rising to 45–55°. The solution was cooled to room temperature and was stirred with 170 ml of a 0.5 M solution of the appropriate cation. The resulting mixture was filtered and the product was recrystallized from *o*-dichlorobenzene. The original toluene solution was stripped to dryness and the residue was triturated with ether to yield a second crop of the same material. Properties of the products are summarized in Table IV.

Transition Metal Difluorobis(3,5-dimethyl-1-pyrazolyl)borates. To sodium 3,5-dimethylpyrazolide (prepared from 16 g (0.167

mole) of 3,5-dimethylpyrazole and sodium hydride) in 300 ml of dry tetrahydrofuran was added 0.083 mole of boron trifluoride etherate and the reaction mixture was refluxed overnight. It was then evaporated to dryness, taken up in water, and extracted once with benzene. The benzene extracts were discarded. The aqueous layer was divided into two halves which were treated, respectively, with 40-ml portions of 0.5 M Ni(OAc)₂ and Co(OAc)₂ solutions. The precipitated solids were filtered, washed with water, and air dried.

The orange nickel chelate, obtained in 1.8 g (10%) yield, was purified by sublimation, mp 349–350°.

Anal. Calcd for C₂₀H₂₈B₂F₄NiN₈: C, 44.7; H, 5.22; N, 20.9; F, 14.2. Found: C, 44.6; H, 5.25; N, 20.9; F, 14.9.

The deep violet cobalt chelate, obtained in 1.8 g (10%) yield, was purified by chromatography on alumina, eluting with methylene chloride. The pure compound melts at 279–280°.

Anal. Calcd for C₂₀H₂₈B₂CoF₄N₈: C, 44.7; H, 5.22; N, 20.9. Found: C, 44.6; H, 5.09; N, 20.6.

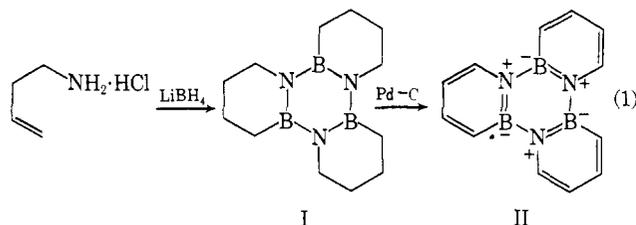
New Heteroaromatic Compounds. XXVI.¹ Synthesis of Borazarenes²

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Abstract: Hydrolysis of 14,16,18-tribora-13,15,17-triazarotriphenylene (II) gave bis(2-borazaryl) ether which reacted with phenylmagnesium bromide to give 2-phenylborazarene and with lithium aluminum hydride to give, apparently, borazarene. Other derivatives of borazarene were obtained by reactions of I with lithium alkyls.

An earlier paper of this series⁵ described the synthesis of 14,16,18-tribora-13,15,17-triazarotriphenylene (II) by the route given in eq 1. Treatment of II with



alkali led to its rapid destruction, as indicated by the disappearance of the characteristic triphenylene-like absorption in the ultraviolet spectrum, and it was thought at that time that the reaction had in fact led to a fission of the central borazine ring of II to give three molecules of 2-hydroxyborazarene (IIIa). This seemed a very interesting observation, for previous studies of the "borazaro" series of heteroaromatics had shown these to be compounds of remarkable stability to hydrolysis and oxidation⁶ and it seemed very likely that the same would prove true of borazarene

itself. Since in compounds of this kind hydroxyl attached to boron can be replaced⁶ by alkyl, aryl, or hydrogen by treatment with appropriate organometallic reagents or metal hydrides, a synthesis of IIIa would be expected to provide a very general route to other borazarene derivatives. Previously only two derivatives of borazarene had been reported, methyl β -(2,3-diphenyl-5-borazaryl)propionate (IV)⁷ and 2-phenylborazarene (IIIb),⁸ both of which were obtained by routes that could not easily be generalized. We have therefore reexamined the reaction of II with alkali, establishing that it does indeed lead to IIIa, and we have studied the preparation and properties of various borazarene derivatives derived in this or analogous ways from II.

The first problem was the synthesis of II itself. Not only were the yields in the original synthesis very low at each of the two key steps (<20%), but they were also very erratic; more often than not, the reactions failed completely. We have therefore reexamined the hydroboration of aminobutene and the dehydrogenation of I to II in detail, using a very wide variety of conditions, hydroborating agents, and dehydrogenation catalysts. The conditions reported here still give poor yields, but these are at least reproducible. It should be added that attempts to dehydrogenate I by chemical means (sulfur, selenium, manganese dioxide, etc.) were uniformly unsatisfactory.

(1) Part XXV: M. J. S. Dewar and R. Jones, *J. Am. Chem. Soc.*, **89**, 2408 (1967).

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