

THE COORDINATION CHEMISTRY OF PYRAZOLE-DERIVED LIGANDS

SWIATOSLAW TROFIMENKO

Plastics Department, E. I. du Pont de Nemours and Co., Wilmington, Delaware 19898

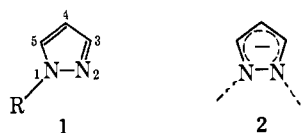
Received February 25, 1972

Contents

| | |
|--|-----|
| I. Introduction | 497 |
| II. Complexes of 2-Monohaptopyrazoles | 497 |
| III. Complexes of 1,2-Dihaptopyrazolide Ion | 499 |
| IV. Polydentate Ligands Containing One Pyrazole Ring and Their Complexes | 501 |
| V. Geminal Poly(1-pyrazolyl) Compounds and Their Complexes | 502 |
| A. Poly(1-pyrazolyl)borates | 502 |
| 1. Bidentate Bis Chelates | 503 |
| 2. Bidentate Mono Chelates | 503 |
| 3. Tridentate Bis Chelates | 504 |
| 4. Tridentate Mono Chelates | 504 |
| 5. Tetradentate Chelates | 505 |
| B. Physical Studies on Transition Metal Poly(1-pyrazolyl)borates | 506 |
| C. Poly(1-pyrazolyl)alkanes | 507 |
| 1. Bidentate Chelates | 507 |
| 2. Tridentate Chelates | 507 |
| VI. Miscellany | 508 |
| VII. Addendum | 508 |

I. Introduction

The pyrazole nucleus, **1**, is thermally and hydrolytically very stable. As a ligand, it coordinates to metals and metalloids through the 2-N, as do 1-alkylpyrazoles. When deprotonated, pyrazole becomes the pyrazolide ion, **2**, which can coordinate



through both nitrogen atoms as an exobidentate¹ ligand of C_{2v} symmetry. The nucleophilicity of the nitrogens and their steric accessibility may be varied through appropriate ring substitution.²⁻⁶ Despite these attractive features and despite

(1) The term "bidentate" alone all too frequently implies "chelate." We propose calling a chelating bidentate ligand "endobidentate" and a bidentate ligand which cannot form a chelate but has to bond to two separate metals or metalloids an "exobidentate" ligand.

(2) G. Dedichen, *Ber.*, **39**, 1831 (1906).

(3) I. I. Grandberg and A. N. Kost, *Dokl. Akad. Nauk SSSR*, **141**, 1087 (1961); *Proc. Acad. Sci. USSR*, **141**, 1251 (1961).

(4) I. I. Grandberg and A. N. Kost, *Zh. Obshch. Khim.*, **32**, 1556 (1962); *J. Gen. Chem. USSR*, **32**, 1542 (1962).

(5) I. I. Grandberg and A. N. Kost, *Zh. Obshch. Khim.*, **32**, 3025 (1962); *J. Gen. Chem. USSR*, **32**, 2974 (1962).

(6) I. I. Grandberg *Zh. Obshch. Khim.*, **32**, 3029 (1962); *J. Gen. Chem. USSR*, **32**, 3029 (1962).

the vigorous development of pyrazole chemistry in general,⁷ the coordination chemistry of pyrazole and of its derivatives received scant attention until the last decade.

This review covers compounds in which a pyrazole ring is N-bonded to a metal or metalloid. Most of the subject matter falls into the following four categories.

(1) Complexes involving a simple, pyridine-like coordination of a pyrazole or substituted pyrazole through the 2-N.

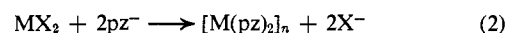
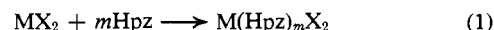
(2) Compounds in which pyrazolide ion, acting as a 1,2-dihapto exobidentate ligand, bridges two identical metals or metalloids.

(3) Asymmetric chelates containing the metal bound to one pyrazole nitrogen and to some other bonding site on a substituent attached to the pyrazole ring. These bidentate ligands may be neutral or uninegative.

(4) Compounds involving geminal poly(1-pyrazolyl) compounds⁸ as ligands. These ligands are neutral or uninegative and they range from bidentate to tetradentate.

II. Complexes of 2-Monohaptopyrazoles

The simplest and most thoroughly studied type of pyrazole complexes are $M(\text{Hpz})_nX_m$ where M is a transition metal, Hpz is a 2-monohaptopyrazole ligand, X is the counterion, and m is the valence of the transition metal, usually 2. These complexes are prepared readily by the reaction of metal salts with pyrazole or substituted pyrazoles in neutral or slightly acid media, since formation of pyrazolide polymers, e.g., $[M(\text{pz})_2]_n$, predominates under basic conditions. The number



of pyrazoles coordinated to the metal depends on a number of factors.

(1) *Coordinating Ability of the Counterion.* Maximal coordination of pyrazole ($m = 6$) is found when X is a noncoordinating anion such as NO_3 , BF_4 , or ClO_4 . Examples of $M(\text{Hpz})_6X_2$ compounds include $M = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Zn},$ and Cd .^{9,10} When X is halide ion, complexes $M(\text{Hpz})_4X_2$ are formed ($M = \text{Ni}, \text{Co},$ and Fe).⁹ The structures of $\text{Ni}(\text{Hpz})_6(\text{NO}_3)_2$, $\text{Ni}(\text{Hpz})_4\text{Cl}_2$, and $\text{Ni}(\text{Hpz})_4\text{Br}_2$ have been estab-

(7) A. N. Kost and I. I. Grandberg, *Advan. Heterocycl. Chem.*, **6**, 347 (1966).

(8) The abbreviation pz will be used to denote the 1-pyrazolyl group. When pz is written between other elements as in $\text{L}_2\text{M}(\text{pz})_2\text{ML}_2$, it will denote the existence of 1,2-dihaptopyrazolide bridges. Similarly, Hpz is pyrazole, 3,5- Me_2pz is 3,5-dimethyl-1-pyrazolyl residue, etc.

(9) N. A. Daugherty and J. H. Swisher, *Inorg. Chem.*, **7**, 1657 (1968).

(10) J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, **88**, 1451 (1969).

lished by X-ray crystallography.¹¹⁻¹⁴ In $\text{Ni}(\text{Hpz})_6(\text{NO}_3)_2$ the Ni ion lies at the center of a nearly regular octahedron of coordinated N atoms (Ni-N distance is 2.125 Å). In the $\text{Ni}(\text{Hpz})_4\text{X}_2$ complexes the halogens are coordinated to the Ni placing it again in an octahedral environment. The pyrazole rings are oriented vertically with respect to the plane defined by the Ni atom and the four coordinated nitrogens, and there exists a hydrogen bond between the 1-N and the halogen in both compounds.

(2) *Nature of the Metal Ion.* Hexakispyrazolecopper(II) complexes could not be prepared under any conditions. Copper(II) formed only tetracoordinate complexes $\text{Cu}(\text{Hpz})_4\text{X}_2$ regardless of the nature of X (Cl, Br, BF_4 , ClO_4 , SO_4 , NO_3).^{9, 15-17} Furthermore, species such as $\text{Cu}(\text{Hpz})_2\text{Cl}_2$ were also obtained as was $\text{Cu}(\text{H}3,5\text{-Me}_2\text{pz})(\text{OAc})_2$.¹⁷ The presence of 4-substituents such as Cl, Br, NO_2 , or of 1-Me did not alter the maximum CuL_4^{2+} stoichiometry.¹⁸

(3) *Substitution on the Pyrazole Ring.* A substituent in the 3 position introduces steric hindrance and makes it difficult to have six 3-substituted pyrazoles coordinated *via* the 2-N to a metal. This difficulty can be circumvented by coordination through a tautomeric 5-substituted structure, where steric hindrance is minimized. In fact, the highest apparent coordination number for a variety of transition metal ions (Mn, Fe, Co, Cd) has been reported¹⁶ in structures of the type $\text{M}(\text{H}3\text{-Mepz})_7(\text{ClO}_4)_2$, although the seventh pyrazole is regarded as being in the second coordination sphere. By contrast, $\text{H}3,5\text{-Me}_2\text{pz}$ which has both positions adjacent to the nitrogens substituted with methyl groups, forms only complexes of the type $\text{M}(\text{H}3,5\text{-Me}_2\text{pz})_4\text{X}_2$.^{16, 19} 4-Methylpyrazole has the methyl group far from the coordination site and, consequently, it behaves like pyrazole itself.¹⁶

Electronic spectra taken in solution⁹ or on single crystals of $\text{Ni}(\text{Hpz})_6^{2+}$ complexes²⁰ give ligand field Dq values of 1065-1080 cm^{-1} and indicate that pyrazole occupies a position similar to that of pyridine or ammonia in the spectrochemical series. 3(5)-Methylpyrazole which has an electron-releasing group should be a stronger coordinating ligand. This is indeed borne out by the ligand field and magnetic parameters of complexes prepared from $\text{H}3(5)\text{Mepz}$ and various M(II) salts (M = Mn, Fe, Co, Ni, Cu, Zn, and Cd).^{16, 21}

A more detailed study of electronic spectra of $\text{M}(\text{H}5\text{-Mepz})_2\text{X}_2$ for M = Mn, Fe, Co, Ni, and Cu, and X = NO_3 , Cl, Br, I, ClO_4 , and BF_4 showed considerable distortion from octahedral symmetry. This was attributed to hydrogen bonding between the ligand and the anion.²² Infrared and Raman spectra of these complexes show the NH vibration to be

strongly dependent on hydrogen bonding which was found to be greatest with chloride anions, followed by Br, I, NO_3 , and BF_4 , while no hydrogen bonding was observed with ClO_4 .²³

In all of the above complexes the coordinating species is 5- rather than 3-methylpyrazole. Final proof for this was obtained by an X-ray structure determination of $\text{Mn}(\text{H}5\text{-Mepz})_4\text{Br}_2$.²⁴ The epr spectra of complexes MnL_4X_2 where L = Hpz or H5-Mepz and X = Cl, Br, I, or NO_3 have been studied and interpreted in terms of a slightly distorted D_{4h} symmetry.²⁵ Likewise, Mössbauer spectra of FeL_6X_2 for L = Hpz or H5-Mepz and X = ClO_4 , Br, or I were found to be in accord with high-spin Fe(II) in distorted octahedral coordination.²⁶ When X = SCN, two isomers were isolated for $\text{ML}_4(\text{SCN})_2$ compounds (M = Mn and Ni). These were thought to be *cis* and *trans* isomers.²⁷

With 3,5-dimethylpyrazole, 3-methyl-5-phenylpyrazole, and 1,3,5-trimethylpyrazole cobalt complexes of the type CoL_2X_2 (X = Cl, Br, or SCN) have been prepared.²¹ A complex anion $[\text{CoBr}_3(\text{H}3,5\text{-Me}_2\text{pz})]^-$ was isolated as the Et_4N salt. The formation and extraction with organic solvents of 3,5-dimethylpyrazole-copper complexes of the type $\text{CuL}_2(\text{SCN})_2$ and $\text{CuL}_4(\text{SCN})_2$ have been studied colorimetrically.^{28, 29} Tetrahedral $\text{ML}_2(\text{NCS})_2$ complexes have been reported for M = Zn and Cd, while $\text{Cu}(\text{H}5\text{-Mepz})_2(\text{NCS})_2$ and $\text{Zn}(\text{Hpz})_3(\text{NO}_3)_2$ were considered as unique.²⁷

Apart from complexes of the first-row transition metals, pyrazole complexes of ruthenium in several oxidation states have been investigated. The blue solution of Ru(II), when treated with pyrazole or 3,5-dimethylpyrazole, produced species such as $\text{RuL}_3\text{Cl}_3^-$, $\text{RuCl}_2\text{L}_3(\text{H}_2\text{O})$, etc., characterized by analyses and conductivity data.³⁰ Pyrazole reacted with RuCl_3 to form the anion $\text{Ru}(\text{Hpz})\text{OHCl}_4^-$ which gave an insoluble silver salt and the neutral species $\text{Ru}(\text{Hpz})_3\text{Cl}_3$.³¹ The reaction of pyrazole with RuCl_4 in acid solution gave only $(\text{H}_2\text{pz})_2^+$ - RuCl_6^{2-} and no Ru-N-coordinated products.³² Complexes of the type L_2AgNO_3 and $\text{L}_2(\text{HgCl}_2)_3$, where L = 3(5)-methylpyrazole, have also been reported.³³

The 1-alkyl-substituted pyrazoles coordinate in the same way as pyrazole itself. This was taken advantage of in identifying 1,3- and 1,5-dimethylpyrazoles from changes in their nmr peaks upon formation of a complex with NiBr_2 .³⁴ It was noted that 5-ethynyl-1-methylpyrazole forms a complex with NiBr_2 but 3-ethynyl-1-methylpyrazole does not, presumably for steric reasons. The fluorescence of a number of 1-substituted pyrazoles complexed with ZnCl_2 and HgX_2 has been investigated.³⁵

(11) C. W. Reiman, A. Santoro, and A. D. Mighell, *Acta Crystallogr., Sect. B*, **26**, 521 (1970).

(12) C. W. Reiman, A. D. Mighell, and F. A. Mauer, *Acta Crystallogr.*, **23**, 135 (1967).

(13) C. W. Reiman, *Chem. Commun.*, 146 (1969).

(14) A. D. Mighell, C. W. Reiman, and A. Santoro, *Acta Crystallogr., Sect. B*, **25**, 595 (1969).

(15) D. Nichols and B. A. Warburton, *J. Inorg. Nucl. Chem.*, **33**, 1041 (1971).

(16) J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, **89**, 605 (1970).

(17) M. Inoue, M. Kishita, and M. Kubo, *Inorg. Chem.*, **4**, 626 (1965).

(18) J. Reedijk, J. C. A. Windhorst, and N. H. M. Van Ham, *Recl. Trav. Chim. Pays-Bas*, **90**, 234 (1971).

(19) S. N. Poddar, *Sci. Cult. (Calcutta)*, **35**, 28 (1969); *Chem. Abstr.*, **71**, 66820q (1969).

(20) C. W. Reiman, *J. Phys. Chem.*, **74**, 561 (1970).

(21) M. J. Bagley, D. Nichols, and B. A. Warburton, *J. Chem. Soc. A*, 2694 (1970).

(22) J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, **89**, 993 (1970).

(23) J. Reedijk, *ibid.*, **90**, 117 (1971).

(24) J. Reedijk, B. A. Stork-Blaisse, and G. C. Verschoor, *Inorg. Chem.*, **10**, 2594 (1971).

(25) R. D. Dowsing, B. Niewenhuijze, and J. Reedijk, *Inorg. Chim. Acta*, **5**, 301 (1971).

(26) J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, **90**, 1285 (1971).

(27) J. Reedijk and J. A. Smit, *ibid.*, **90**, 1135 (1971).

(28) B. Janik, H. Gawron, and J. Weyers, *Mikrochim. Ichnoanal. Acta*, **5-6**, 1142 (1965); *Chem. Abstr.*, **64**, 14947f (1966).

(29) B. Janik, H. Gawron, and J. Weyers, *Mikrochim. Acta*, 950 (1967); *Chem. Abstr.*, **68**, 6914b (1968).

(30) F. Kralik and J. Vrestal, *Collect. Czech. Chem. Commun.*, **27**, 1651 (1962).

(31) F. Kralik and J. Vrestal, *ibid.*, **26**, 1298 (1961).

(32) F. Kralik and J. Vrestal, *ibid.*, **26**, 1293 (1961).

(33) S. G. Matsoyan, E. G. Darbinian, and Y. B. Mitardzhyan, *Arm. Khim. Zh.*, **21**, 998 (1968); *Index Chemicus*, No. 112246 (1969).

(34) E. E. Zaev, V. K. Voronov, M. S. Shvartsberg, S. F. Vasilevsky, Yu. N. Molin, and I. L. Kotlyarevsky, *Tetrahedron Lett.*, **5**, 617 (1968).

(35) I. I. Grandberg, S. V. Tabak, and A. N. Kost, *Zh. Obshch. Khim.*, **33**, 525 (1963); *J. Gen. Chem. USSR*, **33**, 517 (1962).

In a study of selective extraction of transition metal ions into an organic phase from acidic aqueous solutions through complex formation with various 1,3,4,5-tetraalkyl- and 3,4,5-trialkylpyrazoles, it was shown that Fe(III), Zn(II), Cd(II), and Co(II) can be successfully extracted throughout the acidic range while optimum extraction for other ions is strongly pH dependent.³⁶

In addition to complexing with simple transition metal ions pyrazoles have been reported to coordinate with diverse organometallic species. Thus, the reaction of pyrazole with $C_5H_5CoI_2CO$ results in the displacement of CO and the formation of $C_5H_5CoI_2(Hpz)$ as an air-stable green solid.³⁷ Simple coordination by pyrazole to relieve coordinative unsaturation has been reported for $Et_2B(pz)_2Mo(CO)_2-\pi$ -allyl^{38,39} and for compounds such as $H_2B(pz)_2Mn(CO)_3$.⁴⁰ In each of these instances the addition of pyrazole gives rise to an inert gas configuration. Heating of the complex $H_2B(pz)_2Mn(CO)_3-(Hpz)$ converts it to $HB(pz)_3Mn(CO)_3$.⁴⁰

The reaction of $Fe(CO)_5$ with 3,5-dimethylpyrazole is reported⁴¹ to give the air-sensitive $(H3,5-Me_2pz)_2FeCO$ as a pink solid. A π -bonded sandwich structure has been tentatively proposed for this compound; this, however, seems unlikely. The above result contrasts with the reaction of iron pentacarbonyl with pyrazole itself, where $[Fe(pz)_2]_n$ is obtained.⁴² The reaction of iron enneacarbonyl and triiron dodecacarbonyl with pyrazole and 3,5-dimethylpyrazole gave the very unstable $HpzFe(CO)_9$ for which a π -complex structure was proposed, as well as $(Hpz)Fe(CO)_4$ and $(H3,5Me_2pz)Fe(CO)_4$.⁴³ The dimeric compounds $[pzFe(CO)_3]_2$ and $[3,5-Me_2pzFe(CO)_3]_2$, which may have a metallocyclic structure analogous to **5**, have also been reported.⁴³

The reaction of 3,5-dimethylpyrazole with chromium hexacarbonyl yields only the $LCr(CO)_6$ at any reactant ratios, while with tungsten hexacarbonyl either $LW(CO)_6$ or $L_2W(CO)_4$ may be obtained.⁴⁴ Another complex containing both pyrazole and carbonyl ligands is $RuCl_2(CO)_2(Hpz)_2$.^{45,46}

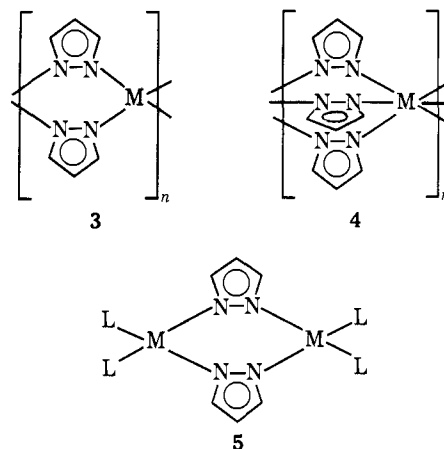
Complex formation between pyrazole and various metal ions has been investigated polarographically. With Cd(II) formation of $Cd(Hpz)_n^{2+}$ complexes was observed for $n = 1, 2, \text{ and } 3$ but not 4, even at high pyrazole concentrations.⁴⁷ In a comparative study of pyrazole and 3,5-dimethylpyrazole complexes with Cd(II) again only three complex species were detected for each.^{48,49} Complex formation between Pb(II) and pyrazole and between Ni(II) and Co(II) and 3,5-dimethyl-

pyrazole was studied. Stability constants were determined for the reversibly reduced Pb complexes and the irreversibly reduced complexes of Ni, as well as complexes of the substituted ligand.⁵⁰ With Zn(II) and pyrazole three weakly complexed species were detected while Cu(II) formed primarily the bis-coordinated species. Ni(II) gave evidence for the formation of all possible complexes up to $Ni(Hpz)_6^{2+}$. With Mn(II) only mono- and bis-coordinated ions were stable, while Fe(II) and Co(II) exhibited presence of complex ions up to $M(Hpz)_4^{2+}$.⁵¹

Association equilibria of pyrazole with protons, Ni(II), and Cu(II) have been studied as a function of ionic strength, and the first stability constants for the Ni(II) and Cu(II) complexes were determined.⁵²

III. Complexes of 1,2-Dihaptopyrazolide Ion

The ability to lose the 1 proton and to function as a uninegative, exobidentate 1,2-dihapto ligand of C_{2v} symmetry is a characteristic feature of pyrazole, distinguishing it from pyridine and other analogous nucleophiles. The geometry of pyrazolide ion permits it to act as a bridge between two identical or dissimilar metals or metalloids. With simply solvated metal ions this bridging leads to polymeric structures, **3**, or possibly **4**. In the case of **3** additional coordination of water, ammonia, etc., may occur placing the metal in an octahedral environment. In the presence of appropriate endcapping groups polymer formation is avoided and monomeric metallocycles, **5**, are produced.



Although pyrazolide ion is 1,2-diazacyclopentadienide ion, there is no evidence that it can form metallocene-type sandwiches, despite several claims to that effect.

Polymeric complexes containing the exobidentate 1,2-dihaptopyrazolide ligand have been known since 1889, when Buchner in his paper on pyrazole⁵³ reported the formation of the insoluble silver pyrazolide, $Ag(pz)$, which he simply denoted as "silver salt." In these early papers no distinction was made between true pyrazolide salts and salts such as $(H_2pz)_2PdCl_4$ where pyrazole exists in the protonated form and is not bonded to the metal. The structure of $Ag(pz)$ has never been established but is probably polymeric as in **6**. A similar structure exists probably in $Cu(pz)$ which has an infrared spectrum

(36) V. M. Dzionko, V. N. Avilina, and O. V. Ivanov, *Dokl. Akad. Nauk. SSSR*, **184**, 98 (1969); *Proc. Acad. Sci. USSR*, **184**, 4 (1969).

(37) D. J. O'Sullivan and F. J. Lalor, *J. Organometal. Chem.*, **25**, C80 (1970).

(38) S. Trofimenko, *J. Amer. Chem. Soc.*, **90**, 4754 (1968).

(39) S. Trofimenko, *Inorg. Chem.*, **9**, 2493 (1970).

(40) A. Bond and M. Green, *J. Chem. Soc. A*, 682 (1971).

(41) A. N. Nesmeyanov, M. I. Ribinskaya, N. S. Kochetkova, V. N. Babin, and G. B. Shulpin, *Dokl. Akad. Nauk SSSR*, **181**, 1397 (1968); *Proc. Acad. Sci. USSR*, **181**, 767 (1968).

(42) F. Seel and V. Sperber, *Angew. Chem.*, **80**, 38 (1968).

(43) V. N. Babin, L. A. Fedorov, N. S. Kochetkova, and Yu. A. Belousov, Abstracts of the Fifth International Conference on Organometallic Chemistry, Moscow, USSR, 1971, Paper 390, Vol. II, p 429.

(44) A. D. Garnovskii, N. E. Kolobova, I. B. Zlotina, G. K. Mitina, K. N. Anisimov, and O. A. Osipov, *ibid.*, 1971, Paper 108, Vol. I, p 291.

(45) M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, *Chem. Commun.*, 1325 (1970).

(46) M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, *J. Chem. Soc. A*, 2820 (1971).

(47) A. C. Andrews and J. K. Romary, *Inorg. Chem.*, **2**, 1060 (1963).

(48) D. R. Crow, *J. Polarogr. Soc.*, **11**, 22 (1965).

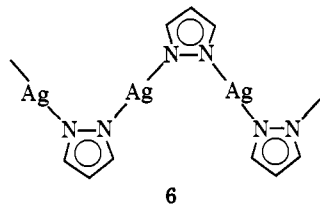
(49) D. R. Crow, *ibid.*, **11**, 67 (1965).

(50) D. R. Crow, *ibid.*, **12**, 101 (1966).

(51) D. R. Crow and J. V. Westwood, *J. Inorg. Nucl. Chem.*, **30**, 179 (1968).

(52) T. R. Musgrave and E. R. Humburg, Jr., *ibid.*, **32**, 2229 (1970).

(53) E. Buchner, *Ber.*, **22**, 842 (1889).



identical with that of $\text{Ag}(\text{pz})$. The colorless $\text{Cu}(\text{pz})$, which may be prepared either from $\text{Cu}(\text{NH}_3)_2^+$ and pyrazolide ion or by pyrolysis of $\text{Cu}(\text{pz})_2$,⁵⁴ may be recrystallized from diglyme and is sublimable *in vacuo*. The mass spectrum shows presence of mainly dimers and trimers in the vapor,⁵⁵ while preliminary X-ray data are compatible with an extended chain structure.⁵⁶

Buchner had also prepared silver salts of 4-bromo-, 4-iodo-, and 4-nitropyrazoles, as well as the HgCl derivative of pyrazole.^{57,58} Almost simultaneously, Balbiano⁵⁹ reported the synthesis of a mercury derivative of pyrazole and of the chloroplatinate, noting conversion of the latter on heating to $\text{Pt}(\text{pz})_2\text{Cl}_2$.

The area of pyrazole-metal compounds remained dormant for almost 40 years, although the synthesis of BrMgpz ⁶⁰⁻⁶² and Kpz ⁶³ was carried out, and these compounds were used to prepare various 1-acylated and alkylated derivatives of pyrazole *via* the reaction with active halogen compounds. The formation of alkali metal pyrazolides and indazolides *via* metalation with alkyllithium or arylsodium and their reactions, *inter alia*, with transition metal halides have been reported recently.⁶⁴ Silver pyrazolides have also been used for the purpose of organic synthesis.⁶⁵⁻⁶⁷

Pyrazolides of many divalent transition metals may be prepared by the reaction of ammoniacal solution of the metal salt with pyrazole. These polymeric chelates are solvated with water and/or ammonia but may be obtained pure by drying *in vacuo*.⁵⁴ A more convenient way to $[\text{M}(\text{pz})_2]_n$ is *via* pyrolysis of the acetates, $\text{M}(\text{Hpz})_2(\text{OAc})_2$.⁵⁵ The polymeric pyrazolides are intractable, thermally very stable solids. Some exhibit thermochromism (Ni, yellow \leftrightarrow orange at 250°; Cu, brown or green \leftrightarrow blue-violet at -196°). The $[\text{Cu}(\text{pz})_2]_n$ polymer may be obtained either as a brown (ammonia method) or green (acetate pyrolysis) solid. The brown modification can be converted to the green one upon heating with excess pyrazole.⁵⁵

Similar polymeric chelates were prepared from C-substituted pyrazoles 4-bromo-, 3,4-dibromo-, 3,4,5-tribromo-, 4-methyl-, 4-isopropyl-, and 4-cyano-. All of them are stable to alkali but are decomposed by acids. The $(3,4,5\text{-Br}_3\text{pz})_2\text{Cu}$ chelate is benzene soluble and exists there as a tetramer.⁵⁴

(54) S. Trofimenko, unpublished results.

(55) W. Mahler, personal communication.

(56) C. T. Fritchie, personal communication.

(57) E. Buchner, *Ber.*, **22**, 2166 (1889).

(58) E. Buchner and M. Fritsch, *Ann.*, **273**, 256 (1893).

(59) L. Balbiano, *Ber.*, **23**, 1103 (1890).

(60) Q. Mingola, *Gazz. Chim. Ital.*, **61**, 449 (1931).

(61) Q. Mingola, *ibid.*, **63**, 242 (1933).

(62) Q. Mingola and F. Ingrassia, *ibid.*, **64**, 279 (1934).

(63) W. Hüchel and H. Bretschneider, *Ber.*, **70**, 2024 (1937).

(64) B. A. Tertov, Z. N. Nazarova, A. D. Garnovskii, M. A. Kasanbueva, A. V. Koblik, Yu. A. Gabarayeva, V. V. Burikin, and P. P. Onyshchenko, Abstracts of the Fifth International Conference on Organometallic Chemistry, Moscow, USSR, 1971, Vol. II, Paper 280, p 141.

(65) H. Reimlinger, A. Noels, J. Jadot, and A. van Overstraeten, *Chem. Ber.*, **103**, 1942 (1970).

(66) H. Reimlinger, A. Noels, and J. Jadot, *ibid.*, **103**, 1949 (1970).

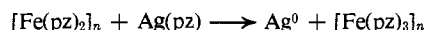
(67) H. Reimlinger, A. Noels, J. Jadot, and A. van Overstraeten, *ibid.*, **103**, 1954 (1970).

The silver derivative $(4\text{-}i\text{-C}_3\text{F}_7\text{pz})\text{Ag}$ is soluble in acetone where it is tetrameric. All silver pyrazolides are remarkably insensitive to light.⁵⁵

The bonding of the metal in pyrazolide complexes is to the 1-N even in cases where alternative coordination sites are available on the pyrazole ring. This was established from infrared spectra of the silver and sodium salts of 3-acylpyrazole⁶⁸ and 3,5-dimethyl-4-acylpyrazole.⁶⁹

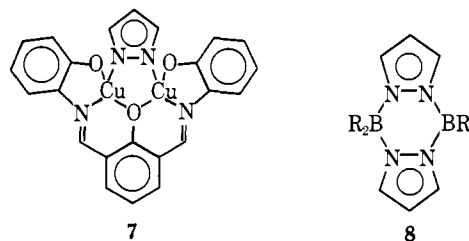
Among the various transition metal pyrazolides the most thoroughly studied one is the very insoluble purple cobalt chelate, $[(3,5\text{-Me}_2\text{pz})_2\text{Co}]_n$, which can be precipitated in analytical purity at pH 7.5-9.0. It has been suggested that precipitation of this complex be used for the gravimetric determination of cobalt.⁷⁰⁻⁷³ By contrast, the related 1-phenyl-3,5-dimethylpyrazole and 3,5-diphenylpyrazole did not react with $\text{Co}(\text{II})$. A sandwich structure has been proposed⁷² to account for the insolubility of $[(3,5\text{-Me}_2\text{pz})_2\text{Co}]_n$, but this explanation seems unlikely. The above compound may also be obtained from the reaction of $(\text{acac})_2\text{Co}$ with hydrazine.²¹ Similarly, insoluble purple cobalt chelates can be made from pyrazolide and 3-methylpyrazolide ions. A tetrahedral, polymeric structure has been suggested for these compounds. *Dq* and *B* parameters have been calculated, and the magnetic moments were found to be normal for tetrahedral complexes.²¹

Pyrazolides of $\text{Fe}(\text{II})$ and $\text{Fe}(\text{III})$ have been prepared by the reaction of pyrazole with a variety of iron derivatives such as $\text{Fe}(\text{CO})_5$, $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$, etc.⁴² While the air-sensitive $[\text{Fe}(\text{pz})_2]_n$ was prepared directly, the stable red-brown $[\text{Fe}(\text{pz})_3]_n$ was obtained either by the reaction



or by treatment of FeCl_3 with Kpz . Both iron pyrazolides are polymeric and as such insoluble except with decomposition.

There are numerous instances in which monomeric compounds contain one or more 1,2-dihaptopyrazolide groups bridging two identical or dissimilar metals or metalloids. The only example of a single bridging pyrazolide ion is the binuclear copper complex 7, synthesized as a possible model for nitrogen fixing systems.⁷⁴



Various different types of metallocycles containing two 1,2-dihaptopyrazolide (or substituted pyrazolide) bridges have been reported. They are of the general structure 5, and include $\text{M} = \text{Rh}$ ($\text{L} = \text{CO}$ and $\text{L}_2 = 1,5\text{-cyclooctadiene}$) and

(68) Yu. N. Scheinker, I. Ambrush, and N. K. Kochetkov, *Dokl. Akad. Nauk, SSSR*, **123**, 709 (1958); *Proc. Acad. Sci. USSR*, **123**, 929 (1958).

(69) V. G. Vinokurov, V. S. Troitskaya, I. D. Solokhina, and I. I. Grandberg, *Zh. Obshch. Khim.*, **33**, 506 (1963); *J. Gen. Chem. USSR*, **33**, 498 (1963).

(70) E. J. Fischer, *Wissen. Veröff. Siemens Konzern*, **4**, 178 (1925).

(71) W. T. Smith and R. L. Shriner, "The Examination of New Organic Compounds," Wiley, New York, N. Y., 1956, p 50.

(72) R. T. Pflaum and L. H. Dieter, *Proc. Iowa Acad. Sci.*, **64**, 235 (1957).

(73) O. Heim, *Ind. Eng. Chem., Anal. Ed.*, **2**, 38 (1930).

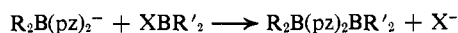
(74) R. Robson, *Aust. J. Chem.*, **23**, 2217 (1970).

Pd ($L = \pi$ -allyl or 2-substituted π -allyl and $L_2 = 1,N$ -dihapto-2-(diethylaminomethyl)phenyl).⁷⁵ Molecular models indicate that these metallocycles are not planar but puckered in the boat form. This is consistent with the observed fluxional nmr spectra, rationalized in terms of rotation of the π -allyl groups at the apices of the boat conformation.

An even larger family of compounds of this type are the pyrazaboles, **8**, which have been briefly discussed elsewhere.⁷⁶ Pyrazaboles are boron-nitrogen heterocycles⁷⁷ which may formally be regarded as composed of two boronium fragments linked by two 1,2-dihaptopyrazolide bridges. They are formed by the reaction of a pyrazole with a borane or borane complex. This method yields symmetrically substituted pyrazaboles.⁷⁸⁻⁸⁰



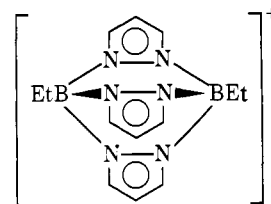
Pyrazaboles containing different substituents on the two boron atoms are synthesized by the reaction of an $\text{R}_2\text{B}(\text{pz})_2^-$ ion with a borane species containing a leaving group such as halide or sulfonate.^{81,82}



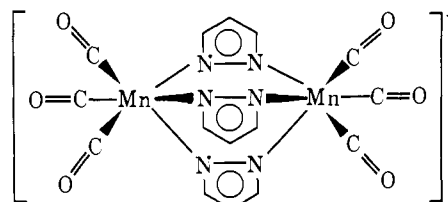
The hydrogens on boron may be replaced by halogens or by aryloxy groups without destruction of the pyrazabole ring. 2,6-Dinitration of 4,4,8,8-tetrafluoropyrazabole with fuming nitric acid has also been accomplished.⁸³ In addition, various transformations of functional groups, *e.g.*, alkaline hydrolysis of a nitrile group, reduction of a nitro group to an amine, conversion of a 2,6-dibromopyrazabole to the 2,6-dilithio derivative, and normal reactivity of the latter as a carbanion, have been reported.⁷⁹ Starting with dipyrazoles linked through the 4 position, pyrazabole polymers have been obtained.⁸⁴

Air-stable aluminum compounds analogous to pyrazaboles have also been prepared from trialkylaluminum and 3,5-dimethylpyrazole⁸⁴ (**5**, $\text{R} = \text{Me}$, $\text{M} = \text{Al}$, $\text{L} = \text{Et}$, mp 117-119°; **5**, $\text{R} = \text{Me}$, $\text{M} = \text{Al}$, $\text{L} = \text{Me}$, mp 141-144°). A similar type of behavior was also observed in the reaction of 3,5-dimethylpyrazole with Me_3M , where $\text{M} = \text{Al}$, Ga , and In .⁸⁵

Two examples exist of an array of three 1,2-dihaptopyrazolide bridges acting, in essence, as one trinegative bidentate ligand of D_{3h} symmetry.⁸⁶ One is the tetrahedral cationic species **9**, the other an octahedral manganese carbonyl anion, **10**. Nmr spectra of these ions are consistent with over-all D_{3h} symmetry for **10** and local D_{3h} symmetry for **9**. The reaction of various pyrazolide ions with $\text{BrMn}(\text{CO})_5$ has been reported to give air-sensitive, ill-characterized products



9

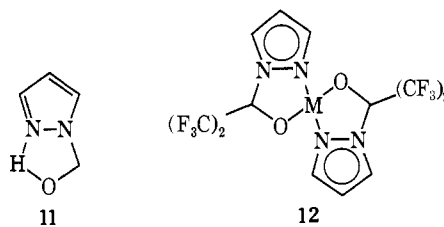


10

along with $\text{Mn}_2(\text{CO})_{10}$.⁸⁷ It is likely that some **10** was formed in these reactions.

IV. Polydentate Ligands Containing One Pyrazole Ring and Their Complexes

The coordinative power of a pyrazole nucleus can be supplemented by other coordinating groups attached either to the 1 or 3(5) positions. Pyrazole forms a stable, hydrogen-bonded adduct **11** with formaldehyde⁸⁸ which raised the possibility that the hydrogen bridge could be replaced with a transition metal ion. However, the reaction of **11** with transi-



11

12

tion metal ions, $\text{M}(\text{II})$, under basic conditions leads to extrusion of formaldehyde and formation of $[\text{M}(\text{pz})_2]_n$ polymers.⁸⁴ On the other hand, with hexafluoroacetone and related negatively substituted ketones, analogous stable chelates such as **12** have been prepared.⁸⁹

Sodium and potassium pyrazolides readily add CS_2 to give the ligand **13** ($\text{Z} = \text{Y} = \text{S}$), analogous to the dithiocarbamate ligand, but chelating *via* a five- rather than four-membered ring.⁹⁰ In this system, chelates **14** derived from divalent transition metals are polymeric, with the thiocarbonyl group coordinating to give an octahedral lattice. An exception is $\text{Fe}(\text{II})$ which forms the deep blue complex ion $[\text{Fe}(\text{pzCS}_2)_3]^-$ isolable as an NR_4^+ salt. Steric effects are of importance; the 3,5-dimethylated ligand forms a monomeric chelate with $\text{Ni}(\text{II})$. Potassium pyrazolide readily forms adducts of structure **13** with CO_2 , ArNCO , and RNCNR and should do so with any $\text{Z}=\text{C}=\text{Y}$ where Z and $\text{Y} = \text{O}$, S , or NR . The CO_2 adduct, stable in the solid state, extrudes CO_2 upon reaction with transition metal ions and yields $[\text{M}(\text{pz})_2]_n$.⁵⁴

The 1-thiocarbamyl-3,5-dimethylpyrazolyl anion gave

(75) S. Trofimenko, *Inorg. Chem.*, **10**, 1372 (1971).

(76) S. Trofimenko, *Accounts Chem. Res.*, **4**, 17 (1971).

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

(78) S. Trofimenko, *ibid.*, **89**, 3165 (1967).

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

(80) S. Trofimenko, *Inorg. Syn.*, **12**, 99 (1970).

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

(82) S. Trofimenko, *J. Amer. Chem. Soc.*, **91**, 2139 (1969).

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

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

(85) A. D. Garnovskii, O. Yu. Okhlobystin, O. A. Osipov, K. M. Yunusov, Yu. V. Kolodyazhnyi, L. M. Golubinskaya, and V. I. Svergun, Abstracts of the Fifth International Conference on Organometallic Chemistry, Moscow, USSR, Aug 1971, Vol. II, Paper 368, p 376.

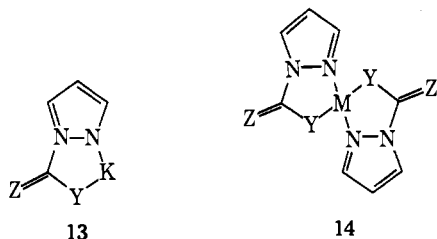
(86) S. Trofimenko, *J. Amer. Chem. Soc.*, **91**, 5410 (1969).

(87) A. Qazi, Ph.D. Dissertation, University of Strathclyde, Glasgow, Scotland, July 1965, pp 34, 35, 73, and 74.

(88) R. Hüttel and P. Jochum, *Chem. Ber.*, **85**, 820 (1952).

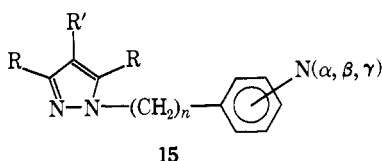
(89) W. Mahler, U.S. Patent 3,265,705 (Aug 9, 1966).

(90) S. Trofimenko, *J. Org. Chem.*, **33**, 890 (1968).



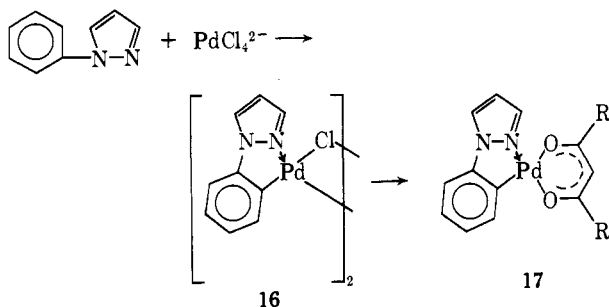
monomeric chelates analogous to **14** with a variety of transition metals,⁹¹ again underscoring the screening effect of the 3,5-methyl groups. Of the two possible modes of bonding to the metal, that through sulfur appears more plausible.

Complexes of SnCl₄ with variously substituted pyrazoles of structure **15**, including 3,5-dimethyl-1-(2-pyridyl)pyrazole



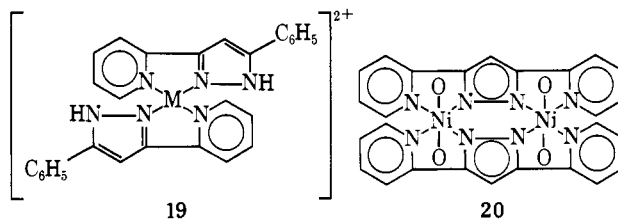
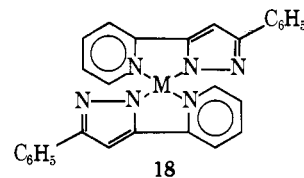
have been reported.⁹² Infrared spectroscopy indicates that coordination takes place through the pyridine N and not through pyrazole.

A special case of a 1-substituted pyrazole acting as a bidentate ligand is 1-phenylpyrazole. It undergoes a remarkable reaction with PdCl₄²⁻ which involves formation of a Pd-C bond in the ortho position, and precipitation of the insoluble, stable dimeric product, **16**. This has been converted to a number of simple derivatives, e.g., **17**.⁵⁴ Compound **17** (R = *tert*-



butyl) has been used in a study of reductive cleavage of aryl-palladium bonds.^{93,94}

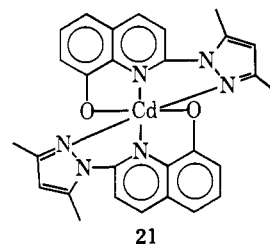
An example of a chelating system derived from a 3-substituted pyrazole is 3-(2-pyridyl)-5-phenylpyrazole (PPPH). Chelates of structure **18** and **19** have been prepared for Ni, Cu, and Co. These thermally very stable compounds are square planar in the case of Ni and Cu and tetrahedral for Co.⁹⁵ The brown-green equilibrium of the Ni compound might involve *cis-trans* isomerism. Octahedral complexes are obtained through the addition of pyridine or other ligands. Thermal and thermomagnetic properties of various Ni complexes such as [Ni(PPP)₂(py)₂], [Ni(PPPH)₂L₂]X₂, Ni(PPPH)₂X₂, and [Ni(PPP)₃]X₂ (X = F, Cl, Br, I, ClO₄, or NO₃; L = pyr-



idine, water, or acetone) have been investigated.⁹⁶ Similarly, the following analogous Co chelates were studied in some detail: [Co(PPPH)₂(OH)₂]X₂, Co(PPPH)₂X₂, and Co(PPP)₃.⁹⁷

A further extension of this ligand type is provided by 3,5-bis(2-pyridyl)pyrazole which on deprotonation gives a tetradentate monoanion of C_{2v} symmetry. With all nitrogen atoms utilized, this ligand gives rise to the lavender binuclear Ni complexes, **20**, where the Ni is in an octahedral environment through coordination with water or alcohol.⁹⁸

A hexadentate ligand containing a pyrazole nucleus, 1-(8-hydroxy-2-quinoly)-3,5-dimethylpyrazole, has been proposed for the determination of cadmium by measuring the luminescence of the chelate **21**. This method⁹⁹ is claimed to be sensitive to 5–50 × 10⁻⁶% Cd.



V. Geminal Poly(1-pyrazolyl) Compounds and Their Complexes

A particularly interesting class of pyrazole-based ligands are geminally poly(1-pyrazolyl)-substituted compounds. Of these, the uninegative poly(1-pyrazolyl)borates, [R_nB(pz)_{4-n}]⁻, and to a lesser extent poly(1-pyrazolyl)alkanes, R_nC(pz)_{4-n}, have been studied in some detail. In principle, elements other than boron or carbon may serve as the site of polysubstitution with 1-pyrazolyl groups. The charge on such a ligand will depend on the nature of the element and the number of pyrazolyl groups linked to it.

A. POLY(1-PYRAZOLYL)BORATES

The coordinating ability of a poly(1-pyrazolyl)borate ion, [R_nB(pz)_{4-n}]⁻, is a consequence of favorable electronic and geometric factors. A dipyrazolylborate ion, R₂B(pz)₂⁻, re-

(91) S. N. Poddar, K. Dey, and N. G. Podder, *Indian J. Chem.*, **8**, 364 (1970).

(92) A. D. Garnovskii, Yu. V. Kolodyaznyi, S. A. Aliyeva, N. F. Krok-hina, I. I. Grandberg, O. A. Osipov, and T. M. Presnyakova, *Zh. Obshch. Khim.*, **40**, 1114 (1970); *J. Gen. Chem. USSR*, **40**, 1104 (1970).

(93) D. A. White and G. W. Parshall, *Inorg. Chem.*, **9**, 2358 (1970).

(94) G. W. Parshall, *Accounts Chem. Res.*, **3**, 139 (1970).

(95) H. Hennig, *J. Prakt. Chem.*, **34**, 64 (1966).

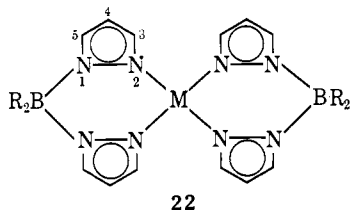
(96) H. Hennig and V. Eckelman, *Z. Anorg. Allg. Chem.*, **363**, 127 (1968).

(97) H. Hennig and I. Daute, *ibid.*, **371**, 212 (1969).

(98) P. W. Ball and A. B. Blake, *J. Chem. Soc. A*, 1415 (1969).

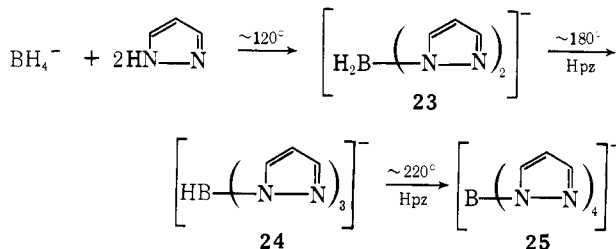
(99) E. A. Bozhevov, L. F. Fedorova, I. A. Krasavin, and V. M. Dziomko, *Zh. Anal. Khim.*, **25**, 1722 (1970); *J. Anal. Chem. USSR*, **25**, 1478 (1970).

sembles a 1,3-diketonate ion and forms chelates such as **22** with divalent transition metal ions. In **22** the nitrogens are fully coordinated and thus unavailable for further coordina-



tion and the area around the metal is screened by substituents in the 3 position. Consequently, chelates **22** are, in contrast to 1,3-diketonates, always monomeric. Furthermore, the B-N and N-M bond lengths and angles in the square planar complexes **22** make these molecules assume a puckered, pseudoboat conformation (although the four nitrogens bonded to the metal lie in a plane) with attendant nonequivalence of the axial and equatorial R groups on boron.

The parent ligands **23**, **24**, and **25** are available by the reaction of an alkali metal borohydride with pyrazole, the extent of substitution depending on the reaction temperature.^{80,100} These salts, unlike any other BR_4^- species, yield on acidification isolable and stable free acids. These may be converted *via* neutralization with NR_4OH to organic-soluble quaternary ammonium salts unavailable by the direct synthetic route.



Ligands containing C substituents are prepared by using an appropriately substituted pyrazole in the above scheme,¹⁰¹ while B-substituted ligands are obtained by starting with a $(BR_nH_{4-n})^-$ species instead of BH_4^- . For steric reasons the reaction of tetraalkyl- or tetraarylborate ions stops at the $R_2B(pz)_2^-$ stage. Ligands of the type $RB(pz)_3^-$ can be prepared, however, starting with an RBH_3^- or RBZ_2 species. Similarly, the reaction of 3,5-dimethylpyrazole with BH_4^- stops completely at the trisubstitution stage.¹⁰¹

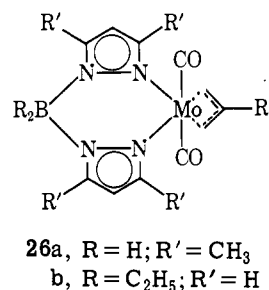
1. Bidentate Bis Chelates

The parent bidentate ligand, $H_2B(pz)_2^-$, forms monomeric chelates, $[H_2B(pz)_2]_2M$, with most divalent first-row transition metal ions. These organic-soluble and sublimable compounds are air stable, except for the Fe(II) and Mn(II) derivatives.⁹⁹ The isomorphous Ni and Cu chelates are square planar, while chelates of Mn, Fe, Co, and Zn are tetrahedral. This assignment rests on optical spectra, magnetic and nmr data,¹⁰² and an X-ray structure determination of $[H_2B(pz)_2]_2Co$.¹⁰³

Presence of alkyl substituents in the 3 position enhances the stability of these chelates. Thus $[H_2B(3,5-Me_2pz)_2]_2M$ chelates ($M = Mn$ or Fe) are stable to air. To some extent this is also true of B-alkylated chelates. For instance, $[Et_2B(pz)_2]_2Ni$ fails to form octahedral complexes by coordinating with, *e.g.*, pyridine (the corresponding parent chelate does it readily). This compound also displays substantial nmr shifts of the pseudoaxial methylene protons toward lower field.¹⁰¹

2. Bidentate Mono Chelates

The stabilizing effect of alkyl substituents on carbon and boron in the bidentate ligands was taken advantage of in synthesizing stable organometallic compounds with noninert gas configuration.^{38,39} For instance, the reaction of the air-sensitive anion $R_2B(3,5-R'pz)_2Mo(CO)_4^-$ with allyl halides gave readily the π -allyl derivatives **26**, possessing a 16-electron configuration.



The same type of product was obtained from substituted allylic halides, from cyclic systems such as cyclohexenyl, and from ligands containing 3,5-Et₂ and 3,5-(C₆H₅)₂ substituents. These orange-red compounds were remarkably stable. Their nmr spectra indicated fluxional behavior similar to that found in the $RB(pz)_3Mo(CO)_2-\pi$ -allyl compounds.¹⁰⁴

The 16-electron structures **26b** 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 spectrum of **26b** showed one of the two BEt_2 methylene groups 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 (2700 cm^{-1}), was interpreted to imply significant interaction between Mo and the pseudoaxial methylene group.

An X-ray structure determination of **26a** confirmed the proposed structure.¹⁰⁵ The $B(NN)_2Mo$ ring is strongly puckered and B-Mo distance is rather short (2.8 Å) compared to the B-M distance in $HB(pz)_3Co_2$ (3.2 Å)¹⁰⁶ or $HB(pz)_3Mo(CO)_2N=NC_6H_5$ (3.45 Å).¹⁰⁷ The distance from the pseudoaxial BH to Mo is unusually short, although not quite in the bonding range.

The reaction of $H_2B(pz)_2^-$ with $BrM(CO)_5$ ($M = Mn$ or Re) yields $H_2B(pz)_2M(CO)_3 \cdot Hpz$ which, on heating, is converted to $HB(pz)_3M(CO)_3$. Phosphines and phosphites replace pyrazole and one CO yielding $H_2B(pz)_2M(CO)_2P_2$, while with

(100) S. Trofimenko, *J. Amer. Chem. Soc.*, **89**, 3170 (1967).

(101) S. Trofimenko, *ibid.*, **89**, 6288 (1967).

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

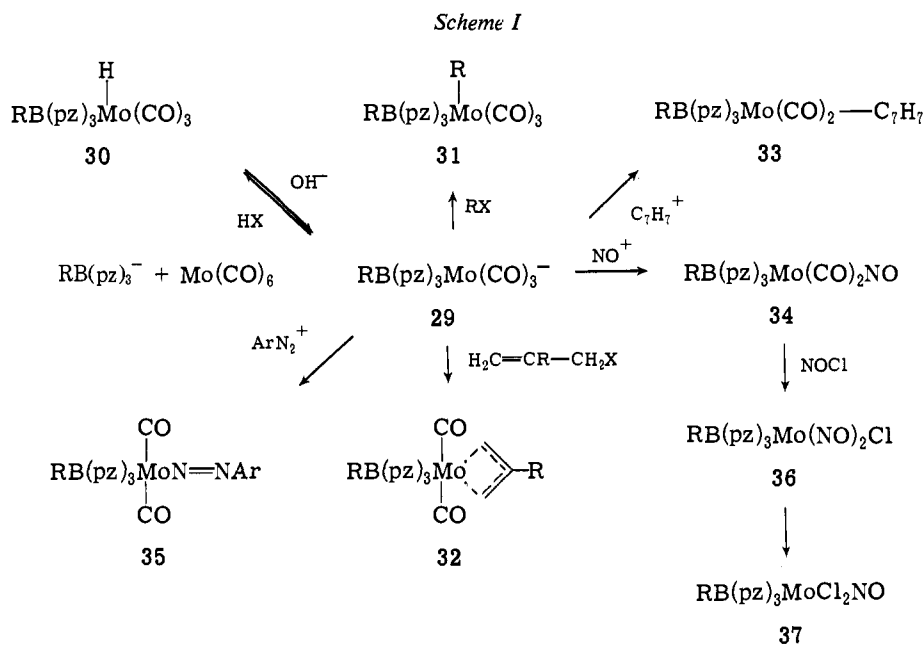
(103) L. J. Guggenberger, C. T. Prewitt, P. Meakin, S. Trofimenko, and J. P. Jesson, *Inorg. Chem.*, in press.

(104) S. Trofimenko, *J. Amer. Chem. Soc.*, **91**, 3183 (1969).

(105) C. A. Kosky, P. Ganis, and G. Avitabile, *Acta Crystallogr., Sect. B*, **27**, 1859, 2493 (1971).

(106) M. R. Churchill, K. Gold, and C. E. Maw, Jr., *Inorg. Chem.*, **9**, 1597 (1970).

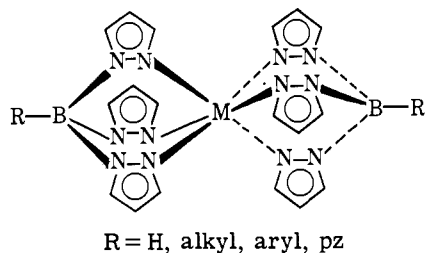
(107) G. Avitabile, P. Ganis, and M. Nemiroff, *Acta Crystallogr., Sect. A*, **27**, 725 (1971).



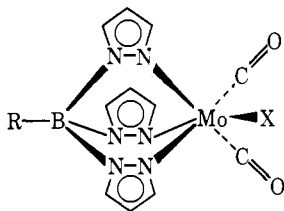
quaternary alkylammonium halides some $\text{H}_2\text{B(pz)}_2\text{M(CO)}_3\text{X}^-$ was formed.⁴⁰

3. Tridentate Bis Chelates

Ligands RB(pz)_3^- form compact octahedral coordination compounds with divalent transition metals, while M(III) ions form the same, but charged, type of structure as in 27. When the R group is another 1-pyrazolyl group the B(pz)_4 ligand



27



28

remains tridentate. In some chelates, such as $[\text{B(pz)}_4]\text{Zn}$, the structure is dynamic as judged by nmr equivalence of all four pyrazolyl groups. The three coordinated pyrazolyl groups in the isomorphous Co derivative, however, do not exchange with the fourth one.¹⁰⁰

The simplest compounds involving a C_{3v} tridentate ligand are the parent $[\text{HB(pz)}_3]_2\text{M}$ derivatives. They are stable to light, air, water, dilute acids, and bases, are sublimable *in vacuo*, and soluble in organic solvents. The overall D_{3d} symmetry for these compounds has been implicit from spectral

and nmr data and has been confirmed by an X-ray crystal structure determination on $[\text{HB(pz)}_3]_2\text{Co}$.¹⁰⁶ The same holds true for compounds derived from symmetrically substituted ligands.

While preparation of mixed ligands, *e.g.*, $\text{HB(pz)}_2\text{pz}'^-$, has not been studied, it is possible to prepare tridentate chelates with less than D_{3d} symmetry by the reaction of $[\text{H}_2\text{B(pz)}_2]_2\text{M}$ with a substituted pyrazole, Hpz' . The compound $[\text{HB(pz)}_2(4\text{-CNpz})]_2\text{Ni}$ was prepared in this fashion⁵⁴ and was converted to the corresponding carboxylic acid *via* alkaline hydrolysis.

4. Tridentate Mono Chelates

The RB(pz)_3^- ligand reacts readily with many organometallic compounds yielding derivatives, exemplified by 28, which are analogous to the "half-sandwiches" based on the cyclopentadienide ligand.^{108,109} This is illustrated best by compounds derived from the group VIb hexacarbonyls, especially those of Mo (Scheme I). Generally, these derivatives correspond to their C_5H_5 counterparts, although some of these half-sandwiches are obtainable only in the RB(pz)_3 system. On the whole, the RB(pz)_3 compounds exhibit greater thermal and chemical stability.

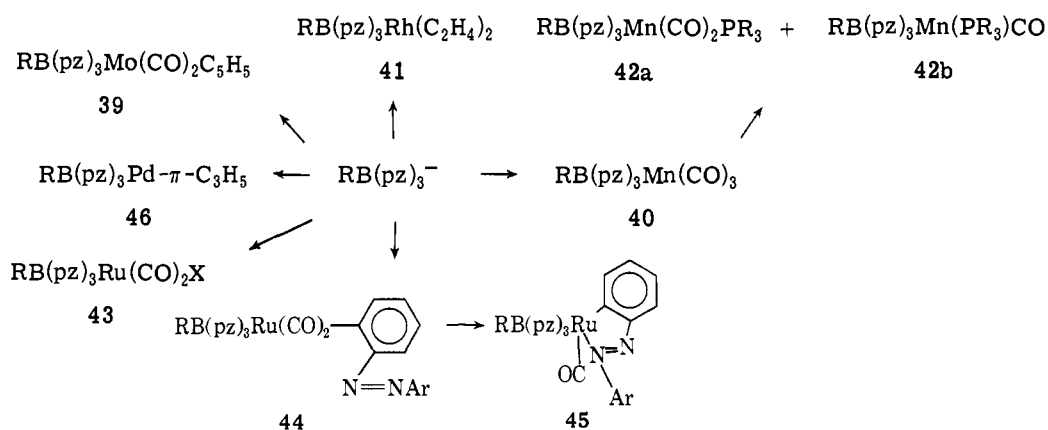
The anions, 29, isolated usually as tetraethylammonium salts, are moderately air stable for R = H or pz. Presence of alkyl groups in the 3 position, as in $\text{HB(3,5-Me}_2\text{pz)}_3\text{Mo(CO)}_3^-$, makes these salts indefinitely air stable. This enhanced stability of the 3-alkyl-substituted derivatives is encountered throughout the polypyrazolylborate area. The anions 29 can be protonated to the air-sensitive free acids, 30, which can be deprotonated with base, while with alkyl halides the seven-coordinate M-alkyl derivatives, 31, are obtained.

The reaction of 29 with allylic halides produces the π -allyl derivatives 32 directly, without isolation of an intermediate σ -allyl species.^{108,109} Although the anion $\text{HB(3,5-Me}_2\text{pz)}_3\text{Mo(CO)}_3^-$ failed to react with allylic halides, the π -allylic

(108) S. Trofimenko, *J. Amer. Chem. Soc.*, **89**, 3904 (1967).

(109) S. Trofimenko, *ibid.*, **91**, 588 (1969).

Scheme II

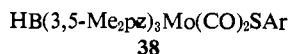
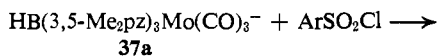


derivative analogous to **32** was prepared by an indirect route.¹⁰⁴ Many of the **32** compounds are thermally stable beyond 250°, and are thus the most thermally stable π -allyl compounds known. Tropylium ion reacts with **29**, forming the C_7H_7 derivative, **33**.

Nitroso and arylazo groups could be readily attached to Mo by treating **29** with a source of NO^+ or with ArN_2^+ .¹¹⁰ In this fashion the stable derivatives **34** and **35** were produced. The structure of **35** has been confirmed by an X-ray study.¹⁰⁷ While the nitrosation reaction proceeded equally well for the parent anions (**29**, R = H or pz) and for the 3-methylated analogs, only the parent anions reacted normally with aryl-diazonium salts. The sterically hindered anion gave, inexplicably, a blue product thought to be $\text{HB}(3,5\text{-Me}_2\text{pz})_3\text{Mo}(\text{CO})_3\text{Ar}$.¹¹¹

The mononitroso derivative **34** reacts readily with nitrosyl chloride to yield the emerald-green dinitrosomonochloride, **36**. The 3,5-dimethylated analog reacts cleanly with further nitrosyl chloride to form the stable, monomeric nitrosodichloride, **37**. While **36** differs from $\text{C}_5\text{H}_5\text{Mo}(\text{NO})_2\text{Cl}$ in being indefinitely stable to storage, no counterpart is known for **37** in the C_5H_5 system.

Another unusual reaction was found to take place between $\text{HB}(3,5\text{-Me}_2\text{pz})_3\text{Mo}(\text{CO})_3^-$ and arylsulfonyl chlorides. Instead of the anticipated sulfones or sulfinates, the monomeric aryl-mercapto derivatives, **38**, were produced. They were also obtained from ArSCl compounds.¹¹¹



The reaction of **37a** with SOCl_2 gave the green compound $\text{HB}(3,5\text{-Me}_2\text{pz})_3\text{MoOCl}_2$, also obtainable from MoOCl_3 and $\text{HB}(3,5\text{-Me}_2\text{pz})_3^-$.¹¹¹

In addition to the variety of group VIB derivatives available *via* the anion **29**, many well-defined, stable organometallic compounds were prepared by simple metathetical reactions of an organometallic halide with an $\text{RB}(\text{pz})_3^-$ ligand. For instance, the compound **33** was made more easily by the reaction of $\text{RB}(\text{pz})_3^-$ with $\text{C}_7\text{H}_7\text{Mo}(\text{CO})_2\text{I}$.¹⁰⁹ Similarly, the reaction of $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$ with $\text{B}(\text{pz})_4^-$ yielded **39**. The suggestion that in this compound the $\text{B}(\text{pz})_4$ ligand is bi-

dentate¹⁰⁹ has been confirmed by two independent X-ray structure determinations.^{112,113}

While attempts to synthesize mixed sandwiches of the type $\text{RB}(\text{pz})_3\text{MC}_5\text{H}_5$, *e.g.*, by the reaction of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{X}$ with $\text{RB}(\text{pz})_3^-$, led invariably to $[\text{RB}(\text{pz})_3]\text{M}$,^{54,114} it has been possible to synthesize a mixed sandwich cation $[\text{pzB}(\text{pz})_3\text{Co}-\text{C}_5\text{H}_5]^+$.¹¹⁵

Examples of organometallic compounds with metals other than the VIB group include the manganese carbonyl derivative **40** and the rhodium-bisethylene complex **41** (Scheme II). The photolytic displacement of CO in compounds **40** by various phosphines to yield **42a,b** has been studied and found to be strongly dependent on steric factors.^{116,117}

The reaction of $\text{HB}(\text{pz})_3^-$ with $\text{Ru}_3(\text{CO})_{12}$, followed by halogenation, gave $\text{HB}(\text{pz})_3\text{Ru}(\text{CO})_2\text{X}$, **43**, where X is Cl, Br, or I. The halogen in these compounds is inert and could not be replaced with carbanionic reagents.¹¹⁴ An X-ray structure determination confirmed the assignment, but did not reveal any unusual features to account for this lack of reactivity.¹¹⁸

Treatment of 2-phenylazophenylruthenium dicarbonyl chloride dimer with $\text{HB}(\text{pz})_3^-$ (as K or Tl salt) resulted in the formation of **44** which, on irradiation, lost one CO with reformation of the N-Ru bond to yield **45**.^{44,45,119}

The π -allyl derivative of Pd, **46**, was obtained by the reaction of π -allylpalladium chloride dimer with $\text{RB}(\text{pz})_3^-$. These compounds were fluxional as *all* pyrazolyl groups in **46** (R = H or pz) and were spectroscopically identical at room temperature. At -40° , however, the coordinated and uncoordinated pyrazolyl groups could be readily discerned.¹⁰⁴

5. Tetradentate Chelates

The $\text{B}(\text{pz})_4^-$ can also act in tetradentate fashion when pairs of N termini are bridged by appropriate four-coordinate species.

(112) S. L. Holt, personal communication.

(113) J. L. Calderon, F. A. Cotton, and A. Shaver, *J. Organometal. Chem.*, **37**, 127 (1972).

(114) M. I. Bruce, D. N. Sharrocks, and F. G. A. Stone, *ibid.*, **31**, 269 (1971).

(115) F. J. Lalor, private communication.

(116) A. R. Schoenberg and W. P. Anderson, Abstracts of 6th Middle Atlantic Regional Meeting of the American Chemical Society, Feb 3-5, 1971, p 53, No. 6.

(117) A. R. Schoenberg and W. P. Anderson, *Inorg. Chem.*, **11**, 85 (1972).

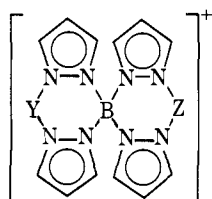
(118) R. J. Doedens, personal communication.

(119) M. I. Bruce, M. Z. Iqbal, D. N. Sharrocks, and F. G. A. Stone, Abstracts of the Fourth International Symposium on Organometallic Chemistry, Bristol, 1969, No. S2.

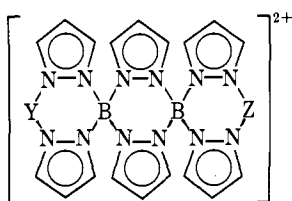
(110) S. Trofimenko, *Inorg. Chem.*, **8**, 2675 (1969).

(111) S. Trofimenko, *ibid.*, **10**, 504 (1971).

For instance, the reaction of $B(pz)_4^-$ with 2 equiv of π -allylpalladium chloride dimer or with diethylboryl sulfonate gives the spiro cations **47** and **48**, respectively, isolable as hexafluorophosphate salts.¹²⁰ The cation **49**, containing two differ-



- 47**, Y = Z = Pd- π -CH₂CRCH₂
48, Y = Z = BEt₂
49, Y = BEt₂; Z = Pd- π -CH₂CRCH₂

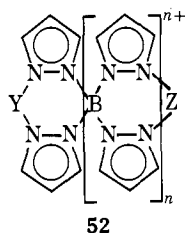


- 50**, Y = Z = BEt₂
51, Y = Z = Pd- π -CH₂CRCH₂

ent bridges, was obtained by the reaction of 4,4-dipyrazolylpyrazabole with π -allylpalladium chloride dimer or of $(pz)_2B(pz)_2Pd$ - π -allyl with diethylboryl sulfonate.

The nmr spectrum of **47** is fluxional, limiting spectra being observed at 87 and -44° . At 87° all four pyrazolyl groups are spectroscopically equivalent, while at -44° two different types of pyrazolyl groups are present, consistent with C_2 symmetry. At higher temperature the ion achieves dynamic D_{2d} symmetry either through rapid exchange of pyrazolyl groups or inversion of the $B(pz)_2Pd$ rings.

An even more complex family of spiro cations, **50** and **51**, was obtained upon treatment of 4,4,8,8-tetrakis(1-pyrazolyl)pyrazabole with sources of incipient cations such as diethylboryl and π -allylPd. They may be regarded as members of a series of cations possessing the general structure **52**.¹²⁰



B. PHYSICAL STUDIES ON TRANSITION METAL POLY(1-PYRAZOLYL)BORATES

Apart from aiding in structure determination, nmr studies were carried out from several points of view. In conjunction with magnetic and Mössbauer data they were used to probe into the spin equilibria encountered with iron(II) poly(1-pyrazolyl)borates. The magnetic moments in these compounds

were dependent on small changes in substituents at the periphery of the molecule. Thus, while $[B(pz)_4]_2Fe$ is diamagnetic at room temperature, $[HB(3,5-Me_2pz)_3]_2Fe$ is fully paramagnetic ($\mu_{eff} \sim 5.2$ BM) and $[HB(pz)_3]_2Fe$ has an intermediate value (2.7 BM). The last magnetic moment is strongly temperature dependent and is due to a spin equilibrium between the $^5A_{1g}$ and $^1A_{1g}$ states.¹²¹ In addition to the above results obtained in solution, similar behavior was found in the solid state^{122,123} and was studied in detail by Mössbauer and magnetic susceptibility techniques down to $4.2^\circ K$.

In the spin equilibrium range the Mössbauer transitions for the high- and low-spin states were clearly observed. It was concluded 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 effect of dipolar interactions, resulting from the magnetic anisotropy of $[HB(pz)_3]_2Co$, on the nmr spectra of the complexing molecule was used to investigate the structure of a labile second-sphere coordination complex between the above cobalt chelate and pyridine or aniline.¹²⁴ 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 4-H. Enthalpies of -2.4 ± 0.2 and -2.9 ± 0.3 kcal/mol were obtained for these complexations.

A study of substituted anilines in the above system revealed that presence of electron-withdrawing substituents leads to stronger, and of electron-donating substituents to weaker, second-sphere coordination complexes.¹²⁵

Various types of dynamic phenomena, amenable to nmr study, have been investigated in polypyrazolylborate complexes. Thus, the fluxional nature of $RB(pz)_3Mo(CO)_2$ - π -CH₂CR'CH₂ and of analogous compounds was studied. The well-resolved limiting spectra indicated the existence of a dynamic process consisting of rotation of the $Mo(CO)_2$ - π -CH₂CR'CH₂ moiety around the B-Mo axis. This makes all three coordinated pyrazolyl groups spectroscopically equivalent at high temperature, but still different from the fourth one (if R = pz). The height of the rotational barrier depends on the nature of substituents in the 3 position and on the π -allyl group. For instance, the lowest barrier was found for R' = Me, while at the other extreme, the cyclopentenyl analog was stereochemically rigid throughout the available temperature range.¹⁰⁴

A quantitative study of the above systems, involving complete line-shape analysis, resulted in the calculation of precise activation parameters.¹²⁶ The behavior of the fourth pz group (for R = pz) was puzzling; while the line-shape analysis indicated its rapid rotation around the B-Mo axis, calculation of nonbonded repulsions between the 5-hydrogens in the eclipsed conformation (through which the planar pz group must pass in the course of rotation) led to the prediction of a very high barrier. To accommodate these dissonant data it was

(121) J. P. Jesson, S. Trofimenko, and D. R. Eaton, *J. Amer. Chem. Soc.*, **89**, 3158 (1967).

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

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

(124) D. R. Eaton, *Can. J. Chem.*, **47**, 2645 (1969).

(125) D. R. Eaton, H. O. Ohorodnyk, and L. Seville, *ibid.*, **49**, 1218 (1971).

(126) P. Meakin, S. Trofimenko, and J. P. Jesson, *J. Amer. Chem. Soc.*, **94**, 5677 (1972).

(120) S. Trofimenko, Abstracts of the Fifth International Symposium on Organometallic Chemistry, Moscow, USSR, 1971, Vol. I, p 17; *J. Coord. Chem.*, in press.

postulated that the B-N bond for the fourth pz group is anomalously long.

A similar rotational mechanism was suggested to account for the temperature-dependent nmr spectra or 16-electron compounds such as **26a**.³⁹

The temperature-dependent nmr spectra or the stereochemically nonrigid system $B(pz)_4Mo(CO)_2C_5H_5$ was studied in order to establish the structure of this compound which could have involved either (a) a tridentate $B(pz)_4$ and $h^3-C_5H_5$ or (b) a bidentate $B(pz)_4$ and $h^5-C_5H_5$. The nmr data, along with an X-ray structure determination, confirmed the b alternative. In terms of the actual dynamic process involved, the data agreed best with inversion of the $B(pz)_2Mo$ ring rather than with a rotational process,³⁹ as in **26a**, or the process found in $C_5H_5(CO)_2LR$ systems.¹²⁷

The same type of inversional processes were found from nmr data to occur in $HB(pz)_3Mo(CO)_2C_5H_5$ and $Et_2B(pz)_2Mo(CO)_2C_5H_5$ compounds, the inversion rate being much rapid in the latter compound. In each case a $h^5-C_5H_5$ was involved and the pyrazolylborate ligand acted as a bidentate.¹²⁸

A similar structural problem exists in the case of $RB(pz)_3Mo(CO)_2C_7H_7$ compounds, where the C_7H_7 ligand could be either h^3 or h^5 . While nmr data were compatible with either alternative, comparison of infrared spectra (CO stretches) with other known systems was more consistent with a $h^3-C_7H_7$ formulation.¹²⁹

A detailed study of optical and paramagnetic resonance data of $[HB(pz)_3]_2Co$ and of its carbon analog $[HC(pz)_3]_2Co^{2+}$ 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.¹³⁰ The principal g tensor components showed a large axial anisotropy as established by single crystal epr results at 4.2°K.

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.¹³¹ 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 the corresponding Ni complexes.

A different theoretical treatment of contact and pseudo-contact shifts in Co-polypyrazolylborate complexes resulted¹³² in predicted contact shifts which were in better agreement with experimental results than those reported earlier. This new treatment of isotropic shifts for the complex $[HB(pz)_3]_2Co$ was checked as a function of temperature and was found to be in excellent agreement with the observed data.¹³³

The solubility products of various transition metal poly-pyrazolylborates were determined in the course of a study to assess the suitability of such ligands as analytical reagents for metals. The solubility products are in the order of 10^{-14} , and thus a gravimetric procedure could be employed in determining Co, Ni, Cu, and Zn. These cations can also be deter-

mined volumetrically in the presence of alkaline earth metals. A spectrophotometric determination of Co in the presence of Ni, Cu, and Zn has been worked out.¹³⁴

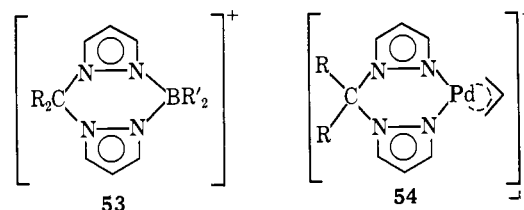
Enthalpies of chelation for Co, Ni, Cu, and Zn with $H_2B(pz)_2^-$, $HB(pz)_3^-$, $H_2B(3-Mepz)_2^-$, and $B(pz)_4^-$ have been measured in water and in acetonitrile. In water, for bidentate ligands, the order of decreasing $-\Delta H$ is $Ni > Cu > Co > Zn$ and for $B(pz)_4^-$ it is $Cu > Ni > Co > Zn$. Quite different orders were observed when ΔH was measured in acetonitrile.¹³⁵

C. POLY(1-PYRAZOLYL)ALKANES

The poly(1-pyrazolyl)alkanes are ligands isosteric and iso-electronic with poly(1-pyrazolyl)borates except for being neutral rather than uninegative. In fact, the coordination chemistry of $R_nC(pz)_{4-n}$ ligands duplicates almost exactly that of their boron counterparts, except that each complex has a charge higher by +1 per ligand. The ligands are synthesized readily either by the reaction of a geminal halide, usually a dihalomethane, with pyrazolide ion or by the acid-catalyzed reaction of acetals or ketals with pyrazoles.

1. Bidentate Chelates

The bidentate ligands $R_2C(pz)_2$ react⁸⁴ with R'_2BX species to yield cations **53**, isosteric with pyrazaboles, and with π -allylpalladium chloride dimer to give cations **54**. In cation **53**, where $R = pz$, the bridging and uncoordinated pz groups are



spectroscopically different by nmr, whereas in the analogous **54** there is rapid exchange which does not slow down until -44° .

2. Tridentate Chelates

The tridentate chelates, based mainly on $HC(pz)_3$, although $C(pz)_4$ and $HC(3,5-Me_2pz)_3$ have also been prepared, behave very much like $HB(pz)_3^-$. With $M(II)$ ions they form water soluble cations, $[HC(pz)_3]_2M^{2+}$, and with various metal carbonyls their behavior mimics exactly that of their boron counterparts even up to the point of stereochemical nonrigidity involving rotation of the $Mo(CO)_2$ - π -allyl moiety being observed in the cation $[HC(pz)_3Mo(CO)_2-\pi\text{-allyl}]^+$.

Ion pairing between $[HC(pz)_3]_2Co^{2+}$ and PF_6^- ion in acetonitrile has been investigated by nmr methods, making use of isotropic ^{19}F shifts of the anion.¹³⁶ It was concluded that the preferred position of the anion lies close to the symmetry axis of the cobalt complex and that a contact ion pair is involved. Epr studies of $[HC(pz)_3]_2Co^{2+}$ have also been carried

(127) J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, **92**, 5852 (1970).

(128) J. L. Calderon, F. A. Cotton, and A. Shaver, *J. Organometal. Chem.*, **38**, 105 (1972).

(129) A. S. Anderson, Ph.D. Thesis, Yale University, 1971.

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

(131) J. P. Jesson, *ibid.*, **47**, 582 (1967).

(132) B. R. McGarvey, *ibid.*, **53**, 86 (1970).

(133) G. N. LaMar, J. P. Jesson, and P. Meakin, *J. Amer. Chem. Soc.*, **93**, 1286 (1971).

(134) S. D. Hersh, Ph.D. Dissertation, University of Delaware, June 1969.

(135) J. R. Jezorek, Ph.D. Dissertation, University of Delaware, June 1969.

(136) D. R. Eaton, L. Seville, and J. P. Jesson, *Can. J. Chem.*, **49**, 2751 (1971).

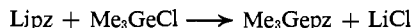
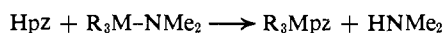
out and correlated with results obtained from the $[\text{HB}(\text{pz})_3]_2\text{Co}$ system.¹³⁰

Altogether, the area of coordination chemistry based on $\text{R}_n\text{C}(\text{pz})_{4-n}$ ligands has not been studied to any appreciable extent, although some work, such as the synthesis of the mixed sandwich cation $[\text{HC}(\text{pz})_3\text{CoC}_5\text{H}_5]^+$, has not yet been reported.¹¹⁵ Nevertheless, work in this area should be fruitful; in particular, comparative studies of pairs of corresponding poly(1-pyrazolyl)alkanes and poly(1-pyrazolyl)borates would be helpful in assessing the effects of charge on the properties of complexes.

VI. Miscellany

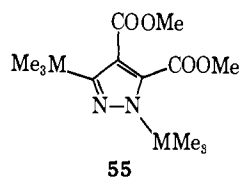
In discussing the X-ray structures of transition metal complexes based on pyrazole and its derivatives it is often useful to refer to the structure of pyrazole itself. In the first determination considerable differences in the C-3-C-4 and C-5-C-4 bond lengths were reported (1.33 vs. 1.41 Å).¹³⁷ This was rationalized in terms of a betaine-like structure. Such an interpretation was questioned and it was suggested that the N-1 and N-2 assignments be reversed.¹³⁸ In the most recent work¹³⁹ the C-3-C-4 and C-5-C-4 distances were essentially equal (both 1.33 Å). The pyrazole nucleus was thus (ignoring the mobile 1-proton) of C_{2v} symmetry.

Diversely substituted pyrazoles containing silyl and germyl groups in the 1 position have been prepared by several types of reactions^{140, 141}



The silyl derivatives are extremely moisture-sensitive liquids. Their nmr spectra indicate nonequivalence of the 3 and 5 positions at room temperature. At about 120° the 3 and 5 positions become spectroscopically equivalent. A 1,2 migration of the silyl group *via* a three-centered transition state has been proposed to account for this.¹⁴¹ A simple reversible dissociation into ion pairs or interchange of silyl groups through the intermediacy of a dimeric form, $\text{R}_3\text{M}(\text{pz})_2\text{MR}_3$, would seem more plausible.

The formation of 1-silylpyrazoles, **55**, containing various substituents, from bis(trimethylsilyl)diazomethane has also been reported.¹⁴² Similar results were also obtained with bis(trimethylstannyl)diazomethane.¹⁴³



M = Si, Sn

(137) H. W. Ehrlich, *Acta Crystallogr.*, **13**, 946 (1960).

(138) A. D. Mighell and C. W. Reiman, *J. Phys. Chem.*, **71**, 2375 (1967).

(139) J. Berthou, J. Elguero, and C. Rerat, *Acta Crystallogr., Sect. B.*, **26**, 1880 (1970).

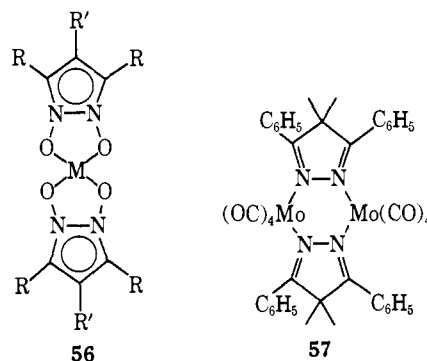
(140) J. Elguero, M. Riviere-Baudet, and J. Satge, *C. R. Acad. Sci., Ser. C*, **266**, 44 (1968).

(141) D. H. O'Brien and C. P. Hsung, *J. Organometal. Chem.*, **27**, 185 (1971).

(142) D. Seyferth and T. C. Flood, *ibid.*, **29**, C25 (1971).

(143) W. F. Lappert and J. S. Poland, *Chem. Commun.*, 156 (1969).

Although devoid of N-M bonds, chelates **56**, derived from 1-hydroxypyrazole 2-oxides should also be mentioned at this point,^{144, 145} as well as complexes **57** derived from isopyrazoles.¹⁴⁶



VII. Addendum. Some Recent Developments

In the area of simple pyrazole coordination compounds the complexes L_3InX_3 (where L = Hpz, H3,5-Me₂pz),¹⁴⁷ (H3,5-Me₂pz)NbCl₅,¹⁴⁸ and Rh(Hpz)₂Cl₂·5H₂O¹⁴⁹ have been prepared and characterized, as have diverse C-substituted Npz and pz complexes of Ag(I) and Cu(I).¹⁵⁰

Vibrational and epr spectra of Fe and In complexes of the types $\text{M}(\text{Hpz})_2\text{Cl}_3$ and $\text{M}(\text{H3-Mepz})_2\text{Cl}_3$ have been analyzed.¹⁵¹ From an esr study of powdered Ni(Hpz)₂X₂ complexes, the parameters *g*, *D*, and *E* for an *S* = 1 system have been evaluated.¹⁵² The coordination of Hpz to Ni²⁺ was found to increase its rate of iodination.¹⁵³ Complexation of Hpz and 1-Mepz to BF₃ has been studied by ¹H and ¹⁹F nmr,¹⁵⁴ and zero-field splittings in Ni(Hpz)₂X₂ were studied.¹⁵⁵

Several methods of preparing $[\text{M}(\text{pz})_2]_n$ polymers have been described, as has the synthesis of complex anions $\text{M}(\text{pz})_4^{2-}$ (M = Zn, Cu, Ni, and Co),¹⁵⁶ and of $[(\text{OC})_4\text{M}(\text{pz})_2\text{M}(\text{CO})_4]^{2-}$ for M = Mo and W.¹⁵⁷

The unstable C₆H₅Fe(CO)₂pz has been reported,¹⁵⁸ as have complexes of the type LFe(CO)₄ for L = Hpz and H3,5-

(144) J. P. Freeman, *J. Heterocycl. Chem.*, **3**, 544 (1966).

(145) J. P. Freeman and J. J. Gannon, *J. Org. Chem.*, **34**, 187 (1969).

(146) H. T. Dieck, I. W. Renk, and H. P. Brehm, *Z. Anorg. Allg. Chem.*, **379**, 169 (1970).

(147) K. M. Yunusov, A. D. Garnovskii, O. A. Osipov, and Yu. V. Kolodyazhnyi, *Zh. Obshch. Khim.*, **41**, 1320 (1971).

(148) L. V. Surpina, A. D. Garnovskii, Yu. V. Kolodyazhnyi, and O. A. Osipov, *ibid.*, **41**, 2279 (1971).

(149) A. W. Addison, K. Dawson, R. D. Gillard, B. T. Heston, and H. Shaw, *J. Chem. Soc., Dalton Trans.*, 589 (1972).

(150) J. Reedijk and H. Okkerson, *Recl. Trav. Chim. Pays-Bas*, in press.

(151) S. A. Cotton and J. F. Gibson, *J. Chem. Soc., Dalton Trans.*, 1696 (1971).

(152) J. Reedijk and B. Niewenhuijse, *Recl. Trav. Chim. Pays-Bas*, **91**, 533 (1972).

(153) J. D. Vaughan and W. A. Smith, Jr., *J. Amer. Chem. Soc.*, **94**, 2460 (1972).

(154) A. Fratiello, R. E. Schuster, and M. Geisel, *Inorg. Chem.*, **11**, 11 (1972).

(155) J. Reedijk, Proceedings of the XIVth International Conference on Coordination Chemistry, Toronto, Canada, 1972, p 318.

(156) J. Rodrian, Ph.D. Dissertation, University of Saarbrücken, 1972.

(157) W. Beck, personal communication.

(158) F. Seel and V. Sperber, *J. Organometal. Chem.*, **14**, 405 (1968).

Me₂pz.¹⁵⁹ A study of site exchanges of nitrogenous bases in a porphinatoruthenium carbonyl system¹⁶⁰ included H3,5-Me₂pz.

Ligands derived from pyrazoles containing an auxiliary donor substituent, e.g., 3-(2-pyridyl)-5-phenylpyrazole (PPPH), received considerable attention recently. For instance, the esr spectrum of Cu(PPP)₂ was studied,¹⁶¹ the anomalous magnetic behavior of Fe(PPP)₂ was investigated,¹⁶² the structure of Ni(PPP)₂ was determined by X-ray crystallography,¹⁶³ and the pH-dependent equilibria of cations and neutral metal complexes of PPPH were studied.¹⁶⁴

Transition metal chelates derived from 3-(2-pyridyl)-5-methylpyrazole were prepared¹⁶⁵ as were those based on pyrazoles also containing a pyrrole nucleus, e.g., 1-(2-pyridyl)-3-(2-pyrryl)-5-methylpyrazole and 3-(2-pyrryl)-5-methylpyrazole.¹⁶⁶ The former ligand produced a seven-membered ring chelate containing an uncoordinated pyrazole moiety. A review containing *inter alia* the above types of compounds has appeared recently.¹⁶⁷

A number of structural studies on poly(1-pyrazolyl)borates has been carried out. From ir and nmr data it was concluded that in H₂B(3,5-Me₂pz)₂Mo(CO)₂C₇H₇ and Et₂B(pz)₂Mo(CO)₂C₇H₇ the C₇H₇ ring is trihapto-bonded to Mo.¹⁶⁸ The structure of the former has also been confirmed by an X-ray

study,^{169,170} which shows the presence of a three-center B-H-Mo bond. The previously mentioned¹¹⁴ compound HB(pz)₃Fe(CO)₂Me was investigated by ir, nmr, and X-ray crystallography and found to be actually HB(pz)₃Fe(CO)₂-COCH₃.¹⁷¹ X-Ray structure determinations have also been carried out on HB(pz)₃Mo(CO)₂NO, HB(pz)₃Mo(CO)₂-π-CH₂CMeCH₂, [EtB(pz)₃BET]PF₆, and Et₂B(4-Brpz)₂BET₂.¹⁷²

Bromination of RB(pz)₃Mo(CO)₂NO yielded predominantly the dimeric RB(pz)₃MoBr₂NO, although some organobromination accompanied by ethanolysis also occurred.¹⁷³ The stable complex (pz)₂B(pz)₂PtMe₂(C₆H₅PMe₂)₂ has been reported,¹⁷⁴ and the rates of establishing spin equilibria in [HB(pz)₃]₂Fe have been studied.¹⁷⁵ Synthetic work in the polypyrazolylborate area included the preparation of perfluoroalkyl derivatives such as H₂B(pz)₂CoR_f(C₆H₅), HB(pz)₂CoR_f(C₆H₅), and HB(pz)₃Fe(CO)₂R_f, of iron derivatives such as [(pz)Fe(CO)₂]₂, (allylpz)Fe(CO)₃, HB(pz)₃Fe(CO)₂-COC₃H₅, HB(pz)₃Fe(CO)₂C₃H₅, and [H₂B(pz)₂]₂Fe(CO)₂, and of the interesting dinitrogen complex H₂B(pz)₂PtMe₃N₂.¹⁷⁶

Various 1-pyrazolylphosphines and -silanes (P(pz)₃, C₆H₅-P(pz)₂, (C₆H₅)₂Ppz, Me₂Si(pz)₂, MeSi(pz)₃) have been synthesized.¹⁷⁷ It has been found that [HC(pz)₃]₂M²⁺ complexes can be prepared in low yield directly from M(Hpz)₆²⁺ and HC(OR)₃.¹⁷⁸ The Al(pz)₄⁻ ligand and some of its transition metal derivatives, as well as RR'Al(pz)₂AlRR' compounds, have been synthesized and characterized.¹⁷⁹

(159) A. N. Nesmeyanov, V. N. Babin, N. S. Kochetkova, and Yu. S. Nekrasov, *Dokl. Akad. Nauk SSSR*, **200**, 601 (1971); *Dokl. Chem.*, **200**, 792 (1972).

(160) S. S. Eaton, G. R. Eaton, and R. H. Holm, *J. Organometal. Chem.*, **39**, 179 (1972).

(161) H. Hennig and R. Kirmse, *Z. Anorg. Allg. Chem.*, **388**, 238 (1972).

(162) H. Hennig, M. Benedix, and R. Benedix, *Z. Chem.*, **11**, 188 (1971).

(163) J. Sieler and H. Hennig, *Z. Anorg. Allg. Chem.*, **381**, 219 (1971).

(164) H. Hennig and D. Hoppach, *Z. Chem.*, **11**, 71 (1971).

(165) H. Hennig and I. Daute, *ibid.*, **11**, 24 (1971).

(166) H. Hennig, R. Daute, and E. Hoyer, "Proceedings of the Symposium on Coordination Chemistry," Jena, 1969, Section C, S-52.

(167) H. Hennig, *Z. Chem.*, **11**, 81 (1971).

(168) J. L. Calderon, F. A. Cotton, and A. Shaver, *J. Organometal. Chem.*, in press.

(169) F. A. Cotton, *Chem. Commun.*, 777 (1972).

(170) F. A. Cotton, M. Jeremic, and A. Shaver, *Inorg. Chim. Acta*, in press.

(171) F. A. Cotton, B. A. Frenz, and A. Shaver, *ibid.*, in press.

(172) E. M. Holt and S. L. Holt, personal communication.

(173) J. A. McCleverty, personal communication.

(174) H. C. Clark and L. E. Manzer, *Inorg. Chem.*, in press.

(175) J. K. Beattie, Proceedings of the XIVth International Conference on Coordination Chemistry, Toronto, Canada, 1972, p 507.

(176) R. B. King, personal communication.

(177) F. Klanberg, personal communication.

(178) J. Reedijk, personal communication.

(179) A. Storr, personal communication.