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Metal derivatives of poly(pyrazolyl)alkanes
I. Tris(pyrazolyl)alkanes and related systems

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Contents

Abstract

A comprehensive surwey of the tris(pyrazolyl)alkanes coordination chemistry, based on the nature of the metal, is presented, together the main synthetic methods and spectroscopic and structural features of this important class of ligands.

Keywords: Metal derivatives; Poly(pyrazolyl)alkanes; Tris(pyrazolyl)alkanes

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Abbreviations: [9]aneS_3, 1,4,7-trithiacyclononane; Ar, aryl; Bipy, $2,2'$-bipyridyl; bn, benzyl; ^{n}Bu, *n*-butyl; ^{t}Bu, *tert*-butyl; Cp, cyclopentadienyl; Cp*, pentamethylcyclopentadienyl; cy, cyclohexyl; COD, 1,5-cyclooctadiene; Et_2O, diethyl ether; EtOH, ethanol; Hacac, 2,4-pentanedione; $HC(pz)_3$, tris(pyrazolyl)methane; $HC(3,5\text{-}Me_2pz)_3$, tris(3,5-dimethylpyrazolyl)methane; HIn, indazole; Ind, indenyl; Hmim, *N*-methylimidazole; Hpz, pyrazole; Hpz^x, a generic substituted-pyrazole where x denotes the substitution according to Trofimenko notation [7]; Me, methyl; nb, bicyclo[2.2.1]heptene; NBD, norbornadiene; Ph, phenyl; PPN^+, bis(triphenylphosphoranylidene)-ammonium cation; ^{i}Pr, iso-propyl; py, pyridine; pyr, pyridyl; $pzTp^x$, a generic tetrakis(pyrazolyl)borate; $RC(pz^x)_3$, a generic tris(pyrazolyl)alkane; SCF, self-consistent-field; tacn, 1,4,7-triazacyclononane; THF, tetrahydrofuran; Tp^x, a generic tris(pyrazolyl)borate; Tht, tetrahydrothiophene; Tps, tris(pyrazolyl)silane; Tpms, tris(pyrazolyl)methanesulfonate

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1. Introduction

Since poly(pyrazol-1-yl)borate ligands were discovered by Trofimenko [1], their coordination chemistry has been extensively developed with particular interest arising out of the ability of this class of ligands to modify or control the steric and electronic environment about the metal center by variation of the pyrazolyl group. From 1967 to date a number of reviews, describing not only synthesis [2,3] and properties of this class of ligands [4,5], but also their coordination chemistry, appeared [6–12]. On the contrary the coordination chemistry of poly(pyrazolyl)alkanes remained for a long time unexplored mainly due to difficulties in the preparation of large quantity of these ligands.

Only recently several researchers have contrasted the chemistry of complexes of the neutral poly(pyrazolyl)alkanes with that previously developed for anionic poly(pyrazolyl)borates. Reger [13] has reviewed some procedures for the synthesis of tris(pyrazolyl)methanes and also reported a summary of their coordination chemistry towards copper(I), silver(I), cadmium(II), lead(II) and thallium. We have now decided to report a comprehensive review of the coordination chemistry of poly(pyrazolyl)alkanes and related ligands. This review covers the results obtained with tris- and tetrakis-(pyrazolyl)alkanes from 1970 to 2003. Following previous work presented by Trofimenko, the subject matter has been divided into three main categories: (1) the chemistry of classical tris- and tetrakis-(pyrazolyl)alkanes organized by periodic table groups; (2) the chemistry of tripodal neutral pyrazolyl-containing systems derived from silane and phosphine oxide; (3) related systems.

In this review, we provide essential information to allow the reader to probe more deeply into the main aspects of the coordination chemistry of these fascinating and flexible ligands. This review would also demonstrate the enormous potential in poly(pyrazolyl)alkanes chemistry, as also the future perspectives in this field. The bis(pyrazol-1-yl)alkane ligands and related systems is subject of the part II.

2. Synthesis and properties of tris(pyrazolyl)alkanes

Tris(pyrazolyl)alkanes (Fig. 1) RC(pz^x)$_3$ constitute a family of stable and flexible polydentate ligands isoelectronic and isosteric with poly(pyrazolyl)borates. These donors can be prepared readily and various substituents may replace each hydrogen atom, so that electronic and steric effects can be varied nearly at will. These molecules contain azole rings which are generally very stable towards chemical attack, for example against both oxidizing and reducing agents.

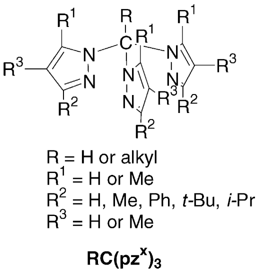


Fig. 1. Generic structure for the tris(pyrazolyl)alkane ligands.

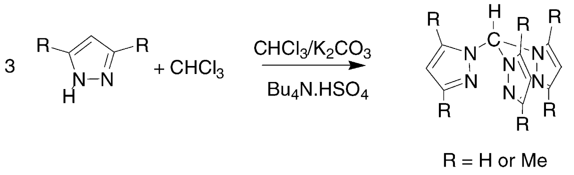


Fig. 2. Elguero’s synthesis [17] of tris(pyrazolyl)methanes.

The simplest member of this family, the tris(pyrazolyl)methane HC(pz)$_3$, was firstly prepared by the reaction of sodium pyrazolate with chloroform in benzene [14]. Two analogous methods were reported in 1970 [15] and in 1990 [16]. A solid–liquid phase transfer procedure involving heating of a mixture of the appropriate pyrazole, chloroform, potassium carbonate and tetrabutylammonium hydrogen sulfate at reflux overnight has been described [17] (Fig. 2).

Higher yields were obtained with a procedure which involves heating a mixture of the pyrazole, water, chloroform, tetrabutylammonium bromide and sodium carbonate at reflux for three days [18]. A modification of Elguero’s procedure for the synthesis of HC(3,5-Me$_2$pz)$_3$, reported the necessity of stirring a mixture of the same reagents at room temperature for a week [19]. Efficient preparations of several poly(pyrazolyl)alkanes were reported five years ago on inorganic synthesis [20].

The synthesis of unsymmetrical HC(pz^x)$_3$ ligands has been also developed [21] and also a new synthetic methods for the preparation of unsymmetrical tris(pyrazolyl)methanes of the type HC(pz)$_2$(pz′) and HC(pz)(pz′)(pz″) throughout an oxidative coupling reaction (Fig. 3) [19].

An approach to tris(pyrazolyl)methanes containing unsymmetrically substituted pyrazoles has been proposed showing that the mixture of regioisomers, obtained, for example when 3(5)-^{t}Bu-pzH has been employed as starting reagent (Fig. 4), treated to equilibrating conditions (refluxing toluene, catalytic acid) converts to a single regioisomer in which steric interactions are minimized [22].

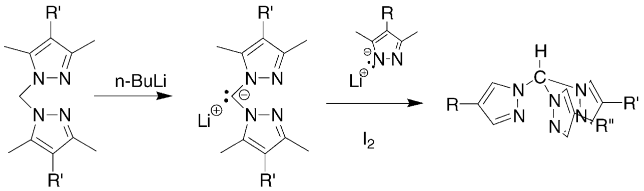


Fig. 3. The oxidative coupling reaction proposed by Armanasco [19] for the synthesis of unsymmetrical tris(pyrazolyl)methanes.

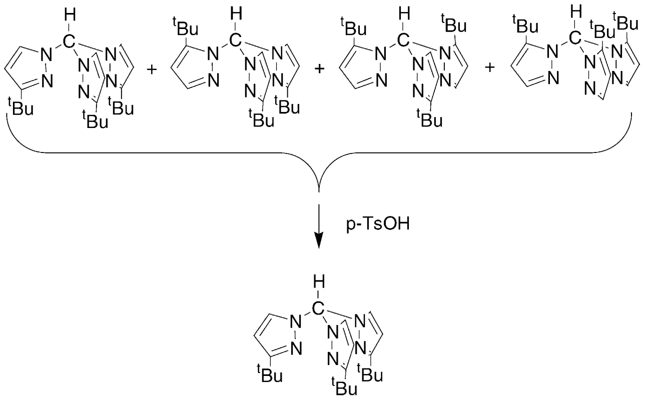


Fig. 4. Acid-catalyzed conversion of unsymnmetrical tris(pyrazolyl)-methanes to a single regioisomer.

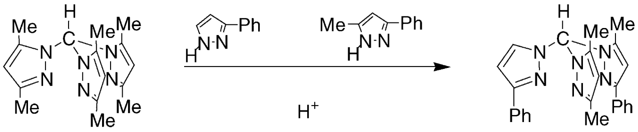


Fig. 5. Synthesis of tris(pyrazolyl)alkanes containg different pyrazoles.

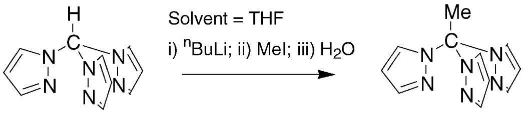


Fig. 6. Proposed method for the methylation of tris(pyrazolyl)methanes.

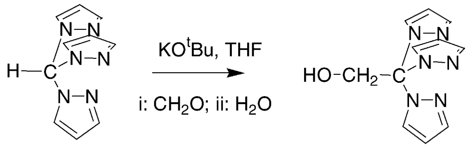


Fig. 7. Introduction of alcohol function group on the bridging carbon of $HC(pz)_3$.

Also the simple $HC(pz)_3$ can be equilibrated with substituted pyrazoles to form new mixed tris(pyrazolyl)methanes (Fig. 5). It has been reported that the products ratio depends on the nature of the starting $RC(pz^x)_3$, the nature of the substituted pyrazole and the relative amount of these two reagents [23].

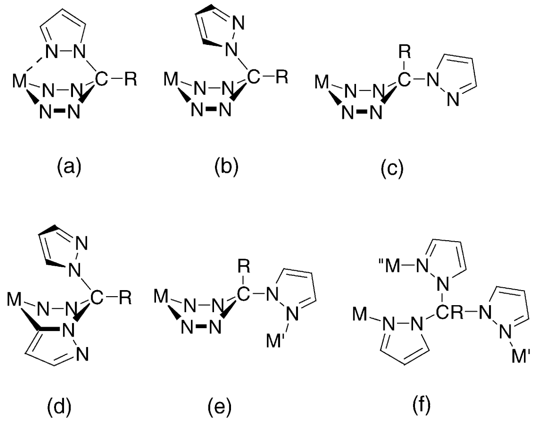
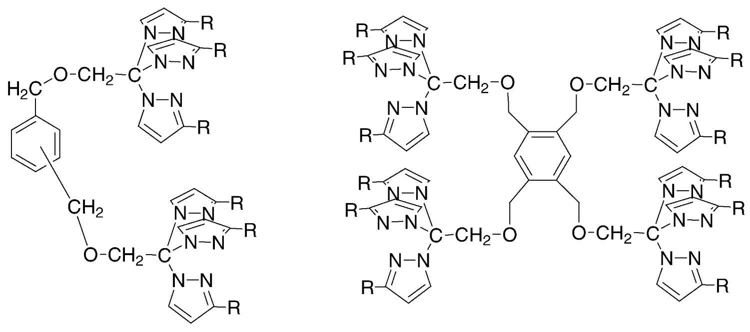


Fig. 9. Selected coordination modes for tris(pyrazolyl)alkanes.

Methylation of $HC(pz)_3$ to form $MeC(pz)_3$ is also possible (Fig. 6), the alkylation being successful when the pyrazole rings contain no alkyl substituents on the 5-position of the rings [24,25].

The acidic methyne hydrogen of $HC(pz)_3$ can be easily removed. After that the ligand has been deprotonated, an alcohol functional group may be introduced using para-formaldehyde and water (Fig. 7). Then $HOCH_2C(pz)_3$ can be used for the synthesis of multitopic semi-flexible ligands with conjugated organic spacers such as I and II (Fig. 8), able to form coordination polymers [26–28]. The ligand II consists, in the solid state, of discrete molecules without significant intermolecular association. Within each $HC(pz^x)_3$ unit, the orientation of the three pyrazolyl ring is a propeller arrangement [28]. An improved synthesis for 1,1,2-(4,4′,4″-tripyrazolyl)ethane from pyrazole and trichloroethanol has been recently reported [29]. The synthesis of tris[3-(6-carboxypyridin-2-yl)pyrazol-1-yl)]methane in a linear multi-step protocol has been reported [30].

The $RC(pz^x)_3$ ligands are suitable for exploring the tendency of metal ions, which generally form square-planar complexes, to extend their coordination environment to square-pyramidal or octahedral via axial interactions. Potential coordination modes includes tridentate (a), and bidentate with the third donor group above the metal centre, but uncoordinated (b), or directed away from the metal cen-



I

II

Fig. 8. Multitopic ligands containing $–C(pz)_3$ units.

tre (c), and also N,C-bidentate (d) bridging tridentate (e–f) as illustrated in Fig. 9.

$RC(pz^x)_3$ produces a relatively strong ligand field, consistent with the rather short M–N bond lengths in the complexes. The pyrazole group acts as moderately strong σ donor and a weak out-of-plane π-donor, with the π-interaction in the plane of the amine ligand probably being close to zero [31]. $HC(pz)_3$ has been also found to stabilize high-oxidation-state organopalladium(IV) complexes [32–34].

A detailed ^{13}C NMR study of some poly(pyrazolyl)alkanes has been reported and the effects of the N-substituents on the ^{13}C chemical shifts of the heterocyclic nuclei have been evaluated [35]. The $\delta(^{13}C)$ of the methane carbon atom are discussed using an interactive model [35]. The $\delta(^{13}C)$ chemical shifts and ^{1}H-^{13}C coupling constants of other poly(pyrazolyl)methanes have been also described four years later. The chemical shifts show high internal consistency: an additive model predicts the chemical shift of the central sp^3 carbon. Coupling constants are also useful tools for the assignment of pyrazolyl carbons, and in addition the $^{1}J(^{1}H–^{13}C)$ coupling of the central carbon can be linearly related to the basicity of the pyrazole substituents [24]. The measurements of small $^{1}H–^{15}N$ and $^{13}C–^{15}N$ coupling constants and isotopic shifts in tris(pyrazolyl)methanes have been performed by ^{1}H-detected, gradient-enhanced ^{15}N and ^{13}C NMR experiments [36].

Structure of the free ligand $HC(3,5\text{-}Me_2pz)_3$ has been reported on 1984 [37]. More recently, the crystal structure of the sublimated form (mp = 424 K) of $HC(3,5\text{-}Me_2pz)_3$ was solved by a Patterson search method [38]. Theoretical calculation (MM2 and MNDO) have been carried out on several conformations of $HC(pz)_3$ and $C(pz)_4$ [39]. The potential surface obtained has been compared with experimental data (lanthanide shift reagents, dipole moment and X-ray structure). The structure of the tetrakis(pyrazolyl)methane has been also determined by X-ray diffraction [39].

Flash vacuum pyrolysis of $HC(pz)_3$ was carried out, α-, γ- and radical eliminations were evaluated. The products formed correspond to a radical reaction [40].

3. Complexes of tris(pyrazolyl)alkanes

3.1. Group IA: Na, Li, K

Tris(pyrazolyl)alkanes are suitable for the stabilization of air-unstable group IA compounds. Two very stable lithium derivatives were described [41]: $[\{HC(3,5\text{-}Me_2pz)_3\}Li(\eta^3\text{-}BH_4)]$ is a neutral octahedral complex, both borohydride and the N_3-donor ligand being tridentate (Fig. 10a), whereas the reaction between $HC(pz)_3$ and $LiBH_4$ yielded an insoluble ionic $[\{HC(pz)_3\}_2Li](BH_4)$. $[\{HC(3,5\text{-}Me_2pz)_3\}Li(\eta^3\text{-}BH_4)]$ is a potential hydrogen source for proton exchange membrane fuel cells [42].

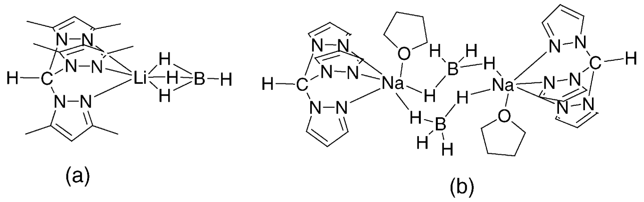


Fig. 10. Group IA metal derivatives of tris(pyrazolyl)alkanes.

The evolution of hydrogen via hydrolysis and the heat of reaction by hydrolysis have been measured [43]. The same authors also reported sodium and potassium compounds: from the reaction of $NaBH_4$ with $HC(pz)_3$ in THF a dimer has been obtained $[\{HC(pz)_3\}(THF)Na(BH_4)]_2$ (Fig. 10b) in which the two tris(pyrazolyl)methanes are tridentate, and the two BH_4 bridge the sodium atom forming two $\mu^1{}_1,\mu^1{}_1$-type bond. The coordination environment in Na atoms is completed by a monodentate THF molecule [44]. Whereas the reaction of $NaBH_4$ with $HC(3,5\text{-}Me_2pz)_3$ yields a 2:1 adduct having an octahedral arrangement with the BH_4 acting as counter-ion. NaI reacts with $HC(pz)_3$ and $HC(3,5\text{-}Me_2pz)_3$ leading to the formation of $[\{HC(pz)_3\}_2Na]I$ and $[\{HC(3,5\text{-}Me_2pz)_3\}_2Na]I$ respectively, which have trigonally distorted octahedral arrangements about the sodium. The reaction of KPF_6 with $HC(3,5\text{-}Me_2pz)_3$ results in the formation of the trigonally distorted six-coordinate octahedral $[\{HC(3,5\text{-}Me_2pz)_3\}_2K][PF_6]$. The low coordination number found is unusual for this large metal ion [45].

3.2. Group IIA: Ca, Sr, Ba

The complex $[\{HC(pz)_3\}_2Sr][BF_4]_2$ has been prepared by the reaction of 1 eq. of $Sr(acac)_2$ with $HBF_4{\cdot}Et_2O$ and 2 eq. of $HC(pz)_3$. $[\{HC(pz)_3\}_2Sr][BF_4]_2$ has a highly distorted structure, with κ^3-bonding of both $HC(pz)_3$ and additional interaction with the metal from the F^- of the BF_4^- counter-ions. The complexes $[\{HC(pz)_3\}_2(Hacac)M](B[3,5\text{-}(CF_3)_2C_6H_3]_4)_2$ (M = Ca and Sr) (Fig. 11a) and $[\{HC(pz)_3\}_2(Me_2CO)Sr](B[3,5\text{-}(CF_3)_2C_6H_3]_4)_2$ (Fig. 11b) were also structurally characterized [45].

A patent has recently described the use of complexes bearing tris(pyrazolyl)methane ligands for the formation of group IIA metal-containing films on a substrate. The compounds prepared were indicated as particularly suitable for the preparation of semiconductor structures [46].

3.3. Group IVB: Ti

Two patents describe Ti-tris(pyrazolyl)alkane derivatives as high-catalysts for polymerization of olefins. They report the synthesis of $[\{HC(pz)_3\}TiCl_3]$ and the polymerization of ethylene using this compound and methylaluminoxane at 313 K for 60 min. A number of compounds of formula $RE(pz)_3MX_3$ (R = H, halide, alkyl, aryl or amino group; E = C, Si, Ge, Sn, Pb; M = Group IVB metal) has been described as catalysts [47]. The synthesis and the use as catalysts of [{HC(pz)$_3$}TiOCl$_2$] has been also described [48].

3.4. Group VB: V, Nb

Cationica six-coordinate species of formula [{HC(pz)$_3$}$_2$ V](Y)$_2$ (Y = Br or PF$_6$) have been prepared and characterized by means of electronic and magnetic measurement by Mani [49]. From the interaction of acetylene complexes [NbCl$_3$(L)(RC≡CR′)] (L = 1,2-dimethoxyethane; R and R′ = Me, Ph or CO$_2$Me] with HC(pz)$_3$ or HC(3,5-Me$_2$pz)$_3$ in the presence of 1 eq. of AgBF$_4$ the cationic complexes [{HC(pz)$_3$}NbCl$_2$(RC≡CR′)][BF$_4$] have been obtained. The structure of these compounds have been determined by spectroscopic methods. NMR studies were also carried out in order to evaluate the fluxional behavior of complexes in solution. The free activation energy values at the coalescence temperature were also calculated [50].

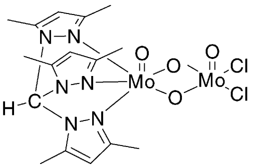


Fig. 12. Structure of the unsymmetrical dimer [{HC(3,5-Me$_2$pz)$_3$} Mo$_2$O$_4$Cl$_2$].

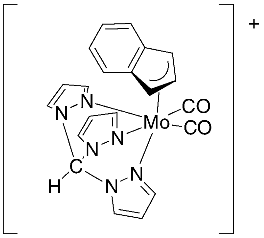
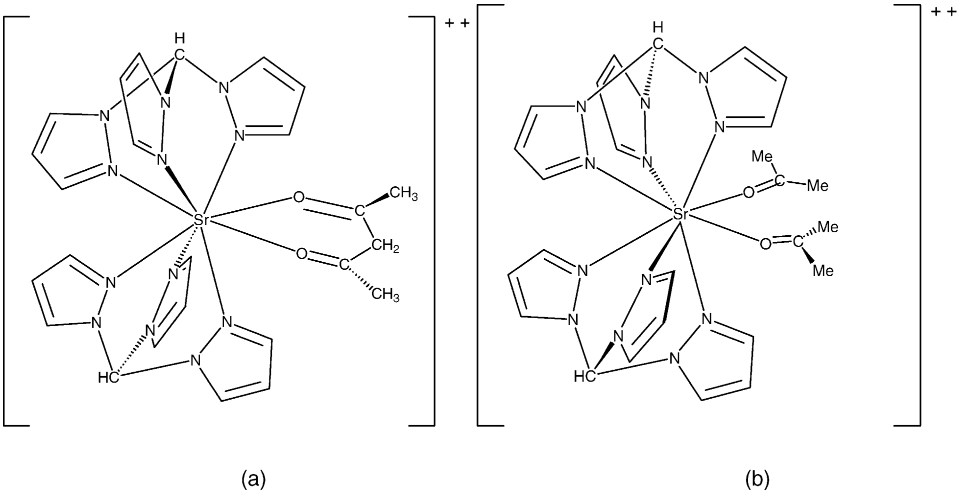


Fig. 13. Ring slippage of the indenyl in [(η^3-ind){κ^3-HC(pz)$_3$} M(CO)$_2$][BF$_4$].

3.5. Group VIB: Cr, Mo, W

The first chromium complex [{HC(pz)$_3$}Cr(CO)$_3$] has been reported by Trofimenko [15]. In the same work he described the molybdenum and tungsten derivatives [{HC(pz)$_3$}M(CO)$_3$] (M = Mo or W), [{HC(3,5-Me$_2$pz)$_3$} Mo(CO)$_3$], [{HC(pz)$_3$}Mo(π-allyl)(CO)$_2$][PF$_6$],[{HC(pz)$_3$} Mo(π-cycloheptatrienyl)(CO)$_2$][PF$_6$], [{HC(pz)$_3$}M(NO) (CO)$_2$][PF$_6$] (M = Mo, or W), [{HC(3,5-Me$_2$pz)$_3$}Mo(NO) (CO)$_2$][PF$_6$] (M = Mo, or W) and [{HC(pz)$_3$}M(N=N–Ar) (CO)$_2$][PF$_6$]. The preparation and properties of [{HC(pz)$_3$}$_2$ Cr][BPh$_4$]$_2$ [51] and the synthesis and structural characterizations of mononuclear and binuclear molybdenum complexes of HC(3,5-Me$_2$pz)$_3$ have been reported [52]. Oxidation of [{HC(3,5-Me$_2$pz)$_3$}Mo(CO)$_3$] by oxidants such as SOCl$_2$, Br$_2$, I$_2$ and HNO$_3$ affords a variety of complexes [{HC(3,5-Me$_2$pz)$_3$}Mo(X)$_3$] (X = Cl, Br, I and O). Upon standing, the reaction mixtures of [{HC(3,5-Me$_2$pz)$_3$}MoOX$_2$]$^+$ produce unsymmetrical dimers [{HC(3,5-Me$_2$pz)$_3$}Mo$_2$O$_4$X$_2$] (Fig. 12). Reaction of MoO$_2$X$_2$(THF)$_2$ (X = Cl or Br) with HC(pz)$_3$ leads to the replacement of both coordinated solvent molecules and one of the chloride ligands to give [{HC(pz)$_3$}MoO$_2$X]X [52]. The turnover frequencies of these complexes in olefin epoxidation, with *t*-butyl hydroperoxide as oxidizing agent, are in the middle of the range observed for MoO$_2$X$_2$L$_2$ complexes with N$_2$-donor ligands L$_2$ [53]. The ring slippage of the indenyl occurs upon dissolution of the complex [(η^5-Ind){κ^2-HC(pz)$_3$}M(CO)$_2$][BF$_4$] (M = Mo or W) in acetonitrile, to give [(η^3-ind){κ^3-HC(pz)$_3$}M(CO)$_2$][BF$_4$] (Fig. 13). The [(η^5-Cp){κ^2-HC(pz)$_3$}Mo(CO)$_2$][BF$_4$] has been also synthesised [54].

The reactivity of 1,1,1-tris(pyrazol-1-yl-methyl)ethane (L), synthesised by reaction of tris(chloromethyl)ethane with sodium pyrazolate, toward (MeCN)$_3$Mo(CO)$_3$ has been investigated [55]. The complex [(L)Mo(CO)$_3$(MeCN)]



(a) (b)

Fig. 11. Structure of the cation in complexes [{HC(pz)$_3$}$_2$(Hacac)Sr](B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$)$_2$ (a) and [{HC(pz)$_3$}$_2$(Me$_2$CO)Sr](B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$)$_2$ (b).

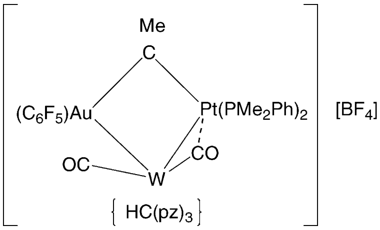


Fig. 14. Structure of the trimetal complex $[WPtAu(C_6F_5)(\mu^3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{HC(pz)_3\}]$.

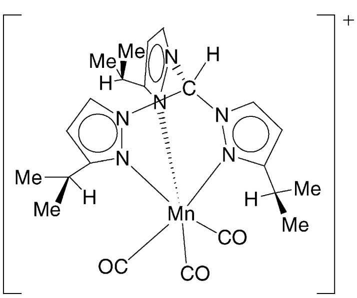


Fig. 16. The sterically hindered $[\{HC(3\text{-}^iPrpz)_3\}Mn(CO_3)]SO_3CF_3$.

formed in which only two of the three donor functions are coordinated [55].

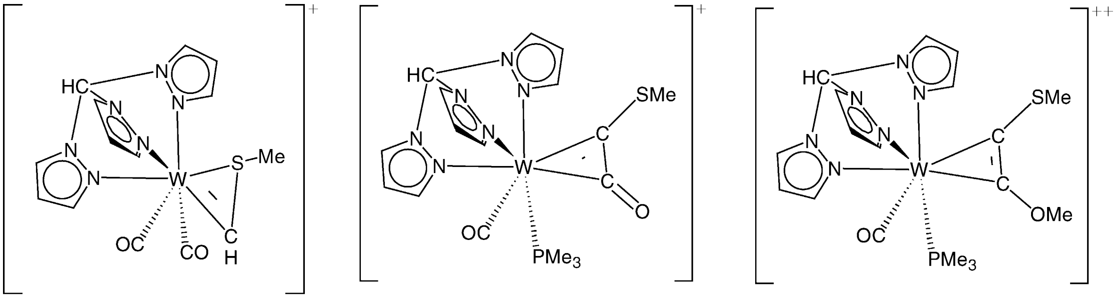
The alkylidyne metal complexes $[\{HC(pz)_3\}M(\equiv CR)(CO)_2][BF_4]$ (M = Mo or W) and $[\{MeC(pz)_3\}W(\equiv CR)(CO)_2][BF_4]$ were synthesised by reaction of the complexes $[M(\equiv CR)(CO)_2]$ in THF with $TlBF_4$ and $HC(pz)_3$. Mixed metal complexes afforded when $[W(\equiv CR)(CO)_2\{HC(pz)_3\}][BF_4]$ reacts with $[Co_2(CO)_8]$, $[Pt(nb)_3]$ and $[Pt(nb)(PMe_2Ph)_2]$. The heterometallic compound $[WPtAu(C_6F_5)(\mu^3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{HC(pz)_3\}]$ (Fig. 14) has been prepared by further addition of $[Au(C_6F_5)(tht)]$ to $[WPt(\mu^3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{HC(pz)_3\}][BF_4]$ [56]. A THF solution of $[\{HC(pz)_3\}W(\equiv CR)(CO)_2][BF_4]$ reacts with Li^nBu and $BF_3.Et_2O$, affording the neutral complexes $[\{(F_3B)(pz)_3\}W(\equiv CR)(CO)_2]$ [57]. The reaction of $[\{(F_3B)(pz)_3\}W(\equiv CR)(CO)_2]$ with some low-valent metal complexes has been also investigated. Some bimetallic and trimetallic derivatives such as $[WPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(COD)\{(F_3B)(pz)_3\}]$ and $[WPtMR(\mu^3\text{-}CMe)(CO)_2(PMe_2\text{-}Ph)_2\{(F_3B)(pz)_3\}]$ were synthesised and investigated by NMR spectroscopy.

It has been demonstrated that the nucleophilic sulfur atom of the CS in $[\{HC(pz)_3\}(CO)_2W(CS)]$ can be methylated with Me_3O^+ to give the thiocarbyne complex **III**. When **III** reacts with PR_3 the η^2-ketenyl complex **IV** formed. Finally methylation of **IV** at the ketenyl oxygen atom yields the acetylene complex **V** (Fig. 15). Protonation of the carbyne atom gave a thiocarbene complex, for which the reactivity towards nucleophiles has been also reported [58].

A number of patents have described the use of tris(pyrazolyl)methane derivatives of formula $[\{RC(pz^x)_3\}Cr(R)_n]$ (R = halide, straight chain or branched alkyl, n = 1–3) as ethylene trimerization catalysts for production of 1-hexene [59]. A catalyst mixture is generally prepared by using a $RC(pz^x)_3\text{–}CrCl_3$ complex activated with methylaluminoxane. The catalyst is used in toluene at 80 °C and allows selective preparation of 1-hexene with high conversion of ethylene [60].

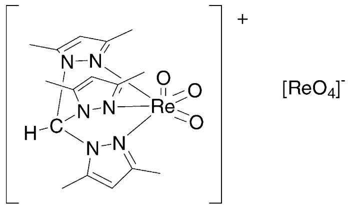
3.6. Group VIIB: Mn, Re

The first manganese complex, $[\{HC(pz)_3\}Mn(CO)_3][PF_6]$, has been reported by Trofimenko [15]. $HC(pz)_3$, $HC(3,5\text{-}Me_2pz)_3$, $HC(3\text{-}^iPrpz)_3$ and $HC(3\text{-}Phpz)_3$ react with $[Mn(CO)_5]SO_3CF_3$ to yield $[\{HC(pz^x)_3\}Mn(CO_3)]SO_3CF_3$ complexes. In $[\{HC(3\text{-}^iPrpz)_3\}Mn(CO_3)]SO_3CF_3$ the ligand is tridentate with the ^{i}Pr groups rotated away from the $Mn(CO)_3$ core of the cation likely due to steric congestion (Fig. 16) [18]. The complexes $\{p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2[Mn(CO)_3]_2(X)_2\}$ (X = BF_4 or CF_3SO_3), $\{m\text{-}C_6H_4\text{-}[CH_2OCH_2C(pz)_3]_2[Mn(CO)_3]_2[BF_4]_2$ and $\{1,2,4,5\text{-}C_6H_2\text{-}[CH_2OCH_2C(pz)_3]_4[Mn(CO)_3]_4[BF_4]_4$ have been prepared by the reaction of the corresponding ligand with $Mn(CO)_5Br$ and AgX in refluxing acetone. The manganese atom is always found in a slightly distorted octahedron. The structurally adaptive ligands in all four complexes support extended three-dimensional (3D) supramolecular structures [61]. The $\{1,2,4,5\text{-}C_6H_2[CH_2OCH_2C(pz)_3]_4\}[Mn(CO)_3]_4\text{-}[BF_4]_4$ forms a 3D sinusoidal architecture with 16 × 7 Å channels organized by π–π stacking and weak C–H···F hydrogen bonds [62].



III **IV** **V**

Fig. 15. Thiocarbine and thiocarbene complexes of W containing $HC(pz)_3$ as supporting ligand.



VI

Fig. 17. Heterolytic Re–O–Re cleavage In Re_2O_7 after reaction with $HC(pz)_3$.

When chelating tripod ligands such as $HC(pz)_3$ reacts with Re_2O_7, heterolytic Re–O–Re cleavage and formation of ionic perrhenate **VI** occurs (Fig. 17) [63]. The rhenium(V) complex $[\{HC(pz)_3\}ReOCl_2]^+$ and the corresponding phosphine oxide adduct $[\{HC(pz)_3\}ReCl_2(OPPh_3)]Cl$ and charge effects on oxygen atom transfer were also described [64]. These complexes are similar to analogous species containing Tp^x ligands.

The rhenacarborane salt $Cs[Re(CO)_3(\eta^7\text{-}7,8\text{-}C_2B_9H_{11})]$ reacts with $AgBF_4$ and $HC(pz)_3$ yielding the complex $[\{\mu\text{-}\kappa^1,\kappa^2\text{-}CH(pz)_3\}\{ReAg(\mu\text{-}10\text{-}H\text{-}\eta^5\text{-}7,8\text{-}C_2B_9H_{10})(CO)_3\}_2]$ which unexpectedly contains a tris(pyrazolyl)methane bridging two $\{ReAg(\mu\text{-}10\text{-}H\text{-}\eta^5\text{-}7,8\text{-}C_2B_9H_{10})(CO)_3\}$ fragments in a κ^1,κ^2-manner (Fig. 18) [65].

$HC(pz)_3$, $HC(3,5\text{-}Me_2pz)_3$, $HC(3\text{-}Phpz)_3$ and a 4:1 $HC(3\text{-}^iPrpz)_3$: $HC(3\text{-}^iPrpz)_2(5\text{-}^iPrpz)$ mixture react with $Re(CO)_5Br$ yielding complexes of formula $[LRe(CO)_3]Br$ ($L = HC(pz^x)_3$). The methyne hydrogen atoms of the $HC(pz)_3$, $HC(3\text{-}^iPrpz)_3$ and $HC(3\text{-}^iPrpz)_2(5\text{-}^iPrpz)$ ligands show deshielded chemical shift values as a result of hydrogen bonding interactions with the bromide counter-ion. Tetrafluoroborate species $[LRe(CO)_3][BF_4]$ species can be obtained when the reaction was carried out in the presence of $AgBF_4$. The hexadentate ligand $p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2$ analogously yields the homobimetallic complex $p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2[Re(CO)_3]_2(Br)_2$ which is organized by π–π and C(H)···π interactions into a two-dimensional supramolecular network of two interpenetrating 'zig–zag' chains [66].

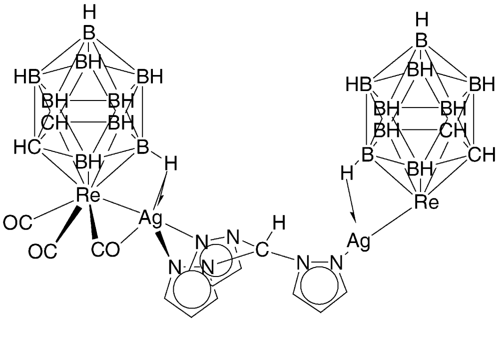
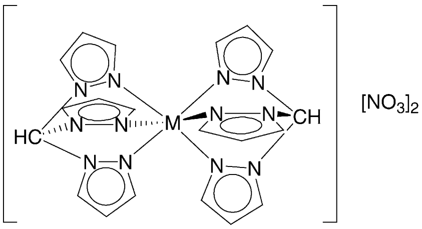


Fig. 18. Structure of a rhenacarborane compound containing $HC(pz)_3$ coordinated in a κ^1,κ^2 manner.



M=Co, Ni, Cu or Zn

Fig. 19. Structure of sandwich-type complexes of formula $[M\{HC(pz)_3\}_2]$.

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

$[Fe\{HC(pz)_3\}_2]Cl_3$, $[Co\{HC(pz)_3\}_2]X_2$ ($X = NO_3$, I, PF_6 or $X_2 = SiF_6$) and $[Ni\{HC(pz)_3\}_2]X_2$ ($X = NO_3$, I_2, PF_6) were firstly reported by Trofimenko [15]. $[M\{HC(pz)_3\}_2][NO_3]_2$ (M = Co or Ni) were also reported and characterized by single-crystal X-ray diffraction and electronic spectroscopy [30] (Fig. 19). A determination at 173 K of $[\{HC(pz)_3\}_2Co][NO_3]_2$ has been reported in 1994 [67]. The reaction of $M([BF_4])_2\cdot xH_2O$ (M = Co, Ni) in a 1:2 ratio with $HC(3,5\text{-}Me_2pz)_3$ yields $[M\{HC(3,5\text{-}Me_2pz)_3\}_2][BF_4]_2$. Over the temperature range from 5 to 350 K or 345 K, Curie law behavior is observed from microcrystalline samples of both compounds showing them to have three and two unpaired electrons. The solid state structure of both complexes are isomorphous at 220 K, monoclinic in the space group $C2/c$. Cooling crystals of the two compounds to low-temperature leads to the observation of the same phase change to triclinic in the new space group $P1$ with nonmerohedral twinning. This change is reversible [68].

Mani [69] reported the synthesis and the characterization (magnetic measurements, electronic absorption spectra, conductivity measurements) of the octahedral mononuclear $[Fe\{HC(pz)_3\}_2]Br_2$ and polynuclear $[Fe\{HC(pz)_3\}(NCS)_2]$. The complexes $[Fe\{HC(3,5\text{-}Me_2pz)_3\}_2][BF_4]_2$, $[Fe\{HC(pz)_3\}_2][BF_4]_2$ and $[Fe\{PhC(pz)_2(pyr)\}_2][BF_4]_2$ have been prepared and their magnetic properties investigated [70,71]. $[Fe\{HC(3,5\text{-}Me_2pz)_3\}_2][BF_4]_2$ is high-spin in the solid state and in solution at 298 K, but undergoes a decrease in magnetic moment at lower temperature [72]. $[Fe\{HC(pz)_3\}_2][BF_4]_2$ is low-spin in the solid-phase at room temperature, but gradually changes over to the high-spin-state upon heating above 295 K and is completely high-spin at ca. 470 K. $[Fe\{PhC(pz)_2(pyr)\}_2][BF_4]_2$ is low-spin at all temperature studied in both the solid-phase and solution. Full multiple scattering calculations of the iron K-edge X-ray absorption near-edge spectra of both $[Fe\{HC(3,5\text{-}Me_2pz)_3\}_2][BF_4]_2$ and $[Fe\{HC(pz)_3\}_2][BF_4]_2$ have been carried out [73]. More recently, a high-pressure iron K-edge X-ray absorption spectral study of the spin-state crossover in $[Fe\{HC(3,5\text{-}Me_2pz)_3\}_2]I_2$ and $[Fe\{HC(3,5\text{-}Me_2pz)_3\}_2][BF_4]_2$ has been described [74]. Also a detailed structural, magnetic and Mössbauer

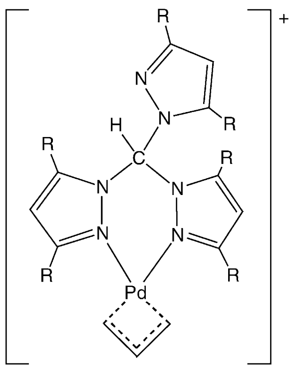


Fig. 20. Palladium(II) allyl derivative of tris(pyrazolyl)alkanes.

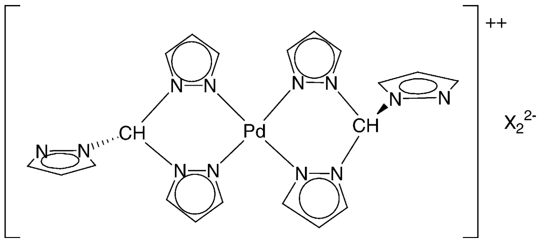


Fig. 22. Square-planar PdN_4 geometry in $[\{HC(pz)_3\}_2Pd]X_2$.

spectral study of $[Fe\{HC(3,5\text{-}Me_2pz)_3\}_2]I_2$ has been reported [75]. If the reaction between $Fe[BF_4]_2{\cdot}6H_2O$ and $HC(3,5\text{-}Me_2pz)_3$ was carried out in 1:1 ligand to metal molar ratio, the complex $[Fe\{HC(3,5\text{-}Me_2pz)_3\}(H_2O)_3][BF_4]_2$, in a distorted octahedral N_3FeO_3 central core, formed, which has a ^1H NMR spectrum characteristic of a paramagnetic high-spin complex [76].

The crystal structure of α and β polymorphs of $[Fe\{HC(pz)_3\}_2][NO_3]_2$ together with a detailed discussion of its visible spectra, variable temperature magnetic measurements, bonding and electrochemistry has been reported [77]. Rapid spin-state interconversion in the bis-complex of $HC(pz)_3$ with Fe(II) has been studied by Mössbauer spectroscopy [78].

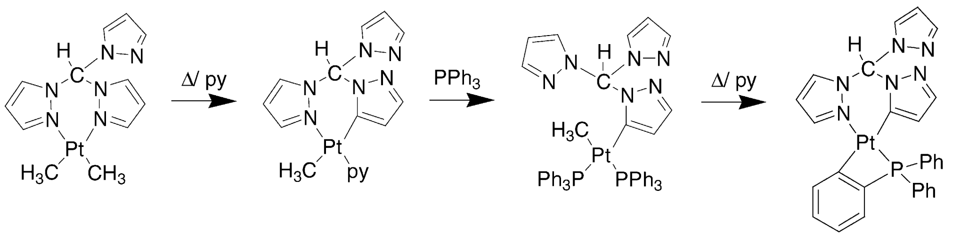
$[Fe\{HC(pz)_3\}_2]^{2+}(Cl)_2$ and $[Fe\{HC(pz)_3\}(NCS)_2]$ have been also prepared [79]. The ^1H NMR spectra of these complexes suggested that they are symmetrical. $[Fe\{HC(pz)_3\}(NCS)_2]$ is monomeric, unlike the previously reported polymeric complex $[Fe\{HC(pz)_3\}(NCS)_2]_n$ [69].

$[MCp^x\{HC(pz1)_3\}]^{n+}$ complexes ($M = Fe$, $n = 1$, $Cp^x = Cp^*$; $M = Co$, $n = 1$ or 2, $Cp^x = Cp$) have been described: $[CoCp\{HC(pz)_3\}]^{2+}$ displays a mixed-sandwich structure with κ^3-$HC(pz)_3$ coordination [80].

Mixed-sandwich complexes of Co, Rh and Ru containing κ^3-poly(pyrazolyl)methanes and η^4-cyclobutadienyl (with Co), η^5-cyclopentadienyl (with Co and Rh) or η^6-arene ligands (Ru) have been prepared [81].

Palladium(II) allyl complexes (Fig. 20) were described in the first paper describing metal derivatives of tris(pyrazolyl)alkanes [15]. $[PtMe_2(COD)]$ reacts with $HC(pz)_3$ (Fig. 21) yielding the complex $[\{HC(pz)_3\}PtMe_2]$ **VII** that upon heating in pyridine undergoes metalation of one pyrazole ring yielding the square-planar complex **VIII** in a *cis*-PtC_2N_2 environment. **VIII** reacts with 2 eq. of PPh_3 yielding **IX**. Finally, **IX** on heating slowly to 458 K converts in **X** in which the PPh_3 was orthometallated (Fig. 21) [82,83]. Five-coordinate complexes $[\{HC(pz)_3\}PtMe(L)][PF_6]$ (L = CO, ethylene, $MeC{\equiv}CPh$, $F_3CC{\equiv}CCF_3$, $MeO_2CC{\equiv}CCO_2Me$) were prepared by the reaction of $PtMeCl(COD)$ with $AgPF_6$ in acetone followed by treatment with $HC(pz)_3$ and L [84]. The structures have been assigned on comparison with those of analogous derivative bearing Tp ligands. The NMR studies indicated that $HC(pz)_3$ is fluxional, the fluxionality decreasing with increasing electron-withdrawing ability of L. The complexes are inert to to the insertion of L into the Pt–Me bond [84]. $[PtMe_3(acetone)_3][PF_6]$ reacts with $HC(pz)_3$ to give $[\{HC(pz)_3\}PtMe_3][PF_6]$ [85].

The reaction of the palladium(II) complex $[\{HC(pz)_3\}PdCl_2]$ with AgX ($X = NO_3$, BF_4 or ClO_4) and an equimolar quantity of $HC(pz)_3$ gave the square-planar complexes $[\{HC(pz)_3\}_2Pd]X_2$ in which the potentially tridentate ligand is however *N*,*N*′-bidentate (Fig. 22). NMR studies indicated fast interconversion between coordinated and uncoordinated pyrazolyl groups [86]. Platinum(II) derivatives of metallated tris(pyrazolyl)methane were also oxidized to Pt(IV) species via oxidative addition of iodomethane [87]. A carbon monoxide derivative $PtMe\{(pz)_2(C_3H_2N_2)CH\text{–}N,C\}(CO)$ and several phosphino complexes $[PtMe\{(pz)_2(C_3H_2N_2)CH\text{–}N,C\}(PR_3)]$, all containing a metallated pyrazolyl ring, have been reported. The complexes $[PtMe\{(pz)_2(C_3H_2N_2)CH\}]_n$ and $PtMe\{(pz)_2(C_3H_2N_2)CH\text{–}N,C\}(pyr)$ have been shown to undergo oxidative addition reactions with organohalides



VII **VIII** **IX** **X**

Fig. 21. Metalation of pyrazolyl ring in platinum derivatives of $HC(pz)_3$.

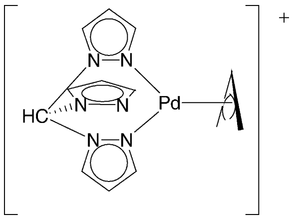


Fig. 23. Structure of $[\{HC(pz)_3\}Pd(\eta^3\text{-}C_3H_5)]^+$.

[88]. Dimethylpalladium(II) and methyl(iodo)palladium complexes of $HC(pz)_3$ were also synthesized and their spectroscopic features compared with those of analogous derivatives of $HC(pyr)_3$, $C(pz)_4$, $HC(pz)_2(pyr)$ and $HC(pz)_2(mim)$ [89]. Structural studies on analogous compounds obtained by using dimethylpyridine and different chelating or unidentate P-donor ligands were reported by the same authors on 1992 [90]. Oxidative addition of RX to $[\{HC(pz)_3\}PdMe_2]$ has led to the isolation of ethyl-, (η^1-benzyl)-, and (η^1-allyl)-palladium(IV) species. The benzyl- and 2-propenyl derivatives are unstable species undergoing facile reductive elimination of ethane yielding organopalladium(II) complexes such as $[\{HC(pz)_3\}Pd(\eta^3\text{-}C_3H_5)]$ (Fig. 23) [91].

The reaction of $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pd(S)_2]X$ ($X = BF_4$, $S =$ acetone) with stoichiometric amounts of $HC(pz)_3$ or $HC(3,5\text{-}Me_2pz)_3$ yields the cationic complexes $[\{HC(pz)_3\}Pd(\eta^3\text{-}C_4H_7)][BF_4]$ and $[\{HC(3,5\text{-}Me_2pz)_3\}Pd(\eta^3\text{-}C_4H_7)][BF_4]$ respectively, that have been studied by NMR spectroscopy. The fluxional bevavior of $[(\eta^3\text{-}C_4H_7)Pd\{(HC\text{-}(pz)_3\}][BF_4]$ has been assigned to a pathway of exchange between the coordinated and the uncoordinated pyrazole ring analogous to a tumbling motion [92]. The reaction of $[PtPh_2(SEt)_2]_2$ with $HC(pz)_3$ and I_2 in dichloromethane gave the octahedral platinum complex $[\{HC(pz)_3\}PtIPh_2]_2[I][I_3]$ containing the N_3-donor ligand facially tricoordinated [93].

$[\{HC(pz)_3\}MMe_3]X$ ($M =$ Pt or Pd; $X = I$ or BF_4), stable at room temperature, were also investigated by NMR spectroscopy. Their solid-state structures were compared with those of analogous complexes containing pyridine and 1-methylimidazole donor rings [94].

Theoretical calculation at the SCF level of geometries for the complexes $[\{HC(pz)_3\}MMe_3]^+$ ($M =$ Pt or Pd) using $(H_2C{=}N{-}NH)_3CH$ as a model for tris(pyrazolyl)methane were also reported [95]. $[\{HC(pz)_3\}M(\eta^1,\eta^2\text{-}C_8H_{12}OMe)]^+$ (Fig. 24) ($M =$ Pt or Pd, were synthesized by the reaction of the dimers $[M(\eta^1,\eta^2\text{-}C_8H_{12}OMe)Cl]_2$ with $HC(pz)_3$. 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 relative cation–anion position (interionic structure) was also investigated in solution by variable temperature ^{19}F, ^1H-HOESY NMR spectroscopy. A remarkable specificity of the interionic contacts is observed in solution: the counter-ion is placed close to the peripheral protons of the pyrazolyl ligands probably due to the partial protection of the apical positions introduced by the non-planar ligands and the delocalization of the positive charge on the pyrazolyl rings. There is an excellent agreement between the solid state and solution results: the anion selectively interacts with the CH and protons of the $HC(pz)_3$ ligand via an assembly of hydrogen bonds [96]. No reaction has been observed between tris(pyrazolyl)methane and pycolyl-bridged dinuclear Pd complexes [97]. (Acetophenone oximato, 2-C,N)- and (benzophenone oximato, 2-C,N)-palladium complexes containing poly(pyrazolyl)methane $C(pz)_4$ and $HC(pz)_3$ were reported by Onishi et al. [98] which also investigated their NMR behavior. In all complexes the pyrazolyl groups were equivalent at high *T* exhibiting stereochemistry non rigidity. A review describes the organometallic chemistry of palladium and platinum with poly(pyrazolyl)alkanes and poly(pyrazolyl)borates [99].

Aquo-ruthenium complexes $[Ru^{II}\{HC(pz)_3\}(bipy)(X)]^{n+}$ ($X =$ Cl, H_2O) containing the tridentate $HC(pz)_3$ and differently substituted 2,2′-bipyridines undergo two pH dependent, chemically reversible one electron oxidations corresponding to the associated Ru^{IV}/Ru^{III} and Ru^{III}/Ru^{II} couples [100]. Their spectroscopic and electrochemical properties have been investigated by means UV–vis, cyclic voltammetry, and coulometry [101]. Mixed-ligand chlororuthenium complexes of formula $[\{HC(pz)_3\}RuCl(L)]Cl$ ($L =$ bipy, *N*,*N*-dimethylpicolylamine, *N*,*N*-dimethylglicinate) were synthesised and tested for the catalytic alkane oxidation: the oxidation of adamantane, cyclooctane or ethylbenzene yielded the hydroxylated products: 1-adamantanol (66%), cyclooctanol (22%) or 1-phenylethanol (48%), respectively [102]. $[\kappa^3\text{-}\{HC(pz)_3\}Ru(H_2O)_3](p\text{-}CH_3C_6H_4SO_3)_2\cdot 1.5H_2O$ has been employed as precursor to the reactive *cis*-di-oxoruthenium(VI) oxidant [103]. The crystal structure of $[\{HC(pz)_3\}Ru(H_2O)_3](p\text{-}CH_3C_6H_4SO_3)_2\cdot 1.5H_2O$ has been also reported [103]. The complex $[\{HC(pz)_3\}Ru(py)_3]^{2+}$ has been synthesised and spectroscopically and electrochemically characterized. The structure in the solid state has been determined by means of X-ray crystallography [104]. The role of the 2,2′-bipyridine ligand in metal to ligand charge transfer (MLCT) excited states and of substituents in the series $[\{HC(pz)_3\}Ru(4,4'\text{-}X_2bipy)(py)]^{2+}$ ($X = C(O)OC_2H_5$, C_6H_5, CH_3, NH_2, H) has been investigated by spectroscopic and photochemical measurements [105].

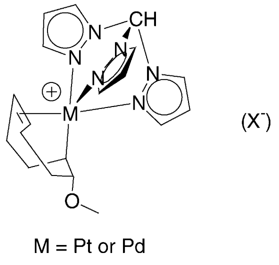


Fig. 24. Structure of $[\{HC(pz)_3\}M(\eta^1,\eta^2\text{-}C_8H_{12}OMe)]^+$.

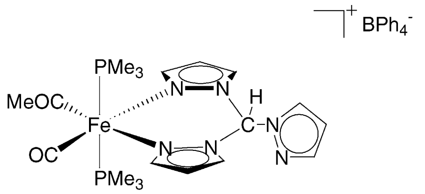


Fig. 25. Structure of *trans*-$[(PMe_3)_2\{\kappa^2\text{-}HC(pz)_3\}M(CO)(COMe)][BPh_4]$.

$HC(pz)_3$ reacts with $M(CH_3)I(CO)_2(PMe_3)_2$ ($M = Fe$, Ru) forming, in the presence of $NaBPh_4$, *trans*-$[(PMe_3)_2\{HC(pz)_3\}M(CO)(COMe)][BPh_4]$ complexes. In this six-coordinate octahedral iron complex $HC(pz)_3$ behaves as a bidentate ligand (Fig. 25). The ion-pair structures and the localization of the counter-ion in solution with respect to the organometallic moiety by the detection of interionic contacts in the ^1H-NOESY and $^{19}F\{^1H\}$-HOESY NMR spectra have been reported together the reactivity of $HC(pz)_3$ toward *fac*-$[Ru(PMe_3)(CO)_3)(Me)I]$ [106]. The *cis*-$[Ru(PMe_3)(CO)_2(COMe)\{\kappa^2\text{-}HC(pz)_3\}][BPh_4]$, that decarbonylates to $[Ru(PMe_3)(CO)(COMe)\{\eta^3\text{-}HC(pz)_3\}][BPh_4]$, has been prepared [107]. Analogous reactions were performed with osmium derivatives, both complexes $[\{\kappa^2\text{-}HC(pz)_3\}Os(PMe_3)(CO)_2(COMe)][BPh_4]$ and $[\{\kappa^2\text{-}HC(pz)_3\}Ru(PMe_3)_2(CO)(COMe)][BPh_4]$ being described. From the reaction of *cis*,*trans*-$[OsI(Me)(CO)_2(PMe_3)_2]$ with AgX and $HC(pz)_3$ the intermediate complexes $[(Me)(CO)_2(PMe_3)_2Os(\mu\text{-}I)Ag\{HC(pz)_3\}][X]$ ($X = CF_3SO_3$ or BF_4) afforded [108]. A dinuclear half-sandwich ruthenium complex $[\{HC(pz)_3\}Ru([9]aneS_3)][CF_3SO_3]_2$ has been reported (Fig. 26) [109].

A fresh acetonitrile solution of $[\{Ru(\eta^6\text{-arene})Cl_2\}_2]$ reacts with $HC(3,5\text{-}Me_2pz)_3$ and $HC(pz)_3$ yielding $[\{\kappa^2\text{-}HC(3,5\text{-}Me_2pz)_3\}Ru(\eta^6\text{-arene})Cl][PF_6]$ (arene = benzene or *p*-xylene) and $[\{\kappa^2\text{-}HC(pz)_3\}Ru(benzene)Cl][PF_6]$ (Fig. 27) [110].

The oxidation state at osmium in $[\{HC(pz)_3\}(Cl)_2Os^{III}(N_2)Os^{II}(Cl)_2)\{HC(pz)_3\}]^+$ has been assigned on the basis of the $\nu(N{=}N)$ stretching vibrations. The synthesis of $[\{HC(pz)_3\}(Cl)_2Os^{VI}(N)][PF_6]$ and $[\{HC(pz)_3\}(Cl)_2Os^{II}(N_2)Os^{II}(Cl)_2)\{HC(pz)_3\}]$ has been also reported [111]. $[\{HC(pz)_3\}(Cl)_2Os^{VI}(N)][PF_6]$ reacts with morpholine, piperidine, diethylamine yielding $[\{HC(pz)_3\}(Cl)_2Os^V(NNR_2)][PF_6]$ (NR_2 = morpholide, piperidide or diethylamide) that has been isolated and characterized structurally (Fig. 28) [112]. A reaction mechanism for this synthesis has been also proposed. These complexes can be chemically or electrochemically oxidized to Os(VI) or reduced to Os(IV) and Os(III). It has been shown that the distorted octahedral arrangement of ligands around the Os atom in the parent nitrido complex is retained in the hydrazido derivative [113]. Redox chemistry of $[\{HC(pz)_3\}(Cl)_2Os^{VI}(N)][PF_6]$ has been investigated exhaustively and it has been demonstrated a stepwise chemistry based on the sequence Os(VI) → Os(IV), Os(IV) → Os(V), and Os(V) → Os(III). $[\{HC(pz)_3\}(Cl)_2Os^{VI}(N)][PF_6]$ undergoes a rapid reaction with PEt_3 yielding the corresponding paramagnetic complex $[\{HC(pz)_3\}(Cl)_2Os^{IV}(NPEt_3)][PF_6]$. One electron oxidation yields $[\{HC(pz)_3\}(Cl)_2Os^V(NPEt_3)]^{2+}$ that undergoes a further group transfer reaction with $Me_2C_6H_3SH$ according to the following equation [114]:

$$\begin{aligned}&[\{HC(pz)_3\}(Cl)_2O_s^V(NPEt_3)]^{2+} + Me_2C_6H_3SH\\&\quad\rightarrow [\{HC(pz)_3\}(Cl)_2O_s^{III}(NCCH_3)]^+\\&\quad + Et_3P{=}N\text{–}SC_6H_3Me_2 + H^+\end{aligned}$$

Electrochemical or chemical reduction of the nitrido complexes $[Os^{VI}\{HC(pz)_3\}(Cl)_2(N)]^+$ in acidic aqueous solution gives the corresponding Os^{II}-amine complex that after air oxidation and work-up, is structurally characterized as $[Os^{III}\{HC(pz)_3\}(Cl)_2(NH_3)][PF_6]$ [115]. Reaction between stoichiometric or excess $[PPN]N_3$ and $[Os^{VI}\{HC(pz)_3\}(Cl_2)N]^+$ in H_2O, CH_3OH, CH_2Cl_2 or CH_3CN proceeds in few seconds to give $[Os^{II}\{HC(pz)_3\}(Cl_2)(N_2)]$. Reduction of the former compound with cobaltocene ($Co(Cp)_2$) in CH_2Cl_2 gave $[\{HC(pz)_3\}(Cl_2)Os^{II}(N_2)Os^{II}(Cl_2)\{HC(pz)_3\}]$. This compound undergoes oxi-

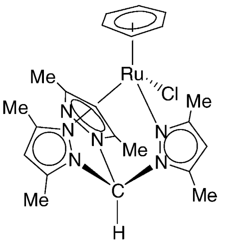


Fig. 27. The cation of $[\{\kappa^2\text{-}HC(pz)_3\}Ru(benzene)Cl]PF_6$.

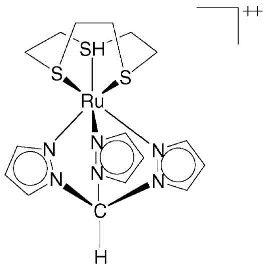


Fig. 26. Structure of the cation in the dinuclear half-sandwich $[\{HC(pz)_3\}Ru([9]aneS_3)][CF_3SO_3]_2$.

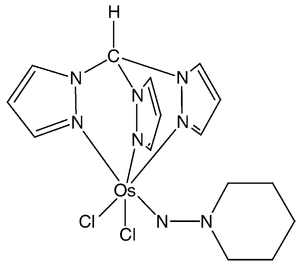


Fig. 28. The κ^3-denticity of $HC(pz)_3$ in $[\{HC(pz)_3\}(Cl)_2Os^V(NNR_2)][PF_6]$.

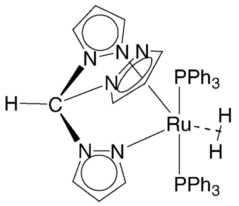


Fig. 29. $[\{HC(pz)_3\}Ru(H_2)(PPh_3)_2][BF_4]_2$.

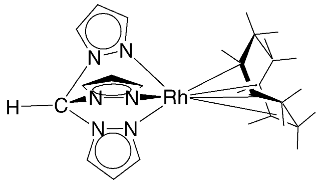


Fig. 30. The distorted trigonal bipyramid of the cation in $[\{HC(pz)_3\}Rh(COD)][RhCl_2(COD)]\cdot 3CHCl_3$.

dation by ferrocenium salts to give the mixed-valence $[\{HC(pz)_3\}(Cl_2)Os^{III}(N_2)Os^{II}(Cl_2)\{HC(pz)_3\}]^+$ [116].

Reaction of $[Os^{VI}\{HC(pz)_3\}(Cl)_2(N)][PF_6]$ with CS_2 and N_3^- in acetone yields the thionitrosyl complex $[Os^{II}\{HC(pz)_3\}(Cl)_2(NS)][PF_6]$ that reacts with PPh_3 giving $[Os^{IV}\{HC(pz)_3\}(Cl)_2(NPPh_3)][PF_6]$ and $S{=}PPh_3$ upon S-transfer. This compound has been shown to undergoes chemical or electrochemical reduction. O-atom transfer to $[Os^{III}\{HC(pz)_3\}(Cl)_2(NS)][PF_6]$ from $^{-}O\text{-}N^{+}Me_3$ yields $[Os^{II}\{HC(pz)_3\}(Cl)_2(NSO)]$ [117].

$[\{HC(pz)_3\}Ru(\eta^6\text{-arene})][PF_6]_2$ has been prepared by a modification of a literature method [118]. The X-ray crystal structure of $[Ru(\eta^6\text{-}p\text{-cymene})\{HC(pz)_3\}][PF_6]_2$ was also determined [119]. Luminescent α-diimine complexes of $HC(pz)_3$ were reported [120]. The *cis*-$[\{HC(pz)_3\}Ru(\alpha\text{-diimine})_2]$ complex exhibits strong visible absorption assigned as a $\pi^*(\text{diimine}) \leftarrow d\pi(Ru)$ metal-to-ligand charge transfer (MLCT) transition. The electronic spectra and voltammetry measurements are compared with those of analogous $(\alpha\text{-diimine})_2Ru(N\text{-donor})$ complexes. It has been reported that the relative π-acceptor abilities of the bidentate coordinated N-donor are: $pzTp < (py)_2 < HC(pz)_3$.

The reactivity of ruthenium complexes $[\{HC(pz)_3\}Ru(L)Cl]PF_6$ ($L = COD$ or NBD) toward mono- and bidentate phosphine ligands (diphenylvinylphosphine, 3,4-dimethyl-1-phenylphosphole, 1,2-bis(diphenylphosphinoethane) has been also investigated [121].

Protonation of $[\{HC(pz)_3\}RuH(PPh_3)_2][BF_4]$ with excess $HBF_4\cdot Et_2O$ in CD_2Cl_2 yielded the dicationic η^2-dihydrogen complex $[\{HC(pz)_3\}Ru(H_2)(PPh_3)_2][BF_4]_2$ (Fig. 29) which is more acidic than its monocationic Tp^x analog (pK_a: 2.8 versus 7.6). The complex $[\{HC(pz)_3\}Ru(H_2)(PPh_3)_2][BF_4]_2$ is unstable towards H_2 loss at ambient temperature. NMR studies revealed that the aqueous acid in $[D_8]$-THF did not fully protonate the metal hydride to form the dihydrogen complex, but a hydrogen-bonded species was obtained [122].

Diamagnetic ligand-bridged species $[\{HC(pz)_3\}Ru^{III}(\mu\text{-}O)(\mu\text{-}L)_2Ru^{III}\{HC(pz)_3\}]^{n+}$ ($L = O_2P(O)(OH)$, $n = 0$; $L = O_2CO$, $n = 0$; $L = O_2CCH_3$, $n = 2$) have been reported. The results of cyclic voltammetric and coulometric experiments show that the complexes undergo both oxidative and reductive processes in solution. Upon reduction, the ligand-bridged structure is lost and the monomer $[\{HC(pz)_3\}Ru(H_2O)_3]^{2+}$ appears quantitatively [123].

Synthesis and spectroscopic studies of ruthenium complexes with poly(pyrazol-1-yl)methane ligands and the crystal structure of $[\{HC(pz)_3\}Ru(Cl)(COD)]Cl\cdot EtOH$ have been reported [124]. The reaction of $[\{HC(pz)_3\}Ru(Cl)_3]$ with pyridine in the presence of NEt_3 afforded $[\{HC(pz)_3\}Ru(py)Cl_2]$ [124]. Field reported two Ru^{II} complexes. The first, $[\{HC(pz)_3\}RuCl(PPh_3)_2]^+$, with a structure analogous to those of neutral ruthenium complexes containing Tp^x ligands, has two PPh_3 in *cis*-position and exhibits dynamic behaviour in solution suggesting restricted rotation about the Ru–P bonds. The structure and stereochemistry of $[\{HC(pz)_3\}Ru(CO)H(PPh_3)]^+$ were fully assigned through NMR experiments [125].

The photochemical and photophysical properties of a series of chromophore-quencher complexes of Ru^{II} based on tris(pyrazolyl)methane, in the context of the various state that are accessible and the intramolecular electron transfer processes that occur following laser-flash excitation, have been described [126].

Three different types of rhodium(I) and iridium(I) complexes have been synthesised: $[\{HC(pz)_3\}M(Cl)(\text{diolefin})]$, $[\{HC(pz)_3\}M(\text{diolefin})][ClO_4]$, $[\{HC(pz)_3\}M(\text{diolefin})][MCl_2(\text{diolefin})]$. The crystal structure of $[\{HC(pz)_3\}M(COD)][MCl_2(COD)]\cdot 3CHCl_3$ showed a square-planar arrangement in the anion and a distorted trigonal bipyramid in the cation (Fig. 30) [127]. The alcohol activation by $[\{HC(pz)_3\}Ir(COD)]^+$ and $[Ir(COD)\{MeC(pz)_3\}]^+$ has been reported [128]: formation of the alkoxycarbonyl derivatives $[IrH\{HC(pz)_3\}(CO_2R)(CO)]^+$ and $[IrH\{MeC(pz)_3\}(CO_2R)(CO)]^+$ ($R' = Me$, Et, ^iPr) from carbon monoxide and alcohols has been widely investigated. The reaction of $HC(pz)_3$ with $[Rh(COD)Cl]_2$ and $AgClO_4$ yields $[Rh(COD)(HC(pz)_3][ClO_4]$. Bubbling carbon monoxide through a methanol solution of this complex leads to the formation of $[Rh(CO)_2(HC(pz)_3][ClO_4]$, which after 30 min refluxing in acetone, yields a dimer of formula $[Rh_2(CO)_3\{(HC(pz)_3\}][ClO_4]_2$ [128] (Fig. 31).

An interesting study on the substitution chemistry of

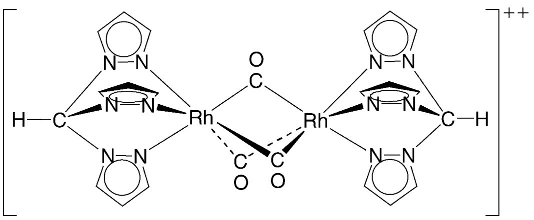


Fig. 31. The dimer $[Rh_2(CO)_3\{(HC(pz)_3\}][ClO_4]_2$.

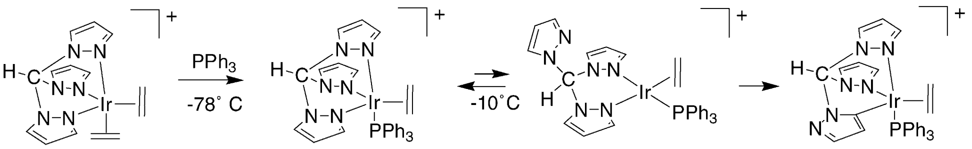


Fig. 32. Cyclometalation reaction of the $HC(pz)_3$ ligand in a formal oxidation of the iridium center by formation of an iridium(III) alkyl hydride complex via activation of a C–H bond.

the square-planar complex $[Rh(CO)_2\{HC(pz)_3\}][PF_6]$ recently showed that interaction with ER_3 (E = Ph or As) ligands yields $[Rh(CO)(PR_3)\{HC(pz)_3\}][PF_6]$ upon carbonyl substitution [129]. Depending on the nature of ER_3 the third pyrazolyl ring is orientated pseudo-parallel to the square-planar metal or exo to that plane. The reactivity toward several alkynes has been also investigated. $[Rh(CO)_2\{HC(pz)_3\}][PF_6]$ reacts with PhC≡CPh yielding $[\{HC(pz)_3\}Rh(CO)(\eta^2\text{-PhC≡CPh})][PF_6]$ whereas with MeC≡CR a cyclopentadienone complex $[\{HC(pz)_3\}Rh(\eta^4\text{-}C_4Me_2R_2C(O)][PF_6]$ formed [129]. Complexes of formula $[\{HC(pz)_3\}Rh(NBD)][PF_6]$, $[\{HC(pz)_3\}Rh(NBD)]Cl$ and $[\{HC(pz)_3\}Rh(NBD)]^+[Rh(NBD)Cl_2]^-$, have been synthesised and characterized by infrared and ^1H and ^{13}C NMR spectroscopy as well as X-ray diffraction analysis. Cationic species have been evidenced in the solid state while equilibria between cationic and neutral species have been established in solution [130].

A previously unknown cyclometalation reaction of the $HC(pz)_3$ ligand in a formal oxidation of the iridium center by formation of an iridium(III) alkyl hydride complex via activation of a C–H bond of a pyrazolyl ring (Fig. 32) has been observed [131]. A series of cationic iridium complexes of $HC(3,5\text{-}Me_2pz)_3$ has been prepared and their structural and spectroscopic properties compared with those of analogous Tp* ligand [132]. $[\{HC(3,5\text{-}Me_2pz)_3\}Ir(C_2H_4)_2][PF_6]$ undergoes olefinic CH-activation under very mild conditions to give first $[\{HC(3,5\text{-}Me_2pz)_3\}IrH(CH{=}CH_2)(C_2H_4)][PF_6]$ and then hydride-crotyl products derived from C–C coupling of the Hydrocarbon ligands of the latter complex (Fig. 33). Hydrogenation reactions and carbene derivatives synthesis were also described. $HC(3,5\text{-}Me_2pz)_3$ is able to bind to Ir(I) and Ir(III) centers as the isosteric and isoelectronic anionic Tp*. The $HC(3,5\text{-}Me_2pz)_3$ complexes display structural properties closely reminescent of those of IrTp* analogues. The trends found support the idea that, in the system based on $Ir(N)_3$ fragments, the energetics of the olefinic C–H bond activation reaction are modulated by the steric properties of the Ir-ancillary ligand moiety [132].

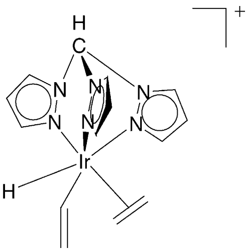


Fig. 33. $[\{HC(3,5\text{-}Me_2pz)_3\}IrH(CH{=}CH_2)(C_2H_4)][PF_6]$ obtained upon olefinic CH-activation in $[\{HC(3,5\text{-}Me_2pz)_3\}Ir(C_2H_4)_2][PF_6]$.

From the reaction of $[RhCl(PPh_3)(\eta^5\text{-}7\text{-}NH_2{}^tBu\text{-}7\text{-}CB_{10}H_{10}]$ and $HC(pz)_3$ in the presence of $TlPF_6$ the complex $[\{HC(pz)_3\}Rh(\eta^5\text{-}7\text{-}NH_2{}^tBu\text{-}7\text{-}CB_{10}H_{10})][PF_2O_2]$ has been obtained. X-ray crystallographic study indicated the pentahapto bonding of the charge-compensated $7\text{-}NH_2{}^tBu\text{-}7\text{-}CB_{10}H_{10}$ molecule and the κ^3-coordination of $HC(pz)_3$ (Fig. 34) [133].

3.8. Group IB: Cu, Ag and Au

The synthesis of $[Cu^I\{HC(3,5\text{-}Me_2pz)_3\}(MeCN)][PF_6]$ and $[Cu^I\{HC(3,5\text{-}Me_2\text{-}4Br\text{-}pz)_3\}(MeCN)][PF_6]$ has been reported [134]. Reversible oxygenation of $[Cu^I\{HC(3,5\text{-}Me_2pz)_3\}(MeCN)][PF_6]$ occurs in solution at 7 °C to yield a 2:1 $\mu\text{-}\eta^2\text{-}\eta^2$-peroxo complex $[Cu_2(\mu\text{-}O_2)\{HC(3,5\text{-}Me_2pz)_3\}_2][PF_6]_2$. Thermal decomposition of this μ-peroxo species yields $[Cu_2(\mu\text{-}OH)_2\{HC(3,5\text{-}Me_2pz)_3\}_2][PF_6]_2$ (Fig. 35) [134]. $[\{HC(pz)_3\}Cu(\eta^1\text{-benzoate})Cl]$ has been structurally characterized (Fig. 36) [135]. Synthesis and structural properties of $[\{HC(pz)_3\}Cu(SCN)_2]$ (Fig. 37)

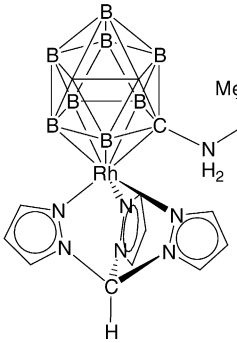


Fig. 34. $[\{HC(pz)_3\}Rh(\eta^5\text{-}7\text{-}NH_2{}^tBu\text{-}7\text{-}CB_{10}H_{10})][PF_2O_2]$.

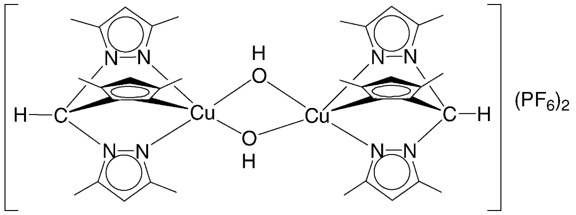


Fig. 35. The μ-peroxo species $[Cu_2(\mu\text{-}OH)_2\{HC(3,5\text{-}Me_2pz)_3\}_2][PF_6]_2$ obtained from thermal decomposition of $[Cu_2(\mu\text{-}O_2)\{HC(3,5\text{-}Me_2pz)_3\}_2][PF_6]_2$.

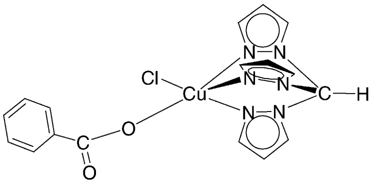


Fig. 36. $[\{HC(pz)_3\}Cu(\eta^1\text{-benzoate})Cl]$.

have been compared with those of $[Cu(tacn)(SCN)_2]$ [136]. From the reaction of $[Cu(NCMe)_4][PF_6]$ with $HC(3,5\text{-}Me_2pz)_3$, $\{HC(3\text{-}Phpz)_3\}$ and $\{HC(3\text{-}^tBupz)_3\}$ the acetonitrile complexes $[\{HC(3,5\text{-}Me_2pz)_3\}Cu(NCMe)][PF_6]$, $[\{HC(3\text{-}Phpz)_3\}Cu(NCMe)][PF_6]$ and $[\{HC(3\text{-}^tBupz)_3\}Cu(NCMe)][PF_6]$ has been obtained. These complexes react with CO yielding stable $[\{HC(3,5\text{-}Me_2pz)_3\}Cu(CO)][PF_6]$, $[\{HC(3\text{-}Phpz)_3\}Cu(CO)][PF_6]$ and $[\{HC(3\text{-}Bu^tpz)_3\}Cu(CO)][PF_6]$ respectively, for which the structure have been determined [137]. $[\{HC(pz)_3\}Cu(PPh_3)]NO_3$ and $[\{HC(3\text{-}Phpz)_3\}Cu(PPh_3)]NO_3$ have been synthesised and structurally characterized. The former exists as a two-dimensional supramolecular network of dimeric units, in which the 2D array is dominated by $CH\cdots\pi$ interactions, the PPh_3 acting as donors and the pz rings as acceptor, whereas in the latter the dimers are formed via a π–π stacking of the phenyl rings of the tris(pyrazolyl)methane ligand and the 2D array is supported by $CH\cdots\pi$ interactions, the phenyl rings acting as donors and the pyrazoly rings as acceptor [138].

The copper complex $[Cu\{HC(3,5\text{-}Me_2pz)_3\}_2][BF_4]_2$ exhibits similar properties to those found for analogous, Fe, Co and Ni compounds [68]. A systematic investigation of the interaction of CuX_2 ($X = ClO_4$, NO_3, Cl, Br, O_2CMe) with excess of $HC(pz^x)_3$ has been reported by us [139]. $[CuX_2\{HC(pz^x)_3CH\}]$, $[\{CuX_2\}_3\{HC(pz^x)_3\}_2]$ or $[Cu\{HC(pz^x)_3CH\}_2]X_2$ complexes have been obtained depending on the substituents on the azolyl moiety and, more particularly, on the nature of the counter-ion. All complexes have been characterized by analytical and spectroscopic measurements (IR, UV, and conductivity measurements) and also in the case of the strongly distorted octahedral $[Cu\{HC(pz^x)_3\}_2]X_2$ species, by X-ray diffraction studies [139].

A novel ion-selective membrane electrodes based on tris(pyrazolyl)methanes has been developed. The $HC(pz)_3$, $HC(3,5\text{-}Me_2pz)_3$, $HC(3\text{-}Phpz)_3$, $HC(3\text{-}^iPrpz)_3$ and $HOCH_2C(pz)_3$ were incorporated as an ionophore in PVC membrane. Some of the electrodes were selective for Cu^{2+} at pH 5.5 [140].

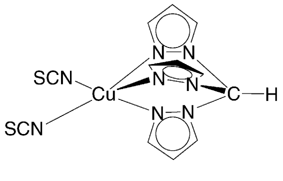


Fig. 37. $[\{HC(pz)_3\}Cu(SCN)_2]$.

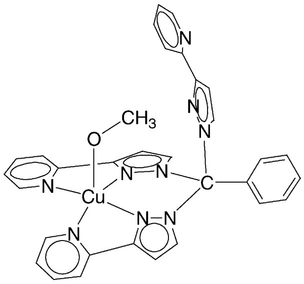


Fig. 38. The four-coordinate podand ligand phenyltris[3-(2-pyridyl)-pyrazol-1-yl]methane (L^{py}) in $[Cu(L^{py})(MeOH)][PF_6]_2$.

The potentially hexadentate podand ligand phenyltris[3-(2-pyridyl)pyrazol-1-yl]methane (L^{py}) has been reported [141]. In $[Cu(L^{py})(MeOH)][PF_6]_2$ the ligand is four-coordinate via two bidentate pyridyl/pyrazolyl arms, the third arm being pendant; the axial methanol ligand completes the square-pyramidal coordination (Fig. 38) [141].

It has been shown that reaction of $Ag(O_3SCF_3)$ with 2 eq. of $\{HC(3,5\text{-}Me_2pz)_3\}$ in THF yields the stable six-coordinate "sandwich" complex $[\{HC(3,5\text{-}Me_2pz)_3\}_2Ag](O_3SCF_3)$ in a trigonally distorted octahedron [142]. The 1:1 adducts $[\{HC(3\text{-}^tBupz)_3\}Ag](O_3SCF_3)$ and $[\{HC(3\text{-}^tBupz)_3\}Ag(CN^tBu)](O_3SCF_3)$ have been also reported (Fig. 39) [142].

The preparation of the silver(I) coordination polymer of a new ligand that links four tris(pyrazolyl)methane groups in one molecule $1,2,4,5\text{-}C_6H_2[CH_2OCH_2C(pz)_3]_4$ has been reported. In this ligand two very relevant properties are present: the important design characteristic of the rigid architecture of facial bonding encoded in each of the four tris(pyrazolyl)methane groups with flexible sidearms on the arene ring that allow different orientation of the binding groups [143]. It has been reported that changes in multitopic tris(pyrazolyl)methane ligand topology influence the architecture of silver(I) supramolecular structure: the reaction between $AgBF_4$ and the ligands $1,2,4,5\text{-}C_6H_2[CH_2OCH_2C(pz)_3]_4$, $o\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2$, and $m\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2$ yield coordination polymers of the formula $\{C_6H_{6-n}[CH_2OCH_2C(pz)_3]_n(AgBF_4)_m\}$ ($n = 4$, $m = 2$; $n = 2$, *ortho* susbstitution, $m = 1$; $n = 2$, *meta* substitution, $m = 2$) [144]. The ligand $o\text{-}C_6H_4[CH_2OCH_2C(3\text{-}Phpz)_3]_2$ interacts with $AgBF_4$ yielding the coordination polymer $o\text{-}C_6H_4[CH_2OCH_2C(3\text{-}Phpz)_3]_2Ag_2([BF_4])_2\}_n$. The supramolecular architecture contains two different type of silver(I) cations arranged in bimetallic units forming 1D coordination polymer. The ligand $o\text{-}C_6H_4[CH_2OCH_2C(3\text{-}Phpz)_3]_2$ coordinates $AgBF_4$ yielding $\{o\text{-}C_6H_4[CH_2OCH_2C(3\text{-}Phpz)_3]_2Ag_2([BF_4])_2\}_n$ which contains two different types of silver(I) cations arranged in bimetallic units forming a 1D coordination polymer [145]. The coordination polymer $\{p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2Ag_2([BF_4])_2\}_n$ has been prepared in THF. It contains two oppo-

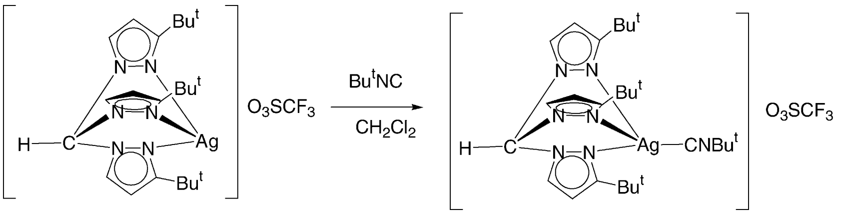


Fig. 39. The 1:1 adducts [{HC(3-^{t}Bupz)$_3$}Ag](O$_3$SCF$_3$) and [{HC(3-^{t}Bupz)$_3$}Ag(CN^{t}Bu)](O$_3$SCF$_3$).

site chirality metallohelicates, formed by a κ^2,κ^1-bonding arrangement of each RC(pz)$_3$ unit that are linked with the bitopic ligand into 2D sheets. The three-dimensional structure is due to C–H · · · F weak hydrogen bonds [146].

From the reaction of the tripodal ligand 1,3,5-Me$_3$C$_6$-[CH$_2$OCH$_2$C(pz)$_3$]$_3$ (Fig. 40) with AgBF$_4$, the inclusion complex [{1,3,5-Me$_3$C$_6$[CH$_2$OCH$_2$C(pz)$_3$]$_3$}$_2$Ag$_3$-(CH$_3$CN)][BF$_4$]$_3$(CH$_3$CN)$_4$ formed. The hexatopic C$_6$-[CH$_2$OCH$_2$C(pz)$_3$]$_6$ yields, upon reaction with the same silver salt, a two-dimensional polymer composed of triangular cage units, again with the encapuslation of CH$_3$CN molecule [147].

The compound [{HC(3-Phpz)$_3$}Ag][BF$_4$] has been shown to crystallize in four different forms depending on the crystallization solvent. Both mononuclear and coordination polymers formed [148].

We have reported [149] that the reaction of AgX (X = ClO$_4$, NO$_3$, O$_3$SMe) with excess of HC(pz^x)$_3$ (Hpz^x = Hpz, Hpz^{4Me}, 3,5-Me$_2$pzH, Hpz^{Me3}) can yield 1:1, 2:1 or 3:2 complexes, the ligand to metal ratio being dependent on the number and position of the methyls on the azole ring and primarily on the nature of the counter-ion X. [{HC(pz)$_3$}Ag(NO$_3$)]$_n$ 1:1 crystallizes with two formula units devoid of crystallographic symmetry as the asymmetric unit of the complex which is an infinite, unsolvated, two-dimensional polymer, lying parallel to the *ac* plane. In [{HC(3,5-Me$_2$pz)$_3$}$_2$Ag][NO$_3$], each ligand behaves as a tripod, the silver atom being in a strongly distorted octahedral environment [149].

Me$_2$AuNO$_3$ reacts with HC(pz)$_3$ yielding the square-planar *cis*-[{HC(pz)$_3$}AuMe$_2$]NO$_3$ in which the potentially tridentate ligand is coordinated in bidentate N$_2$-fashion [150].

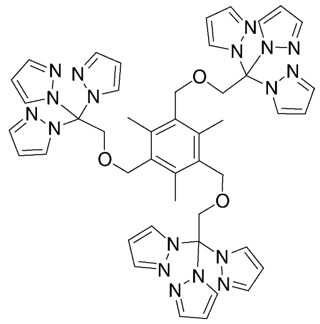


Fig. 40. The polydentate 1,3,5-Me$_3$C$_6$[CH$_2$OCH$_2$C(pz)$_3$]$_3$.

3.9. Group IIB: Zn, Cd, Hg

Our group reported the first Zn^{II}, Cd^{II} and Hg^{II} mercury derivatives of HC(pz)$_3$ [151,152] and also a comparison with analogous derivatives containining bis(pyrazolyl)alkanes [153]. The preparation of isoelectronic mixed-ligand complexes such as [{HC(3,5-Me$_2$pz)$_3$}Cd{HB(3,5-Me$_2$pz)$_3$}][BF$_4$] [154] allowed a direct comparison of the two ligand types in the same complex [155]. The ligands *o*-, *m*-, *p*-C$_6$H$_4$[CH$_2$OCH$_2$C(pz)$_3$]$_2$ react with [Cd$_2$(THF)$_5$][BF$_4$]$_4$ yielding coordination polymers [{C$_6$H$_4$[CH$_2$OCH$_2$C(pz)$_3$]$_2$-Cd}[BF$_4$]$_2$]$_n$ in which RC(pz)$_3$ is tridentate, bonded to two different cadmium(II) atoms, forming a coordination polymer containing six-coordinate, pseudo-octahedral cadmium(II) centers [156].

Attempts to prepare [{HC(pz)$_3$}ZnL]$^+$ species (L = uninegative anion) yielded only distorted octahedral [{HC(pz)$_3$}$_2$Zn]$^{++}$ [157]. A number of tris(pyrazolyl)- and tris(indazolyl)-methane ligands and their interaction with Zn salts that spans the range from no reaction at all to hydrolytic destruction [158] have been described. It has been reported that with Zn halides [{HC(3,5-Me$_2$pz)$_3$}ZnBr$_2$], [{HC(3-Me$_2$CH–In)$_3$}ZnBr$_2$], and [{HC(3-Me$_2$CH–In)$_3$}ZnCl$_2$] can be synthesised. The octahedral ionic 2:1 complex [{HC(3,5-Me$_2$pz)$_3$}$_2$Zn][ClO$_4$]$_2$ has been structurally characterized. [{HC(3-Me$_2$CH–In)$_3$}Zn(NO$_3$)$_2$] is in an octahedral zinc coordination environment with mono and bidentate NO$_3$ groups and a tridentate tris(indazolyl)methane. The reaction of [{HC(3-Me$_2$CH–In)$_3$}ZnBr$_2$] with AgClO$_4$ yield the labile [{HC(3-Me$_2$CH–In)$_3$}ZnBr][ClO$_4$] and the unstable [{HC(3-Me$_2$CH–In)$_3$}Zn(OH$_2$)][ClO$_4$]$_2$.

Tris(azolyl)alkanes have been investigated for their interaction with the zinc enzyme carbonic anhydrase (CA). Several types of activities were detected, but CA inhibitory properties were discovered for the very sterically demanding derivatives [159].

A detailed report of the interaction between zinc and cadmium(II) salts with HC(pz^x)$_3$ ligands appeared recently in literature. Compounds [{HC(pz^x)$_3$}$_2$M]X$_2$, and [{HC(pz^x)$_3$}MX$_2$] (M = Zn or Cd, X = ClO$_4$, NO$_3$, Cl, Br, I or CH$_3$COO), have been characterized by X-ray, IR, NMR and ESI MS spectroscopy [160].

1,3,5-Me$_3$C$_6$[CH$_2$OCH$_2$C(pz)$_3$]$_3$ forms with Cd^{2+} a complex having a double, open cage structure holding two Et$_2$O molecules [147].

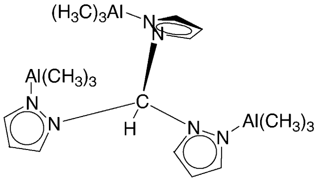


Fig. 41. $\{HC(pz)_3\}[AlMe_3]_3$.

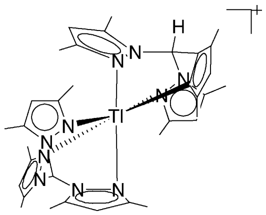


Fig. 42. The octahedral coordination environment in the cation of $[\{HC(3,5\text{-}Me_2pz)_3\}_2Tl]PF_6$ where the lone pair is stereochemically inactive.

3.10. Group IIIA: Al, Ga, In, Tl

$HC(pz)_3$ readily coordinates 3 eq. of Me_3Al giving $\{HC(pz)_3\}[AlMe_3]_3$ (Fig. 41). ^1H NMR studies also evidenced the formation of mono- and bis-adducts $\{HC(pz)_3\}[AlMe_3]$ and $\{HC(pz)_3\}[AlMe_3]_2$ as from the reaction of $HC(pz)_3$ with less than 3 eq. of $AlMe_3$ [161].

Both the 2:1 and 1:1 ligand:metal complexes of thallium(I), $[\{HC(3,5\text{-}Me_2pz)_3\}_2Tl][PF_6]$ and $[\{HC(3,5\text{-}Me_2pz)_3\}Tl][PF_6]$ that have been characterized in the solid state by X-ray crystallography. $[\{HC(3,5\text{-}Me_2pz)_3\}_2Tl][PF_6]$ has an octahedral structure with a stereochemically inactive lone pair (Fig. 42) whereas in $[\{HC(3,5\text{-}Me_2pz)_3\}Tl][PF_6]$ the structure of the cation is a trigonal pyramid [162].

3.11. Group IVA: Sn, Pb

No compounds have been described containing tris-(pyrazolyl)methanes bonded to Ge and Si acceptors through the pyridinic nitrogen whereas a number of tin and lead compounds have been reported in literature.

Two diorganotin(IV) dihalide derivatives of $HC(pz)_3$, $[\{HC(pz)_3\}R_2SnCl_2]$ ($R = Et$ or Me) in which the donor likely acts as bidentate were reported. However, these compounds are scarcely characterized [163]. Reger et al. [164] described $[\{HC(3,5Me_2pz)_3\}Pb][BF_4]_2$, containing a three-coordinate lead center, $[\{HC(3,5Me_2pz)_3\}_2Pb][BF_4]_2$, that has trigonally distorted octahedral environment with the lone pair sterochemically inactive, $[\{HC(pz)_3\}_2Pb][BF_4]_2$ an asymmetric six-coordinate lead center with very different Pb–N distances and finally the highly asymmetric mixed ligands species $[\{HC(3,5Me_2pz)_3\}\{HB(3,5\text{-}Me_2pz)_3\}Pb][BF_4]$ and $[\{HC(3,5Me_2pz)_3\}\{HB(pz)_3\}Pb][BF_4]$, the former being described as a distorted square base pyramid. The reaction of $Sn(O_3SCF_3)_2$ with 1 meq. of $HC(3,5\text{-}Me_2pz)_3$ in THF yields the complex $\{HC(3,5\text{-}Me_2pz)_3\}Sn(O_3SCF_3)_2$. $Pb(acac)_2$ react with 2 eq. of $[H(Et_2O)]\{[3,5\text{-}(CF_3)_2C_6H_3]_4\}$ and 2 eq. of $HC(pz)_3$ or $HC(3,5\text{-}Me_2pz)_3$ yielding, respectively, $[\{HC(3,5\text{-}Me_2pz)_3\}_2Pb]\{[3,5\text{-}(CF_3)_2C_6H_3]_4\}_2$, which is a ionic species in a trigonally distorted octahedral environment with the lone pair on the lead stereochemically inactive and $[\{HC(pz)_3\}_2Pb]\{[3,5\text{-}(CF_3)_2C_6H_3]_4\}_2$, ionic in a distorted octahedral environment, but with a stereochemically active lone pair on lead(II) [165].

The reaction of $RSnCl_3$ and SnX_4 with equimolar amounts of $HC(pz^x)_3$ yields ionic 1:1 $[\{HC(pz^x)_3\}SnRCl_2]^+[SnRCl_4]^-$ or $[\{HC(pz^x)_3\}SnX_3]^+[SnX_5]^-$ and 2:1 $[\{HC(pz^x)_3\}SnRCl_2{}^+]_2[SnRCl_5]^{2-}$ or $[\{HC(pz^x)_3\}SnX_3{}^+]_2[SnX_6]^{2-}$ (Fig. 43). These stable complexes have been characterized in the solid state (X-ray, IR, MS-FAB) as well as in solution (^1H and ^{119}Sn NMR, conductivity, and molecular weight determinations) [166].

3.12. Lanthanides

The crystal structure of $[NBu_4]^+[Ce^{III}(NO_3\text{-}\kappa^2\text{-}O,O')_4\{\kappa^3\text{-}HC(pz)_3\}]$ showed an 11-coordinate Ce(III) complex [167]. Eu, Ga and Tb derivatives of tris[3-(6-carboxypyridin-2-yl)pyrazol-1-yl)]methane and their luminescence properties have been reported [168].

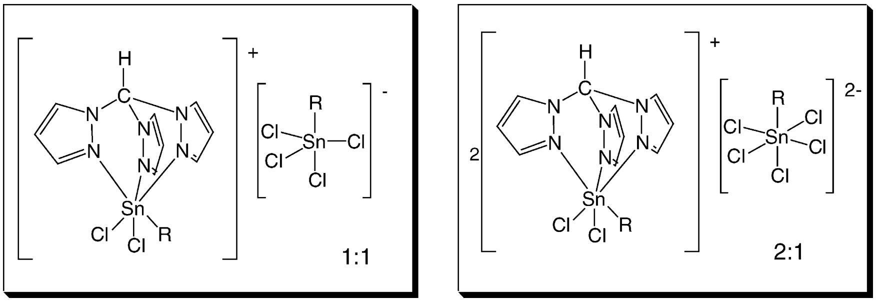


Fig. 43. The ionic 1:1 $[\{HC(pz^x)_3\}SnRCl_2]^+[SnRCl_4]^-$ and 2:1 $[\{HC(pz^x)_3\}SnRCl_2{}^+]_2[SnRCl_5]^{2-}$ complexes obtained from the reaction of $RSnCl_3$ with $HC(pz^x)_3$.

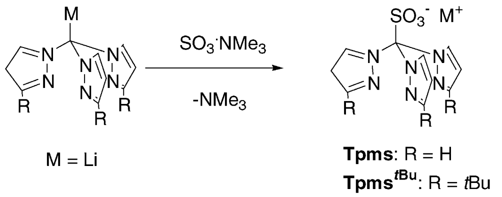


Fig. 44. Synthesis of the tripodal nitrogen-donor water-soluble ligands (tris(pyrazolyl)- and tris(3-*tert*-butylpyrazol)-methanesulfonic.

4. Related systems

4.1. Tris(pyrazolyl)methane–sulphonate derivatives

The methine proton of $HC(pz)_3$ is sufficiently acidic to be removed by ^{n}BuLi, and the resulting reactive intermediate readily reacts with electrophiles. Kläui et al. [169] synthesised two anionic tripodal nitrogen water-soluble ligands (tris(pyrazolyl)- and tris(3-*tert*-butylpyrazol)-methanesulfonic acids, Tpms and $Tmps^{tBu}$, respectively) by addition of lithiated $HC(pz)_3$ to a sulfurtrioxide–trimethylamine complex (Fig. 44). Tpms has a methanesulfonate unit which imparts very good stability toward hydrolysis and an increased solubility in polar solvents and is stable over a wide range of pH values in aqueous solution. In contrast to $HC(pz)_3$ Tpms is almost exclusively soluble in water and only moderately soluble in methanol. It has been reported that tetrahedral complexes with transition metals that are C_{3v}-symmetric can be obtained with the $Tmps^{tBu}$ derivative. Tpms yields a Rh complex $[(Tpms)Rh(CO)(PMe_3)]$ which is the only known catalyst with a tripodal ligand which is active in the catalytic carbonylation of benzene [170]. The Tpms coordinates Rh(I) in a κ^2 or κ^3 mode [171]. This family of ligands interacts with M(II) salts yielding $[(Tmps^{tBu})ZnX]$ (X = Cl, Br, I or Et, O_2CMe) (Fig. 45) $[(Tmps^{tBu})NiX]$ (X = Cl, Br), $[(Tmps^{tBu})CoCl(Hpz^{tBu})]$, $[(Tmps^{tBu})Cu(CO)]$, $[(Tmps)Cu(CO)]$, $[(Tmps^{tBu})Zn(\mu\text{-}O_2CMe)(\mu\text{-}OH)Zn(Tmps^{tBu})]$, the former being one of the very few structural models of the dinuclear zinc enzymes phospholipase C and phosphotriesterase [172].

Heterometal cubane-type MFe_3S_4 clusters trigonally symmetrized with Tpms capping ligand have been recently reported [173].

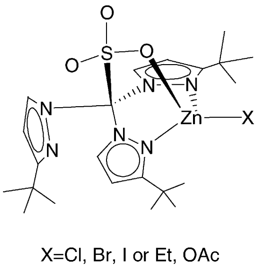


Fig. 45. The $[(Tmps^{tBu})ZnX]$ complexes, synthetic models for dinuclear zinc enzymes phospholipase C and phosphotriesterase.

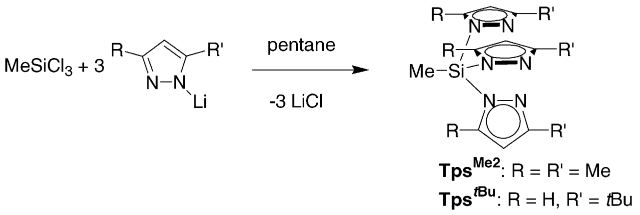


Fig. 46. An efficient synthesis for the tris(pyrazolyl)silanes Tps^{Me2} and Tps^{tBu}.

The interaction of Tpms with CuCl in the presence of PR'_3 gives copper(I) coordination compounds of formula $[Cu(Tpms)(PR'_3)]$. Whereas a copper(II) species $[(Cu(Tpms)_2]$ formed when R is cyclohexyl. $[Cu(Tpms)(PPh_3)]$ is the first example of structurally characterised complex containing Tpms coordinated to a metal ion in an unusual κ^3-*N*,*N*′,O fashion [174].

4.2. Other tetrakis(pyrazolyl)alkane derivatives

Protonation of $CpMo(\eta^3\text{-}C_3H_5)(CO)_2$ followed by reactions with $C(pz)_4$ yields $[CpMo(CO)_2(\mu\text{-}Cpz_4)][BF_4]$ which reacts with $ClReO_3$ to yield $[CpMo(CO)_2(\mu\text{-}Cpz_4)\text{-}\{Re(Cl)O_3\}][BF_4]$ [175].

4.3. Tris(pyrazolyl)silane

Synthesis of pyrazolylsilane ligands was mentioned in a old review [176]. An efficient synthesis of Tps^{Me2} and Tps^{tBu} has been recently described [177] (Fig. 46). $[(Tps)Cu(NCMe][PF_6]$ has been prepared and characterized analytically and spectroscopically [177], which also prepared octahedral tricarbonyl complexes from the reaction of labile nitrile adducts $[M(CO)_3(NCMe)_3]$ (M = Cr, Mo) or $[W(CO)_3(NCEt)_3]$ and Tps in MeCN or THF [178]. The cone angle of the silane ligand is moderately larger than that of Tp, and also approaches the value estimated for well-known “tetrahedral enforcer” ligands such as Tp^{tBu}. Tps^{Me2} can be also prepared by the transilylation reaction of methyltrichlorosilane with 3 eq. of (3,5-dimethylpyrazolyl)trimethylsilane [179].

4.4. Tris(pyrazolyl)phosphineoxide

The tris(pyrazolyl)phosphine oxide ligand $O{=}P(Me_2pz)_3$ (Fig. 47a) was prepared by substitution of the chloride of

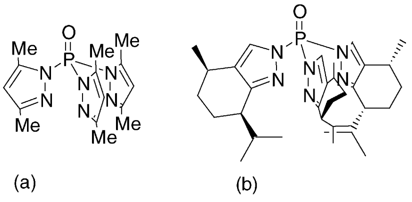


Fig. 47. Tris(pyrazolyl)phosphine oxide ligands $O{=}P(Me_2pz)_3$ (a) and $O{=}P(Menthpz)_3$ (b).

$OPCl_3$ by the appropriate pyrazole in the presence of triethylamine in refluxing benzene. Its reaction with Mo–π-allyl complexes has been investigated. Hydrolysis of one pyrazolyl group was found in the crystal structure of one of the complexes obtained [180].

Optically active and C_3-symmetric tris(pyrazolyl)phosphine oxide ligands such as $O{=}P(Menthpz)_3$ (Fig. 47b) were prepared by procedures analogous to those reported for achiral variants [181].

Acknowledgements

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