THE COORDINATION CHEMISTRY OF PYRAZOLE-DERIVED LIGANDS

SWIATOSLAW TROFIMENKO

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

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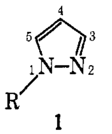
I. Introduction

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 exobidentate[1] 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 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.



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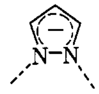

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This review covers compounds in which a pyrazole ring is N-bonded to a metal or metalloid. Most of the subject matter falls into the following four categories.

(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) compounds[8] 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 $M(Hpz)_nX_m$ where M is a transition metal, Hpz is a 2-*monohapto*pyrazole 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.*, $[M(pz)_2]_n$, predominates under basic conditions. The number of pyrazoles coordinated to the metal depends on a number of factors.

$$MX_2 + m\text{Hpz} \longrightarrow M(\text{Hpz})_mX_2 \qquad (1)$$

$$MX_2 + 2\text{pz}^- \longrightarrow [M(\text{pz})_2]_n + 2X^- \qquad (2)$$

(*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 $M(Hpz)_6X_2$ compounds include M = Mg, Mn, Fe, Co, Ni, Zn, and Cd.[9,10] When X is halide ion, complexes $M(Hpz)_4X_2$ are formed (M = Ni, Co, and Fe).[9] The structures of $Ni(Hpz)_6(NO_3)_2$, $Ni(Hpz)_4Cl_2$, and $Ni(Hpz)_4Br_2$ have been estab-

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[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.

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[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).

[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 $L_2M(pz)_2ML_2$, it will denote the existence of 1,2-*dihapto*pyrazolide 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 $Ni(Hpz)_6(NO_3)_2$ 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 $Ni(Hpz)_4X_2$ 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 $Cu(Hpz)_4X_2$ regardless of the nature of X (Cl, Br, BF_4, ClO_4, SO_4, NO_3).[9,15-17] Furthermore, species such as $Cu(Hpz)_2Cl_2$ were also obtained as was $Cu(H3,5\text{-}Me_2pz)(OAc)_2$.[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 reported[16] in structures of the type $M(H3\text{-}Mepz)_7(ClO_4)_2$, although the seventh pyrazole is regarded as being in the second coordination sphere. By contrast, $H3,5\text{-}Me_2pz$ which has both positions adjacent to the nitrogens substituted with methyl groups, forms only complexes of the type $M(H3,5\text{-}Me_2pz)_4X_2$.[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 solution[9] or on single crystals of $Ni(Hpz)_6^{2+}$ complexes[20] 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 H3(5)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 $M(H5\text{-}Mepz)_2X_2$ 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 $Mn(H5\text{-}Mepz)_4Br_2$.[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 $ML_4(SCN)_2$ 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 $[CoBr_3(H3,5\text{-}Me_2pz)]^-$ was isolated as the Et_4N salt. The formation and extraction with organic solvents of 3,5-dimethylpyrazole–copper complexes of the type $CuL_2(SCN)_2$ and $CuL_4(SCN)_2$ have been studied colorimetrically.[28,29] Tetrahedral $ML_2(NCS)_2$ complexes have been reported for M = Zn and Cd, while $Cu(H5\text{-}Mepz)_2(NCS)_2$ and $Zn(Hpz)_3(NO_3)_2$ 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 $RuL_3Cl_3^-$, $RuCl_2L_3(H_2O)$, etc., characterized by analyses and conductivity data.[30] Pyrazole reacted with $RuCl_3$ to form the anion $Ru(Hpz)OHCl_4^-$ which gave an insoluble silver salt and the neutral species $Ru(Hpz)_3Cl_3$.[31] The reaction of pyrazole with $RuCl_4$ in acid solution gave only $(H_2pz)_2^+$-$RuCl_6^{2-}$ and no Ru–N-coordinated products.[32] Complexes of the type L_2AgNO_3 and $L_2(HgCl_2)_3$, 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]

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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 $Et_2B(pz)_2Mo(CO)_2$-π-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 reported[41] to give the air-sensitive $(H3,5\text{-}Me_2pz)_2FeCO$ 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 $HpzFe(CO)_3$ 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 $[3,5\text{-}Me_2pzFe(CO)_3]_2$, which may have a metallocyclic structure analogous to **5**, have also been reported.[43]

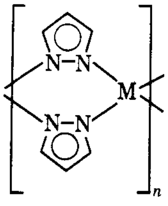
The reaction of 3,5-dimethylpyrazole with chromium hexacarbonyl yields only the $LCr(CO)_5$ at any reactant ratios, while with tungsten hexacarbonyl either $LW(CO)_5$ or $L_2W(CO)_4$ may be obtained.[44] Another complex containing both pyrazole and carbonyl ligands is $RuCl_2(CO)_2(Hpz)_2$.[45,46]

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, 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-dimethylpyrazole 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.



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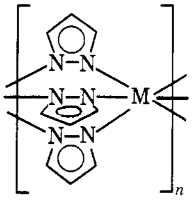

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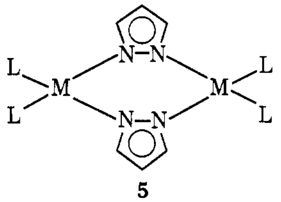

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Although pyrazolide ion is 1,2-diazacyclopentadienide ion, there is no evidence that it can form metallocene-type sandwiches, despite several claims to that effect.

Polymeric complexes containing the exobidentate 1,2-dihaptopyrazolide ligand have been known since 1889, when Buchner in his paper on pyrazole[53] 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

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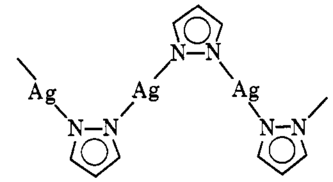

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identical with that of Ag(pz). The colorless Cu(pz), which may be prepared either from $Cu(NH_3)_2^+$ and pyrazolide ion or by pyrolysis of $Cu(pz)_2$,[54] may be recrystallized from diglyme and is sublimable *in vacuo*. The mass spectrum shows presence 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, Balbiano[59] reported the synthesis of a mercury derivative of pyrazole and of the chloroplatinate, noting conversion of the latter on heating to $Pt(pz)_2Cl_2$.

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 $[M(pz)_2]_n$ is *via* pyrolysis of the acetates, $M(Hpz)_4(OAc)_2$.[55] The polymeric pyrazolides are intractable, thermally very stable solids. Some exhibit thermochromism (Ni, yellow ⟷ orange at 250°; Cu, brown or green ⟷ blue-violet at −196°). The $[Cu(pz)_2]_n$ 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 $(3,4,5\text{-}Br_3pz)_2Cu$ chelate is benzene soluble and exists there as a tetramer.[54] The silver derivative $(4\text{-}i\text{-}C_3F_7pz)Ag$ 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-acylpyrazole[68] and 3,5-dimethyl-4-acylpyrazole.[69]

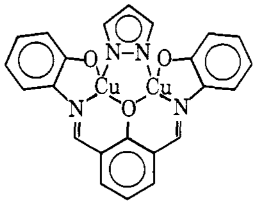
Among the various transition metal pyrazolides the most thoroughly studied one is the very insoluble purple cobalt chelate, $[(3,5\text{-}Me_2pz)_2Co]_n$, which can be precipitated in analytical purity at pH 7.5–9.0. It has been suggested that precipitation of this complex be used for the gravimetric determination of cobalt.[70–73] By contrast, the related 1-phenyl-3,5-dimethylpyrazole and 3,5-diphenylpyrazole did not react with Co(II). A sandwich structure has been proposed[72] to account for the insolubility of $[(3,5\text{-}Me_2pz)_2Co]_n$, but this explanation seems unlikely. The above compound may also be obtained from the reaction of $(acac)_2Co$ 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 Fe(II) and Fe(III) have been prepared by the reaction of pyrazole with a variety of iron derivatives such as $Fe(CO)_5$, $[C_5H_5Fe(CO)_2]_2$, etc.[42] While the air-sensitive $[Fe(pz)_2]_n$ was prepared directly, the stable red-brown $[Fe(pz)_3]_n$ was obtained either by the reaction

$$[Fe(pz)_2]_n + Ag(pz) \longrightarrow Ag^0 + [Fe(pz)_3]_n$$

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]



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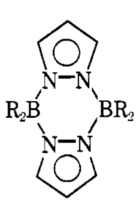

8

Various different types of metallocycles containing two 1,2-*dihapto*pyrazolide (or substituted pyrazolide) bridges have been reported. They are of the general structure **5**, and include M = Rh (L = CO and L_2 = 1,5-cyclooctadiene) and

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(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. Mingoia, *ibid.*, **63**, 242 (1933).
(62) Q. Mingoia and F. Ingraffia, *ibid.*, **64**, 279 (1934).
(63) W. Hückel and H. Bretschneider, *Ber.*, **70**, 2024 (1937).
(64) B. A. Tertov, Z. N. Nazarova, A. D. Garnovskii, M. A. Kasanbieva, 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).
(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 = π-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 heterocycles[77] which may formally be regarded as composed of two boronium fragments linked by two 1,2-*dihapto*pyrazolide bridges. They are formed by the reaction of a pyrazole with a borane or borane complex. This method yields symmetrically substituted pyrazaboles.[78–80]

$$\text{Hpz} + \text{BR}_3 \longrightarrow \text{R}_2\text{B(pz)}_2\text{BR}_2 + \text{RH}$$

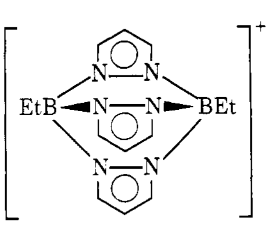
Pyrazaboles containing different substituents on the two boron atoms are synthesized by the reaction of an $R_2B(pz)_2^-$ ion with a borane species containing a leaving group such as halide or sulfonate.[81,82]

$$\text{R}_2\text{B(pz)}_2^- + \text{XBR}'_2 \longrightarrow \text{R}_2\text{B(pz)}_2\text{BR}'_2 + \text{X}^-$$

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-dimethylpyrazole[54] (**5**, R = Me, M = Al, L = Et, mp 117–119°; **5**, R = Me, M = Al, L = Me, mp 141–144°). A similar type of behavior was also observed in the reaction of 3,5-dimethylpyrazole with Me_3M, where M = Al, Ga, and In.[85]

Two examples exist of an array of three 1,2-*dihapto*pyrazolide bridges acting, in essence, as one trinegative bistridentate 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 $BrMn(CO)_5$ has been reported to give air-sensitive, ill-characterized products along with $Mn_2(CO)_{10}$.[87] It is likely that some **10** was formed in these reactions.



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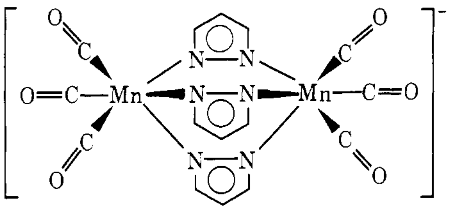
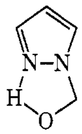


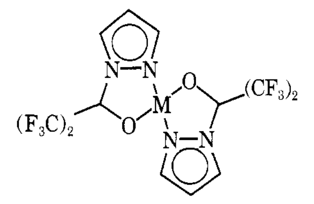
10

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 formaldehyde[88] which raised the possibility that the hydrogen bridge could be replaced with a transition metal ion. However, the reaction of **11** with transition metal ions, M(II), under basic conditions leads to extrusion of formaldehyde and formation of $[M(pz)_2]_n$ polymers.[54] On the other hand, with hexafluoroacetone and related negatively substituted ketones, analogous stable chelates such as **12** have been prepared.[89]



11



12

Sodium and potassium pyrazolides readily add CS_2 to give the ligand **13** (Z = Y = 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 Fe(II) which forms the deep blue complex ion $[Fe(pzCS_2)_3]^-$ isolable as an NR_4^+ salt. Steric effects are of importance; the 3,5-dimethylated ligand forms a monomeric chelate with Ni(II). Potassium pyrazolide readily forms adducts of structure **13** with CO_2, ArNCO, and RNCNR and should do so with any Z=C=Y where Z and Y = O, S, or NR. The CO_2 adduct, stable in the solid state, extrudes CO_2 upon reaction with transition metal ions and yields $[M(pz)_2]_n$.[54]

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

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(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.

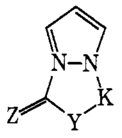
(86) S. Trofimenko, *J. Amer. Chem. Soc.*, **91**, 5410 (1969).

(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).



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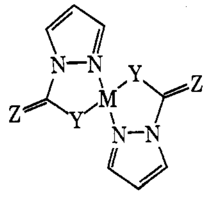
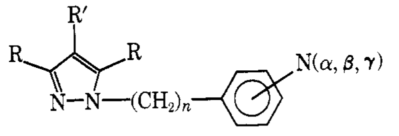


14

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.

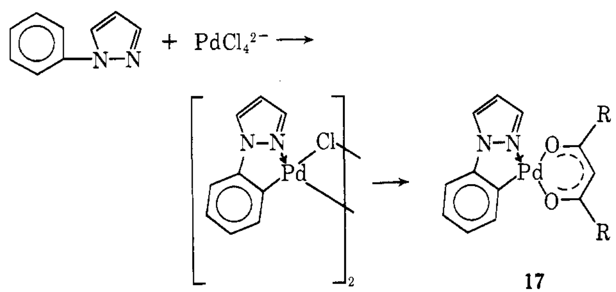
Complexes of $SnCl_4$ with variously substituted pyrazoles of structure **15**, including 3,5-dimethyl-1(2-pyridyl)pyrazole



15

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

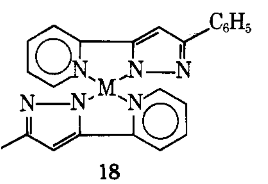
A special case of a 1-substituted pyrazole acting as a bidentate ligand is 1-phenylpyrazole. It undergoes a remarkable reaction with $PdCl_4^-$ which involves formation of a Pd–C bond in the ortho position, and precipitation of the insoluble, stable dimeric product, **16**. This has been converted to 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]



16

17

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 $[Ni(PPP)_2(py)_2]$, $[Ni(PPPH)_2L_2]X_2$, $Ni(PPPH)_2X_2$, and $[Ni(PPP)_3]X_2$ (X = F, Cl, Br, I, ClO_4, or NO_3; L = pyridine, water, or acetone) have been investigated.[96] Similarly, the following analogous Co chelates were studied in some detail: $[Co(PPPH)_2(OH)_2]X_2$, $Co(PPPH)_2X_2$, and $Co(PPP)_3$.[97]



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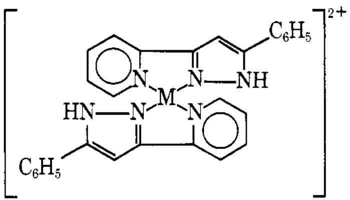

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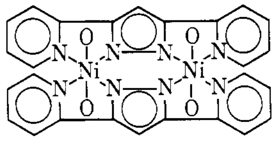
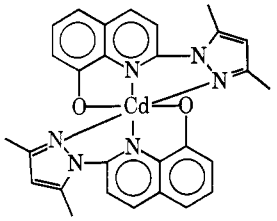


20

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-quinolyl)-3,5-dimethylpyrazole, has been proposed for the determination of cadmium by measuring the luminescence of the chelate **21**. This method[99] is claimed to be sensitive to 5–50 × 10^{-6}% Cd.



21

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, $R_2B(pz)_2^-$, re-

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(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. Krokhina, 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).

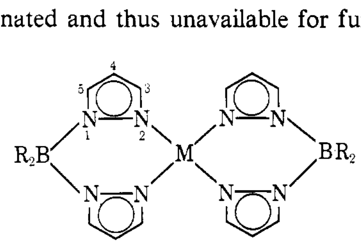
(96) H. Hennig and V. Eckelman, *Z. Anorg. Allg. Chem.*, **363**, 127 (1968).

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

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

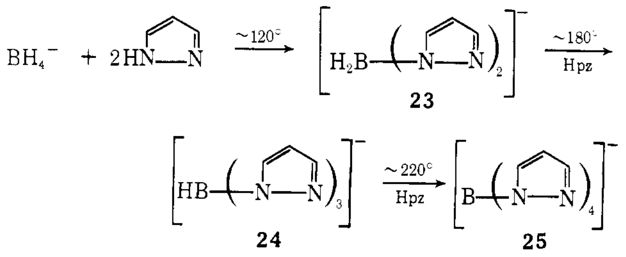
(99) E. A. Bozhevolnov, L. F. Fedorova, I. A. Krasavin, and V. M. Dziomko, *Zh. Anal. Khim.*, **25**, 1722 (1970); *J. Anal. Chem. USSR*, **25**, 1478 (1970).

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 coordination 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.



22

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]

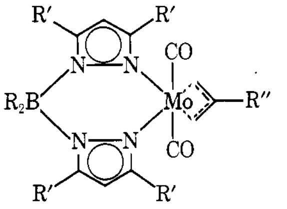
1. Bidentate Bis Chelates

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 $[H_2B(3,5\text{-}Me_2pz)_2]_2M$ 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 $R_2B(3,5\text{-}R'_2pz)_2Mo(CO)_4^-$ with allyl halides gave readily the π-allyl derivatives **26**, possessing a 16-electron configuration.



26a, R = H; R′ = CH_3
b, R = C_2H_5; R′ = H

The same type of product was obtained from substituted allylic halides, from cyclic systems such as cyclohexenyl, and from ligands containing 3,5-Et_2 and 3,5-$(C_6H_5)_2$ substituents. These orange-red compounds were remarkably stable. Their nmr spectra indicated fluxional behavior similar to that found in the $RB(pz)_3Mo(CO)_2$-π-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

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(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.

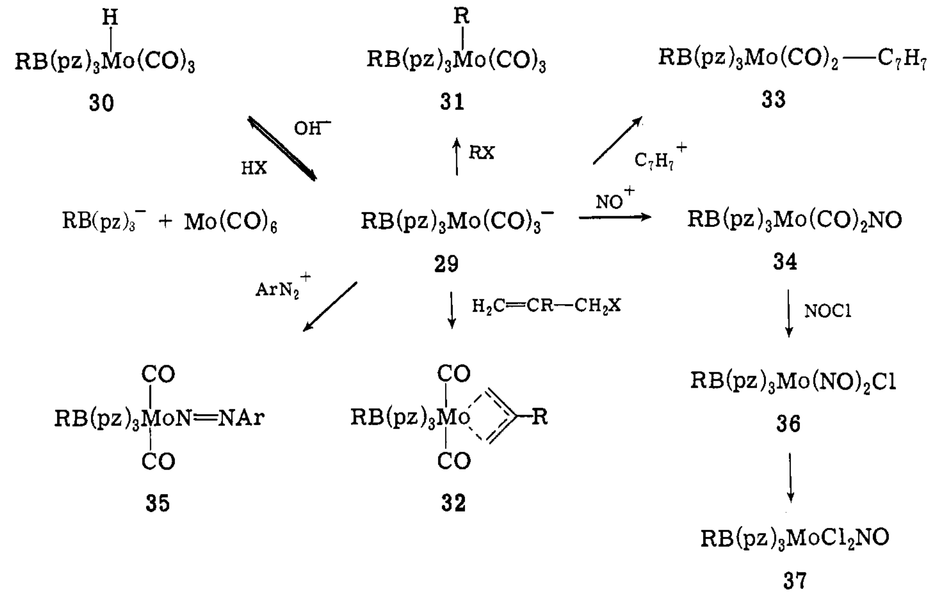
(104) S. Trofimenko, *J. Amer. Chem. Soc.*, **91**, 3183 (1969).

(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).

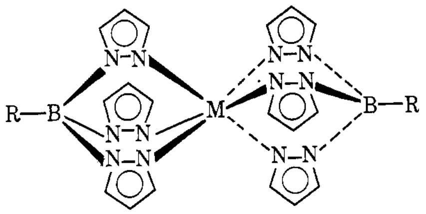
Scheme I



quaternary alkylammonium halides some $H_2B(pz)_2M(CO)_3X^-$ was formed.[40]

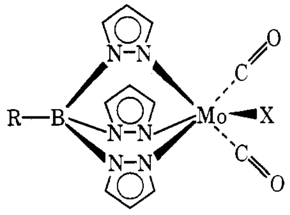
3. Tridentate Bis Chelates

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 remains tridentate. In some chelates, such as $[B(pz)_4]_2Zn$, 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]



R = H, alkyl, aryl, pz

27



28

The simplest compounds involving a C_{3v} tridentate ligand are the parent $[HB(pz)_3]_2M$ derivatives. They are stable to light, air, water, dilute acids, and bases, 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 $[HB(pz)_3]_2Co$.[106] The same holds true for compounds derived from symmetrically substituted ligands.

While preparation of mixed ligands, *e.g.*, $HB(pz)_2pz'^-$, has not been studied, it is possible to prepare tridentate chelates with less than D_{3d} symmetry by the reaction of $[H_2B(pz)_2]_2M$ with a substituted pyrazole, Hpz′. The compound $[HB(pz)_2(4\text{-}CNpz)]_2Ni$ was prepared in this fashion[54] 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 $HB(3,5\text{-}Me_2pz)_3Mo(CO)_3^-$, 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 $HB(3,5\text{-}Me_2pz)_3Mo(CO)_3^-$ failed to react with allylic halides, the π-allylic

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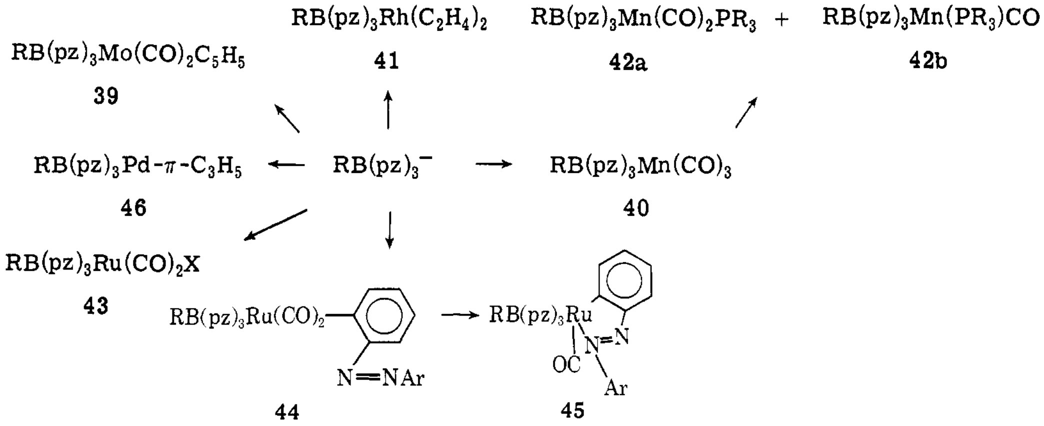
(108) S. Trofimenko, *J. Amer. Chem. Soc.*, **89**, 3904 (1967).
(109) S. Trofimenko, *ibid.*, **91**, 588 (1969).

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 aryldiazonium salts. The sterically hindered anion gave, inexplicably, a blue product thought to be $HB(3,5\text{-}Me_2pz)_3Mo(CO)_3Ar$.[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 $C_5H_5Mo(NO)_2Cl$ 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 $HB(3,5\text{-}Me_2pz)_3Mo(CO)_3^-$ and arylsulfonyl chlorides. Instead of the anticipated sulfones or sulfinates, the monomeric arylmercapto derivatives, **38**, were produced. They were also obtained from ArSCl compounds.[111]

$$\underset{\mathbf{37a}}{HB(3,5\text{-}Me_2pz)_3Mo(CO)_3^-} + ArSO_2Cl \longrightarrow \underset{\mathbf{38}}{HB(3,5\text{-}Me_2pz)_3Mo(CO)_2SAr}$$

The reaction of **37a** with $SOCl_2$ gave the green compound $HB(3,5\text{-}Me_2pz)_3MoOCl_2$, also obtainable from $MoOCl_3$ and $HB(3,5\text{-}Me_2pz)_3^-$.[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 $RB(pz)_3^-$ ligand. For instance, the compound **33** was made more easily by the reaction of $RB(pz)_3^-$ with $C_7H_7Mo(CO)_2I$.[109] Similarly, the reaction of $C_5H_5Mo(CO)_3Cl$ with $B(pz)_4^-$ yielded **39**. The suggestion that in this compound the $B(pz)_4$ ligand is bidentate[109] has been confirmed by two independent X-ray structure determinations.[112,113]

While attempts to synthesize mixed sandwiches of the type $RB(pz)_3MC_5H_5$, *e.g.*, by the reaction of $C_5H_5Fe(CO)_2X$ with $RB(pz)_3^-$, led invariably to $[RB(pz)_3]_2M$,[54,114] it has been possible to synthesize a mixed sandwich cation $[pzB(pz)_3Co\text{-}C_5H_5]^+$.[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 $HB(pz)_3^-$ with $Ru_3(CO)_{12}$, followed by halogenation, gave $HB(pz)_3Ru(CO)_2X$, **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 $HB(pz)_3^-$ (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 $RB(pz)_3^-$. 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 $B(pz)_4^-$ can also act in tetradentate fashion when pairs of N termini are bridged by appropriate four-coordinate species.

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

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

[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.

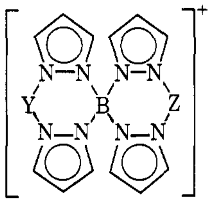
[116] A. R. Schoenberg and W. P. Anderson, Abstracts of 6th Middle Atlantic Regional Meeting of the American Chemical Society, Feb 3–5, 1971, p 53, No. 6.

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

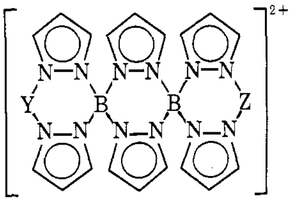
[118] R. J. Doedens, personal communication.

[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.

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, isoluble as hexafluorophosphate salts.[120] The cation **49**, containing two different 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.



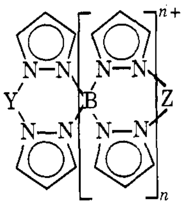
47, $Y = Z = Pd\text{-}\pi\text{-}CH_2CRCH_2$
48, $Y = Z = BEt_2$
49, $Y = BEt_2$; $Z = Pd\text{-}\pi\text{-}CH_2CRCH_2$



50, $Y = Z = BEt_2$
51, $Y = Z = Pd\text{-}\pi\text{-}CH_2CRCH_2$

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]



52

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, $[HB(3,5\text{-}Me_2pz)_3]_2Fe$ 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°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 NH_2 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-$CH_2CR'CH_2$ 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-$CH_2CR'CH_2$ 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

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

(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).

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 $Et_2B(pz)_2$-$Mo(CO)_2C_5H_5$ 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 $RB(pz)_3$-$Mo(CO)_2C_7H_7$ 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 pseudocontact shifts in Co–polypyrazolylborate complexes resulted[132] 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 polypyrazolylborates 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 determined 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]

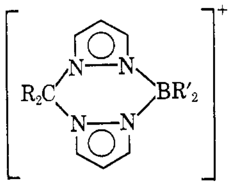
Enthalpies of chelation for Co, Ni, Cu, and Zn with $H_2B(pz)_2^-$, $HB(pz)_3^-$, $H_2B(3\text{-}Mepz)_2^-$, and $B(pz)_4^-$ have been measured in water and in acetonitrile. In water, for bidentate ligands, the order of decreasing $-\Delta H$ is Ni > Cu > Co > Zn and for $B(pz)_4^-$ it is Cu > Ni > Co > 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 isoelectronic 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 $R_2C(pz)_2$ react[84] 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°.



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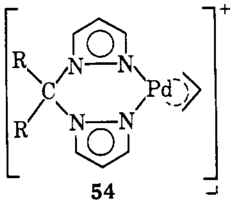

54

2. Tridentate Chelates

The tridentate chelates, based mainly on $HC(pz)_3$, although $C(pz)_4$ and $HC(3,5\text{-}Me_2pz)_3$ 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 $[HC(pz)_3Mo(CO)_2$-π-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

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(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 $[HB(pz)_3]_2Co$ system.[130]

Altogether, the area of coordination chemistry based on $R_nC(pz)_{4-n}$ ligands has not been studied to any appreciable extent, although some work, such as the synthesis of the mixed sandwich cation $[HC(pz)_3CoC_5H_5]^+$, 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 work[139] 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]

$$Hpz + R_3M\text{-}NMe_2 \longrightarrow R_3Mpz + HNMe_2$$

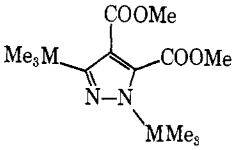
$$Lipz + Me_3GeCl \longrightarrow Me_3Gepz + LiCl$$

$$2Hpz + (Et_3Ge)_2O \longrightarrow Et_3Gepz + H_2O$$

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, $R_3M(pz)_2MR_3$, 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]

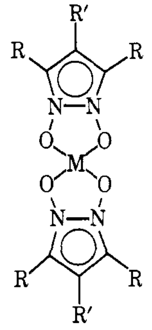
$$(Me_3M)_2CN_2 + MeOOCC{\equiv}CCOOMe \longrightarrow$$



55

M = Si, Sn

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]



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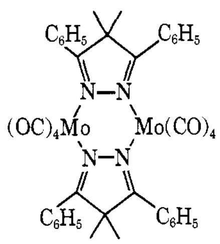

57

VII. Addendum. Some Recent Developments

In the area of simple pyrazole coordination compounds the complexes L_3InX_3 (where L = Hpz, H3,5-Me_2pz),[147] (H3,5-Me_2pz)$NbCl_5$,[148] and $Rh(Hpz)_4Cl_2Cl \cdot 5H_2O$[149] 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 $M(Hpz)_3Cl_3$ and $M(H3\text{-}Mepz)_3Cl_3$ have been analyzed.[151] From an esr study of powdered $Ni(Hpz)_6X_2$ complexes, the parameters *g*, *D*, and *E* for an $S = 1$ system have been evaluated.[152] The coordination of Hpz to Ni^{2+} was found to increase its rate of iodination.[153] Complexation of Hpz and 1-Mepz to BF_3 has been studied by ^1H and ^{19}F nmr,[154] and zero-field splittings in $Ni(Hpz)_4X_2$ were studied.[155]

Several methods of preparing $[M(pz)_2]_n$ polymers have been described, as has the synthesis of complex anions $M(pz)_4{}^{2-}$ (M = Zn, Cu, Ni, and Co),[156] and of $[(OC)_4M(pz)_2M(CO)_4]^{2-}$ for M = Mo and W.[157]

The unstable $C_5H_5Fe(CO)_2pz$ has been reported,[158] as have complexes of the type $LFe(CO)_4$ for L = Hpz and H3,5-

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(137) H. W. 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. Hrung, *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).

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Me_2pz.[159] A study of site exchanges of nitrogenous bases in a porphinatoruthenium carbonyl system[160] included H3,5-Me_2pz.

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 prepared[165] 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 $H_2B(3,5\text{-}Me_2pz)_2Mo(CO)_2C_7H_7$ and $Et_2B(pz)_2Mo(CO)_2C_7H_7$ the C_7H_7 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 mentioned[114] compound $HB(pz)_3Fe(CO)_2Me$ was investigated by ir, nmr, and X-ray crystallography and found to be actually $HB(pz)_3Fe(CO)_2COCH_3$.[171] X-Ray structure determinations have also been carried out on $HB(pz)_3Mo(CO)_2NO$, $HB(pz)_3Mo(CO)_2\text{-}\pi\text{-}CH_2CMeCH_2$, $[EtB(pz)_3BEt]PF_6$, and $Et_2B(4\text{-}Brpz)_2BEt_2$.[172]

Bromination of $RB(pz)_3Mo(CO)_2NO$ yielded predominantly the dimeric $RB(pz)_3MoBr_2NO$, although some organobromination accompanied by ethanolysis also occurred.[173] The stable complex $(pz)_2B(pz)_2PtMe_2(C_6H_5PMe_2)_2$ 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 $H_2B(pz)_2CoR_f(C_5H_5)$, $HB(pz)_3CoR_f(C_5H_5)$, and $HB(pz)_3Fe(CO)_2R_f$, of iron derivatives such as $[(pz)Fe(CO)_2]_2$, $(allylpz)Fe(CO)_3$, $HB(pz)_3Fe(CO)_2COC_3H_5$, $HB(pz)_3Fe(CO)_2C_3H_5$, and $[H_2B(pz)_2]_2Fe(CO)_2$, and of the interesting dinitrogen complex $H_2B(pz)_2PtMe_3N_2$.[176]

Various 1-pyrazolylphosphines and -silanes ($P(pz)_3$, $C_6H_5P(pz)_2$, $(C_6H_5)_2Ppz$, $Me_2Si(pz)_2$, $MeSi(pz)_3$) have been synthesized.[177] It has been found that $[HC(pz)_3]_2M^{2+}$ complexes can be prepared in low yield directly from $M(Hpz)_6{}^{2+}$ 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]

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