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Coordination Chemistry Reviews 249 (2005) 663–691

COORDINATION CHEMISTRY REVIEWS

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Review

Metal derivatives of poly(pyrazolyl)alkanes☆ II. Bis(pyrazolyl)alkanes and related systems

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Received 27 February 2004; accepted 3 August 2004

Contents

Abbreviations: acacH, 2,4-pentanedione; OAc, acetate; Bipy, 2,2′-bipyridyl; Bn, benzyl; Bp^x, a generical bis(pyrazolyl)borate; ^{i}Bu, iso-butyl; ^{n}Bu, normal-butyl; ^{t}Bu, terz-butyl; camphpzH, 7,8,8-trimethyl-4,5,6,7-tetrahydromethano-2-indazole; COD, 1,5-cyclooctadiene; Cp, a generical cyclopentadienyl; cy, cyclohexyl; dme, 1,2-dimethoxyethane; dmf, dimethylformmamide; dppe, 1,2-diphenylphosphinoethane; en, etilendiammina; Et, ethyl; Et_2O, diethyl ether; EtOH, ethanol; Fo, formyl; Hin, indazole; hfacH, hexafluoroacetylacetone; $H_2C(pz)_2$, bis(pyrazolyl)methane; $H_2C(pz^x)_2$, a generical bis(pyrazolyl)methane; Ind, indenyl; Me, methyl; mim, 1-methylimidazol-2-yl; ox, oxalate; *o*-pd, orthophenylendiammine; phen, 1,10-phenanthroline; pip, piperidine; $pzTp^x$, a generical tetrakis(pyrazolyl)borates; py, pyridyl; pyr, pyridine; $(R_2C)_n(pz^x)_2$ or $RR'C(pz)_2$, a generical bis(pyrazolyl)-*N*,*N*′-alkane; tfo, trifluoroacetate; tfs, trifluoromethanesulfonate; thi, thienyl; Htz, 1,2,4-triazole; THF, tetrahydrofuran; Tmed, tetramethylethylendiamine; tpnm, tris(2-pyridyl)methoxymethane; Tp^x, tris(pyrazolyl)borate

☆ Part I is Ref. [1].

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doi:10.1016/j.ccr.2004.08.017

Abstract

This review summarizes the literature concerning metal complexes of bis(pyrazolyl)alkane ligands $R_2C(pz^x)_2$ and follows a previous article describing the coordination chemistry of tris(pyrazolyl)alkanes [C. Pettinari, R. Pettinari, Coord. Chem. Rev., in press]. A comprehensive survey of bis(pyrazolyl)alkanes coordination chemistry, based on the nature of the metal, is presented, together with the main synthetic methods and spectroscopic and structural features of this important class of ligands.

Keywords: Poly(pyrazolyl)alkane; Coordination chemistry; Metal derivatives

1. Introduction

Bis(pyrazolyl)alkanes $(R_2C)_n(pz^x)_2$ (Fig. 1) constitute a family of stable and flexible bidentate ligands, isoelectronic and isosteric with the well-known bis(pyrazolyl)borates, also discovered by Trofimenko [2]. These molecules form a variety of coordination compounds with main group and transition metals. Their coordinating behaviour is often very different from that shown by Bp^x, $(R_2C)_n(pz^x)_2$ being able to yield stable adducts containing six M–N–N–C–N–N and seven M–N–N–C–C–N–N membered rings (Fig. 2), basic salts, mercuriated products, cleavage of the carbon (sp^3)–N bond and "agostic" interaction M···H–C between the metal center and protons of the bridging methylene groups. While bipy or phen metal adducts are likely to contain an approximately planar, five membered –M–N–C–C–N moiety, upon coordination of $(R_2C)_n(pz^x)_2$ to a metal, a six- or a seven-membered cycle is formed for which a boat conformation is forecast. Nevertheless, both the internal and external angles of the formally related M–(N–N)$_2$–E moieties (where E is not carbon) are known to be able to undergo wide variations. X-ray studies, carried out on several μ-pyrazolato-*N*,*N*′-derivatives [3–5], showed that the six-membered ring is not always in the boat conformation, but can undergo a severe folding as in bis(3,5-dimethylpyrazolyl)borato-*N*,*N*′](η^3-cycloheptatrienyl)(dicarbonyl)molybdenum [4], or can be a distorted chair as in dimeric [bis(cyclopentadienyltitanium)(μ-pyrazolato-*N*,*N*′)]$_2$ [5a] or dihydrobis(3,5-dimethylpyrazolyl)borate(η^3-allyl)dicarbonylmolybdenum [5b]. Related studies with pyrazaboles showed that energy differences between chair, boat, or planar conformations of a M–(N–N)$_2$–E (M = E = boron) are small, and that the solid state configuration is mainly determined by packing effects [3].

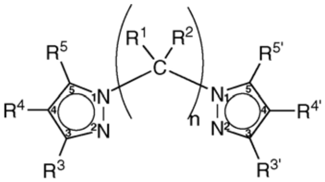


Fig. 1. General structure of bis(pyrazol-1-yl)alkane ligands.

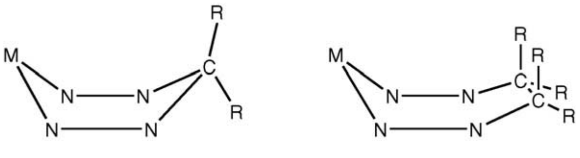


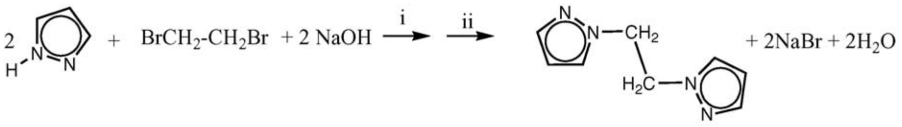
Fig. 2. Six and seven-membered rings formed by bis(pyrazolyl)alkanes after metal coordination.

The $(R_2C)_n(pz^x)_2$ ligands can be readily prepared and various substituents may replace each hydrogen atom, so that electronic and steric effects can be varied nearly at will. A steady stream of new derivatives was recently reported, however at this moment no complete and systematic review has appeared. We report a comprehensive survey of the coordination chemistry of bis(pyrazolyl)alkanes (and related systems containing only two pyrazolyl rings), based on the nature of the metal, together the principal synthetic methods and spectroscopic and structural properties of this class of ligands.

2. Syntheses and properties of bis(pyrazolyl)alkanes

The synthesis of $H_2C(pz)_2$ was first reported by Trofimenko [2]. This ligand can be prepared by reaction of Hpz with CH_2Cl_2 in an autoclave at 150 °C. At 200 °C this reaction leads to 4,4′-dipyrazolylmethane, which upon reaction with boranes, forms a pyrazabole polymer. Some $R_2C(pz^x)_2$ have also been prepared from the reaction of potassium salts of the azole with methylene iodide. The use of strong bases often has allowed higher yields [6].

Elguero and co-workers improved the Trofimenko method some years later. They showed that *N*,*N*′-pyrazolylmethanes can be prepared by reaction of azoles with CH_2Cl_2 under phase transfer catalysis (PTC) conditions [7]. Substituted bis(pyrazolyl)methanes $(H_2C)_n(pz^x)_2$ (x = H, NO_2, 4-Br, 4-NO_2, NH_2, 5-NH_2) were prepared by reaction of the correspondingly substituted pyrazoles with CH_2Cl_2 or by direct attack on the pyrazolyl rings [8].



i : PTC = NBu_4Br; solvent = toluene; T = 60-80°C, time = 24-72 h
ii: extraction with CH_2Cl_2; recrystallisation solvent = dichloromethane; sublimation

Fig. 3. General synthetic method for the synthesis of bis(pyrazol-1-yl)alkane ligands [9].

A general and simple procedure for the synthesis of bis(pyrazolyl)alkane ligands, reported by Elguero and co-workers, is described in Fig. 3 [9].

Substituted bis(pyrazolyl)methanes can also be prepared by lithiation of geminal bis(pyrazolyl)alkanes. The ligand $H_2C(pz)_2$ can be lithiated on the bridging CH_2 to give carbanions which react with a variety of electrophiles. Lithiation can also be directed to the five-position of the heterocyclic ring [10].

The reactions of azoles and benzazoles with dihalomethane and dihaloethanes for the synthesis of bis(azolyl)-methanes and -ethanes have also been performed in the absence of solvent by solid–liquid phase transfer catalysis [11]. No solvent was used during the reaction and, when possible, during the work-up. Comparison with classical methods indicates that the most important advantages of PTC without solvent are higher yields and milder conditions. PTC in the absence of solvent is a general procedure for the preparation of bis(azolyl)methanes and showed no dependence on the nature of the azole. In addition the absence of solvent allows the use of dibromomethane also with the less reactive azoles because the alkylation agent is used in an equimolar amount and not in a large excess (as a solvent). Nevertheless, the regioselectivity obtained by this method is similar to that described by classical methods [11].

The ligands $(1,2\text{-}C_2H_4)(pz)_2$, $(1,2\text{-}C_2H_4)(4\text{-}Brpz)_2$, $(1,2\text{-}C_2H_4)(4\text{-}NO_2pz)_2$, $(1,2\text{-}C_2H_4)(3\text{-}NO_2pz)_2$ were prepared by reaction of Hpz^x with 1,2-dibromoethane or 1-chloro-2-(pyrazol-1-yl)ethane by PTC (Fig. 4) and characterized by ^1H and ^{13}C NMR spectroscopy [12].

Reaction of 3-(2-py)pzH with CH_2Br_2 and NaOH under PTC yielded $H_2C(3\text{-}(2\text{-}py)pz)_2$, containing two bidentate pyrazolyl-pyridine arms linked to a methylene spacer [13]. The ligand $(1,3\text{-}C_3H_6)(3\text{-}(2\text{-}py)pz)_2$ was prepared by reaction of 3-(2-py)pzH with 1,3-dibromopropane under the same PTC conditions [14].

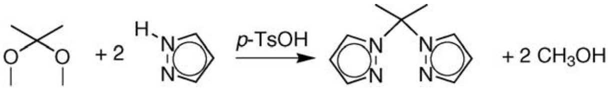


Fig. 5. Synthesis of bis(pyrazolyl)alkanes with ketals or acetals [16].

While the reaction of 3-^{t}BupzH with CH_2Br_2 under PTC conditions afforded $H_2C(3\text{-}^tBupz)_2$, the reaction of 3-^{i}PrpzH with CH_2Br_2 under the same conditions yielded three isomers: $H_2C(5\text{-}^iPrpz)_2$, $H_2C(3\text{-}^iPrpz)(5\text{-}^iPrpz)$ and $H_2C(3\text{-}^iPrpz)_2$. The sterically hindered $H_2C(5\text{-}^iPrpz)_2$ was obtained in the highest yield [15].

When the pz^x rings are bridged by larger alkyl group (isopropylidene) the ligands were better prepared by acid-catalyzed reaction of pyrazole or C-substituted pyrazole with acetals or ketals (Fig. 5) [16]. When an unsymmetrically substituted pyrazole was employed, the sterically favoured isomer was generally obtained. This procedure was applied to the synthesis of chiral bis(pyrazolyl)methanes such as $R_2C(camphpz)_2$ (Fig. 6) [16,17].

The metal catalyzed reaction of 1,1′-carbonyldipyrazoles with aldehydes or ketones to give 1,1′-alkylidenedipyrazoles and carbon dioxide is sensitive to electronic and steric substituents [18].

The ligand $1,2\text{-}(C_2H_4)(3\text{-}Fopz)_2$ (Fig. 7) was synthesized by reaction of 3-formylpyrazole with 1,2-ditosylate-ethane and KO^{t}Bu at −40 °C in THF [19].

Otero reported the multistep synthesis of the polyfunctional ligand $H_2C(5\text{-}Ph_2Ppz)_2$ and $Me_3SiCH(5\text{-}Ph_2Ppz)_2$ (Fig. 8) [20].

Unsymmetrical bis(pyrazolyl)alkanes can be easily prepared by using a procedure reported by Elguero in 1986 [21]. The unsubstituted Hpz can be first converted into its 1-hydroxymethyl derivative by reaction with formaldehyde. Then reaction with thionyl chloride yields the 1-chloromethyl derivative which is isolated as its hygroscopic hydrochloride salt. Under solid–liquid

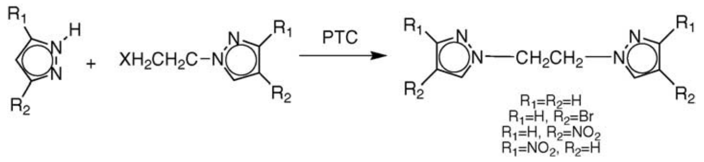


Fig. 4. Synthesis of bis(pyrazolyl)ethanes under PTC conditions [12].

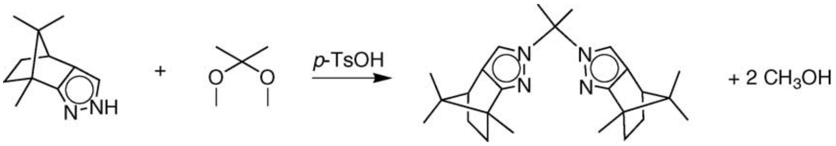


Fig. 6. Synthesis of $Me_2C(camphpz)_2$ [16,17].

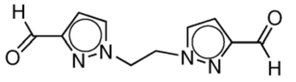


Fig. 7. 1,2-$(CH_2)_2$(3-Fopz)$_2$ [19].

PTC conditions the 1-chloromethylpyrazole reacts with equimolar quantities of a substituted pyrazole such a 3,4,5-Me_3pzH to selectively produce the unsymmetrical bis(pyrazolyl)methane $R_2C(pz)(pz^x)$ [21].

A conformational study on bis(pyrazolyl)methane by using crystallography, lanthanide shift reagents L.S.R., dipole moments and theoretical calculations were reported by Claramunt et al. [22] whereas Bonati and Bovio [23a], Pettinari et al. [23b] and Castellano and co-workers [24] reported X-ray single crystal studies of two bis(pyrazolyl)methane ligands.

^{1}H and ^{13}C NMR studies of substituted bis(pyrazolyl)methane $R_2C(pz^x)_2$ and the effects of the various N-substituents on the ^{13}C chemical shifts of the heterocyclic nuclei were reported by Elguero [25]. The chemical shifts of the methane C atom are discussed using an interactive model. Some ^{1}H–^{13}C coupling constants were measured [26].

Selected example of $R_2C(pz^x)_2$ coordination modes are reported in Fig. 9. Selected synthetic methods for a number of $R_2C(pz^x)_2$ ligands are listed in Table 1.

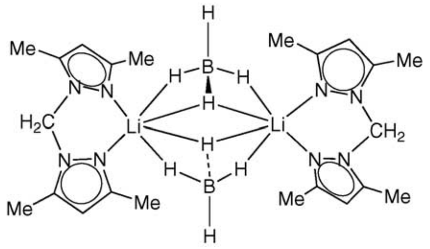


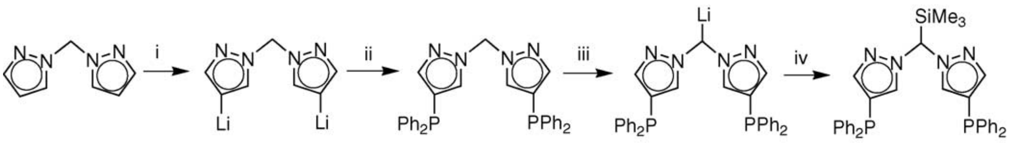
Fig. 10. $[\{H_2C(3,5\text{-}Me_2pz)_2\}Li(\mu\text{-}\eta^3\text{-}BH_4)]_2$ [27].

3. Metal derivatives of bis(pyrazolyl)alkanes

3.1. Group IA: Na, Li

Reaction of equimolar amounts of $LiBH_4$ and $H_2C(pz^x)_2$ yields coordination compounds that are much more stable in air than $LiBH_4$. In the dimer $[\{H_2C(3,5\text{-}Me_2pz)_2\}Li(\mu\text{-}\eta^3\text{-}BH_4)]_2$ the $[BH_4]$ acts as a bridging group through one η^3-H and two η^2-H (Fig. 10). The reaction of $LiBH_4$ with $H_2C(pz)_2$ ligand yields $[\{H_2C(pz)_2\}Li(BH_4)]_2$ [27].

The hydride derivative $[\{H_2C(3,5\text{-}Me_2pz)_2\}Li(\mu\text{-}\eta^3\text{-}BH_4)]_2$ was also investigated as potential new hydrogen source for protein exchange membrane fuel cells. The



i: 2 ^{n}BuLi, THF, -70°C, 30min; ii: 2Ph_2PCl, THF, r.t., 12h; iii) 2 ^{n}BuLi, THF, -70°C, 1h; iv) Me_3SiCl, THF, r.t., 12h

Fig. 8. The multistep synthesis of the polyfunctional ligand $H_2C(5\text{-}Ph_2Ppz)_2$ and $Me_3SiCH(5\text{-}Ph_2Ppz)_2$ [20].

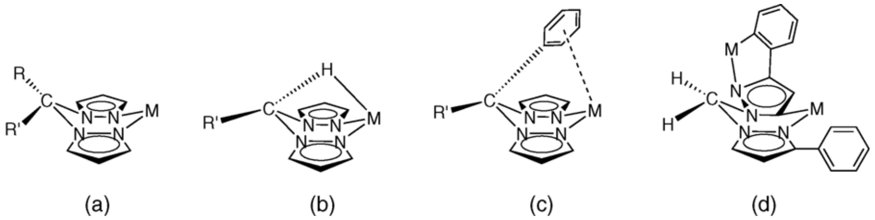
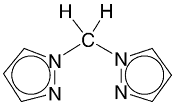
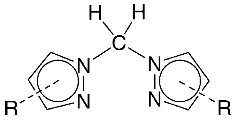
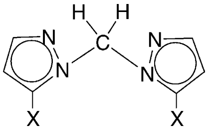
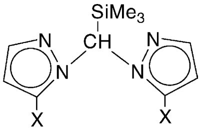
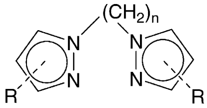
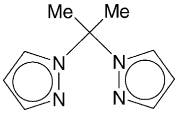
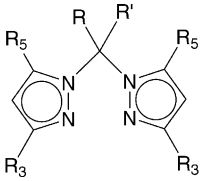
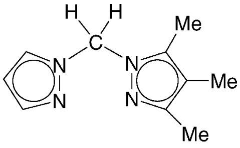


Fig. 9. Selected example of $R_2C(pz^x)_2$ coordination mode.

Table 1
The most relevant synthetic methods describing the synthesis of bis(pyrazolyl)alkane ligands

Starting reagents	Solvents and reaction conditions	Ligands	Refs.
Hpz	CH_2Cl_2 autoclave 150 °C		[2]
Hpz + NBu_4Br	CH_2Cl_2 PTC reflux, 12 h		[7,8,9]
$H_2C(pz)$ + ^nBuLi + XY	THF: (i) −70 °C, 30 min; (ii) r.t., 12 h		[10,20]
$H_2C(pz^x)_2$ + $SiMe_3Cl$	THF r.t., 12 h		[20]
$Br(CH_2)_nBr$ + NaOH + NBu_4X	Toluene PTC 70 °C, 72 h		[14]
2,2-Dimethoxypropane + $2Hpz^x$ + *p*-TsOH	CH_3OH reflux		[16]
$OC(pz^x)_2$ + RR′CO (R and R′ = H, alkyl, or aryl)	THF $CoCl_2$		[18]
1-$(ClCH_2)$pz + 3,4,5-Me_3pzH + NBu_4Br	PTC CH_2Cl_2 reflux		[21]

evolution of hydrogen via hydrolysis and the heat of reaction by hydrolysis have been measured [28]. $[\{H_2C(3,5\text{-}Me_2pz)_2\}Li(\mu\text{-}\eta^3\text{-}BH_4)]_2$ and $[\{H_2C(pz)_2\}Li(BH_4)]_2$ were tested for use as hydrogen storage media for portable fuel cell applications [29].

The reaction of $[NaCr(bipy)(ox)_2(H_2O)]\cdot 2H_2O$ with $H_2C(pz)_2$ in methanol leads to formation of $\{[NaCr(bipy)(ox)_2]_2(H_2C(pz)_2)\cdot 2H_2O\}_n$. This compound exists as an open railroad framework polymer with channels of 15.0 × 7.3 Å [30].

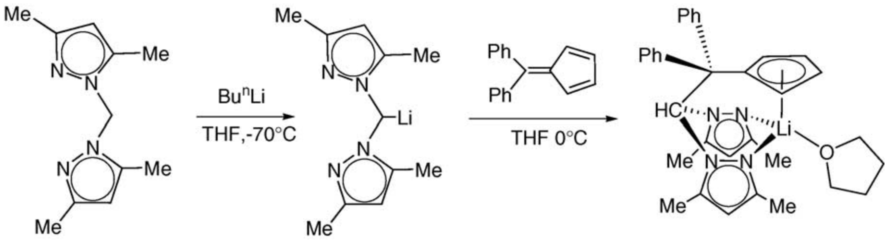


Fig. 11. Synthesis of $[Li\{2,2\text{-}(3,5\text{-}Me_2pz)_2\text{-}1,1\text{-diphenylethylcyclopentadienyl}\}(THF)]$ [31].

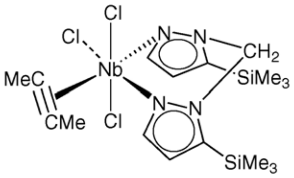


Fig. 12. [NbCl$_3$(H$_2$C(5-SiMe$_3$pz)$_2$)(MeC≡CMe)] [34].

Otero reported that deprotonation of the methylene group of H$_2$C(3,5-Me$_2$pz)$_2$ with ^{n}BuLi, followed by reaction with 6,6-diphenylfulvene, yielded the lithium compound [Li{2,2-(3,5-Me$_2$pz)$_2$-1,1-diphenylethylcyclopentadienyl}(THF)] (Fig. 11) [31].

3.2. Group IVB: Zr

The lithium compound [Li{2,2-(3,5-Me$_2$pz)$_2$-1,1-diphenylethylcyclopentadienyl}(THF)] reacts at −70 °C in a 1:1 molar ratio with ZrCl$_4$ in THF to give [ZrCl$_3${2,2-(3,5-Me$_2$pz)$_2$-1,1-diphenylethylcyclopentadienyl}] [31].

3.3. Group VB: V, Nb

Six-coordinate vanadium(II) complexes [V{H$_2$C(pz)$_2$}$_2$X$_2$] (X = Cl, Br, I, NCS) and [V{H$_2$C(3,5-Me$_2$pz)$_2$}$_2$X$_2$] (X = Br, NCS) were synthesized by reaction of V(II) salts with the corresponding R$_2$C(pz^x)$_2$. Polymeric six-coordinate [V{H$_2$C(pz)$_2$}$_2$Cl][BPh$_4$], monomeric five-coordinate [V{3,5-Me$_2$pz)$_2$}$_2$Cl]X (X = BPh$_4$, PF$_6$) and monomeric six-coordinate [V{H$_2$C(pz)$_2$}$_3$][BPh$_4$]$_2$ complexes were also reported [32].

A hydrolytic cleavage of a C(sp^3)–N bond was observed when the reaction between VOCl$_2$ and Me$_2$C(pz)$_2$ was carried out in hydroalcoholic solvents, the adduct [(pzH)$_2$VOCl$_2$] being the only product clearly identified in the reaction solution [33].

From the reaction of [NbCl$_3$(dme)$_n$] with H$_2$C(pz)$_2$, H$_2$C(3,5-Me$_2$pz)$_2$, and H$_2$C(5-SiMe$_3$pz)$_2$, the binuclear complexes [NbCl$_3$(L)$_2$] (L = bis(pyrazol)alkane) were formed. Mononuclear acetylene complexes [NbCl$_3$(L)(RC≡CR′)] (R, R′ = Me, Ph and/or CO$_2$Me) were obtained from either the reaction of [{NbCl$_3$(L)}$_2$] with acetylenes or from the reaction of [NbCl$_3$(dme)(RC≡CR′)] with the appropriate bis(pyrazolyl)alkane. The structures of these compounds (Fig. 12) were determined by spectroscopic methods. NMR studies were also carried out in order to evaluate the fluxional behaviour of the complexes in solution [34].

[NbCl$_3$(dme)]$_n$ reacts with H$_2$C(5-PPh$_2$pz)$_2$ to give the binuclear complex [NbCl$_3${H$_2$C(5-PPh$_2$pz)$_2$}]$_2$. The reaction of H$_2$C(5-PPh$_2$pz)$_2$ with the mononuclear species [NbCl$_3$(dme)(RC≡CR′)] gave the corresponding derivatives [NbCl$_3${H$_2$C(5-PPh$_2$pz)$_2$}(RC≡CR′)] (R = R′ = Ph; R = R′ = SiMe$_3$; R = Ph, R′ = Me; R = Ph, R′ = SiMe$_3$) containing the bis(pyrazolyl)alkane ligand coordinated in a bidentate *N*,*N*-fashion [20].

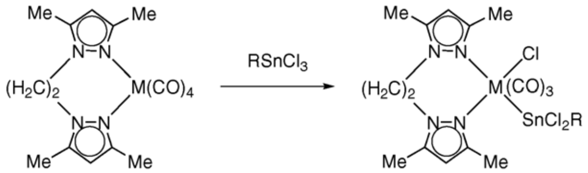


Fig. 13. The seven-coordinate oxidative addition compound [M{H$_2$C(pz)$_2$}(CO)$_3$(Cl)(RSnCl$_2$)] [40].

3.4. Group VIB: Cr, Mo, W

Five and six-coordinate Cr(II) complexes [Cr{H$_2$C(pz)$_2$}Cl$_2$], [Cr{H$_2$C(pz)$_2$}$_2$X$_2$] (X = Br, I), and [Cr{H$_2$C(pz)$_2$}$_2$X][BPh$_4$] (X = Cl, Br) [Cr{H$_2$C(3,5-Me$_2$pz)$_2$}$_2$Cl][BF$_4$], [Cr{H$_2$C(3,5-Me$_2$pz)$_2$}$_2$X][BPh$_4$] (X = Br, I), and [Cr{H$_2$C(3,5-Me$_2$pz)$_2$}$_2$X]X (X = Br, I) were reported by Mani and Morassi on 1979 [35].

H$_2$C(3,5-Me$_2$pz)$_2$ reacts with M(CO)$_6$ (M = Cr, Mo, W) yielding [M{H$_2$C(3,5-Me$_2$pz)$_2$}(CO)$_4$]. In [Mo{H$_2$C(3,5-Me$_2$pz)$_2$}(CO)$_4$], the four carbonyls and the bidentate ligand adopt a *quasi*-octahedral arrangement around the Mo atom [36]. The tetracarbonyl molybdenum complex can be converted to [Mo{H$_2$C(3,5-Me$_2$pz)$_2$}(CO)$_2$(π-C$_3$H$_5$)Br] by reaction with allyl bromide [37].

Thermolysis of [M{H$_2$C(3,5-Me$_2$pz)$_2$}(CO)$_4$] (M = Mo, W) in dme gave dinuclear compounds, [M{H$_2$C(3,5-Me$_2$pz)$_2$}(CO)$_3$]$_2$. These dimers reacted with MeCN to give mononuclear compounds, [M{H$_2$C(3,5-Me$_2$pz)$_2$}(CO)$_3$(NCMe)]. The same products can be obtained from the reaction of [M{H$_2$C(3,5-Me$_2$pz)$_2$}(CO)$_4$] with MeCN [38].

The multidentate ligands H$_2$C(3-MeS-5-C(CH$_3$)$_3$pz)$_2$, H$_2$C(3-MeS-5-(*p*-MeOPh)pz)$_2$, H$_2$C(3-MeS-5-Phpz)$_2$, H$_2$C(3-Ph-5-(MeS)pz)$_2$, H$_2$C(3-MeS-5-(*p*-MeOPh)pz)(3′-(*p*-MeOPh)-5′-(MeS)pz), H$_2$C(3-(*p*-MeOPh)-5-MeSpz)$_2$ prepared by Tang under PTC conditions [39] reacted with M(CO)$_6$ (M = Cr, Mo or W) always affording [M{H$_2$C(pz^x)$_2$}(CO)$_4$] derivatives. An X-ray crystal structure study indicated that the sulfur atoms in these complexes do not coordinate to the metal centers, and that S-rich H$_2$C(pz^x)$_2$ generally act as bidentate chelating N$_2$-donor towards M(CO)$_6$ species [39].

Derivatives [M{(1,2-C$_2$H$_4$)(3,5-Me$_2$pz)$_2$}(CO)$_4$] (M = Mo, W) were recently synthesized by the direct reaction of (1,2-C$_2$H$_4$)(3,5-Me$_2$pz)$_2$ with M(CO)$_6$. The X-ray structure of [W{(1,2-C$_2$H$_4$)(3,5-Me$_2$pz)$_2$}(CO)$_4$] showed the seven-membered ring W–N–N–C–C–N–N in the boat conformation [40]. Upon treatment with RSnCl$_3$ these complexes gave the seven-coordinate oxidative addition products [M{H$_2$C(pz)$_2$}(CO)$_3$(Cl)(RSnCl$_2$)] (Fig. 13) [40]. Gioia Lobbia and Bonati reported the synthesis of [M{H$_2$C(pz)$_2$}(CO)$_4$] complexes (M = Cr, Mo, W) from the reaction of M(CO)$_6$ with H$_2$C(pz)$_2$ in toluene solution [41].

H$_2$C(3,5-Me$_2$-4-Brpz)$_2$, H$_2$C(4-Brpz)$_2$, H$_2$C(3,5-Me$_2$-4-Clpz)$_2$ and H$_2$C(4-Clpz)$_2$ react with M(CO)$_6$ (M = Cr or Mo) to yield the corresponding [M{H$_2$C(pz^x)$_2$}(CO)$_4$] [42].

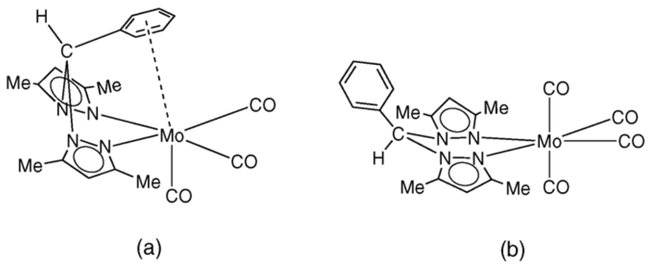


Fig. 14. $[Mo\{PhHC(3,5\text{-}Me_2pz)_2\}(CO)_3]$ (a) and $[Mo\{PhHC(3,5\text{-}Me_2pz)_2\}(CO)_4]$ (b); (a) is the first intramolecular coordination compound with a weakly bound η^2-arene [44].

A convenient synthesis of the paramagnetic 16-electron molybdenum(II) carbonyl derivatives, $[Mo\{H_2C(pz^x)_2\}(CO)_2Br_2]$ ($H_2C(pz^x)_2$ = $H_2C(pz)_2$, $H_2C(3,5\text{-}Me_2pz)_2$, $CH_2(3,4,5\text{-}Me_3pz)_2$) were reported by Shiu and co-workers. $[Mo\{(\eta^2\text{-}H_2C(3,5\text{-}Me_2pz)_2)\}(CO)_2Br_2]$ have a *quasi*-octahedral geometry with Br atoms in *trans*-position [43].

$[Mo\{PhHC(3,5\text{-}Me_2pz)_2\}(CO)_4]$ and $[Mo\{PhHC(3,5\text{-}Me_2pz)_2\}(CO)_3]$ (Fig. 14), were prepared and structurally characterized. A comparison of the C–C bond lengths of the Ph fragment in the both compounds showed the second one to be the first intramolecular coordination compound with a weakly bound η^2-arene [44].

$Ph_2C(3,5\text{-}Me_2pz)_2$, which is more sterically hindered than $PhHC(3,5\text{-}Me_2pz)_2$, interacts with $[Mo(CO)_6]$ yielding readily the η^2-arene compounds $[\{Ph_2C(3,5\text{-}Me_2pz)_2\}Mo(CO)_3]$ (Fig. 15). This η^2-ligation seems to stabilize the coordination of $Ph_2C(3,5\text{-}Me_2pz)_2$ in $[\{Ph_2C(3,5\text{-}Me_2pz)_2\}Mo(CO)_2(N_2C_6H_4NO_2\text{-}p)][BPh_4]$ and $[\{Ph_2C(3,5\text{-}Me_2pz)_2\}Mo(CO)_2(N_2Ph)][BF_4]$ obtained from the reaction of $[\{Ph_2C(3,5\text{-}Me_2pz)_2\}Mo(CO)_3]$ with the appropriate diazonium salt. However only $[Mo(CO)_3\{P(OMe_3)\}_3]$ was derived from the reaction of $[\{Ph_2C(3,5\text{-}Me_2pz)_2\}Mo(CO)_3]$ with $P(OMe)_3$ [45].

Bulky donors such as $H_2C(3,5\text{-}Me_2\text{-}4\text{-}Bnpz)_2$, $H_2C(3\text{-}{}^tBupz)_2$, $H_2C(3(5)\text{-}Phpz)_2$, $H_2C(3\text{-}Phpz)(5\text{-}Phpz)$ react with $[Mo(pip)_2(CO)_4]$ or $[Mo(CO)_6]$ yielding $[\{H_2C(pz^x)_2\}Mo(CO)_4]$ species. Their structural features suggest that the presence of a bulky substituent such as a Ph or a ^{t}Bu group on the pyrazolyl moiety may produce strong nonbonded interaction in $[\{H_2C(pz^x)_2\}Mo(CO)_4]$ and inhibit the formation of stable complexes such as $[\{H_2C(3\text{-}{}^tBupz)_2\}Mo(CO)_4]$ or $[\{H_2C(3\text{-}Phpz)_2\}Mo(CO)_4]$.

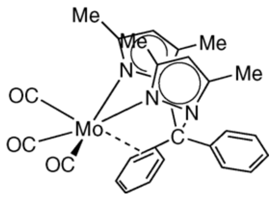


Fig. 15. The η^2-arene compounds $[\{Ph_2C(3,5\text{-}Me_2pz)_2\}Mo(CO)_3]$ [45].

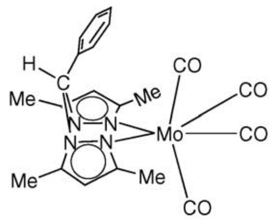


Fig. 16. $[\{PhHC(3,5\text{-}Me_2pz)_2\}Mo(CO)_4]$ in which the Ph is *cis* to the most distorted carbonyl [46].

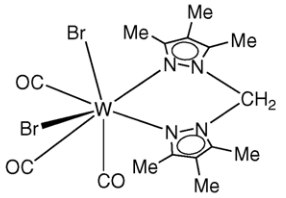


Fig. 17. A seven-coordinate carbonyl halide $[M(CO)_3X_2\{\eta^2\text{-}R_2Cpz^x)_2\}]$ [47].

Whereas in $[\{PhHC(3,5\text{-}Me_2pz)_2\}Mo(CO)_4]$ the phenyl substituent at the bridging carbon end of the six-membered-boat metallacycle, formed by $H_2C(pz^x)_2$ with the central atom, is *cis* to the most distorted carbonyl [46] (Fig. 16).

Synthesis and structural characterization of six- and seven-coordinate carbonyl halides (Fig. 17) of molybdenum(II) and tungsten(II) $[M(CO)_2X_2\{\eta^2\text{-}R_2C(pz^x)_2\}]$ and $[M(CO)_3X_2\{\eta^2\text{-}R_2C(pz^x)_2\}]$ (X = I, Br; $R_2C(pz^x)_2$ = $H_2C(pz)_2$, $H_2C(3,5\text{-}Me_2pz)_2$, $H_2C(3,4,5\text{-}Me_3pz)_2$, $PhHC(pz)_2$, $PhHC(3,5\text{-}Me_2pz)_2$) have been reported. It was suggested that the coordination numbers could be explained in terms of the interplay of the steric and electronic effects [47].

The π-allyldicarbonyl complexes $[Mo\{R_2C(pz^x)_2\}(CO)_2(\pi\text{-}allyl)Br]$ were prepared either directly by the allyl bromination of $[Mo\{PhHC(3,5\text{-}Me_2pz)_2\}(CO)_3]$ or $[Mo\{R_2C(pz^x)_2\}(CO)_4]$ ($R_2C(pz^x)_2$ = $H_2C(pz)_2$, $H_2C(3,5\text{-}Me_2pz)_2$, $PhHC(pz)_2$, $PhHC(3,5\text{-}Me_2pz)_2$) or indirectly by reaction of $[Mo(MeCN)_2(CO)_2(\pi\text{-}allyl)Br]$ with $R_2C(pz^x)_2$. The peculiar structural features of $[Mo\{PhHC(3,5\text{-}Me_2pz)_2\}(CO)_2(\pi\text{-}allyl)Br]$ confirm unequivocally the solvent-dependent coordination stability of pyrazole-derived bidentate ligands, in $[Mo\{R_2C(pz^x)_2\}(CO)_2(\pi\text{-}allyl)Br]$ (Fig. 18) [48].

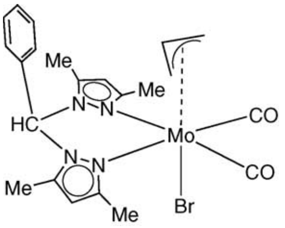


Fig. 18. $[Mo\{R_2C(pz^x)_2\}(CO)_2(\mu\text{-}allyl)Br]$ [48].

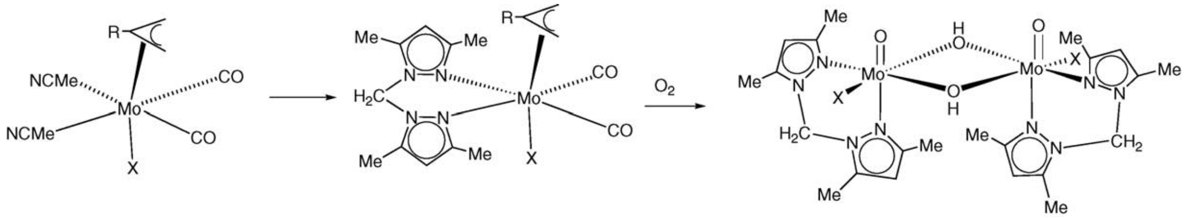


Fig. 19. The Mo_2O_4 core found in bis(pyrazolyl)alkane molybdenum compounds [49].

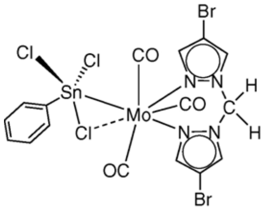


Fig. 20. The chlorine-bridged Mo–Sn bond in [Mo{H_2C(4-Brpz)$_2$}(CO)$_3$(μ-Cl)($SnCl_2Ph$)] [51].

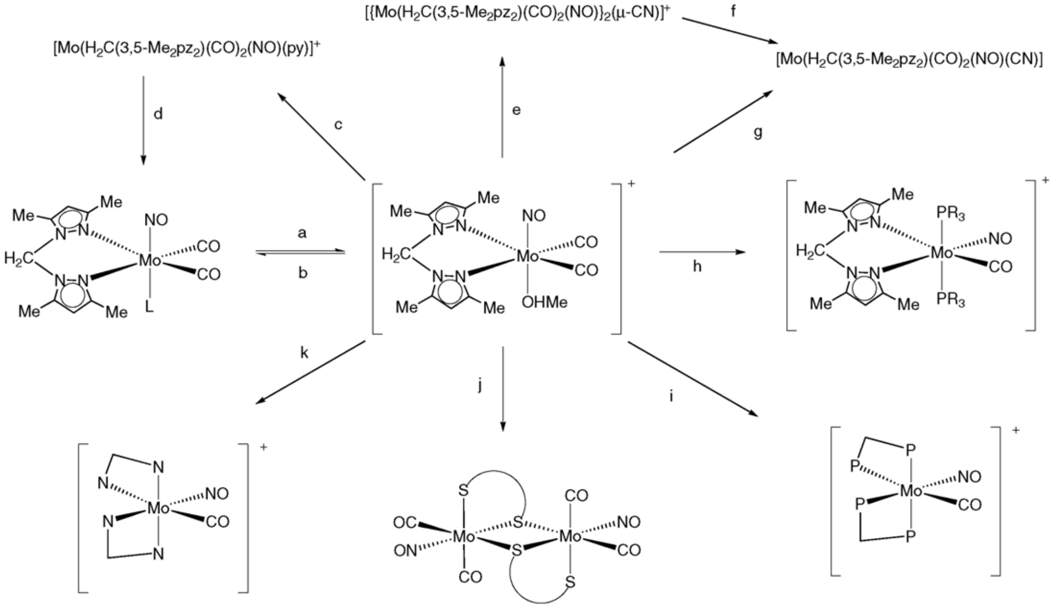
Sarkar and co-workers reported a mild aerial oxidation of Mo(II) π-allyl complexes containing $H_2C(3,5\text{-}Me_2pz)_2$ that produces new dimeric Mo(V) oxo complexes with a Mo_2O_4 core (Fig. 19) [49]. These Mo(II) complexes can activate dioxygen and lead to catalytic oxidation of triphenylphosphine with high efficiency [49].

[M{$H_2C(pz)_2$}(CO)$_4$] (M = Mo, W) was found to react with $RSnCl_3$ (R = Ph, Cl) yielding [M{$H_2C(pz)_2$}(CO)$_3$(Cl)$SnCl_2Ph$] and [M{$H_2C(pz)_2$}(CO)$_3$(Cl)$SnCl_3$]. Analogously the reaction of [M{$H_2C(3,5\text{-}Me_2pz)_2$}(CO)$_4$] with $PhSnCl_3$ and $SnCl_4$ produces [M{$H_2C(3,5\text{-}Me_2pz)_2$}(CO)$_3(Cl)SnCl_2Ph$] and [M{$H_2C(3,5\text{-}Me_2pz)_2$}(CO)$_3(Cl)SnCl_3$], respectively. These complexes were stable in air in the solid state, and, in solution, can be stored for a long period without decomposition [50].

Electronic and steric features of the x substituents on $H_2C(pz^x)_2$ remarkably influence the structures of the products. In [{$H_2C(3,5\text{-}Me_2\text{-}4\text{-}Brpz)_2$}W(CO)$_3(Cl)SnCl_3$] no chlorine-bridged W–Sn bond is observed whereas one chlorine-bridged Mo–Sn bond is present in [Mo{H_2C(4-Brpz)$_2$}(CO)$_3$(μ-Cl)($SnCl_2Ph$)] (Fig. 20) [51].

The Mo(VI) *cis*-dioxo complex [Mo{$Me_2C(pz)_2$}O_2Cl_2] has been obtained by reaction of $MoO_2Cl_2(THF)_2$ with $Me_2C(pz)_2$ and characterized by X-ray. The catalytic use in olefin epoxidation, *t*-butyl hydroperoxide being the oxidizing agent, has been investigated. The turnover frequencies are in the range of 150–460 [mol epoxide/(mol catalyst × h)]. This activity is in the middle of the range observed for $MoO_2X_2L_2$ complexes containing N-donor ligands [52].

The presence of a nitrosyl group in [Mo{$H_2C(3,5\text{-}Me_2pz)_2$}(NO)(HOMe)(CO)$_2$][$BF_4$] can help to tighten



a) NaL or KL (L = Cl, I, N_3, NO_3, SCN, $MeCO_2$); b) for L = I, $NOBF_4$; c) py; d) NaCl, NaBr or NaI; e) 1/2 KCN; f 1/2 KCN; g) KCN; h) 2 PR_3; i) 2 dppm; J) $Na^+Et_2NCS_2^-$, $Na^+Me_2NCS_2^-$ or $NH_4^+C_4H_8NCS_2^-$; k) bpy, phen or Me_2bpy

Fig. 21. The reactivity of [Mo{$H_2C(3,5\text{-}Me_2pz)_2$}(NO)(HOMe)(CO)$_2$]($BF_4$) towards halide, pseudohalide, phosphines and N-donors [53].

the $H_2C(3,5-Me_2pz)_2$ ligation during nucleophilic substitution reactions in spite of the inherent ring strain present in the six-membered-boat metallacycle formed between $H_2C(3,5-Me_2pz)_2$ and the central metal atom. Flexibility of the metallacycle is still present even with this electronic tightening in all the $H_2C(3,5-Me_2pz)_2$-ligated metal nitrosyl products. Shiu hypothesized that steric effects of $H_2C(3,5-Me_2pz)_2$, inherent ring strain and flexibility of the metallacyle, and finally the electronic effect of NO can contribute to formation of different products from the reactions of $[Mo\{H_2C(3,5-Me_2pz)_2\}(NO)(HOMe)(CO)_2][BF_4]$ with halide, pseudohalide, phosphines and N-donors (Fig. 21) [53].

From the reaction of $[W(\equiv CMe)(CO)_4]$ with $H_2C(pz)_2$ in the presence of $TlBF_4$ the complex $[W(\equiv CMe)(CO)_3\{H_2C(pz)_2\}][BF_4]$ was obtained [54].

$H_2C(3,5-Me_2-4-Brpz)_2$, $H_2C(4-Brpz)_2$, $H_2C(3,5-Me_2-4-Clpz)_2$ and $H_2C(4-Clpz)_2$ react with $W(CO)_6$ and form (bis(4-halopyrazol)methane)tetracarbonyltungsten(0) complexes analogous to those reported for Mo(0) [42].

The substituent effects on infrared absorption was evaluated by Shiu et al. [55]. The flexibility of the six-membered metallacycle boat allows adjustment of the chelate structure to minimize the nonbonded repulsive interactions. Structural modifications alter the electron ability so that no regular trend in carbonyl stretching values for $[M\{R_2C(pz^x)_2\}(CO)_4]$ (where L = $H_2C(pz)_2$, $H_2C(3,5-Me_2pz)_2$, $H_2C(3,4,5-Me_3pz)_2$, and M = Cr, W) is observed; the electron ability of the resulting ligand does not become necessarily stronger with increasing number of methyl groups on the pyrazolyl rings [55].

Bis(pyrazol)methane ligands with bulky substituents like $H_2C(3,5-{}^iPr_2pz)_2$ and $H_2C(3,5-{}^iBu_2pz)_2$ reacted with $M(CO)_6$ (M = Cr, Mo or W) under UV irradiation also yielding bis(pyrazol)methane tetracarbonylchromium, molybdenum or tungsten species. Treatment of the molybdenum or tungsten complexes with $SnCl_4$ also gives Mo–Sn or W–Sn heterobimetallic complexes [56].

3.5. Group VIIB: Mn, Re

The first manganese compound reported in literature was $[Mn_2\{H_2C(3,5-Me_2pz)_2\}_4F_2][BF_4]_2$ [57]. Tang and co-workers reported the synthesis and crystal structure of $[Mn\{CH_2(3,5-Me_2pz)_2\}(N_3)_2]_n$, a one-dimensional coordination polymer containing azido-bridged ligands (Fig. 22). Magnetic measurements have indicated that, in agreement with the structural data, the chain shows a regular alternation of ferromagnetic and antiferromagnetic interactions and shows antiferromagnetic interactions in the interchains [58].

The pyren derivatives $H_2C(3-pz^{pyrene})_2$, $H_2C(3-pz^{pyrene})(5-pz^{pyrene})$ and $({}^nPr)HC(pz^{pyrene})_2$ ligands react with $Re(CO)_5Br$ forming $[Re\{H_2C(pz^{pyrene})_2\}(CO)_3Br]$ and $[Re\{({}^nPr)HC(pz^{pyrene})_2\}(CO)_3Br]$ (Fig. 23). These compounds show extensive π-stacking of pyrenyl group.

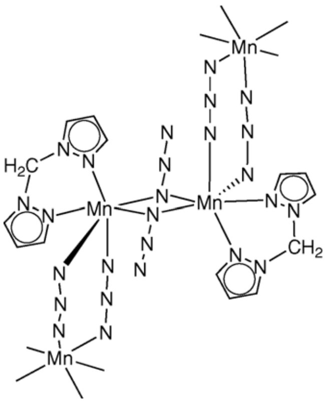


Fig. 22. $[Mn\{CH_2(3,5-Me_2pz)_2\}(N_3)_2]_n$, a one-dimensional coordination polymer containing azido-bridged ligands [58].

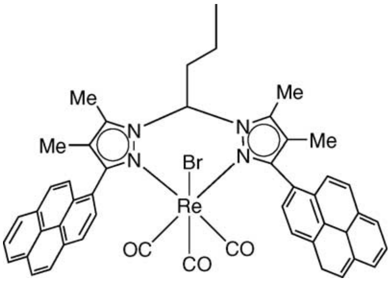


Fig. 23. $[Re\{({}^nPr)HC(pz^{pyrene})_2\}(CO)_3Br]$ [59].

The crystal structure of $[Re\{Me_2C(pz)_2\}(CO)_3Br]$ was also reported [59].

3.6. Group VIII: Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt

In 1978 Reedijk described the synthesis and characterization of the five-coordinate dimeric nickel(II) thermochromic complex $[Ni\{H_2C(3,5-Me_2pz)_2\}Cl_2]_2$ [60] for which the crystal structure was determined (Fig. 24) [61]. This compound shows ferromagnetic exchange interactions.

The same authors described then the synthesis and the characterization of transition metals derivatives $[M\{H_2C(3,5-Me_2pz)_2\}X_2]$ (M = Co or Ni; X = Cl or Br) and $[M\{H_2C(3,5-Me_2pz)_2\}_2X_2]$ (M = Fe, Co, Ni, X = ClO_4; M = Co, Ni, X = NO_3; M = Ni, X = Cl, Br) [62]. The perchlorato compounds appear to have one bidentate ClO_4 and one ionic ClO_4. The M:$H_2C(3,5-Me_2pz)_2$ 1:2 species appear to occur either in octahedral geometry, leaving

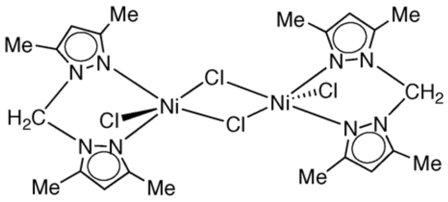


Fig. 24. The dimer $[Ni\{H_2C(3,5-Me_2pz)_2\}Cl_2]_2$ [61].

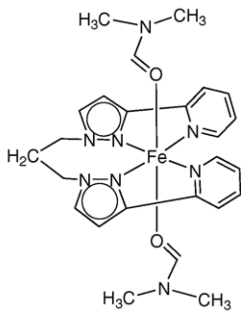


Fig. 25. The high-spin d^6 *trans*-[Fe(H_2C)$_3$(3-(2py)-pz)$_2$(dmf)$_2$][ClO_4]$_2$ [14].

two *cis* position free or occupied by weakly coordinating anions, or in a tetrahedral geometry without space for other ligands.

Poly(pyrazolyl)alkanes are neutral ligands and for this reason were considered as appropriate mimics of the naturally occurring histidine residues found in metalloenzymes. They have several advantages in the synthesis of iron complexes containing N-donor ligands to respect poly(pyrazolyl)borate ligands that show interaction of the B–H residue with the metal center [63].

[Fe{H_2C(3,5-Me_2pz)$_2$}X_2] (X = Cl, Br), [Fe{H_2C(3,5-Me_2pz)$_2$}$_2$$X_2$] (X = I, NCS), and the ionic [Fe{H_2C(3,5-Me_2pz)$_2$}$_2$X][BPh_4] (X = Cl, Br, I) were prepared by Mani in 1979 [64].

Difluoro-bridged dimers [M_2{H_2C(3,5-Me_2pz)$_2$}$_4$$F_2$][$BF_4$]$_2$ where M = Fe, Co, Ni were prepared by Verbiest et al. [57]. These compounds were synthesized by partial decomposition of the M(BF_4)·6H_2O in ethanol in the presence of the N_2-donor ligand. The perchlorato derivatives [M_2{H_2C(3,5-Me_2pz)$_2$}$_4$$F_2$][$ClO_4$]$_2$ (M = Co, Ni) were also reported [57].

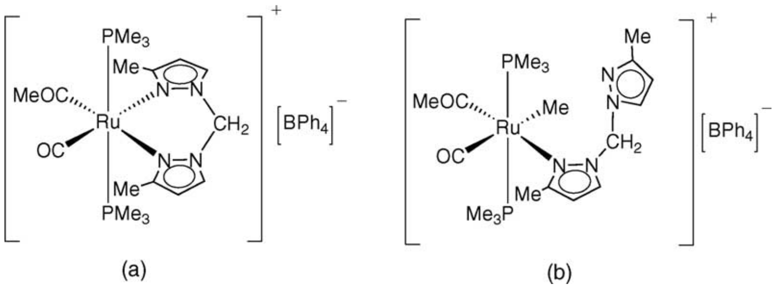
Trans-[Fe{H_2C(pz)$_2$}(PMe_3)$_2$(CO)(COMe)][BPh_4] [65], [Fe{H_2C(pz)$_2$}$_2$(NCS)$_2$] [66], *cis*-[Fe{H_2C(pz)$_2$}$_2$$Cl_2$] [66] and [Fe{$H_2C(pz)_2$}$_2$Cl][$BPh_4$] [66] were recently reported. The ion pair structure of the former compound and the localization of its counter-ion in solution with respect to the metal center were determined by the detection of interionic contacts in the ^{1}H-NOESY and ^{19}F{^{1}H}-HOESY NMR spectra. [Fe{H_2C(pz)$_2$}$_2$(NCS)$_2$], *cis*-[Fe{H_2C(pz)$_2$}$_2$$Cl_2$], and [Fe{$H_2C(pz)_2$}$_2$Cl][$BPh_4$] display temperature dependent paramagnetism.

(1,3-C_3H_6)(3-(2py)-pz)$_2$ reacted with iron(II) sulfate heptahydrate and aqueous $NaClO_4$ in MeOH yielding the high-spin d^6 *trans*-[Fe(H_2C)$_3$(3-(2py)-pz)$_2$(dmf)$_2$][ClO_4]$_2$ complex (Fig. 25) upon recrystallization from dmf. In this compound containing (1,3-C_3H_6)(3-(2py)-pz)$_2$ is coordinated equatorially [14].

Murray and co-workers very recently reported a number of six-coordinate bi- and tri-podal iron(II) chelates [Fe{(py)HC(pz)$_2$}$_2$][NO_3]$_2$ and [Fe{(py)HC(pz)$_2$}$_2$][PF_6]$_2$. The electronic properties of these compounds were investigated by optical spectroscopic measurements and a low-spin d^6 behaviour was indicated [67].

The neutral six-coordinate Ru(II) complex [$RuCl_2${(H_2C(pz)$_2$}(COD)] was synthesized from [{$RuCl_2$(COD)}$_n$] and H_2C(pz)$_2$. [$RuCl_2${H_2C(pz)$_2$}(COD)] is a saturated species in which the H_2C(pz)$_2$ is easily replaced by phosphines and CO [68]. [$RuCl_2${H_2C(pz)$_2$}(COD)] reacts with $LiBEt_3H$ to give the hydride [RuH(Cl){H_2C(pz)$_2$}(COD)] [69]. This compound, a good starting material in substitution processes with hydrogen and N-donors [70], catalyzes both the hydrogenation of unsaturated substrates such as cyclohexene, cyclohexanone, acetone and propanal [71]. The reaction of [RuHCl{H_2C(pz)$_2$}(COD)] with one equivalent of Ag(tfs) afforded the triflate-containing [RuH(tfs){H_2C(pz)$_2$}(COD)] which, upon reaction with PMe_2Ph, yielded the *trans*-[RuH(PMe_2Ph){H_2C(pz)$_2$}(COD)](tfs), which isomerizes easily to *cis*-[RuH(PMe_2Ph){H_2C(pz)$_2$}(COD)](tfs). The *trans*-[RuH{P(OMe)$_3$}{H_2C(pz)$_2$}(COD)](tfs) also readily isomerizes to *cis*-[RuH{P(OMe)$_3$}{H_2C(pz)$_2$}(COD)](tfs) and *cis*- and *trans*-[RuHL{H_2C(pz)$_2$}(COD)](tfs) (L = pyridine, 4-picoline, or 3,5-lutidine) [71].

Trans,*cis*-Ru(PMe_3)$_2$(CO)$_2$(Me)I reacts with H_2C(pz)$_2$, in the presence of $NaBPh_4$, affording *trans*-[Ru(PMe_3)$_2$(CO)(COMe){H_2C(pz)$_2$}][BPh_4]. *trans*,*cis*-Ru(PMe_3)$_2$(CO)$_2$(Me)I also reacts with H_2C(5,5′-Mepz)$_2$ or H_2C(3,5-Me_2pz)$_2$ forming respectively *trans*-[Ru(PMe_3)$_2$(CO)(COMe){H_2C(5,5′-Mepz)$_2$}][BPh_4] and *trans*-[Ru(PMe_3)$_2$(CO)(COMe){H_2C(3,5-Me_2pz)$_2$}][BPh_4]. Whereas the reaction of *trans*,*cis*-[Ru(PMe_3)$_2$(CO)$_2$(Me)I] with H_2C(3,3′-Me_2pz)$_2$ yields a mixture of *trans*,*cis*-[Ru(PMe_3)$_2$(CO)$_2${η^1-H_2C(3,3′-Mepz)$_2$}(Me)][BPh_4] and



(a) (b)

Fig. 26. *Trans*-[Ru(PMe_3)$_2$(CO)(COMe){H_2C(3,3′-Mepz)$_2$}]BPh_4 (a) and *trans*,*cis*-[Ru(PMe_3)$_2$(CO)$_2${η^1-H_2C(3,3′-Mepz)$_2$}(Me)]BPh_4 (b) [65].

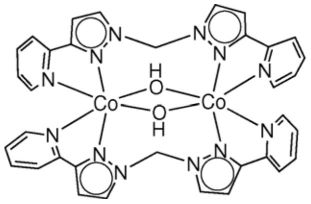


Fig. 27. $[Co_2(H_2C(3\text{-}(2\text{-}py)pz)_2)_2(\mu\text{-}OH)_2][ClO_4]_2$ containing a $Co_2(\mu\text{-}X)_2$ core spanned by two tetradentate bis(pyrazolyl)methane ligands [13].

trans-$[Ru(PMe_3)_2(CO)(COMe)\{H_2C(3,3'\text{-}Mepz)_2\}][BPh_4]$ (Fig. 26) [65]. *Fac*$[Ru(PMe_3)(CO)_3(Me)I]$ reacts with $H_2C(pz)_2$ in the presence of $NaBPh_4$, affording *cis*-$[Ru\{H_2C(pz)_2\}(PMe_3)(CO)_2(COMe)][BPh_4]$. This complex decarbonylates leading to a mixture of the three stereoisomers of *cis*-$[Ru\{H_2C(pz)_2\}(PMe_3)(CO)_2Me][BPh_4]$. *Fac*,*cis*-$[Ru(PMe_3)(CO)_3I_2]$ reacts with $H_2C(pz)_2$ affording *cis*-$[Ru\{H_2C(pz)_2\}(PMe_3)(CO)_2I][BPh_4]$. The stereochemistry of these compounds, the dynamic processes existing between them, and their interionic structures were investigated by the phase-sensitive ^1H NOESY NMR techniques [72].

The role of the $R_2C(pz^x)_2$ substituents on the rate constant of aqua ligand substitution of $[Ru(H_2O)\{H_2C(pz)_2\}(tpmm)]^{2+}$ and $[Ru(H_2O)\{Me_2C(pz)_2\}(tpmm)]^{2+}$ was investigated. A 9.4×10^5-fold increase in the rate constant of ligand substitution at pH = 6.86 was observed when $H_2C(pz)_2$ was replaced with $Me_2C(pz)_2$. This remarkable increase was unexpected, with only a H-to-Me spectator ligand substituent change and is primarily due to steric interaction. The crystal structures of $[Ru(Cl)\{H_2C(pz)_2\}(tpmm)][BF_4]$ and $[Ru(Cl)\{Me_2C(pz)_2\}(tpmm)][BF_4]\cdot CH_2Cl_2$ were also reported [73].

Reaction of *cis*,*trans*-$[OsI(Me)(CO)_2(PMe_3)_2]$ and *fac*-$[OsI(Me)(CO)_3(PMe_3)]$ with silver salts (AgX) and $H_2C(pz)_2$ affords $[Os(COMe)\{H_2C(pz)_2\}(CO)(PMe_3)Y][BPh_4]$ (Y = PMe_3, CO) [74].

$H_2C(pz)_2$ and $Me_2C(3\text{-}Mepz)_2$ reacted with CoX_2 salts to give $[Co\{H_2C(pz)_2\}_2X_2]\cdot 2H_2O$ (X = Cl, Br, I, NO_3, ClO_4) and $[Co\{Me_2C(3\text{-}Mepz)_2\}X_2]$ (X = Cl, Br, I) [75].

Mixed-ligands complexes $[Co\{Me_2C(pz)_2\}(acacH)X_2]$, $[Co\{Me_2C(pz)_2\}(hfacH)X_2]$ (X = NO_3 or ClO_4), and $[Co\{Me_2C(3(5)\text{-}Mepz)_2\}Co(acac)][ClO_4]$ were also prepared [76]. The number of pyrazolyl rings coordinated to the metal depends on the nature of the β-diketonates and the oxo acid ion [76].

Elguero and co-workers synthesized $[Co\{1,2\text{-}C_2H_4(pz)_2\}Cl_2]$ and $[M\{1,2\text{-}C_2H_4(pz)_2\}(NO_3)_2]$ (M = Co or Ni) [77]. In $[Ni\{1,2\text{-}C_2H_4(pz)_2\}(NO_3)_2]$, the metal is found in a distorted octahedron whose apices are a N from the bis(pyrazolyl)ethane and an O atom from the NO_3.

Reaction of $H_2C(3\text{-}(2\text{-}py)pz)_2$ with $Co(ClO_4)_2$ gave a centrosymmetric dinuclear complex $[Co_2\{H_2C(3\text{-}(2\text{-}py)pz)_2\}_2(\mu\text{-}OH)_2][ClO_4]_2$ that was structurally characterized. The $Co_2(\mu\text{-}X)_2$ core is spanned by two tetradentate bis(pyrazolyl)methane ligands (Fig. 27), each of which coordinates one bidentate arm to each metal [13].

Oro et al. reported the rhodium(I) complexes $[RhCl\{H_2C(pz)_2\}(diolefin)_2]$, $[Rh(CO)_2\{H_2C(pz)_2\}][RhCl_2(CO)_2]$, $[\{Rh(diolefin)(PPh_3)\}_2\{H_2C(pz)_2\}][(ClO_4)_2]$, $[Rh(CO)_2\{H_2C(pz)_2\}][ClO_4]$ and $[Rh(CO)\{H_2C(pz)_2\}(PPh_3)][ClO_4]$. In the crystal structure of $[Rh(COD)\{H_2C(pz)_2\}][ClO_4]\cdot 1/2\ C_2H_4Cl_2$ the Rh atom is in a distorted square-planar coordination the COD ring being in a twisted boat conformation [78].

Addition of $H_2C(3,5\text{-}Me_2pz)_2$ to $[(\eta^4\text{-}COD)Rh(acetone)_2][BF_4]$ affords the complex $[Rh\{H_2C(3,5\text{-}Me_2pz)_2\}(COD)][BF_4]$, which can be carbonylated under mild conditions into $[Rh\{H_2C(3,5\text{-}Me_2pz)_2\}(CO)_2][BF_4]$. One of the CO ligands in this compound can be easily displaced by PPh_3, $PMePh_2$, or $P(OMe)_3$. The X-ray crystal structures of $[Rh\{H_2C(3,5\text{-}Me_2pz)_2\}(CO)_2][BF_4]$ and $[Rh\{H_2C(3,5\text{-}Me_2pz)_2\}(CO)(PPh_3)][BF_4]$ were determined, the rhodium being in a square-planar environment. These compounds can be used as catalysts in the hydroformylation and hydroaminomethylation of olefins [79]. The reaction rate of hydroaminomethylation reaction can be significantly increased on addition of a hydride-donating species such as $[RuH_2(PPh_3)_4]$ [79].

Ir(COD) and $Ir(CO)_2$ derivatives containing $H_2C(pz)_2$ and $H_2C(3,5\text{-}Me_2pz)_2$ have been synthesized and characterized by NMR and X-ray spectroscopy [80]. The $[Ir\{H_2C(pz^x)_2\}(CO)_2][BPh_4]$ species are effective catalysts for the alcoholysis of a range of alcohols and hydrosylanes, including secondary and tertiary hydrosilanes, under mild conditions.

Mesubi investigated the coordinating behaviour of $Me_2C(pz)_2$ also towards Ni(II) salts. $Me_2C(pz)_2$ in the presence of poorly coordinating polyanions such as BF_4 and PF_6. They readily react to give stable $[Ni\{Me_2C(pz)_2\}_2X][BF_4]$ or $[Ni\{Me_2C(pz)_2\}_2X][PF_6]$ (X = Cl, NO_3, OAc) [81]. The complexes obtained were characterized by magnetic moments, electronic and IR spectroscopy. An octahedral structure is proposed for $[Ni\{Me_2C(pz)_2\}_2X]^+$ (X = NO_3, AcO), the X group acting as bidentate ligand.

Mixed-ligand complexes $[Ni\{Me_2C(pz)_2\}_2(L)X]$ (LH = acacH or hfacH; X = Cl or NO_3) and $[Ni\{Me_2C(3(5)\text{-}Mepz)\}_2(acac)]X$ (X = Br or ClO_4) were also prepared [76].

The crystal structure of the bimetallic hexacyanoferrate(III) complex $[(Ni\{H_2C(pz)_2\}_2)_3(Fe(CN)_6)_2]\cdot 7H_2O$ (Fig. 28) forming discrete pentanuclear clusters, each cluster being connected to neighboring clusters in the crystal lattice via a novel hydrogen-bonded “cluster” of seven water molecules, was reported by Murray and co-workers [82].

The crystal structure of $[Ni\{(thi)CH(pz)_2\}_2(O(O')NO)][NO_3]$ has also been reported [83]. The thienyl group is not coordinated to the metal existing in an distorted octahedral environment from four pyrazolyl groups and a chelating nitrate. The compound $[Ni_2\{H_2C(3\text{-}(2\text{-}py)pz)_2\}_2(\mu\text{-}OAc)_2][PF_6]$ was recently reported, but not structurally characterized [13].

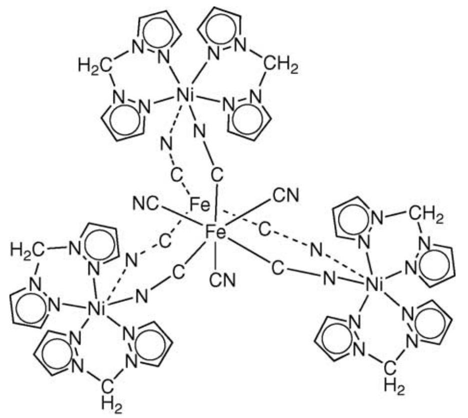


Fig. 28. The bimetallic hexacyanoferrate(III) $[(Ni\{H_2C(pz)_2\}_2)_3(Fe(CN)_6)_2]\cdot 7H_2O$ [82].

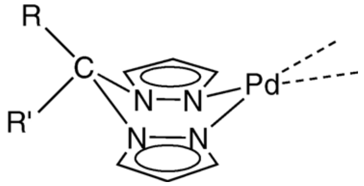


Fig. 29. Boat conformation in the six-membered palladacycle.

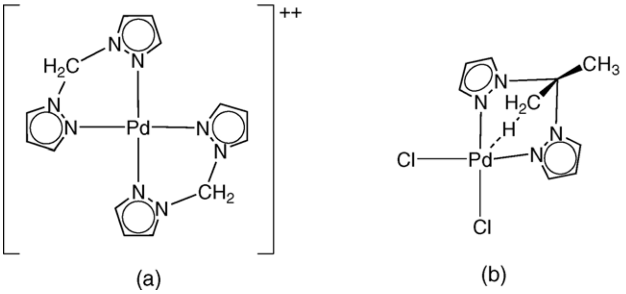

(a)
(b)

Fig. 30. Bis(chelation) in $[Pd\{H_2C(pz)_2\}_2]^{2+}$ (a) and Pd···H–C (agostic) interaction in $[Pd\{Me_2C(pz)_2\}Cl_2]$ (b) [85].

Bis(pyrazol)methanes were widely used also in palladium chemistry. Coordination of $R_2C(pz^x)_2$ to Pd occurs to form a six-membered metallacycle that always adopts a boat conformation (Fig. 29). When H or Me substituents are present in the bridging spacer between the pyrazolyl rings, boat-to-boat interconversion usually takes place. When more sterically hindered substituents are on the bridging carbon boat-to-boat interconversion is absent. When methyl groups are present in the three- and/or five-positions of the pyrazolyl rings an enhancement of the rigidity of the boat conformation was generally found [84].

The first palladium complex was obtained by Trofimenko from reaction of $R_2C(pz)_2$ with $[(\pi\text{-allyl})PdX]_2$ (X = halide) dimer which yields cationic $[Pd\{R_2C(pz)_2\}(\pi\text{-allyl})]^+$ species [2].

The neutral $[Pd\{H_2C(pz)_2\}Cl_2]$, $[Pd\{H_2C(3,5\text{-}Me_2pz)_2\}Cl_2]$ and $[Pd\{Me_2C(pz)_2\}Cl_2]$ and the cationic species $[Pd\{H_2C(pz)_2\}_2]^{2+}$, $[Pd\{H_2C(3,5\text{-}Me_2pz)_2\}_2]^{2+}$ and $[Pd\{Me_2C(pz)_2\}_2]^{2+}$ were synthesized by Minghetti et al. [85]. Crystal structures of $[Pd\{H_2C(3,5\text{-}Me_2pz)_2\}Cl_2]$ and $[Pd\{H_2C(pz)_2\}_2]^{2+}$ (Fig. 30a) were also reported and a weak Pd···H–C (agostic) interaction was found in $[Pd\{Me_2C(pz)_2\}Cl_2]$ (Fig. 30b) [85].

Cyclopalladation has been found to occur in a palladium derivative of $R_2C(pz^x)_2$ functionalized with malonyl residues (Fig. 31a). When the ligand reacts directly with $[PdCl_4]^{2-}$ a compound containing the ligand coordinated in N_2-chelating fashion is formed (Fig. 31b) [86].

Ligands $RR'C(pz)_2$ (R = R′ = H, Me; R = H, R′ = Me) form complexes $[PdMe_2\{RR'C(pz)_2\}]$ and $[PdIMe\{RR'C(pz)_2\}]$ showing variable temperature NMR spectra in accordance with a boat-to-boat inversion of the chelate ring [87]. $[PdMe_3(L)]I$ complexes (L = $(py)HC(pz)_2$ or $(mim)HC(pz)_2$) were prepared by oxidative addition of MeI to $[PdMe_2(L)]$ [84].

Venanzi and co-workers reported the synthesis of palladium complexes $[Pd(\eta^3\text{-}C_3H_5)(L)][PF_6]$ (L = bis(4R-methyl-7R-isopropyl-4,5,6,7-tetrahydro-N_2-indazolyl)methane, bis(4R-methyl-7R-isopropyl-4,5,6,7-tetrahydro-N_1,N_2-indazolyl)methane and bis(4R-methyl-7R-isopropyl-4,5,6,7-tetrahydro-N_1-indazolyl)methane (Fig. 32) and used them as catalytic precursors for asymmetric allylic alkylation [88].

Reaction between $Pd(OAc)_2$ and bis(arylpyrazolyl)methanes: $H_2C(3\text{-}RC_6H_4pz)_2$, $H_2C(3\text{-}RC_6H_4pz)(5\text{-}RC_6H_4pz)$ (R = H, OMe or Br) affords metallacycles $H_2C(3\text{-}RC_6H_4pz)_2Pd_2$ and $[H_2C(3\text{-}RC_6H_4pz)(5\text{-}RC_6H_4pz)]Pd_2$ (Fig. 33). Monomeric compounds $[Pd_2(acac)_2\{H_2C(3\text{-}RC_6H_4pz)_2\}]$, $[Pd_2(acac)_2\{H_2C(3\text{-}RC_6H_4pz)(5\text{-}RC_6H_4pz)\}]$ formed when the acetate-bridged palladacycles reacted with Tl(acac) [89]. The authors also discussed the preferential formation of a

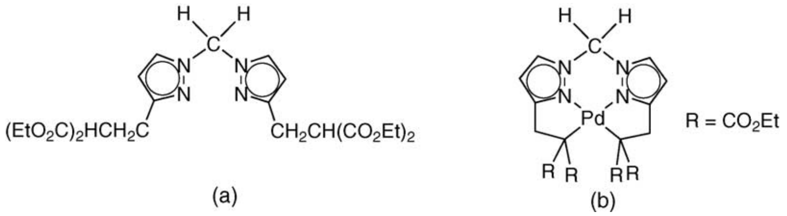

(a)
(b)

Fig. 31. Cyclopalladation (a) and N_2-chelation (b) in bis(pyrazolyl)alkanes functionalized with malonyl residues [86].

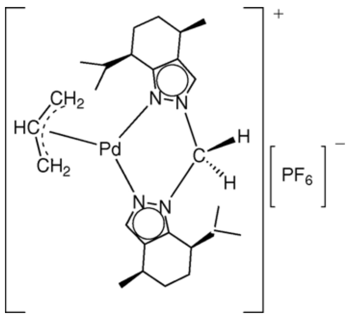


Fig. 32. [Pd(η^3-C_3H_5)(L)][PF_6] (L = bis(4R-methyl-7R-isopropyl-4,5,6,7-tetrahydro-N_1-indazolyl)methane) [88].

six-membered metallacycle in the first step of the reaction [89].

Otero and co-workers reported the synthesis and the characterization of the allylpalladium complexes [(η^3-C_4H_7)Pd{$H_2C(pz)_2$}][BF_4], [(η^3-C_4H_7)Pd{$H_2C(pz)_2$}][PF_6], [(η^3-C_4H_7)Pd{$H_2C(3,5\text{-}Me_2pz)_2$}][$PF_6$] and also investigated their fluxional behaviour [90]. Two conformers of [(η^3-C_4H_7)Pd{$H_2C(3,5\text{-}Me_2pz)_2$}][$PF_6$] were detected at low-temperature and they interchange when the temperature is increased.

$H_2C(5\text{-}PPh_2pz)_2$ reacts with [$PdCl_2(PhCN)_2$] forming [Pd{$H_2C(5\text{-}PPh_2pz)_2$}Cl_2], where a P,P-chelation of the ligand was observed. A dynamic conformation of the six- and eight-membered metallacycles formed was found [20].

The reaction of $(CH_3CN)_2PdCl_2$ with the corresponding bis(pyrazolyl)methane yields [Pd{$Ph_2C(3\text{-}{}^tBupz)_2$}$Cl_2$] and [Pd{$Ph_2C(pz)_2$}$Cl_2$]. [Pd{$Ph_2C(3\text{-}{}^tBupz)_2$}$Cl_2$] adopts a boat conformation and retards the chelate ring inversion relative to the derivative of $Ph_2C(pz)_2$. The reaction of [Pd{$Me_2C(pz)_2$}Me_2] with [$HNMe_2Ph$][$B(C_6F_5)_4$] yields [Pd{$Me_2C(pz)_2$}Me(NMe_2Ph)][$B(C_6F_5)_4$] while the reaction with [$H(OEt_2)_2$][B{3,5-$(CF_3)_2C_6H_3$}$_4$] yields [Pd{$Me_2C(pz)_2$}Me(OEt_2)][B{3,5-$(CF_3)_2C_6H_3$}$_4$]. [Pd{$Me_2C(pz)_2$}Me($CH_2 = CH_2$)][$B(C_6F_5)_4$] undergoes ethylene insertion at $-10\,^\circ$C and oligomerizes ethylene (1 atm) to predominantly linear internal C8 to C24 olefins at 23 °C [91].

Complexes [Pd{$H_2C(pz^x)_2$}$(CH_3CN)_2$][ClO_4]$_2$ ($H_2C(pz^x)_2$ = $H_2C(pz)_2$ and $H_2C(3,5\text{-}Me_2pz)_2$) were prepared and the reactivity towards a variety of neutral N- and

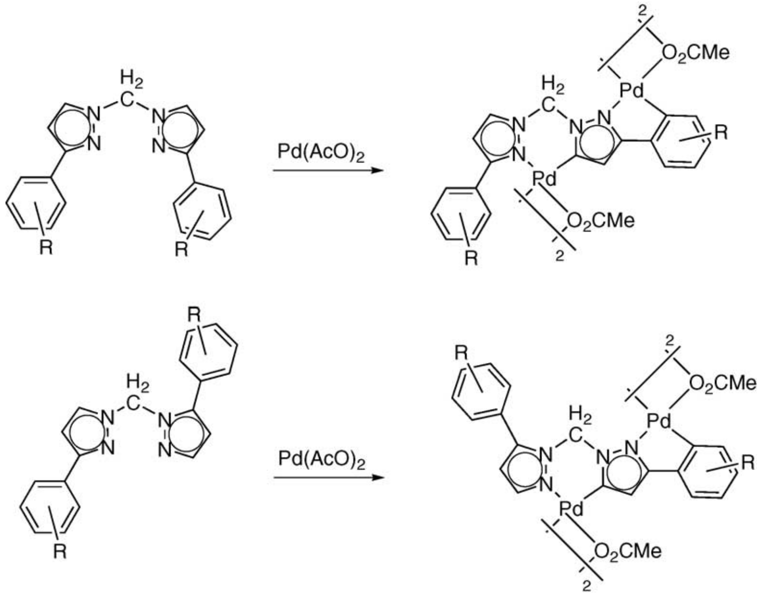


Fig. 33. The metallacycles $H_2C(3\text{-}RC_6H_4pz)_2Pd_2$ and [$H_2C(3\text{-}RC_6H_4pz)(5\text{-}RC_6H_4pz)$]$Pd_2$ [89].

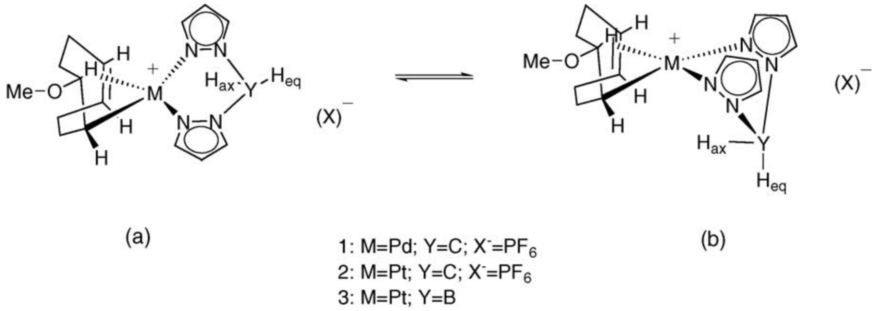


Fig. 34. [M{$H_2C(pz)_2$}(η^1,η^2-$C_8H_{12}OMe$)]$^+$ [95].

P-donor ligands L (L = pyr, PPh_3, PEt_3) or L^2 (L^2 = dppe, en, tmed, bipy, *o*-pd) investigated. Dimeric complexes $[\{H_2C(pz')_2\}Pd(\mu\text{-}OH)_2Pd\{H_2C(pz^x)_2\}][ClO_4]_2$ were isolated that react with L^3 (L^3 = acac, salicylaldehyde, 2-pyrrolcarbaldehyde, 2-pyridine-methoxo, picolinate, 8-hydroxyquinolinate) forming the mononuclear species $[Pd\{H_2C(pz^x)_2\}(L^3)][ClO_4]$ [92]. Dinuclear complexes $[\{Pd\{H_2C(pz')_2\}_2(\mu\text{-}ox)][ClO_4]_2$ and $[\{Pd(\mu\text{-}L^4)\{H_2C(pz^x)_2\}_2][ClO_4]_2$ (L^4 = pz^x, tz, *p*-thiocresolate, thiophenolate) were analogously formed [93]. Deprotonation of a secondary amine by the hydroxo-complexes in the presence of carbon disulfide yields the dithiocarbammate complexes $[Pd(S_2CNR_2)\{H_2C(pz^x)_2\}][ClO_4]$ [93].

The two α-R substituted ligands $PhHC(3,5\text{-}Me_2pz)_2$ and $(py)HC(3,5\text{-}Me_2pz)_2$ were used in the synthesis of new palladium(II) compounds $[PdXX'\{RHC(pz^x)_2\}]$ (R = Ph, X = X′ = Cl; X = X′ = Me; X = Cl, X′ = Me; X = X′= C_6F_5. R = 2-py, X = X′ = Cl; X = Cl, X′ = Me; X = X′ = C_6F_5) $[Pd(\eta^3\text{-}2\text{-}CH_3\text{-}C_3H_4)\{RHC(3,5\text{-}Me_2pz)_2\}]X$ (R = Ph, X = PF_6; R = 2-py, X = tfs) and $[Pd\{(py)HC(3,5\text{-}Me_2pz)_2\}_2][BF_4]_2$ (R = Ph, 2-py). $RHC(pz^x)_2$ adopts a rigid conformation the R group being in an axial position and, as a consequence, no boat-to-boat interconversion is observed. The pyridyl group is always uncoordinated, the $RHC(pz^x)_2$ acting as N_2-bidentate donor [94].

$[M\{H_2C(pz)_2\}(\eta^1,\eta^2\text{-}C_8H_{12}OMe)]^+$ (Fig. 34) (M = Pt or Pd, were synthesized by the reaction of the dimers $[M(\eta^1,\eta^2\text{-}C_8H_{12}OMe)Cl]_2$ with $H_2C(pz)_2$. These complexes were characterized in solution by multinuclear and multidimensional low-temperature NMR spectroscopy and in the case of the palladium complex by X-ray single crystal studies in the solid state. The interionic structure was also investigated in solution at room and low-temperature by ^{19}F, ^1H-HOESY and ^{31}P NMR spectroscopy. These complexes exhibit some dynamic processes investigated by low-temperature NMR experiments and undergo both exchange of the two pyrazolyl rings and inversion of the six-membered chelate rings. Two isomers are present in solution and both exchange their pyrazolyl rings [95].

Clark et al. prepared $[Pt\{R_2C(pz^x)_2\}Me_2X_2]$ (X = I or NO_3; $R_2C(pz^x)_2 = H_2C(pz)_2$, $Me_2C(pz)_2$ $H_2C(3,5\text{-}Me_2pz)_2$) [96]. The reaction of Me_3PtX (X = Cl or I) with $H_2C(3,5\text{-}Me_2pz)_2$ yields $[Pt\{H_2C(3,5\text{-}Me_2pz)_2\}Me_3I]$ containing an octahedral Pt atom with one Me group *trans* to iodine and two methyl groups *trans* to the N atoms of $R_2C(pz^x)_2$ (Fig. 35) [97].

Minghetti et al. also reported some platinum derivatives of $R_2C(pz^x)_2$: they synthesized neutral $[Pt\{H_2C(pz)_2\}Cl_2]$, $[Pt\{H_2C(3,5\text{-}Me_2pz)_2\}Cl_2]$, and cationic $[Pt\{H_2C(pz)_2\}_2]^{2+}$ and $[Pt\{H_2C(3,5\text{-}Me_2pz)_2\}_2]^{2+}$ complexes but their efforts to synthesize platinum derivatives containing $Me_2C(pz)_2$ failed [85]. In fact when $Me_2C(pz)_2$ reacts with $PtCl_2$, $(RCN)_2PtCl_2$ and $K_2[PtCl_4]$ breaking of the ligand and formation of simple adducts of pyrazole such as *cis*- or *trans*-$Pt(pzH)_2Cl_2$ or species containing the ligand [HN=C(R)pz] were isolated in contrast with the behaviour found for the palladium analogues [98].

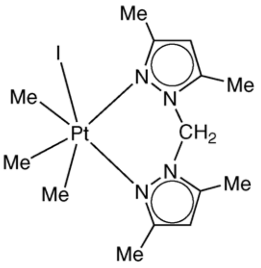


Fig. 35. $[Pt\{H_2C(3,5\text{-}Me_2pz)_2\}Me_3I]$ [97].

Iodomethane reacts with $[M\{H_2C(pz)_2\}Me_2]$ (M = Pd, Pt) yielding *fac*-$[M\{H_2C(pz)_2\}IMe_3]$ that undergo fluxional behaviour involving inversion of the six-membered chelate rings [99]. $[PtMe_3I]_4$ react with $NaSSPPh_2$ and gave $[PtMe_3(SSPPh_2)]_2$ which reacts immediately with $H_2C(pz)_2$ leading to $[Pt\{H_2C(pz)_2\}Me_3(SSPPh_2)]$ [100] upon cleavage of the sulfur bridges.

Canty and Byers prepared a number of bis(pyrazolyl)alkane ligands where one of the bridging methylene hydrogens was replaced by other substituents. The reactivity of the tripod ligands $(py)HC(pz)_2$ and $(mim)HC(pz)_2$ towards $PdMe_2$(II) and MeIPd(II) acceptors was investigated and compared with that of $HC(pz)_3$, $HC(py)_3$, and $C(pz)_4$ [101].

$[Pt(IV)I_2Me_2]$ derivatives of $(py)HC(pz)_2$ and $(mim)HC(pz)_2$ were reported. They exist as a mixture of isomers containing bi- and tri-dentate $R_2C(pz^x)_2$. Whereas $(thi)HC(pz)_2$ forms a complex with $[PtI_2Me_2]$ containing the potentially tripodal ligand only coordinated in bidentate N_2-chelating fashion. In these complexes the ligand are *trans* to the *cis*-$PtMe_2$ group and have one uncoordinated donor group (Fig. 36) [102].

$[PtMe_2(\mu\text{-}SEt_2)]_2$ undergoes oxidative addition reactions with chloro-2,2′-bis(pyrazol)propanes to form platinum(IV) complexes $[PtClMe_2\{(pz)_2CR(CHX)\text{-}N,N',C''\}]$ (R = Me, CH_2Cl, X = H; R = Me, X = Cl), the ligands acting as tripodal [NCN]-systems (Fig. 37). An X-ray single crystal study showed these complexes in a distorted octahedral geometry, *fac*-$PtClC_3N_2$, with $(pz)_2CMeCH_2$- and $(pz)_2C(CH_2Cl)CH_2$-forming N–Pt–N and N–Pt–C angles at platinum ca. 7–12° less than 90° [103].

In the cationic complexes $[PtIR_2(L\text{-}N,N',N'')]^+$ (L = $(mim)HC(pz)_2$ and $(py)HC(pz)_2$) the tridentate ligands L are

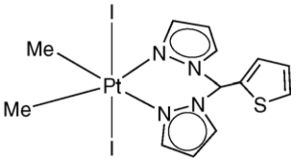


Fig. 36. The $[Pt(IV)I_2Me_2]$ derivative of $(thi)HC(pz)_2$ [102].

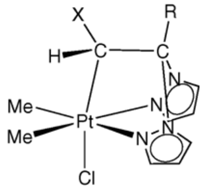


Fig. 37. $[PtClMe_2\{(pz)_2CR(CHX)\text{-}N,N',C''\}]$ in which the ligand acts as tripodal [NCN]-donor [103].

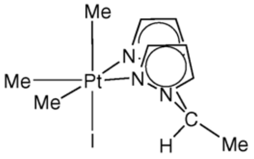


Fig. 38. $[M\{MeHC(pz)_2\text{-}N,N'\}Me_3I]$ [105].

facially coordinated with an octahedral $PtIC_2N_3$ geometry around platinum(IV) [104].

Conformational studies were made on this kind of complexes. In *fac*-$[PtIMe_3\{MeHC(pz)_2\text{-}N,N'\}]$ the metal center is in an octahedral configuration. The ^1H NMR spectra of $[M\{MeHC(pz)_2\text{-}N,N'\}Me_3I]$ (M = Pt or Pd) indicated that these complexes exist in only one configuration in solution. The large downfield shift of the methine resonance, compared with the same proton in $[MMe_2\{HC(pz)_2Me\text{-}N,N'\}]$, is consistent with a conformation of the six-membered chelate ring that places the methine proton adjacent to the iodine atom (Fig. 38) [105].

The platinum complex $[PtCl_2\{H_2C(5\text{-}PPh_2pz)_2\}]$ was prepared and structurally characterized. A distorted square-planar geometry was found in which a proton (H_{endo}) of the bridging methylene is in close proximity to the metal center with a boat-boat conformation of the metallacycle [20].

3.7. Group IB: Cu, Ag, Au

The complexes $[Cu\{H_2C(3,5\text{-}Me_2pz)_2\}_2(ClO_4)_2]$, $[Cu\{H_2C(3,5\text{-}Me_2pz)_2\}_2(NO_3)_2]$, and $[Cu\{H_2C(3,5\text{-}Me_2pz)_2\}_2X_2]$ (X = Cl or Br) were prepared 25 years ago by Reedjik and Verbiest [62].

$Cu(H_2O)_6(BF_4)_2$ reacted with 3,5-Me_2pzH in ethanol yielding $[Cu_2F_2(BF_4)_2(3,5\text{-}Me_2pzH)_6]$ which upon reaction with $H_2C(3,5\text{-}Me_2pz)_2$ forms the first dimeric fluoro-bridged copper(II) compound $[Cu_2\{H_2C(3,5\text{-}Me_2pz)_2\}_4F_2][BF_4]_2$ (Fig. 39) [106].

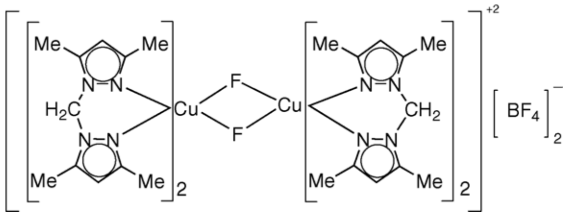


Fig. 39. The dimeric fluoro-bridged copper(II) compound $[Cu_2\{H_2C(3,5\text{-}Me_2pz)_2\}_4F_2](BF_4)_2$ [106].

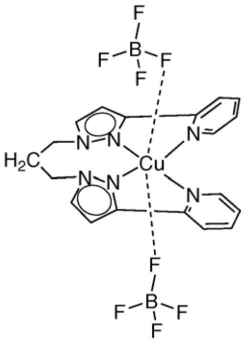


Fig. 40. The distorted tetrahedral $[Cu(1,3\text{-}C_3H_6)(3\text{-}(2\text{-}py)pz)_2][BF_4]_2$ [14].

$[Cu\{Me_2C(pz)_2\}Cl_2]$, prepared by Mesubi [107], reacts readily with pseudohalide ions yielding $[Cu\{Me_2C(pz)_2\}X_2]$ (X = SCN, NCO, N_3) and with PF_6 and BPh_4 to give $[Cu\{Me_2C(pz)_2\}_2X]X'$ (X′ = PF_6, X = Cl, Br or NO_3; X′ = BPh_4, X = Cl). The reaction of $[Cu\{Me_2C(pz)_2\}Cl_2]$ with acac, S_2CNR_2 (R = Me, Et), Bp or Tp leads always to the displacement of $Me_2C(pz)_2$ from the metal coordination sphere [107]. $[Cu\{Me_2C(pz)_2\}X_2]$ (X = Cl, Br or OAc) $[Cu\{Me_2C(pz)_2\}(ClO_4)_2]\cdot H_2O$, $[Cu\{Me_2C(pz)_2\}SO_4\cdot 2H_2O]\cdot H_2O$, and $[Cu\{Me_2C(pz)_2\}_2X]X$ (X = NO_3 or ClO_4) were isolated and characterized by the same author [108] which also prepared $[Cu\{H_2C(pz)_2\}X_2]\cdot nH_2O$ and $[Cu\{H_2C(3,5\text{-}Me_2pz)_2\}X_2]\cdot nH_2O$ (X = Cl, Br, NO_3, OAc, or X_2 = SO_4, n = 0, 1, 3 or 5) [109].

The dinuclear complex $[Cu_2\{H_2C(3\text{-}(2\text{-}py)pz)_2\}_2(\mu\text{-}OH)_2][PF_6]_2$ analogous to Co, Ni and Zn species was described by Mann [13]. Whereas $(1,3\text{-}C_3H_6)(3\text{-}(2\text{-}py)pz)_2$ reacts with copper(II) acetate hydrate and aqueous $NaBF_4$ in MeOH yielding $[Cu(1,3\text{-}C_3H_6)(3\text{-}(2\text{-}py)pz)_2][BF_4]_2$ in which the cation is found in a significant tetrahedral distortion (Fig. 40) arising from the inability of the ligand to be planar [14].

Synthesis, spectroscopic characterization, X-ray crystal structure determination, and magnetic study of the azido-bridged one-dimensional molecular railroad copper(II) compound of formula $[Cu_4\{H_2C(pz)_2\}_2(N_3)_8]_n$ (Fig. 41) which contains the Cu_4N_6 defective double cubane unit were re-

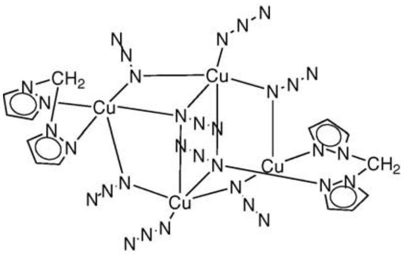


Fig. 41. The azido-bridged one-dimensional molecular railroad copper(II) compound $[Cu_4\{H_2C(pz)_2\}_2(N_3)_8]_n$ [110].

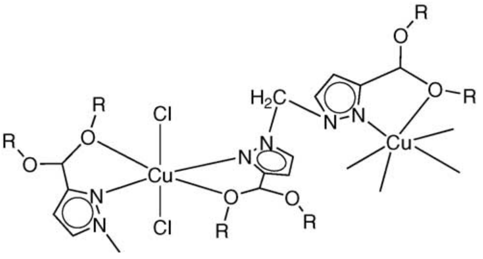


Fig. 42. $[Cu(1,2\text{-}C_2H_4)(3\text{-}CH\text{-}(OCH_3)_2pz)_2Cl_2]_x$ [19].

ported. Three different coordination modes of the azide group occur in the compound [110].

The polynuclear copper(II) complexes $[Cu\{1,2\text{-}C_2H_4)(3\text{-}CH\text{-}(OCH_3)_2pz\}_2X_2]_x$ and $[Cu\{(H_2C)_2(3\text{-}CH\text{-}(OCH_2CH_3)_2pz)_2\}X_2]_x$ (X = Cl or Br) were obtained from the reaction of bis(3-dimethoxymethylpyrazolyl)ethane $(1,2\text{-}C_2H_4)(3\text{-}CH\text{-}(OCH_3)_2pz)_2$, and bis(3-diethoxymethylpyrazolyl)ethane $(1,2\text{-}C_2H_4)(3\text{-}CH\text{-}(OCH_2CH_3)_2pz)_2$ with the corresponding CuX_2 salt. The X-ray crystal structures of $[Cu\{(1,2\text{-}C_2H_4)(3\text{-}CH\text{-}(OCH_3)_2pz)_2\}Cl_2]_x$ (Fig. 42) and $[Cu\{(1,2\text{-}C_2H_4)(3\text{-}CH\text{-}(OCH_3)_2pz)_2\}Br_2]_x$ showed that two of the four oxygen atoms of the acetal fragments are axially semi-coordinated to the copper(II) ions, adjusting the coordination sphere around the metal ion to a very distorted octahedron. The equatorial plane in $[Cu\{1,2\text{-}C_2H_4)(3\text{-}CH\text{-}(OCH_3)_2pz\}_2Cl_2]_x$ is a *trans*-CuN_2Cl_2 chromophore, while in $[Cu\{1,2\text{-}C_2H_4)(3\text{-}CH\text{-}(OCH_3)_2pz\}_2Br_2]_x$ it is a *cis*-CuN_2Br_2 species with a large in-plane distortion [19].

The interaction of $H_2C(pz^x)_2$ with $[CuY(PR'_3)_2]$ ($H_2C(pz^x)_2$ = $H_2C(pz)_2$, $H_2C(3,5\text{-}Me_2pz)_2$; Y = NO_3, BF_4, ClO_4, halide; R = aryl or cy) [111,112] yields ionic $[Cu\{H_2C(pz^x)_2\}(PR'_3)_2]Y$ or neutral $[CuY\{H_2C(pz^x)_2\}(PR'_3)]$ derivatives upon displacement of Y or PR'_3, respectively, from the copper coordination sphere. The stoichiometry and structure of the complexes are dependent on the nature of the substituent on the azolyl group and also on the nature of the counter-ion Y. Displacement of the nitrate is observed with the less hindered and less basic ligand of this family $H_2C(pz)_2$. Nevertheless, one PR'_3 may be displaced from $[CuNO_3(PR'_3)_2]$ by the more bulky and more basic $H_2C(3,5\text{-}Me_2pz)_2$. By contrast, no difference in behaviour was observed from the reaction with the arsine and stibine derivatives $[CuNO_3(AsPh_3)_3]$ and $[CuNO_3(SbPh_3)_3]$ which always reacts with $H_2C(pz^x)_2$ yielding $[CuNO_3\{H_2C(pz^x)_2\}(EPh_3)]$. Displacement of all the phosphine ligands to yield $[Cu\{H_2C(pz^x)_2\}_2]Y$ is possible although forcing conditions are required, i.e. strong excess of the N_2-donor ligand in refluxing benzene. The compounds $[Cu\{H_2C(pz^x)_2\}_2]Y$ can be more efficiently prepared from $[CuNO_3(SbPh_3)_3]$ taking advantage of the decreasing strength of the metal-E bond in the sequence P, As and Sb [111].

Bis(pyrazolyl)-methanes and -ethanes react with AgX species (X = NO_3, ClO_4, tfs, O_3SMe, OAc, BF_4) yielding complexes of different stoichiometry dependent on the nature of X [113,114]. The bis(pyrazolyl)alkane/silver ratio rises from 0.5 in $[(Ag(tfs))_2\{(1,2\text{-}C_2H_4)(4\text{-}NO_2pz)_2\}]$ [114] to 2 in the distorted tetrahedral $[Ag\{Me_2C(pz)_2\}_2][ClO_4]$ (Fig. 43) [113]. The $H_2C(pz)_2$ ligand reacts with $AgNO_3$ yielding a 1:1 neutral species whereas with Ag(OAc) a polynuclear $[Ag(pz)]_n$ species is formed, presumably following hydrolysis of the acetate and breaking of the bridging C–N bond in the organic ligand.

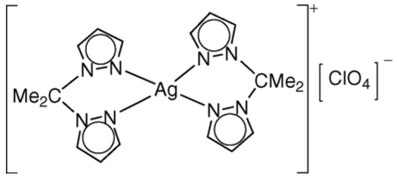


Fig. 43. The distorted tetrahedral $[Ag\{Me_2C(pz)_2\}_2]ClO_4$ [113].

Ward and co-workers also reported the synthesis and the structural characterization of $[Ag\{1,3\text{-}C_3H_6)(3\text{-}(2\text{-}py)\text{-}pz\}_2][NO_3]$ and $[Ag\{1,3\text{-}C_3H_6)(3\text{-}(2\text{-}py)\text{-}pz\}_2][ClO_4]$ [14].

The only gold compound described to date is $[Au(Me)_2\{H_2C(3,5\text{-}Me_2pz)_2\}][NO_3]$ that however was not structurally characterized [115].

A bitopic ligand, 1,1′-bis(dipyrazolylmethyl)ferrocene, $Fe[(C_5H_4)HC(pz)_2]_2$ was reported by Reger to form the $\{Fe[(C_5H_4)HC(pz)_2]_2AgBF_4\}_n$, $\{Fe[(C_5H_4)HC(pz)_2]_2AgPF_6\}_n$, $Fe[(C_5H_4)HC(pz)_2]_2AgSO_3CF_3\}_n$, and $\{Fe[(C_5H_4)HC(pz)_2]_2AgSbF_6\}_n$ coordination polymers (Fig. 44) with three-dimensional supramolecular structures organized by weak hydrogen bonds, $\pi\cdots\pi$ stacking, and $CH\cdots\sigma$ interactions [116].

Tetrakis[(4-ethyl)pyrazolyl]propane $H_2C[HC(4\text{-}Etpz)_2]_2$, prepared by a transamination reaction, reacts with $Ag(NO_3)$ yielding the complex $[Ag_2\{\mu\text{-}H_2C[HC(4\text{-}Etpz)_2]_2\}_2]_3[Ag(NO_3)_4]_2$, containing dimeric units in which two silver cations are sandwiched between two $H_2C[HC(4\text{-}Etpz)_2]_2$ ligands and the counterion [117].

Supramolecular structures dominated by cooperative π–π stacking/CH–π hydrogen bonding interactions have been formed using $CH_2[HC(pz)_2]_2$ as

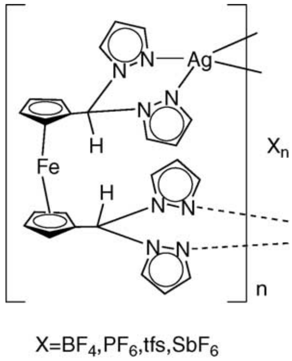


Fig. 44. The $\{Fe[(C_5H_4)HC(pz)_2]_2AgBF_4\}_n$, $\{Fe[(C_5H_4)HC(pz)_2]_2AgPF_6\}_n$, $Fe[(C_5H_4)HC(pz)_2]_2AgSO_3CF_3\}_n$, and $\{Fe[(C_5H_4)HC(pz)_2]_2AgSbF_6\}_n$ coordination polymers [116].

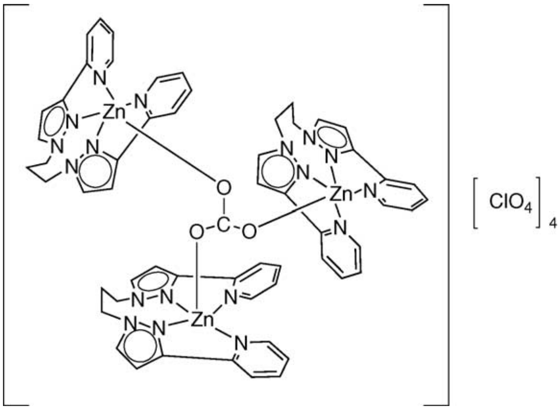


Fig. 45. Symmetric μ^3-bridging mode of carbonate in $[(Zn(1,3\text{-}C_3H_6)\{3\text{-}(2\text{-}py)pz\}_2)_3(\mu^3\text{-}CO_3)][ClO_4]_4$ [14].

ligand. When this ligand reacts with Ag(tfs) $[Ag_2\{\mu\text{-}CH_2[HC(pz)_2]\}_2](tfs)_2$ is obtained. Whereas the reaction with $AgNO_3$ produces the trimetallic complex $[Ag_3\{\mu\text{-}CH_2[HC(pz)_2]_2\}_2][NO_3]_3(CH_3CN)_2$ [118].

$[Ag\{1,3\text{-}C_3H_6)(3\text{-}(2\text{-}py)pz\}_2][NO_3]$ and $[Ag(1,3\text{-}C_3H_6)(3\text{-}(2\text{-}py)pz)_2][ClO_4]$ were also reported [14].

3.8. Group IIB: Zn, Cd, Hg

$[Zn\{H_2C(3,5\text{-}Me_2pz)_2\}X_2]$ (X = Cl or Br) $[Zn\{H_2C(3,5\text{-}Me_2pz)_2\}_2(ClO_4)_2]$, $[Cd\{H_2C(3,5\text{-}Me_2pz)_2\}_2(ClO_4)_2]$ and $[Zn\{H_2C(3,5\text{-}Me_2pz)_2\}_2(NO_3)_2]$ have been firstly reported by Reedijk and Verbiest [62].

Elguero and co-workers synthesized also the two zinc complexes $[Zn\{(1,2\text{-}C_2H_4)(3,5\text{-}Me_2pz)_2\}Cl_2]$ and $[Zn(1,2\text{-}C_2H_4)(3,5\text{-}Me_2pz)_2I_2]$ [77].

Our group reported a systematic study of the interaction of $H_2C(pz)_2$ [119,120], $H_2C(3,5\text{-}Me_2pz)_2$ [121,122], $H_2C(4\text{-}Mepz)_2$ [123], $H_2C(3,4,5\text{-}Me_3pz)_2$ [124], $(1,2\text{-}C_2H_4)(pz)_2$ [125,126] $(1,2\text{-}C_2H_4)(3,5\text{-}Me_2pz)_2$ [127], $Me_2C(pz)_2$ [33,128,129] with ZnX_2, CdX_2 and HgX_2 metal salts (X = Cl, Br, I, CN, SCN, OAc, CF_2CO_2, NO_3, SO_3CF_3). Also the reactivity of bis(4-halopyrazolyl)alkanes towards the same acceptors has been investigated [130]. A table summarizing the results obtained, the ligand to metal ratio and the main spectroscopic and structural features of zinc, cadmium and mercury complexes of bis(pyrazolyl)alkanes has been also presented [127].

$[Zn_2(H_2C\{3\text{-}(2\text{-}py)pz\}_2)_2(\mu\text{-}OH)_2][PF_6]_2$ [13] and $[(Zn(1,3\text{-}C_3H_6)\{3\text{-}(2\text{-}py)pz\}_2)_3(\mu^3\text{-}CO_3)][ClO_4]_4$ [145] have been also reported. The latter complex, structurally characterized, contains a rare example of symmetric μ^3-bridging mode of carbonate (Fig. 45) [14].

Reedjik reported also a difluoro-bridged dimer $[Cd_2\{H_2C(3,5\text{-}Me_2pz)_2\}_4F_2][BF_4]_2$ [57]. Canty compares $[MeHg\{H_2C(pz)_2\}][NO_3]$ [131] with analogous complexes containing analogous N-donor ligands but with only one pz ring in order to determine the coordination behaviour of the bis(pyrazolyl)alkane in solution [132]. In $[MeHg\{H_2C(pz)_2\}][NO_3]$ the ligand $H_2C(pz)_2$ is coordinate in a chelate fashion to MeHg(II) yielding an irregular three-coordination for Hg. The cationic and the anionic moieties are grouped to form $\{[MeHg\{H_2C(pz)_2\}]NO_3\}_2$ dimeric units via Hg···O interactions [133].

3.9. Group IIIA: B, In

The bidentate ligands $R_2C(pz^x)_2$ react with R'_2BX compounds, where X is a leaving group, to form boronium cations $[R_2C(pz^x)_2BR'_2]^+$ [2].

In $[In_2\{H_2C(3\text{-}(2\text{-}py)pz)_2\}Cl_4(\mu\text{-}OH)_2]$, the ligand $H_2C(3\text{-}(2\text{-}py)pz)_2$ reverts to its more usual bridging mode. This complex contains two pseudo-octahedral In^{III} centers with *cis*,*cis*,*cis*-$N_2O_2Cl_2$ coordination environments, and is a rare example of hydroxide ligands bridging two In(III) centers [13].

3.10. Group IVA: Sn, Pb

We [23b] and Gioia Lobbia et al. [134,135] have reported systematically the results of the interaction of $R_2C(pz^x)_2$ with tin and organotin(IV) acceptors. Mesubi also has described some di- and mono-organotin chloride complexes $[Sn\{H_2C(pz)_2\}R_2Cl_2]$ or $[Sn\{H_2C(pz)_2\}RCl_3]$ [136].

$R_2C(pz^x)_2$ (in detail: $H_2C(pz)_2$, $H_2C(4\text{-}Clpz)_2$, $H_2C(4\text{-}Brpz)_2$, $H_2C(3,5\text{-}Me_2\text{-}4\text{-}Clpz)_2$, $H_2C(3,4,5\text{-}Me_3pz)_2$, $H_2C(3,5\text{-}Me_2pz)_2$, $(CH_2)_2(3,5\text{-}Me_2pz)_2$, $H_2C(4\text{-}NO_2pz)_2$, $H_2C(3,5\text{-}Me_2\text{-}4\text{-}Bnpz)_2$ [137] reacts with $[CH_2(SnPhBr_2)_2]$, yielding adducts of $[PhBr_2\{R_2C(pz^x)_2\}SnCH_2SnPhBr_2]$ (Fig. 46). The electronic and steric features of the substituents on the pyrazole rings markedly influences the donating ability of bis(pyrazol)alkanes towards the organotin acceptor.

$H_2C(3\text{-}^tBupz)_2$, $H_2C(5\text{-}^iPrpz)_2$, $H_2C(3\text{-}^iPrpz)(5\text{-}^iPrpz)$ and $H_2C(3\text{-}^iPrpz)_2$ react with diorganotin halides in petroleum ether yielding six-coordinate $[Sn\{H_2C(pz^x)_2\}Ph_2X_2]$. The crystal structures of $[Sn\{H_2C(3\text{-}^iPrpz)(5\text{-}^iPrpz)\}Ph_2Br_2]$ and $[Sn\{H_2C(5\text{-}i\text{-}Prpz)_2\}Ph_2Br_2]$ indicated that the ^iPr group in the three-position of the pyrazole ring decreases the coordination ability of $H_2C(3\text{-}^iPrpz)(5\text{-}^iPrpz)$ [138].

C-organostannyl- and organosilyl-derivatives of substituted bis(pyrazolyl)alkane (Fig. 47) were synthesized and characterized spectroscopically. Lithiation and subsequent

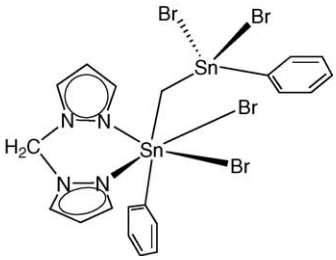


Fig. 46. $[PhBr_2\{R_2C(pz^x)_2\}SnCH_2SnPhBr_2]$ [137].

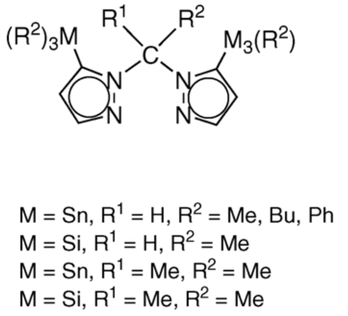


Fig. 47. *C*-organostannyl- and organosilyl-derivatives of substituted bis(pyrazolyl)alkane [139].

substitution by R_3M takes place at the 5,5′-positions for both bis-heterocycles, and this is confirmed by the X-ray structure of 1,1′-[5,5′-$(Ph_3Sn)C_3N_2]_2CH_2$ [139].

The crystal structure of $[PhBr_2Sn\{CH_2(4\text{-}Clpz)_2\}CH_2S\text{-}nPhBr_2]$ showed that bis(4-chloropyrazol)methane acts as a chelating bidentate ligand to only one tin atom [140].

The mononuclear complex $[Pb\{H_2C(3\text{-}2\text{-}py\text{-}pz)_2\}_2(\mu\text{-}OH)_2][ClO_4]_2$ contains the ligand $H_2C(3\text{-}(2\text{-}py)pz)_2$ coordinated in a tetradentate chelating fashion, and the metal center in a very irregular eight-coordinate geometry due to the additional presence of a stereochemically active lone pair [13]. The eight-coordinate $[Pb(1,3\text{-}C_3H_6)(3\text{-}(2\text{-}py)pz)_2(NO_3)_2]$ complex was prepared by a similar procedure [14]. Table 2 summarizes metal derivatives of $R_2C(pz^x)_2$ and their principal; applications.

4. Other systems containing at least two pyrazolyl rings

4.1. Bis(pyrazolyl)acetate derivatives

Otero et al. [141] have developed a synthetic route in order to isolate a new class of tridentate scorpionate mixed functionalized ligands. They reported that a mixture of a chilled (−70 °C) solution of $H_2C(3,5\text{-}Me_2pzH)_2$ in THF reacts with 1 equiv of ^{n}BuLi and CO_2, yielding the lithium compound $[\{Li(H_2O)\text{-}(bdmpza)\}_4]$ (Fig. 48) containing the anionic bis(3,5-dimethylpyrazolyl)acetate ligand. The bis(pyrazolyl)acetates are tridentate ligands closely related to the tris(pyrazolyl)methane, but with one of the pyrazole groups replaced by a carboxylate group. We have inserted them in this review due to the fact that they contain two pyrazolyl rings and their synthesis starts from bis(pyrazol)methanes. In the paper quoted above, Otero reported that $[\{Li(H_2O)\text{-}(bdmpza)\}_4]$ reacts with a niobium complex to give the niobium complex $[NbCl_2(bdmpza)(PhC{\equiv}CMe)]$ [140]. $[\{Li(H_2O)\text{-}(bdmpza)\}_4]$ and 2,2′,-bis(3,5-dimethylpyrazol-1-yl)ethanol (Hbdmpze) react with $[NbCl_3(dme)]_n$ to give the binuclear complexes $[Nb(Cl)(bdmpza)_2]_2$ and $[Nb(Cl)(bdmpze)_2]_2$. A number of $[NbCl_2(bdmpza)(RC{\equiv}CR')]$ and $[NbCl_2(bdmpze)(RC{\equiv}CR')]$ derivatives were also described. $[NbCl_2(bdmpza)(PhC{\equiv}CMe)]$ reacts with LiCp′ (Cp′ = $C_5H_4SiMe_3$) yielding the mixed-ligand complex [NbCp′Cl(bdmpza)]-bis(pyrazol)acetate (bpza), bis(3,5-dimethylpyrazol)acetate (bdmpza) and bis(3,5-di-*tert*-butylpyrazol)acetate (bdtbpza) are the most frequently used ligands (Fig. 49). However different alkyl substituents can also be introduced into the pyrazolyl rings. Burzlaff and his group developed and investigated this field exhaustively.

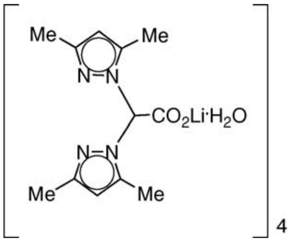


Fig. 48. $H_2C(3,5\text{-}Me_2pzH)_2$ in THF reacts with ^{n}BuLi and CO_2, yielding the lithium compound $[\{Li(H_2O)\text{-}(bdmpza)\}]$ [141].

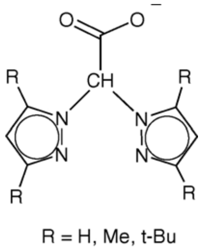


Fig. 49. General structure of bis(pyrazol-1-yl)acetates.

Reaction of bdmpza with $FeCl_2$ gave the 2:1 complex $[(bdmpza)_2Fe]$. In contrast the sterically more hindered ligand bdtbpza coordinates only once to iron leading to [(bdtbpza)FeCl] which may serve as a structural model complex for the active sites of mononuclear nonheme iron oxidase and oxygenases [142]. From the reaction of bis(pyrazolyl)acetates with $Fe(BF_4)_2{\cdot}6H_2O$, $FeCl_2$ and $[NEt_4]_2[Cl_3FeOFeCl_3]$ the dimeric $[Fe(bdtbpza)Cl]_2$ and the monomeric 1:1 complexes $[NEt_4][Fe(bpza)Cl_3]$ and $[NEt_4][Fe(bdmpza)Cl_3]$ were respectively synthesized [143]. bpza and bdtbpza also interact with iron(II) salts, $[(bpza)_2Fe]$ and $[(bdtbpza)_2Fe]$ being respectively formed [143]. $[(bpza)_2Fe]$, $[(bdmpza)_2Fe]$ and $[(bdtbpza)_2Fe]$ are high-spin. No spin crossover to the low-spin state was observed in the temperature range 5–350 K. $[NEt_4][Fe(bpza)Cl_3]$ and $[NEt_4][Fe(bdmpza)Cl_3]$ are iron(III) high-spin complexes.

bpza and bdmpza react with perrhenic acid yielding $[(bpza)ReO_3]$ and $[(bdmpza)ReO_3]$, respectively. The latter compound exhibits a monomeric distorted octahedral structure with a $[N,N,O]ReO_3$ central core [144]. $[(bpza)Re(CO)_3]$, $[(bpza)Mn(CO)_3]$, $[(bdmpza)Mn(CO)_3]$ and $[(bdmpza)Re(CO)_3]$ have also been reported. $[(bdmpza)Re(CO)_3]$ reacts with $NOBF_4$ affording $[(bdmpza)Re(CO)_2(NO)][BF_4]$ [145]. $[(bpza)Mn(CO)_3]$ and $[(bdmpza)Mn(CO)_3]$ were synthesized by reaction of

Table 2
Metal complexes of bis(pyrazolyl)alkane ligands and their applications

Metal	Ligand	Applications	Refs.
Li	H$_2$C(pz)$_2$	New potential hydrogen sources for PEM fuel cells	[27,29]
	H$_2$C(3,5-Me$_2$pz)$_2$		[27,28,29,31]
Na	H$_2$C(pz)$_2$	Coordination polymers	[30]
Zr	Bpzcp[a]		[31]
V	H$_2$C(pz)$_2$		[32]
	H$_2$C(3,5-Me$_2$pz)$_2$		[32]
	Me$_2$C(pz)$_2$		[33]
Nb	H$_2$C(pz)$_2$		[34]
	H$_2$C(3,5-Me$_2$pz)$_2$		[34]
	H$_2$C(5-SiMe$_3$pz)$_2$		[34]
	H$_2$C(5-PPh$_2$pz)$_2$		[20]
Cr	H$_2$C(pz)$_2$		[35,41,55]
	H$_2$C(3,5-Me$_2$pz)$_2$		[35,36,55]
	H$_2$C(3,4,5-Me$_3$pz)$_2$		[55]
	H$_2$C(3-MeS-5-C(CH$_3$)$_3$pz)$_2$		[39]
	H$_2$C(3-MeS-5-(*p*-MeOPh)pz)$_2$		[39]
	H$_2$C(3-MeS-5-Phpz)$_2$		[39]
	H$_2$C(3-Ph-5-(MeS)pz)$_2$		[39]
	H$_2$C(3-MeS-5-(*p*-MeOPh)pz)(3′-(*p*-MeOPh)-5′-(MeS)pz)		[39]
	H$_2$C(3-(*p*-MeOPh)-5-MeSpz)$_2$		[39]
	H$_2$C(3,5-Me$_2$-4-Xpz)$_2$ (X = Cl or Br)		[42]
	H$_2$C(4-Xpz)$_2$ (X = Cl or Br)		[42]
	H$_2$C(3,5-^{i}R$_2$pz)$_2$ (R = Pr or Bu)		[56]
Mo	H$_2$C(pz)$_2$		[40,41,43,47,48,50,55]
	H$_2$C(3,5-Me$_2$pz)$_2$	Molybdenum biological models	[36,37,38,43,47,48,49,50,53,55]
	H$_2$C(3,4,5-Me$_3$pz)$_2$		[43,55]
	H$_2$C(3-MeS-5-C(CH$_3$)$_3$pz)$_2$		[39]
	H$_2$C(3-MeS-5-(*p*-MeOPh)pz)$_2$		[39]
	H$_2$C(3-MeS-5-Phpz)$_2$		[39]
	H$_2$C(3-Ph-5-(MeS)pz)$_2$		[39]
	H$_2$C(3-MeS-5-(*p*-MeOPh)pz)(3′-(*p*-MeOPh)-5′-(MeS)pz)		[39]
	H$_2$C(3-(*p*-MeOPh)-5-MeSpz)$_2$		[39]
	(1,2-C$_2$H$_4$)(3,5-Me$_2$pz)$_2$		[40]
	H$_2$C(3,5-Me$_2$-4-Brpz)$_2$		[42,51]
	H$_2$C(4-Xpz)$_2$ (X = Cl or Br)		[42]
	H$_2$C(3,5-Me$_2$-4-Clpz)$_2$		[42]
	Me$_2$C(pz)$_2$	Potential catalysts for cyclooctene epoxidation	[52]
	PhHC(pz)$_2$		[47,48]
	PhHC(3,5-Me$_2$pz)$_2$		[44,47,48]
	Ph$_2$C(3,5-Me$_2$pz)$_2$		[45]
	H$_2$C(3,5-Me$_2$-4-Bnpz)$_2$		[46]
	H$_2$C(3-^{t}Bupz)$_2$		[46]
	H$_2$C(3(5)-Phpz)$_2$		[46]
	H$_2$C(3-Phpz)(5-Phpz)		[46]
	H$_2$C(3,5-^{i}R$_2$pz)$_2$ (R = Pr or Bu)		[56]
W	H$_2$C(pz)$_2$		[40,41,47,50,54,55]
	H$_2$C(3,5-Me$_2$pz)$_2$		[36,38,47,50]
	H$_2$C(3,4,5-Me$_3$pz)$_2$		[55]
	H$_2$C(3-MeS-5-C(CH$_3$)$_3$pz)$_2$		[39]
	H$_2$C(3-MeS-5-(*p*-MeOPh)pz)$_2$		[39]
	H$_2$C(3-MeS-5-Phpz)$_2$		[39]
	H$_2$C(3-Ph-5-(MeS)pz)$_2$		[39]
	H$_2$C(3-MeS-5-(*p*-MeOPh)pz)(3′-(*p*-MeOPh)-5′-(MeS)pz)		[39]
	H$_2$C(3-(*p*-MeOPh)-5-MeSpz)$_2$		[39]
	(1,2-C$_2$H$_4$)(3,5-Me$_2$pz)$_2$		[40]
	H$_2$C(3,5-Me$_2$-4-Brpz)$_2$		[42,51]
	H$_2$C(4-Xpz)$_2$ (X = Cl or Br)		[42]
	H$_2$C(3,5-Me$_2$-4-Clpz)$_2$		[42]

Table 2 (*Continued*)

Metal	Ligand	Applications	Refs.
	$H_2C(4-Brpz)_2$		[51]
	$PhHC(pz)_2$		[47]
	$PhHC(3,5-Me_2pz)_2$		[47]
	$H_2C(3,5-{}^iR_2pz)_2$ (R = Pr or Bu)		[56]
Mn	$H_2C(3,5-Me_2pz)_2$	Magnetic properties	[57,58]
Re	$H_2C(3-pz^{pyrene})_2$	Luminescent properties	[59]
	$H_2C(3-pz^{pyrene})(5-pz^{pyrene})$		[59]
	$({}^nPr)HC(pz^{pyrene})_2$		[59]
	$Me_2C(pz)_2$		[59]
Fe	$H_2C(pz)_2$		[65,66,81]
	$H_2C(3,5-Me_2pz)_2$		[57,62,64]
	$(1,3-C_3H_6)(3-(2py)-pz)_2$		[14]
	$(Py)HC(pz)_2$		[67]
	$(C_5H_4)HC(pz)_2$		[115]
Ru	$H_2C(pz)_2$	Ion pair structures and counterion localization in solutions	[65,68,69,70,71,72,73]
	$H_2C(n,m-Me_2pz)_2$ (n = 3 or 5, m = 3 or 5)		[65]
	$Me_2C(pz)_2$		[73]
Os	$H_2C(pz)_2$		[74]
Co	$H_2C(pz)_2$		[75]
	$H_2C(3,5-Me_2pz)_2$		[57,62]
	$Me_2C(3-Mepz)_2$		[75,76]
	$Me_2C(5-Mepz)_2$		[76]
	$1,2-C_2H_4(pz)_2$		[77]
	$H_2C(3-(2-py)pz)_2)_2$		[13]
Rh	$H_2C(pz)_2$		[78]
	$H_2C(3,5-Me_2pz)_2$	Hydroformylation and hydroaminomethylation catalysts	[79]
Ir	$H_2C(pz)_2$	Silane alcoholysis catalysts	[80]
	$H_2C(3,5-Me_2pz)_2$	Silane alcoholysis catalysts	[80]
Ni	$H_2C(3,5-Me_2pz)_2$		[57,60,61,62]
	$1,2-C_2H_4(pz)_2$		[77]
	$Me_2C(pz)_2$		[76,81]
	$H_2C(n-Mepz)_2$ (n = 3 or 5)		[76]
	$(thi)CH(pz)_2)$		[83]
	$H_2C(3-(2-py)pz)_2)_2$		[13]
Pd	$H_2C(pz)_2$		[2,85,87,90,92,93,95,99]
	$H_2C(3,5-Me_2pz)_2$		[85,90,92,93]
	$H_2C(5-Ph_2pz)_2$		[20]
	$Me_2C(pz)_2$		[85,87,91]
	$H_2C(3-CH_2CH(C_2OEt)_2pz)_2$	Cyclopalladation	[86]
	$MeHC(pz)_2$		[87,105]
	$(L)HC(pz)_2$ (L = py or mim)		[84,101]
	bis(4R-methyl-7R-isopropyl-4,5,6,7-tetrahydro-N_1-indazolyl)methane	Asymmetric allylic alkylation	[88]
	$H_2C(3-RC_6H_4pz)_2$	Double palladation	[89]
	$H_2C(3-RC_6H_4pz)(5-RC_6H_4pz)$		[89]
	$Ph_2C(pz)_2$		[91]
	$Ph_2C(3-{}^tBupz)_2$		[91]
	$PhHC(3,5-Me_2pz)_2$		[94]
	$(py)HC(3,5-Me_2pz)_2$		[94]
Pt	$H_2C(pz)_2$	Oxidative addition	[85,95,96,99,100]
	$H_2C(3,5-Me_2pz)_2$		[85,96,97]
	$Me_2C(pz)_2$		[96,98]
	$MeHC(pz)_2$		[105]
	$(L)HC(pz)_2$ (L = py or mim)		[102,104]
	$CMe(CH_2Cl)(pz)_2$	Oxidative addition	[103]
	$C(CH_2Cl)_2(pz)_2$		[103]
	$H_2C(5-Ph_2pz)_2$		[20]
Cu	$H_2C(pz)_2$		[109,110,111,112]
	$H_2C(3,5-Me_2pz)_2$		[62,106,109,111,112]
	$Me_2C(pz)_2$		[107,108]
	$H_2C(3-(2Py)pz)_2$		[13]
	$(1,3-C_3H_6)(3-(2-py)pz)_2$		[14]

Table 2 (*Continued*)

Metal	Ligand	Applications	Refs.
	$(1,2-C_2H_4)(3-CH-(OR)_2pz)_2$ (R = Me or Et)		[19]
Ag	$H_2C(pz)_2$		[113,114]
	$H_2C(3,5-Me_2pz)_2$		[113,114]
	$(1,2-C_2H_4)(4-NO_2pz)_2$		[114]
	$Me_2C(pz)_2$		[113]
	$(1,3-C_3H_6)(3-(2-py)-pz)_2$	Coordination polymers	[14]
	$(C_5H_4)HC(pz)_2$	Coordination polymers	[116]
	$H_2C[HC(4-Etpz)_2]_2$	Coordination polymers	[117]
	$CH_2[HC(pz)_2]_2$	Coordination polymers	[118]
	$(1,3-C_3H_6)(3-(2-py)pz)_2$		[14]
Au	$H_2C(3,5-Me_2pz)_2$		[115]
Zn	$H_2C(pz)_2$		[119,120,127]
	$H_2C(3,5-Me_2pz)_2$		[62,121,122]
	$H_2C(4-Mepz)_2$		[123]
	$H_2C(3,4,5-Me_3pz)_2$		[124]
	$(1,2-C_2H_4)(pz)_2$		[125,126]
	$(1,2-C_2H_4)(3,5-Me_2pz)_2$		[77,127]
	$Me_2C(pz)_2$		[33,128,129]
	$H_2C(3-(2Py)pz)_2$		[13]
	$(1,3-C_3H_6)\{3-(2-py)pz\}_2$		[14,146]
Cd	$H_2C(pz)_2$		[119,120,127]
	$H_2C(3,5-Me_2pz)_2$		[57,121,122]
	$H_2C(4-Mepz)_2$		[123]
	$H_2C(3,4,5-Me_3pz)_2$		[124]
	$(1,2-C_2H_4)(pz)_2$		[125,126]
	$(1,2-C_2H_4)(3,5-Me_2pz)_2$		[127]
	$Me_2C(pz)_2$		[33,128,129]
Hg	$H_2C(pz)_2$		[119,120,127,131,132,133]
	$H_2C(3,5-Me_2pz)_2$		[121,122]
	$H_2C(4-Mepz)_2$		[123]
	$H_2C(3,4,5-Me_3pz)_2$		[124]
	$(1,2-C_2H_4)(pz)_2$		[125,126]
	$(1,2-C_2H_4)(3,5-Me_2pz)_2$		[127]
	$Me_2C(pz)_2$		[33,128,129]
	$H_2C(4-Xpz)_2$ (X = Cl or Br)		[130]
B	$H_2C(pz^x)_2$		[2]
In	$H_2C(3-(2-py)pz)_2$		[13]
Sn	$H_2C(pz)_2$		[50,136,2323b,134]
	$H_2C(3,5-Me_2pz)_2$		[50,2323b,135]
	$H_2C(4-Brpz)_2$		[51,137]
	$H_2C(4-Clpz)_2$		[137,140]
	$H_2C(3,5-Me_2-4-Xpz)_2$ (X = Cl or Bn)		[137]
	$H_2C(3,5-Me_2-4-Brpz)_2$		[51]
	$H_2C(3,4,5-Me_3pz)_2$		[137]
	$(CH_2)_2(3,5-Me_2pz)_2$		[137]
	$H_2C(4-NO_2pz)_2$		[137]
	$H_2C(3-{}^tBupz)_2$		[138]
	$H_2C(n-{}^iPrpz)_2$ (n = 3 or 5)		[138]
	$H_2C(3-{}^iPrpz)(5-{}^iPrpz)$		[138]
Pb	$H_2C(3-(2-py)pz)_2$		[13]
	$(1,3-C_3H_6)(3-(2-py)pz)_2$		[14]

[a] 2,2-$(3,5-Me_2pz)_2$-1,1-diphenylethylcyclopentadienyl.

$[BrMn(CO)_5]$ with the corresponding ligand in THF [145]. The X-ray crystal structure of Hbpza, $[(bdmpza)Mn(CO)_3]$, $[(bpza)Re(CO)_3$ and $[(bdmpza)Re(CO)_3]$ was reported [145].

It is well-known that zinc complexes containing *N*,*N*,*O*-ligands can serve as models for the active site of zinc-containing enzymes that bind the metal ion with two histidine groups and one aspartate or glutamate group such as carboxypeptidase A, thermolysin and other proteases. For this reason the interaction of bis(pyrazolyl)acetate with zinc(II) salts was widely investigated.

Reaction of bdmpza with $ZnCl_2$ gave a 2:1 complex $[(bdmpza)_2Zn]$ that was structurally characterized. On the other hand the sterically more hindered ligand bdtbpza coordinates only once to zinc(II) resulting in the complex [(bdtbpza)ZnCl] [144]. The same authors also reported the synthesis and characterization of the new chiral ligand (3,5-di-tert-butylpyrazol-1-yl)(3′,5′-

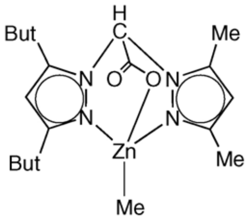


Fig. 50. The [Zn(bpa^{tBu2,Me2})(CH_3)] complex used as precursor for structural model complexes of the active site of zinc enzymes [146].

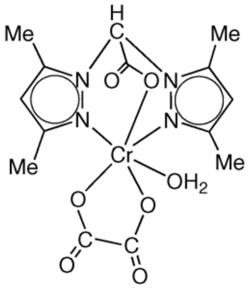


Fig. 51. [Cr(ox)(bdmpza)(H_2O)] forming an infinite two-dimensional network through O—H· · ·O hydrogen bonds [149].

dimethylpyrazol)acetic acid (Hbpa^{tBu2,Me2}) and its complexes [Zn(bpa^{tBu2,Me2})Cl], [Zn(bpa^{tBu2,Me2})(CH_3)] and [Zn(bpa^{tBu2,Me2})(OAc)] as also of the species [Zn(bdtbpza)(CH_3)], [Zn(bdtbpza)(CH_2CH_3)], [Zn(OAc)(bdtbpza)] [146]. [Zn(bpa^{tBu2,Me2})(CH_3)] (Fig. 50) can be used as precursor for structural model complexes of the active site of zinc enzymes. [Zn(bpa^{tBu2,Me2})$_2$] was formed on a side reaction, and exhibits a distorted square-pyramidal coordination with one 3,5-di-*tert*-butylpyrazol group slightly bent away from the Zn-N axis and the other having a weak interaction with the zinc ion from the base direction of the pyramid. The [Zn(bpa^{tBu2,Me2})Cl] crystallizes as a dimer [146].

Ruthenium trichloride hydrate reacted with Hbpza and excess PPh_3 yielding [Ru(bpza)Cl(PPh_3)$_2$]. Whereas the bulkier bdmpza forms [Ru(bdmpza)Cl_2(PPh_3)]. Reaction of bpza or bdmpza with [$RuCl_2$(PPh_3)$_3$] forms, respectively [Ru(bpza)Cl(PPh_3)$_2$] and [Ru(bdmpza)Cl(PPh_3)$_2$] [147]. These complexes were all characterized by X-ray structure determination [145]. [(bdmpza)$(CO)_2$W≡C–C≡C–$SiMe_3$] and [(bdmpza)$(CO)_2$W≡C–C≡C–C_6H_5] were synthesized in a stepwise fashion from [$W(CO)_6$] and Li[C≡CR], $(CF_3CO)_2O$ and M(bdmpza) [147]. The electron-donating potential of the tripodal bdmpza was compared with that of Tp^x and tmeda ligands. bdmpza is shown to be a weaker electron donor than Tp^x but displays stronger electron-donating abilities than Cp [148].

[Cr(ox)(bdmpza)(H_2O)] was synthesized and structurally characterized. In this compound (Fig. 51), which forms an infinite two-dimensional network through O–H· · ·O hydrogen bonds, bdmpza acts as a tridentate donor whereas ox as a chelating bidentate ligand [149].

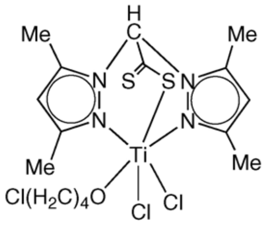


Fig. 52. The alkoxide species [{$TiCl_2$($O(CH_2)_4Cl$)(κ^3-bdmpza)}] and [{$TiCl_2$($O(CH_2)_4Cl$)(κ^3-bdmpzdta)}] [152].

Two copper(II) complexes were also reported, [Cu(bdmpza)$_2$] and [Cu(bdmpza)$_2$]·$2H_2O$. The central coordination sphere in both compounds is fulfilled by two bdmpza ligands, which are centrosymmetrically oriented around the copper ion, thus forming a *trans*-CuN_4O_2 elongated octahedral chromophore. In [Cu(bdmpza)$_2$]·$2H_2O$ the water molecules are hydrogen-bonded to the noncoordinate carboxylate oxygen atoms [150]. The complexes [$TiCl_3$(bdmpza) and [$TiCl_2$(THF)(bdmpza]Cl] were synthesized and shown to catalyze, with methylaluminoxane, the polymerization of ethylene [151].

Otero recently reported the preparation of new scorpionate ligands, always in the form of lithium derivatives, namely [{Li(H_2O)-(bdmpzdta)}$_4$], [{Li(H_2O)-(bdphpza)}$_4$], [{Li(H_2O)-(bdphpzdta)}$_4$] (bdmpzdta = bis(3,5-dimethylpyrazol)dithioacetate, bdphpza = bis(3,5-diphenylpyrazol)acetate, bdphpzdta = bis(3,5-diphenylpyrazol)dithioacetate) [151].

A series of titanium complexes was prepared from the reaction of $TiCl_4$(THF)$_2$ with [Li(H_2O)-(bdmpza)$_4$] and above reported lithium salts, [$TiCl_3$(κ^3-bdmpza)], [$TiCl_3$(κ^3-bdmpzdta)], [$TiCl_2$(κ^3-bdmpzdta)$_2$], [$TiCl_2$(THF)(κ^3-bdmpza)]Cl and [$TiCl_2$(THF)(κ^3-bdmpzdta)]Cl. [$TiCl_2$(THF)(κ^3-bdmpza)]Cl and [$TiCl_2$(THF)(κ^3-bdmpzdta)]Cl undergo a nucleophilic THF ring-opening reaction to give respectively the alkoxide species [$TiCl_2$($O(CH_2)_4Cl$)(κ^3-bdmpza)] and [$TiCl_2$($O(CH_2)_4Cl$)(κ^3-bdmpzdta)] (Fig. 52). Several alkoxides of formula [$TiCl_2$(OR)(κ^3-bdmpza)] and [$TiCl_2$(OR)(κ^3-bdmpzdta)] were also described [152]. A new enantiopure chiral ligand was prepared by introducing a carboxylate group at the bridging carbon atom of bis(camphorpyrazol)methane. A prochiral center is formed, rather than an additional stereocenter [152].

The tripodal ligand bis(5-tert-butyl-3-methylpyrazol-2-yl)acetic acid (HL) was prepared in order to model the 2-His-1-carboxylate facial triad found in the active sites of metalloenzymes such as carboxypeptidase A. Pseudotetrahedral compounds [Zn(L)Me], [Zn(L)Cl], [Zn(L)OAc], [Zn(L)NCS], were reported and characterized. Also the four-(solution) or five-coordinate [Zn(L)(OH_2)]$^+$, and the five-coordinate [Zn(L)acetohydroxamate] were described [153].

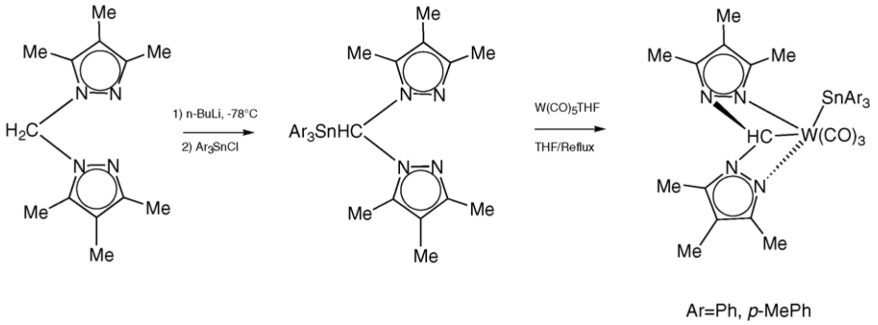


Fig. 53. $\{HC(3,4,5\text{-}R_3pz)_2\}(CO)_3W\text{–}SnX_3$ [154].

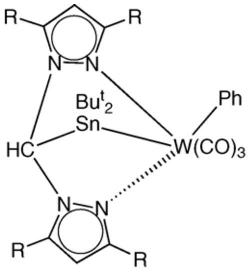


Fig. 54. A novel k^3-[N,Sn,N] coordination mode in $(^tBu)_2SnHC(3,4,5\text{-}R_3pz)_2W(CO)_3(Ph)$ [155].

4.2. Bis(3,4,5-trimethylpyrazol)methide derivatives

The modification of $H_2C(3,4,5\text{-}Me_3pz)_2$ by substitution of organotin groups on the central carbon atom was readily carried out by reaction of $LiHC(3,4,5\text{-}Me_3pz)_2$ with a triaryltin chloride as shown in Fig. 53. The compounds $[X_3Sn\{HC(3,4,5\text{-}R_3pz)_2\}]$ (R = H, Me, Et, ^{i}Pr; X = Ph, p-MePh, Et, ^{i}Pr, ^{t}Bu) react with $[W(CO)_5THF]$ yielding heterodinuclear complexes $[\{HC(3,4,5\text{-}R_3pz)_2\}(CO)_3W\text{–}SnX_3]$, containing four-membered metallacycles, in which bis(3,4,5-triorganopyrazol)methide acts as an unprecedented tridentate monoanionic κ^3-[N,C,N] chelating ligand (Fig. 53) [154].

When there are alkyl substituents in the four-position of pyrazole rings, some decarbonylation intermediates $[X_3Sn(HC(3,4,5\text{-}R_3pz)_2)W(CO)_4]$ can be isolated. Also the reaction of trialkylstannylbis(pyrazol)methanes, $X_3Sn(HC(3,4,5\text{-}R_3pz)_2)$ (X = Et or ^{i}Pr), with $[W(CO)_5THF]$ yields only complexes $[X_3Sn(HC(3,4,5\text{-}R_3pz)_2)W(CO)_4]$, in which bis(pyrazol)methanes act as *N,N*-chelating bidentate ligands. However, treatment of phenyldi(*tert*-butyl)-stannylbis(pyrazol)methanes, $(^tBu)_2PhSn(HC(3,4,5\text{-}R_3pz)_2$ (R = Me or H), with $[W(CO)_5THF]$ produces $(^tBu)_2SnHC(3,4,5\text{-}R_3pz)_2W(CO)_3(Ph)$, in which a novel k^3-[N,Sn,N] coordination mode as well as asymmetric semibridging carbonyl between the W–Sn bond is observed (Fig. 54) [155].

Analogously poly(pyrazol)alkanes modified by organogermyl and organosilyl groups on the bridging carbon atom, reacted with $W(CO)_5(THF)$ also yielding new heterobimetallic species [156].

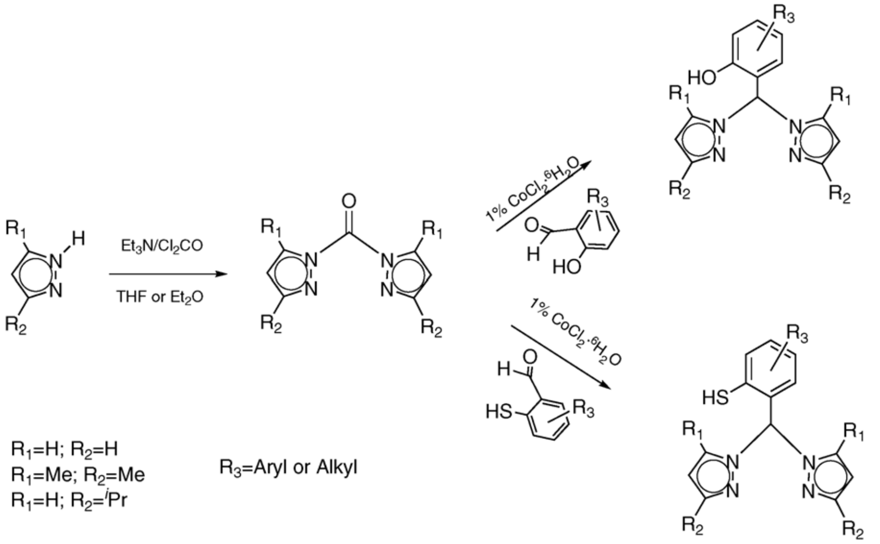


Fig. 55. Synthesis of hydroxyarylbis(pyrazolyl)methanes [157].

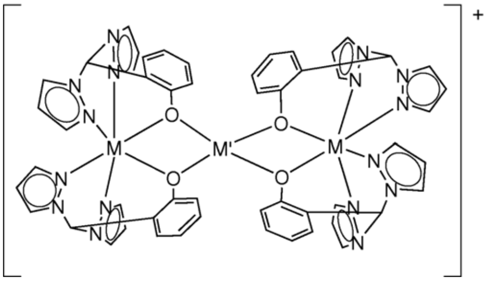


Fig. 56. The homo and heterotrimetallic trinuclear species $[M(bpzOPh)_2M'(bpzOPh)_2M]$ [159].

4.3. *Hydroxyarylbis(pyrazolyl)methane derivatives and related compounds*

Carrano, using the Peterson synthesis of dipyrazolylalkanes by bis(pyrazolyl)ketones and aliphatic or aromatic carbonyl compounds, have developed a synthetic strategy for producing a new class of scorpionate ligands related to the tris(pyrazolyl)methane system but with one of the pyrazole groups replaced by a phenol, thiophenol or other functionalized aryl and alkyl groups (Fig. 55). (2-Hydroxyphenyl)bis(pyrazolyl)methane (HbpzOPh), (2-hydroxyphenyl)bis(3,5-dimethylpyrazolyl) methane (HbdmpzOPh) and (2-hydroxyphenyl)bis(3-isopropylpyrazolyl)methane (HbprpzOPh) ligands were prepared and their reactivity toward $CoCl_2{\cdot}6H_2O$ investigated. $[Co(bpzOPh)_2]{\cdot}2.5MeOH{\cdot}1.5H_2O$, $[Co(bdmpzOPh)_2]{\cdot}0.5H_2O$, $[Co(HbprpzOPh)_2Cl_2]$ and $[Co_3(\mu^3\text{-}OH)(\mu\text{-}bprpzOPh)_2(HbprpzOPh)(H_2O)][BF_4]$ were described [156]. In a second paper Carrano reported the coordination chemistry of the same ligands towards Ni(II) salts. $[Ni(bpzOPh)_2]{\cdot}MeCN$, $[Ni(bdmpzOPh)_2]{\cdot}xS$ ($x = 0.5$, S = MeOH; $x = 2$, S = H_2O), $[Ni(\mu_2\text{-}bdmpzOPh)_2NiCl_2]{\cdot}xS$ ($x = 2$, S = H_2O; $x = 2$, S = CH_2Cl_2), $[Ni_3(\mu_3\text{-}Cl)(\mu\text{-}bprpzOPh)_2(HbprpzOPh)(MeOH)]Cl{\cdot}MeOH{\cdot}xS$ ($x = 4$, S = H_2O; $x = 1.42$, $x = {}^iPr_2O$) and $[Ni_3(\mu_3\text{-}OH)_2(\mu\text{-}bprpzOPh)_3][BF_4]{\cdot}2Me_2CO$ were synthesized and characterized. This work demonstrated that the degree of steric hindrance on the pyrazole rings mediates the nuclearity of the isolated Ni(II) complex [158].

Homo- and heterometallic mono-, di, and trinuclear Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} complexes of HbpzOPh, and its derivatives have been reported. ^1H NMR spectra of the paramagnetic Co^{II} and Ni^{II} sandwich species $[M(bpzOPh)_2]$ indicated the presence of isomeric *cis–trans* equilibria of these complexes in solution, and the presence of some of the *cis* isomer in solution seems to support the formation of new heterometallic trinuclear species of the type $[M(bpzOPh)_2M'(bpzOPh)_2M][BF_4]$ (M = octahedral, M′ = tetrahedral center = Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} (Fig. 56) [159].

Reaction of $Cu(OAc)_2$ with the anionic 2-hydroxy-3-tert-butyl-methylphenyl)bis(3,5-dimethylpyrazolyl)methane (tbmpzOPh) yields the complex [Cu(tbmpzOPh)(OAc)] in which the Cu is found in a distorted five-coordinate geometry, the two pz rings and the bidentate OAc occupying the pseudoequatorial plane with the phenoxy oxygen in an apical position [160].

HbpzOPh, HbdmpzOPh, HbprpzOPh react with $Cu(BF_4)_2{\cdot}6H_2O$ yielding mono and diphenolate complexes $[Cu(HbpzOPh)_2(solvent)][BF_4]_2{\cdot}H_2O$, $[Cu(HbdmpzOPh)(bdmpzOPh)][BF_4]{\cdot}H_2O$, $[Cu(bdmpzOPh)_2]{\cdot}MeCN{\cdot}H_2O$ with relevance to galactose oxidase and Cu(II) transferrin and $[Cu_2(\mu_3\text{-}bprpzOPh)(HbprpzOPh)(\mu\text{-}OH)(H_2O)][BF_4]_2$, an unusual disymmetric dinuclear monophenolate, monohydroxide bridged complex with five and four copper coordination [161].

The reactivity of HtbmpzOPh towards Zn, Co and Cd nitrate salts was investigated, the complexes $[(HtbmpzOPh)Zn(NO_3)_2]$, $[(HtbmpzOPh)Cd(pzH)(NO_3)_2]$ and $[(tbmpzOPh)Cd(pzH)(NO_3)]$ being obtained. In the former complex the Zn adopts a pseudotetrahedral four-coordinate geometry where HtbmpzOPh acts as bidentate with a protonated and uncoordinate phenoxy arm. The Co derivatives is pseudooctahedral, the phenoxy arm being deprotonated and coordinate, whereas the Cd complex is seven coordinated, the phenoxy being protonated and not coordinated as in the zinc species [162].

The synthesis and characterization of iron and cobalt complexes of HbpzOPh, HbdmpzOPh, and HtbmpzOPh are reported. $[Fe(bpzOPh)_2][ClO_4]$, $[Fe(bdmpzOPh)_2][ClO_4]$, $[Fe(tbmpzOPh)_2][ClO_4]$, $[Fe(tbmpzOPh)_2]$, $[Fe(tbmpzOPh)_2][BPh_4]$, $[Co(bpzOPh)_2][Ag(MeCN)][BF_4]_3$, $[Co(bdmpzOPh)_2]$ $[Ag(MeCN)][BF_4]_3$ were investigated by X-ray diffraction studies and electrochemistry. The electrochemical methods show that there is an oxidation state and ligand dependent *cis*/*trans* isomerization in these compounds [163]. HbpzOPh has been employed to prepare a series of linear trimetallic systems with the general structural motif $[M_3(bpzOPh)_4]^{2+}$ (Fig. 56) where M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. Variable temperature magnetic data indicate that Ni, Cu, and Mn complexes display modest antiferromagnetic coupling between the metal centers, while the cobalt derivative is strongly ferromagnetically coupled [164].

Trinuclear thiolate bridged Ni(II) systems $[Ni_3(bpzSPh)_4]^{2+}$ (HbpzSPh = 2-sulfanylphenyl)bis(pyrazolyl)methane) which contains a linear NiS_2NiS_2Ni moiety are prepared. In the presence of alkyl- or aryl-nitriles, such as MeCN, the $[Ni_3(bpzSPh)_4]^{2+}$ cation undergoes cleavage and rearrangement reactions to give $[Ni_2(bpzSPh)_2(MeCN)_4]^{2+}$ or $[Ni_2(bpzSPh)_2(MeCN)_2(H_2O)_2]^{2+}$ [165].

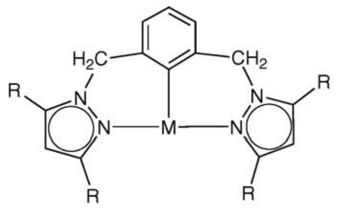
The dimer $[Co_2(bpzSPh)_2(MeCN)_4][BPh_4]_2$ was also reported [165].

The synthesis and characterization of zinc complexes of the heteroscorpionate ligands (3-tert-butyl-2-hydroxy(or thio)-5-methylphenyl)bis(3,5-dimethylpyrazolyl)methane (HL^O or HL^S) containing pentafluorothiophenol (SPh^{F5}) were described by Carrano and Hammes. The stoichiometry of the complexes obtained is strongly dependent on the ratio of the pentafluorothiophenol used [166]. The same ligands were employed in the synthesis of $[Zn(L^{O})I]$, $[Zn(L^{O})Cl]$, $Zn(HL^{O})I_2]$, $[Zn(L^{O})Me]$, $[Zn(L^{O})OAc]$, $[Zn(L^{O})SPh]$, $[Zn(L^{O})SBn]$, $[Zn(L^{S})Me]$, $[Zn(L^{S})SPh]$, and $[Zn(L^{S})_2]$. Comparison was made with analogous compounds containing other scorpionate ligands and preliminary reactivity studies with HX, MeI or trimethylphosphate that suggest sensible difference between N_3-, N_2O-, and N_2S-donor set ligands [167]. The nickel compounds $[Ni(L^{O})Cl]$, $[Ni(L^{O})acac]$, $[Ni(L^{O})OAc]$, $[Ni(L^{O})acac(Hpz)]$, $[Ni(L^{O})acac(MeOH)]$ and $[Ni(L^{O})2]$ were synthesized and characterized and the heteroscorpionate ligand was demonstrated to support a tetrahederal environment for Ni(II) but not to be a tetrahedral enforcer [168].

Carrano also reported the synthesis and characterization of the tridentate "heteroscorpionate" mixed functionality ligand (2-thiophenyl)bis(pyrazolyl)methane (HbpzmSPh) and used this ligand in the synthesis of iron(III), cobalt(III) and vanadium(III) complexes [169]. A series of zinc complexes of (2-methylethanethiol-bis-3,5-dimethylpyrazolyl)methane (bpzmSH) such as [Zn(bpzmS)Me] [170], [Zn(bpzmS)I], $[Zn(bpzmS)(BF_4)]$ and $[Zn(bpzmS)(SPh^{F5})]$ [171] were reported and methylated in solution to give $[Zn(bpzmSCH_3)I_2]$, $[Zn(bpzmSCH_3)I]BF_4$ and $[Zn(bpzmSCH_3)(SPh^{F5})I]$ and the coordination properties of the resulting thioether investigated [171].

HbpzOPh and HbdmpzOPh form respectively cationic allylpalladium complexes of formula $[Pd(\eta^3\text{-}C_4H_7)(HbpzOPh)]tfo$ and $[Pd(\eta^3\text{-}C_4H_7)(HbdmpzOPh)]tfo$ in which the ligands adopt a rigid boat conformation after coordination to the Pd center and the hydroxyaryl group in the axial position of the metallacycle. Analogous complexes $[Pd(\eta^3\text{-}C_4H_7)(HC(R)(pz^{x})_2)]tfo$ (R = cy, anisol-2-yl, ferrocenyl) were also described. Two isomeric forms were identified in solution (endo and exo) that differ in the orientation of the allyl ligand. The R group is in a free rotation regime when R is a phenylic group whereas it has a restricted rotation when R is an hindered group. The isomerization process was affected by the presence of coordinating anions (Cl^-) or by a change in the complex concentration [172]. Also palladium polyfluorophenyl complexes, such as $[Pd(C_6F_5)_2\{HC(R)(pz^{x})_2\}]$ (R = ferrocenyl) were prepared. For the $HC(R)(pz)_2$ and $HC(R)(3,5\text{-}Me_2pz)_2$ complexes only one isomer was found with the R group in an *axial* orientation. For the derivative $Pd(2,3,4,6\text{-}C_6HF_4)_2(pzpm)$, containing a planar ligand, two atropisomers are observed even at high temperature, which excludes the existence of polyfluorophenyl rotation [173].

Intramolecular coordination by the six-membered monoanionic N,C,N chelating system 2,6-(pyrazolylmethyl) phenyl (Fig. 57) and substituted derivatives can give rise to facial and meridional coordination, exhibited by structural studies of facial coordination in the platinum(IV) complex $[PtBrMe_2\{2,6\text{-}(pzCH_2)_2C_6H_3\}]\cdot 1{:}2C_6H_6$ and meridional coordination in the platinum(II) complex $[PtBr\{2,6\text{-}(3,5\text{-}Me_2pzCH_2)_2C_6H_3\}]$ showing close to 'ideal' geometry for the $[N–C–N]^-$ donor sets Pt(IV) species is obtained by oxidative addition of $2,6\text{-}(3,5\text{-}Me_2pzCH_2)_2C_6H_3Br$ to $[PtMe_2(SEt_2)_2]_2$ whereas reaction with $[Pt(p\text{-}Tol)_2(SEt_2)_2]_2$ gave $[PtBr\{2,6\text{-}(3,5\text{-}Me_2pzCH_2)_2C_6H_3\}]$.



M = Pt, Pd or Ru; R = H or Me

Fig. 57. The six-membered monoanionic N,C,N chelating system 2,6-(pyrazol-1-ylmethyl)phenyl [174].

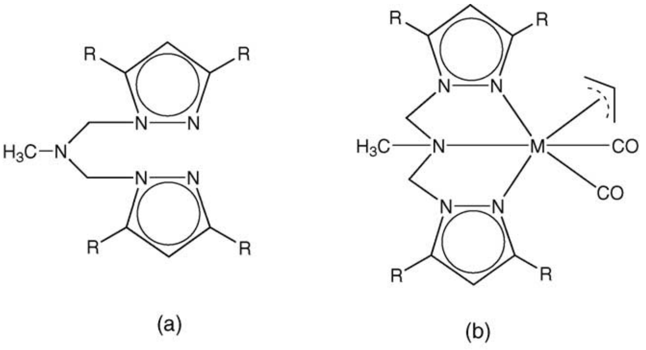
The ligand $\{1,3\text{-}(pzCH_2)_2C_6H_4\}$ undergoes cyclometalation with Pd(II) acetate to form $[Pd(OAc)\{2,6\text{-}(pzCH_2)_2C_6H_3\text{-}N,N',C''\}]$ containing the ligand as a planar [N–C–N]-donor [101].

1,3-(Bis(pyrazol)methyl)benzene derivatives were shown to react with Pd and Ru acceptors, undergoing cyclometalation reactions [175].

Mukherjee recently began research devoted to the investigation of *m*-xylyl based ligands capable of providing two *N*-coordination and arene hydroxylation mainly towards Cu(II) acceptors [176–180].

4.4. Bis(pyrazolyl)amine

Poly(pyrazolyl)amines (Fig. 58a) are multidentate ligands closely related to scorpionates. Organotransition-metal complexes of chromium(II), molybdenum(II), and tungsten(II) with formula $[LM(CO)_2(\pi\text{-}C_3H_5)][PF_6]$ (Fig. 58b) [L = $\{CH_3N(H_2C(pz)_2\}$, M = Cr, Mo, W; L = $(CH_3N(H_2C(3,5\text{-}Me_2pz)_2)$, M = Mo, W] were prepared. In $[\{CH_3N(H_2C(3,5\text{-}Me_2pz)_2\}Mo(CO)_2(\pi\text{-}C_3H_5)][PF_6]$ each cation can be described as pseudooctahedral, the allyl moiety occupying only one coordination site [181]. $[Cr\{CH_3N(H_2C(pz)_2\}(CO)_2(\eta^3\text{-}allyl)][PF_6]$ con-



(a)

(b)

R = H or Me

Fig. 58. Poly(pyrazolyl)amine (a) and their metal complexes $[LM(CO)_2(\pi\text{-}C_3H_5)]PF_6$ (b) [182].

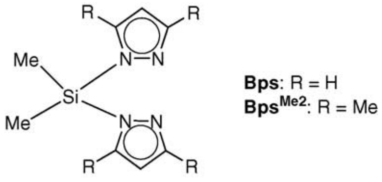


Fig. 59. General structure of the bis(pyrazolyl)sylane (Bps) ligands [186].

tains an η^3-allyl group symmetrical with respect to $\{CH_3N(H_2C(pz)_2\}$. This symmetric structure was compared with the unsymmetrical structure reported for $[Mo\{CH_3N(H_2C(pz)_2\}(CO)_2(\eta^3\text{-allyl})][PF_6]$ [182].

$\{(CH_3N(CH_2pz)_2\}$ and $\{CH_3N(CH_2)(3,5\text{-}Me_2pz)_2\}$ reacted with $M(CO)_6$ or $M(CO)_3(MeCN)_3$ in MeCN to give respectively *fac*-$[\{CH_3N(CH_2(pz)_2)\}M(CO)_3]$ and *fac*-$[\{(CH_3N(CH_2)(3,5\text{-}Me_2pz)_2)\}M(CO)_3]$ in good yields (M = Cr, Mo, W). These complexes are compared with the related polypyrazolylborate complexes of the group VI metal carbonyls [183]. $AgNO_3$ reacted at room temperature within minutes with $M\{CH_3N(CH_2(3,5\text{-}Me_2pz)_2)_2\}(CO)_3$ (M = Mo, W) to give $[M\{CH_3N(CH_2(3,5\text{-}Me_2pz)_2\}(CO)_2(NO)]^+$ in MeCN [184]. The reaction between $[Cr\{CH_3N(CH_2(3,5\text{-}Me_2pz)_2)\}(CO)_3]$ and an excess of $[NO][BF_4]$ in MeCN gives the air-stable 17-electron monomeric product $[Cr\{CH_3N(CH_2(3,5\text{-}Me_2pz)_2)\}(NO)(NCMe)_2][BF_4]_2$ [185].

4.5. Bis(pyrazolyl)sylanes

The bis(pyrazolyl)sylanes (Bps) (Fig. 59) can be synthesized from the reaction of Me_2SiCl_2 with two molar equivalents of the corresponding alkali metal pyrazolates [186]. Bps and Bps^{Me2}, isolated in good yield, are stable in dry air for at least 6 months and they are soluble in aliphatic and aromatic hydrocarbons, acetonitrile, dichloromethane and ethers. They slowly decompose in acetone or in the presence of solvents with acidic protons such as water and alcohols. Bps and Bps^{Me2} were used to prepare zinc(II) derivatives.

4.6. Bis(pyrazolyl)metallates

Several bis(pyrazolyl)metallates involving platinum(II) and palladium(II) of general formula (bidentate donor)$M(pz^x)_2$ (Fig. 60) were described and spectroscopically characterized. They can be considered as potentially bidentate ligands [187,188]. Tetrafluoroboric acid often protonates both pyrazolato groups, affording [(bidentate donor)$M(Hpz^x)_2]^{2+}$ cations, whose reactivity [189], e.g. with $[BH_4]^-$ and spectroscopic properties [190] were investigated. Heteropolymetallic compounds derived from (bidentate phosphine)$M(pz^x)_2$) were recently reported and structurally characterized. These sterically hindered ligand afforded very soluble trinuclear and pentanuclear tetrahedral complexes [191,192]. Fast atom bombardment mass spectrometry of some of these derivatives have been were also reported [193].

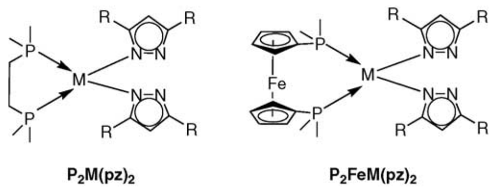


Fig. 60. General structure for the bis(pyrazolyl)metallates.

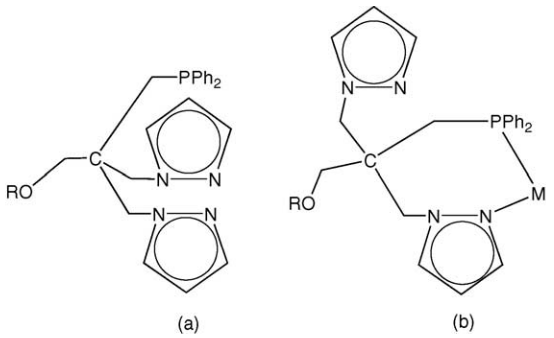


Fig. 61. Structure of the ligands $(CH_2OR)C(CH_2PPh_2)(CH_2pz)_2$ (R = H or Et) and their metal complexes [194].

4.7. Other systems

The ligands $(CH_2OR)C(CH_2PPh_2)(CH_2pz)_2$ (R = H or Et) (Fig. 61) a their reactivity towards $Mo(MeCN)_3(CO)_3$ were reported by Huttner. Both ligands act as bidentate N,P-donors, one pyrazolyl ring not being coordinated [194].

5. Concluding remarks

Since the Trofimenko discovery a number of papers on bis(pyrazolyl)alkanes coordination chemistry has been published. These ligands have shown a coordinating behaviour often paralleling that of the isosteric and isoelectronic bis(pyrazolyl)borates. Their behaviour has been very different from that of the well-known, always N_2-donor but rigid, chelating ligands bipyridyl and phenanthroline. Complexes with many metal ions have been reported, however several gaps are present in the periodic table, for example the group IIA, Ti, Hf, Ta, Tc, Ga, In, Tl and lanthanide metal derivatives of bis(pyrazolyl)alkanes could be the subject of new investigations. Further developments in this areas will undoubtedly build on the ability of these systems to exercise a great degree of the control on the metal environment and also to test their potential application as catalysts or in the production of new materials for electronic devices.

Acknowledgements

University of Camerino and “Fondazione Carima” are gratefully acknowledged.

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