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STUDY OF POLY (pyrazol-1-yl) BORATES LIGANDS AND THEIR COMPLEXES

ASIF IQBAL BHAT[1]

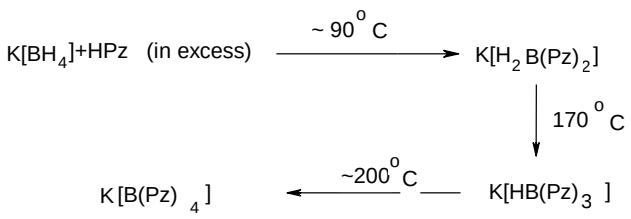
Department of Chemistry, Sri Pratap College, Srinagar, Jammu And Kashmir, India

ABSTRACT

Poly (pyrazol-1-yl) borates are a unique class of chelating agents. They possess unusual ligand properties, which are intermediate between the classical sigma bonding chelating ligands such as acetylacetonate and the pi-bonding cyclopentadienid anion. The Poly(pyrazol-1-yl)borates and their analoges have made significant contributions the development of both coordination and organometallic compounds. On the basis of their coordinating ability, Poly(pyrazol-1-yl)borate ligands are classified into three categories: 1) Bidentate ligands derived from $[R_2B(pz)_2]^-$, Where R= H, CH_3, or Aryl group, 2) Tridentate ligands derived from $[RB(pz)_3]^-$, which usually forms very stable complex. However, in some cases the ligand may coordinate to the metal in a bidentate fashion, 3) The ligand $[B(pz)_4]^-$ contain four coordination sites but it usually coordinates in a tridentate manner. It may also form bidentate complexes, in some cases. In such cases the uncoordinated pyrazolyl group retain their chelating ability and it is possible to prepare dinuclear species of the type $M(pz)_2B(pz)_2$ (M= identical or dissimilar metal and the ligand is bis bidentate.

KEYWORDS: Borates, Ligands, poly (pyrazol-1-yl)

The parent poly [pyrazol-1-yl]borate ligand $[H_nB(Pz)_{4-n}]$ has been obtained by the reaction of potassium tetrahydridoborate, $K[BH_4]$ with an excess of molten pyrazole at varying temperature according to the following scheme:

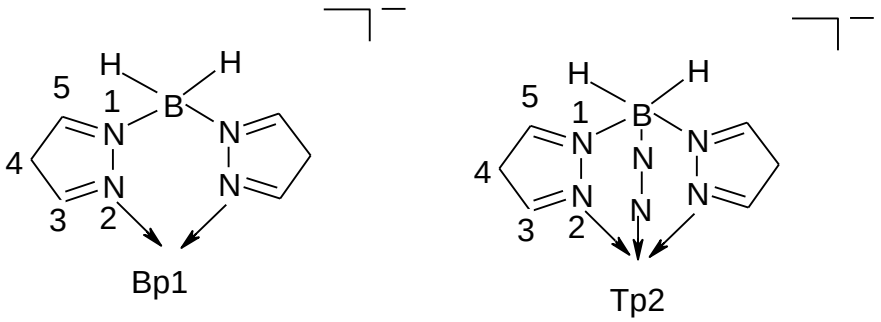


The di- and tri-substituted ligands have been isolated by stoping the reaction at appropriate temperatures. They yield isolable free acids upon acidification wherein the proton is chelated. The compounds were water-soluble and hydrolytically stable .The stability increases with the decreasing number of hydrogen atoms attached to boron. These ligands can be varied manifold by putting diverse substituents on the boron or carbon atoms of the pyrazole ring. A number of such ligands have been prepared involving $[BR_nH_{4-n}]^-$ species in place of BH_4^- and substituted pyrazoles in place of simple pyrazole.

Since the first report of Trofimenko (1966), a very large number of papers have appeared describing the synthesis and the application of poly(pyrazolyl)borates, in an extraordinarily wide range of chemistry, from modeling the active site of metalloenzymes, through analytical chemistry and organic synthesis, to catalysis and material science (Trofimenko, 1969).

Poly(pyrazolyl)borate ligands (scorpionates) are versatile ligands in physio-chemical, bio-inorganic and structurally oriented coordination chemistry (Trofimenko, 1993; Byers *et al.*, 1992; Kitajima and Tolman, 1995; Parkin, 1995; Reger, 1996; Etienne, 1996; Janiak, 1998; Janiak *et al.*, 1995). 'Scorpionate ligand'- a term coined by Trofimenko, in the late 1960s to describe describe the term the poly(pyrazol-1-yl)borates where the ligand grabs the metal with two identical claws $[=(Pz)_2]$ and a curving tail (pseudo axial R) which is curved towards the metal to sting it in close analogy to these features in the scorpion. The parent compounds are dihydrobis(pyrazolyl)borate (Bp, 1, Fig. 1) and hydrotris(pyrazolyl)borate (Tp, 2, Fig. 2). Thallium(I) derivatives of poly(pyrazolyl)borate ligands are important (i) as a means of isolation and characterization of new scorpionate ligands and (ii) as a mild (less reducing) and often more stable ligand transfer reagent in place of alkali metal salts of scorpionate ligands (Janiak *et al.*, 1995).

[1]Corresponding author



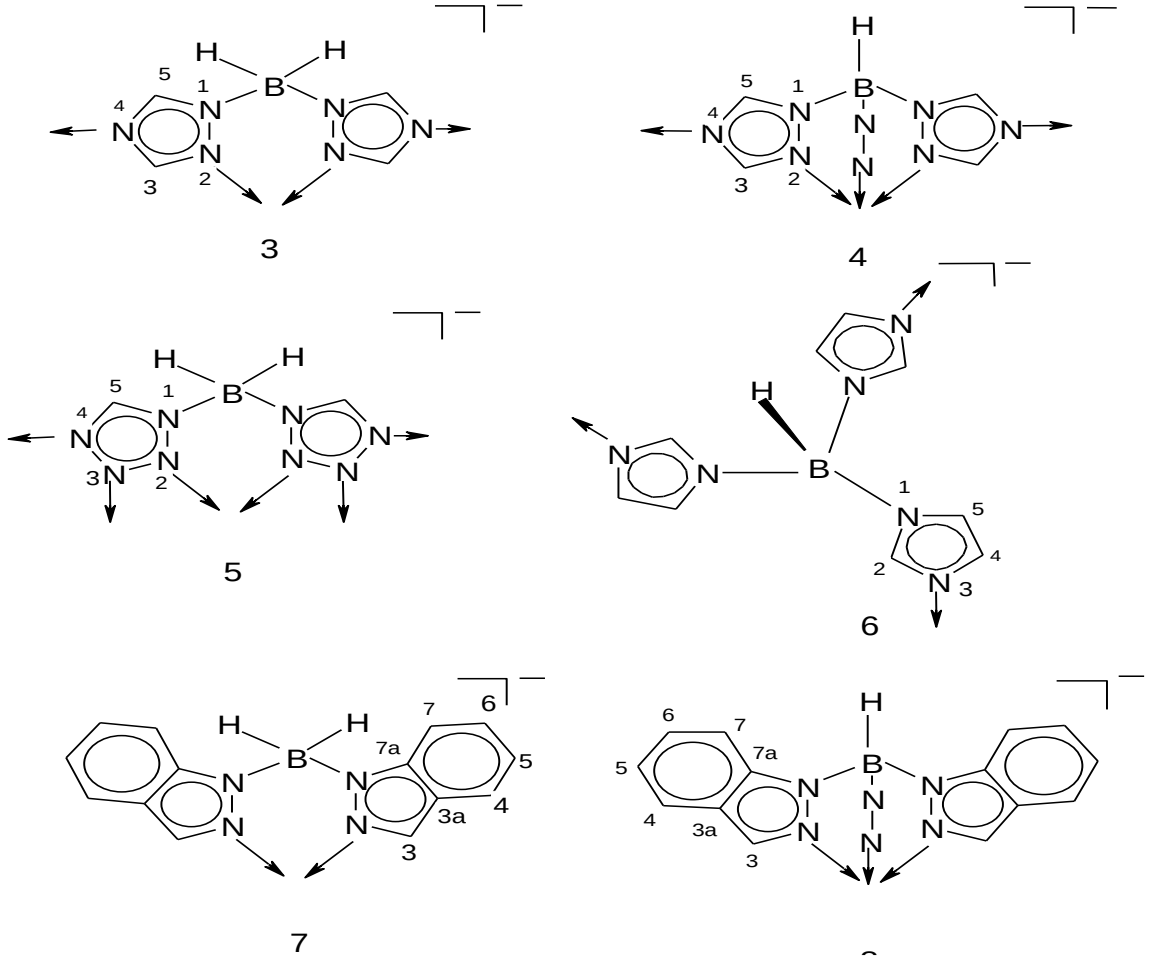
(⁻N—N-) denotes the third pyrazole ring which is oriented to the rear

Figure 1

Figure 2

The modified scorpionate ligands are bis- and tris(1,2,4-triazolyl) borate (**3** and **4**, Fig. 3) (Janiak and Hemling, 1994; Janiak *et al.*, 1995; Janiak *et al.*, 1996), bis(tetrazolyl)borate (**5**, Fig. 3) (Reglinski *et al.*, 1999; Bhandari *et al.*, 2000), bis- and tris(imidazolyl)borate (**6,** Fig. 3) (Janiak *et al.*, 1998; Trofimenko *et al.*, 1992; Han and Parkin, 1990; Han *et al.*, 1990; Han and Parkin, 1990) or bis-and tris(indazolyl)borate (**7** and **8**, Fig. 3) (Han *et al.*, 1991). Examples of modified poly(pyrazolyl)borate ligands studied so far are fluorinated tris(pyrazolyl)borate and tris(mercaptoimidazolyl)borate (Han and Parkin, 1992).

Thallium(I) complexes are also used by others to investigate supramolecular metal–ligand structures (Trofimenko *et al.*, 1987).

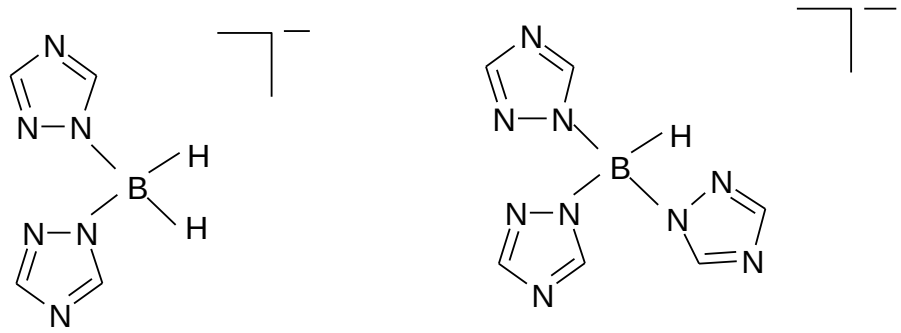


(N-N) denotes the third triazolyl ring or imidzolyl ring which is oriented to the rare

Figure 3

In recent years the use of scorpionate N3-donor hydrotris(pyrazolyl) borate ligands has yielded indispensable precursors for more elaborate coordination and organometallic species (Alsfasser *et al.*, 1990). This family of ligands having found important applications in fields of bioinorganic, inorganic and organometallic chemistry (Eichhorn and Armstrong, 1990).

Tris(4-halopyrazolyl)borates (Perkinson *et al.*, 1991) and the bis- and tris(pyrazolyl)borates bearing trifluoromethyl substituents were a few examples in the literature of scorpionate



Structure of the ligands employed in this work

Figure 4

Ligands incorporating electronically noninnocent substituents. With the latter class of ligands, it has been shown that the strongly electron-withdrawing CF_3 substituents reduce the electron density on the coordinated metal ion (Jeffery *et al.*, 1991).

The first example of second generation scorpionate ligands is Tp^{tBu} prepared from 3-tert-butylpyrazole and KBH_4. Its four coordinated tetrahedral complex of the type Tp^{tBu} MX [M= Mn(II) to Zn(II); X= Cl, NCS, NCO, N_3] were prepared. The ligand Tp^{tBu} give rise to several new and unique type of complexes somer of which were characterized by X-Ray crystallography (Kitajima *et al.*, 1990. The first tris[tris(pyrazolyl)borato] beryllium derivative Tp^{tBu} BeR (R = Cl, Br, I, H, SH) were synthesized (Dias *et al.*, 1997) As a model of nitrate reductase, the five coordinate Tp^{tBu} $CuNO_2$ and tetrahedral Tp^{tBu}-$CuOSO_2CF_3$ were synthesized and their structures established by X-ray data. (Trofimenko *et al.*, 1992) The structural of the tetrahedral $Tp^{tBu}CuCl$ and $Tp^{tBu}Cd_2$ have also been determined. An unusual complex trans- $Tp^{tBu}Ni[(C_6H_4\text{-p-Me})(PMe_3)_2]$ in which Tp^{tBu} functions as a monodentate ligand was prepared and its structure established by X-ray crystallography.

The ligand hydrotris(3-tert.butyl-5-methylpyrazolyl)borate, Tp^{Ph} was one of the first "second generation" homoscorpionate (Trofimenko, 2004). Several of its complexes were prepared (McCaffin *et al.*, 1991; Kitajima *et al.*, 1989; Jewson *et al.*, 1999). The ligand hydrotris(3,5-diphenylpyrazolyl)-borate,TP^{Ph2} and its Cu(II) complex was also prepared (Janiak *et al.*, 2000). The hydrotris[3-(p-anisyl)pyrazolyl] borate, Tp^{Pan} and their tetrahedral complexes of the type Tp^{PTol} MX and Tp^{Pan} MX [M = Co(II), Ni(II), Zn (II); X = NCS, NCO, N_3] have been reported (Graziani *et al.*, 2002).

Tris(pyrazolyl)borates $[HB(Pz)_3]$ constitute one of the most versatile ligands in chemistry (Kisko *et al.*, 1999). In fact, complexes of tris(pyrazolyl)borates are now known for most of the elements in the periodic table. The vast majority of these involve the use of ligands with a hydride group on the boron atom (e.g., $[HB(Pz)_3]^-$, $[HB(3,5\text{-}(Me)_2Pz)_3]^-$ $[HB(3\text{-}(Mes)Pz)_3]^-$ (1, Fig. 5), $[HB(3\text{-}(t\text{-}Bu)Pz)_3]$). Relatively few tris(pyrazolyl)borate systems featuring B-alkyl or B-aryl substituents have also been isolated (Kisko *et al.*, 1998). Most of these ligands, however, are based on the parent pyrazole (e.g., $[PhB(Pz)_3]^-$ (2, Fig. 5), $[(\eta^5\text{-}C_5H_5)Fe\{\eta^5\text{-}\ C_5H_4B(Pz)_3\}]^-$). B-hydride free ligands that also contain sterically demanding substituents at the pyrazolyl moiety 3-position (e.g., $[t\text{-}BuB(_3\text{-}(t\text{-}Bu)Pz)_3]^-$ (3 Fig. 5) and $[PhB(3\text{-}(t\text{-}Bu)Pz)_3]^-$ (4, Fig. 5) are rare. (Jesson *et al.*, 1967; Beattie *et al.*, 1978) Such ligands are very attractive because they not only lack the reactive and sometimes problematic B–H functionality, but they also provide excellent protection for labile or reactive metal adducts.

Low frequency IR spectra of HB(Pz or 3,5-$Me_2Pz)_3M$ [M = Fe(III), Co(II), Ni(II), Cu(II), Zn(II)] have been recorded and assigned (Hutchinson *et al.*, 1979). With Fe(III),Cr(III), & Co(II) metal ions, the $RB(Pz)_3$ ligand formed $[L_2M]^+$ complexes rather than neutral L_3M complexes.

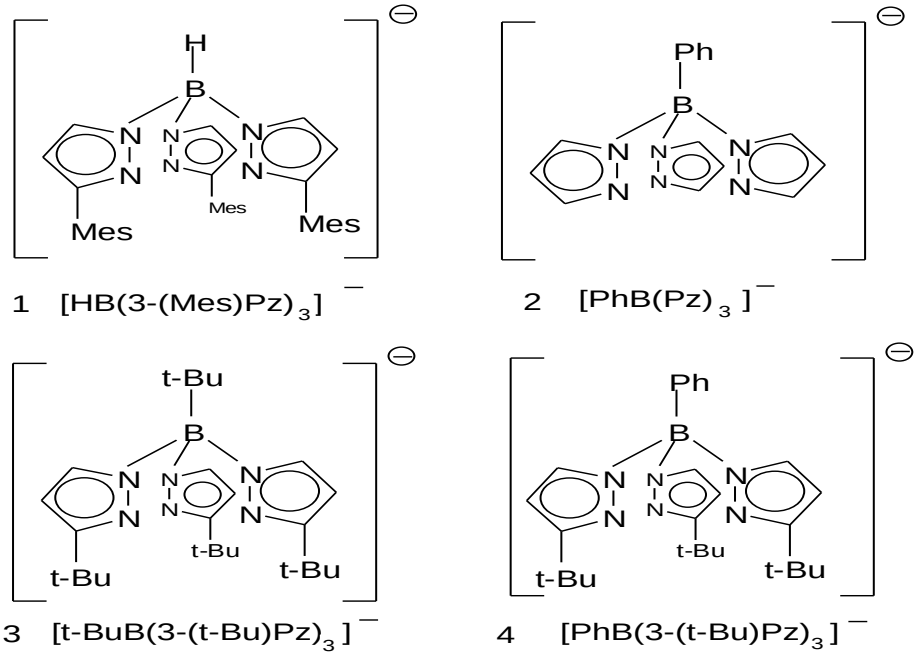


Figure 5

The spin equilibrium in Fe $[HB(Pz)_3]_2^-$ has been studied by resonance and pulsed ultrasonic method (Sharp and Bard, 1983), and its high temperature crossover by Mossbauer, Far – IR and variable temperature magnetic susceptibility measurements (Santini *et al.*, 2010). This complex has been subjected to cyclic Volta metric studies in liquid SO_2, where Fe(II) has been oxidized to Fe(IV)state (Trofimenko, 2007). An intresting dinuclear complex, $HB(Pz)_3Fe$-(μ-$OAc)_2$-(μ-O)Fe $HB(Pz)_3$ has also beenprepared in one step as a model for binuclear iron centre of the heamerythrin (Trofimenko, 1999) similar complexes with formato and oxalate bridges fas been synthesized. The oxygen bridge can be protonated and deprotonated (Ghosh *et al.*, 1989) and the structure of the oxo-bridged and hydroxo-bridged compounds have been determined by the X-ray crystallography. (Dias *et al.*, 1995) $HB(3,5\text{-}Me_2Pz)_3CuCO$ complex was found to be more stable than $HB(Pz)_3CuCO$. A number of complexes have been obtained by replacing the CO group in this compound by R_3P, R_3As, and R_3Sb etc. An unusual complex containing Cu-Mo band has been obtained by the reaction of $HB(Pz)_3CuCO$ and $H_2Mo(C_{2\,h5})$ (Dias *et al.*, 1997).

A new class of scorpionate ligands, with cyano-substituted pyrazole rings have been synthesized, bis(pyrazolyl)borate ligand, Bp^{4CN} (Dias *et al.*, 1996), cyano-substituted scorpionate ligand containing an additional phenyl substituent in the 3-position, $Bp^{Ph,4CN}$ (Ghosh *et al.*, 1999). Fig. 6

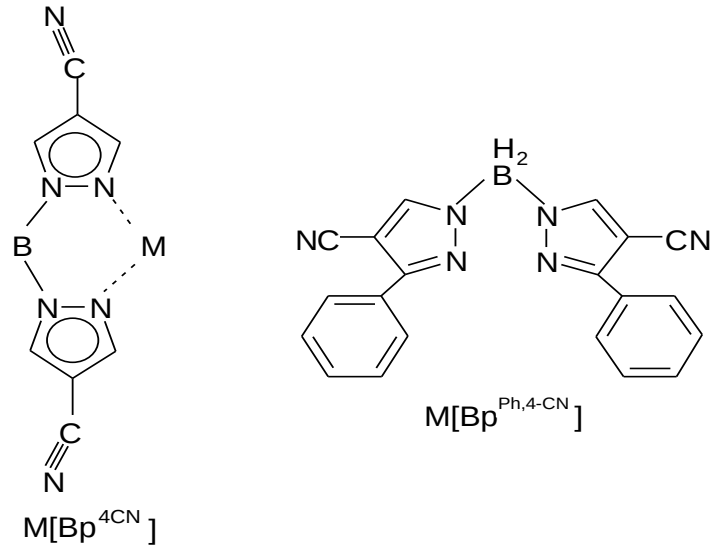


Figure 6

The special nature of the Bp^{4CN} ligand became dramatically apparent when simple monomeric biscomplexes, $M[Bp^{4CN}]_2$, with first-row transition metals were prepared (Gorun and Stibrany, 1997). These complexes were prepared by the reaction of $Tl[Bp^{4CN}]$, with MX_2 (X) Cl, OAc, ClO_4 in methylene chloride. Instead of the typical organic-soluble deep purple tetrahedral cobalt(II) complexes, or orange-red square planar nickel(II) ones, which were obtained with all known Bp^x ligands, except for those containing coordinating substituents in the 3-position such as pyridyl, bipyridyl, or 2,4-(dimethoxy)phenyl insoluble materials were obtained, with colors characteristic of octahedral structures.

The infrared spectra of these as well as of the nickel(II) and iron(II) analogues, were essentially superimposable. While the preference for octahedral coordination by cobalt and nickel may be understandable, it was surprising that zinc, which is often content with being fourcoordinate and tetrahedral, still opted for the octahedral structure. Unlike the less-substituted Bp^{4CN}, $Bp^{Ph,4CN}$ ligand is capable of forming homoleptic mononuclear complexes. The synthesis and structural characterization of Co(II) and Cu(II) complexes has been reported (Albinati *et al.*, 1997).

The fluorination of "classical" ligands is a powerful tool for the modification of the coordination sphere of inorganic and organometallic complexes. Both the physical and chemical properties of metal complexes can be dramatically altered by incorporating fluorine into the ligands. Metal adducts of the fluorinated ligands often show very different physical and chemical properties relative to their nonfluorinated analogues. For example, polyfluorinated ligands commonly improve the volatility, oxidation resistance, thermal stability, and fluorocarbon solubility of their metal adducts. (Schneider *et al.*, 1998) They have also been known to improve the activity and/or selectivity of certain metal-catalyzed reactions (Gorun *et al.*, 2000; Dias and Jin, 2000) Fluorinated ligands are highly desired for applications in fluorous-biphase and supercritical CO2 media (Fekl *et al.*, 2000; Lupinetti *et al.*, 2001). Weakly coordinating, fluorinated anions also play an important role in chemistry (Rangan *et al.*, 2009). Consequently, there is a considerable interest in the synthesis and applications of fluorinated ligands. Despite the importance and wide utility of poly(pyrazolyl) borate ligands, relatively little is known about their fluorinated versions. Over the past few years, the synthesis and use of several poly(pyrazolyl)borates containing fluoroalkyl substituents have been reported. Among the many varieties of poly(pyrazolyl)borates, the tris(pyrazolyl)borate ligand has attracted the most interest, perhaps due to its close analogy to the ubiquitous cyclopentadienyl system (Diaconu *et al.*, 2002). The vast majority of studies involving the metal complexes of tris(pyrazolyl)borates are limited to the parent ligand $[HB(Pz)_3]^-$ (Dias *et al.*, 2003) or their alkyl-substituted derivatives such as $[HB(3,5\text{-}(CH_3)_2Pz)_3]^-$ and $[HB(3,5\text{-}(i\text{-}Pr)_2Pz)_3]$- (or to a lesser extent the aryl-substituted ligands) (Rodriguez *et al.*, 1997). Fluorination of the popular hydridotris(pyrazolyl)borate class of ligands (Matsumi *et al.*, 1998), has only recently received attention (Matsumi *et al.*, 1998). The synthesis of potassium hydridotris(3,5bis(trifluoromethyl)pyrazolyl) borate ($KTp^{(CF3)2}$, isolated as an adduct of dimethylacetamide, $KTp^{(CF3)2}$, DMAC) was reported in 1995 by Dias and co-workers (Paine and Narula, 1990). However, the use of this ligand in transition-metal and organometallic chemistry has been limited. For example, while metal carbonyl, alkene, alkyne, and arene complexes of this ligand have been reported, metal alkyl complexes containing this fluorinated Tp ligand have been conspicuously absent (Matsumoto and Chujo, 2003; Bartlett, 1986). The synthesis and full characterization including an X-ray crystal structure of the Pt(IV) trimethyl complex of hydridotris(3,5-bis-trifluoromethyl)pyrazolyl)borate, $Tp(CF_3)_2PtMe_3$ has been reported [92]. To properly evaluate the effect of fluorination of the "classic" TpR_2 (hydridotris (3,5-dialkylpyrazolyl)borate) ligand on the structural and spectroscopic properties of the organometallic fragent, Scott Lovell *et al* have also characterized the known nonfluorinated analogue $TpMe_2PtMe_3$ ($TpMe_{2=}$ hydridotris(3,5-dimethylpyrazolyl)borate) (Khalil *et al.*, 1996) by X-ray crystallography and NMR spectroscopy.

Tris(pyrazolyl)borate ligands bearing fluoro substituents are rare, and the examples in the literature include $[HB(3\text{-}(CF_3)Pz)_3]^-$, $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ (where $B(3,5\text{-}(CF_3)_2Pz)_3$hydrotris(3,5-bis(trifluoromethyl) (pyrazolyl)borate), and $[HB(3\text{-}(CF_3),5\text{-}(CH_3)Pz)_3]^-$ (Shiu *et al.*, 1993; Chen *et al.*, 1994). Ligands such as $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ are electron deficient and show interesting chemistry. For example, $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ has been used in the stabilization of low-valent main group species such as $[HB(3,5\text{-}(CF_3)_2Pz)_3]$In (Kläui *et al.*, 2000) and in the isolation of rare metal carbonyl complexes, e.g., $[HB(3,5\text{-}(CF_3)_2Pz)_3]$AgCO (Kimblin *et al.*, 2000). The partially trifluoromethylated $[HB(3\text{-}(CF_3)\text{-}5\text{-}(CH_3)Pz)_3]^-$ ligand has also shown to be useful in stabilizing a rare hydridovinyl species, $[HB(3\text{-}(CF_3),5\text{-}(CH_3)Pz)_3]Ir(H)(CO)(CH{=}CH_2)$ (Dias *et al.*, 1995). The synthesis of two new tris(pyrazolyl)borate ligands containing $-C_2F_5$ and $-C_3F_7$ substituents on the pyrazolyl group 3-positions have been reported by H. V. Rasika Dias *et al.* (1996). In order

to investigate the relative electronic properties of [HB(3-$(C_2F_5)Pz)_3]^-$ and [HB(3-$(C_3F_7)Pz)_3]^-$, they have synthesized their copper(I) carbonyl complexes and compared the C-O stretching frequency data to those of the previously reported tris(pyrazolyl)boratocopper(I) carbonyl complexes. The preparation of precursor pyrazoles and the X-ray crystal structures of the sodium salt of ligand, [HB(3-$(C_2F_5)Pz)_3$]CuCO, and [HB(3-$(C_3F_7)Pz)_3$]CuCO are reported (Dias and Jin, 1996).

The synthesis and use of several poly (pyrozoyl borates) containing fluoroalkyl substituents include $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]^-$, $[HB(3\text{-}(CF_3)Pz)_3]^-$, [HB(3-(C_2F_5)-Pz)$_3]^-$, $[HB(3\text{-}(C_3F_7)Pz)_3]^-$, and $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ (Dias and Jin, 1995). Their metal adducts show very interesting properties. For example, the copper(I) carbonyl and ethylene adducts [HB(3,5-$(CF_3)_2Pz)_3$]CuCO (Dias *et al.*, 2000) and [HB(3,5-$(CF_3)_2Pz)_3$]Cu(η^2-$C_{2\ h4}$) (Dias *et al.*, 1996) are air and thermally stable solids. It is also possible to obtain the corresponding silver(I) complexes (Dias and Lu, 1995; Dias and Gorden, 1996). The [HB(3,5-$(CF_3)_2Pz)_3$]AgCO is an example of a metal carbonyl where the bonding between the metal and the CO is essentially of σ-type (with little to no л-backbonding) (Dias *et al.*, 1997). Its carbonyl stretching frequency (ν_{CO} 2178 cm^{-1}) is higher than that of free CO (2143 cm^{-1}-). [HB(3,5-$(CF_3)_2Pz)_3$]CuNNN(1-Ad) and [HB(3,5-$(CF_3)_2Pz)_3$] AgN(1-Ad)NN represent rare, thermally stable organo azide–metal complexes (Del *et al.*, 1995).

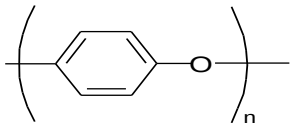
The $[HB(3\text{-}(CF_3),5\text{-}(CH_3)Pz)_3]^-$ ligand (2 where R=CH_3), which was reported by Graham *et al*, has also shown to be useful in stabilizing rare, reactive and/or labile molecules like the hydridovinyl species [HB(3-(CF_3),5-$(CH_3)Pz)_3$]Ir(H)-(CO)(CH=CH_2) (Albinati *et al.*, 1997). Metal adducts of fluorinated poly(pyrazolyl)borates also catalyze various transformations (e.g., [HB(3,5-(CF_3)2Pz)$_3$]Cu(η^2- $C_{2\ h4}$) for aziridination; [HB(3,5-$(CF_3)_2Pz)_3$]Ag(THF) for C–Cl bond activation; [HB(3-(CF_3),5-$(CH_3)Pz)_3$]Cu for oxidation (Schneider *et al.*, 1998). Overall, fluorinated poly-(pyrazolyl)borates are of significant current interest and are useful for many important applications (Gorrell and Parkin, 1990; Dias and Thankamani, 2013; Hu and Gorun, 2001). Recently the synthesis of a new fluorinated tris(pyrazolyl)borate ligand $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]^-$ has been reported. Solid state structures of several tris(pyrazolyl)borato sodium complexes featuring oxygen-based donors like THF, Et_2O and H_2O have been also reported (Dias *et al.*, 2000). The ligand electronic effects were investigated using the IR spectroscopic data of the copper(I) carbonyl complex [HB(3-(CF_3),5-$(Ph)Pz)_3$]CuCO. H. V. Rasika Dias *et al* had synthesised and characterized the potassium salt of a highly fluorinated bis(pyrazolyl)borate ligand, (dihydridobis (3,5bis(trifluoromethyl) pyrazolyl)borate) and used it in the synthesis of copper(II) and zinc(II) complexes, $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]_2Cu$ and $[H_2B(3,5\text{-}(CF_3)2\text{-}Pz)_2]_2Zn$ (Dias *et al.*, 2003). These compounds have been characterized by X-ray crystallography. In order to study the effects of replacing methyls with trifluoromethyl groups on the pyrazole rings of bis(pyrazolyl)borate ligands, they have also investigated the crystal structure of the corresponding methylated species, $[H_2B(3,5\text{-}(CH_3)_2Pz)_2]_2Zn$.

There are many known alkali-metal tetrahydroborates (Diaconu *et al.*, 2002), some of these salts had been used in poly(pyrazolyl)borate chemistry (Rodriguez *et al.*, 2000). These salts were used for the synthesis of a copper(I) bis(pyrazolyl)borate, $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]Cu(PPh_3)_2$, directly from a copper tetrahydroborate salt and 3,5-$(CF_3)_2$PzH (where 3,5-$(CF_3)_2$PzH) = 3,5- bis(trifluoromethyl)pyrazole), thereby circumventing the need for an alkali-metal derivative such as $[H_2B(3,5\text{-}(CF_3)_2Pz)$. The structure and geometry of these complexes were revealed by the crystallography. $[H_2B(3,5\text{-}(CF_3)2Pz)_2]^-$ ligand in [H2B(3,5-(CF3)$_2$ Pz)$_2$]Cu($PPh_3)_2$ coordinates to copper through only one nitrogen atom. The geometry at the copper may be described as trigonal planar with a Cu-N bond length of 2.057(2) Å and Cu-P distances of 2.2388 (7) and 2.2690 (7) Å. One of the hydrogens on boron also shows a weak interaction with the copper atom (Cu-H) 2.01(2) Å; Cu, B) 2.891 Å. This contact is not strong enough to distort the geometry at copper from trigonal planar as evident from the sum of the angles at Cu, 358.8°.

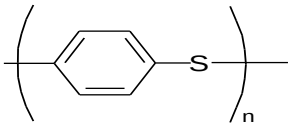
The tetrakis(pyrazol-1-yl)borate anion BPz_4^- , is a substituted variant of the hydrotris analogue and form similar octahedral complexes as $M[HBPz_3]_2$. These complexes are, however, thermally more stable and have somewhat low solubility than those of the corresponding hydrotris complexes. The BPz_4^- can also act in a tetrahedral four coordinate species (Roth *et al.*, 1990). This ligand like the hydrotris ligand yield half sandwich compounds (Dodds *et al.*, 2004). The free acid B(3,5-$Me_2Pz)_4H$ has also been reported (Sun *et al.*, 2002). Several complexes of the type $B(Pz)_4Mn(CO)_2L$ (L = substituted phosphines) were studied by IR and NMR spectroscopy and thermal decomposition (Mészáros *et al.*, 2001). $B(Pz)_4CuCO$ compound has also been prepared where all the Pz groups are NMR equivalents. The structure of $B(Pz_4)TIR_2$ (R=Et & Bu) indicates that all Pz groups exchange rapidly at room temperature. However in $[Co(Pz)_4]_2$ the fourth uncoordinated Pz group maintains the separate NMR identity. The reaction of 2-

picolyl bridged Pd complex with $B(Pz)_4^-$ favoured stereochemically rigid products (Antiñolo *et al.*, 1999; Bucher *et al.*, 1995; Onishi *et al.*, 1983). The dinuclear $[Cl_2PdL]_2$ gave different products with $B(Pz)_4^-$ depending on L. Several BPz_4AgL species where L= PR_3, $P(OR)_3$, AsR_3 and SbR_3 have been prepared .The complex $B(Pz)_4TaMe_3Cl$ has been studied by X-ray crystallography. The stereochemical nonrigidity of $B(Pz)_4PtMeCO$ has been studied by ^1H, and ^{13}C NMR. The complex $B(Pz)_4PtMeL$, where L = acetylene were also prepared (Ruiz *et al.*, 2002). Similarly, the complex $B(Pz)_4AuCl_2$ have also been obtained (Vicente *et al.*, 2002). Low frequency IR spectra of $[B(Pz)_4]_2M$ complexes where M= Fe , Co, Ni, Cu, Zn have been studied (Huchinson *et al.*, 1976). Detailed ^1H, ^{13}C, ^{15}N and ^{11}B NMR spectra of $K[B(Pz)_4]$ have been reported (Lopez *et al.*, 1990). Numerous lanthanide complexes of the type $Ln[B(Pz)_4]_3$ have been reported (Domingos *et al.*, 1995). Several compounds where $B(Pz)_4$ act as bidentate ligand have been reported (Hallett *et al.*, 2010). The free acid, $B[3,5\text{-}Me_2(Pz)_4H]$ has also been isolated. Similarly, $KB(indazolyl)_4$ and its 5-nitroindazolyl analogue and several of their metal complexes have been synthesized.

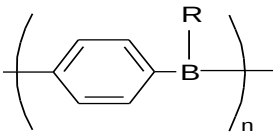
Conjugated organoboron polymers such as poly (*p*-phenylene-borane)s (PPBs), Fig. 7 were synthesized via the empty л orbital of the boron atom by means of hydroboration polymerization (Dias and Jin, 1995) or polycondensation (Dias *et al.*, 1997) exhibited unique characteristics such as intense fluorescence emission, excellent third-order non-linear optical behaviour, and n-type electrochemical activity with fairly high stability toward air and moisture. Thus, they are expected as a novel type of optical and electronic materials. The higher thermal stability is also expected due to the absence of a retrohydroboration (-β-elimination) (Lupinetti *et al.*, 2001) process during their thermal degradation. These characteristics of the polymers might allow their application for various electronic devices.



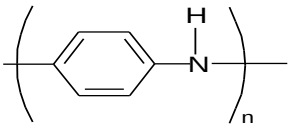
Poly(phenylene-oxide) (PPO)



Poly(phenylene-sulfide) (PPS)



Poly(phenylene-borane) (PPB)



Polyaniline (PANI)

Hetroatom-containing (Polyphenylenen)s

Figure 7

Recently, the poly(cyclodiborazane)s Fig. 8 containing transition metals such as palladium and platinum in their backbone (Dias *et al.*, 2000) were prepared by hydroboration polymerization with tripylborane. These polymers exhibited an extension of π-conjugation via transition metal and boron atom. They are also expected to show third-order non-linear optical properties.

Matsumoto and Chujo (2003) have prepared a series of poly(cyclodiborazane)s by hydroboration polymerization Fig. 9.

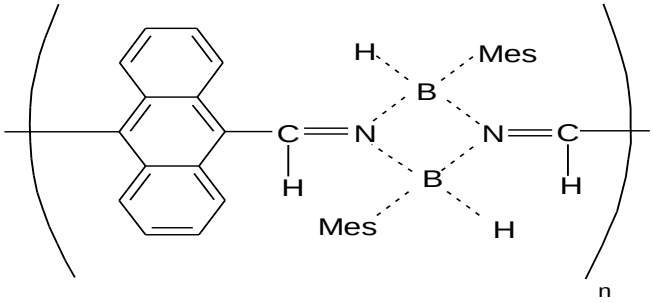


Figure 8

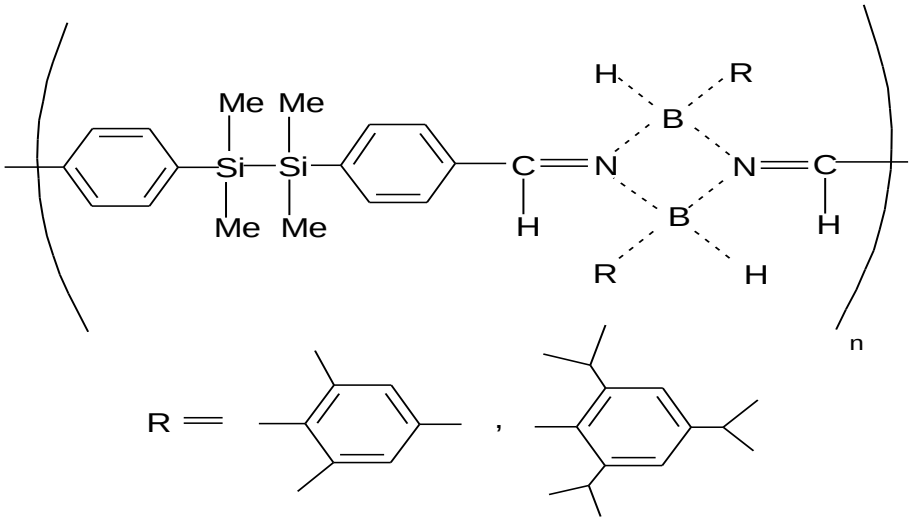
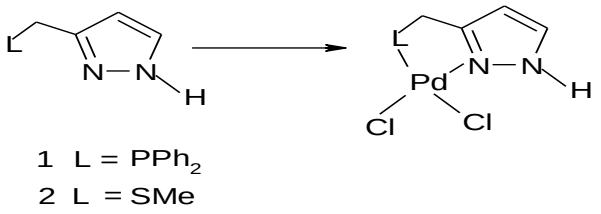


Figure 9

The obtained polymers showed great stability toward air and moisture, and interestingly, an effective expansion of π-conjugation was observed in the case where the ICT structures were constructed in the backbone. The optical and electronic properties of the polymers showed potential for application as high performance materials.

Many metalloenzymes activate substrates using a combination of one or more metal ions and nearby functional groups capable of donating or accepting one or more hydrogen bonds or protons. Pyrazole complexes have not been studied in this context. However, very limited literature data on the acidifying effect of metal complexation suggest that suitably designed pyrazole metal ions and proton donors or acceptors at near-physiological pH: the free ligand exhibits a p*K*a of 14.2, whereas pyrazole complexes of $Cr(III)(NH_3)_5$, $Co(III)(NH_3)_5$, and $Ru(III)(NH_3)_5$ have p*K*a values in the range 5.98-7.21.8. In order to anchor a metal ion firmly on a pyrazole derivative, Grotjahn *et al.* (2003) have designed polydentate ligands (1 and 2) to form stable chelates involving one soft ligating atom (P or S) and one pyrazole N, while leaving the other pyrazole N and its attached hydrogen available for donating a hydrogen bond or a proton to another ligand on the metal Fig. 10. Although hundreds of Polydentate ligands containing pyrazoles are known (Casado *et al.*, 2005; Turculet *et al.*, 2004), virtually all of them feature a pyrazole ring substituted at one nitrogen, probably because of the ease of synthesizing such systems.



1 L = PPh_2
2 L = SMe

Figure 10

The ligands featuring one pyrazole ring substituted at carbon with a single -CH_2SCH_3 or -CH_2PPh_2 group, along with their square-planar, mononuclear complexes to a *cis*dichloropalladium (II) fragment have been reported ()[70].

The novel hybrid pyrazolate/phosphine anionic ligand $[CH_2{=}CHCH_2B(CH_2PPh_2)\ (pz)_2]^-$ has been synthesized (Dias and Polach, 2000). Coordination of this ligand to metals in a *fac* tridentate fashion occurs in the complexes $[CH_2{=}CHCH_2B(CH_2PPh_2)(pz)_2M\ (cod)]$, prepared by reactions of the lithium salt of the ligand with $[M(\mu\text{-}Cl)(cod)]_2$ (M = Rh, Ir). They are pentacoordinated, with the rhodium complex showing a distorted trigonal-bipyramidal structure in the solid state, as determined by X-ray diffraction methods. Furthermore, the ligand has been linked to the periphery of a carbosilane dendrimer, resulting in the polyanionic dendrimer $[Li(TMED)]_4$ $[Si\{(CH_2)_3SiMe_2(CH_2)_3B(CH_2PPh_2)\ (pz)_2\}_4]$, which leads further to the corresponding metallodendrimer with four rhodium atoms. $[PhB(CH_2PR_2)_3]$- (R)Ph,iPr) have more recently seen their genesis, creating new systems that have already provided interesting cases of C-H and Si-H bond activation (Dias and Wang, 2000). However, despite the development of several generations of scorpionate ligands and the increasing interest in the synthesis and use of "heteroscorpionate" ligands derived from bis(pyrazolyl) methane (Dias and Z., 2000), there are few

and old examples of boron based hybrid pyrazolate ligands containing two pyrazolyl bridges and one imethylamino, or arylmercapto or alkoxy bridges. A novel hybrid pyrazolate/phosphine bringing together hard (N) and soft (P) donor atoms in pyrazolylborate systems have been designed an efficiently synthesised [CH_2=$CHCH_2B(CH_2PPh_2)(pz)_2$] (Dias and Jin, 2000). The rhodium and iridium complexes of [CH_2=$CHCH_2B(CH_2PPh_2)(pz)_2$] have also been synthesized.

Although Coordination compounds of 1,2,4- than a century, the beginning of their study, however, dates from the late 1970s. This is well after the publication of the first crystal structure of the polynuclear $CuCl_2$(Htrz) in 1961 and the trinuclear $Ni_3(Htrz)_6$ $(H_2O)_6$]-$(NO_3)_6$.2 H_2O in 1968 (Dias and Ayers, 2002). Potts in his review article (Ayers and Dias, 2002) have noted the use of triazole complexes of silver for application in the photographic industry, although quite a number of complexes with other metals have had already been described at that time. The chemistry of 1,2,4-triazole complexes and the knowledge of their structures and properties, however, have increased rather quickly since the early 1980s. Several important properties of the triazoles are the cause of the wide spread interest. Because of the position of the donor atoms in the five membered rings, the triazoles appear to possess the possibility of linking (transition) metal ions together. The triazole ligands thereby constitute a bridge between the metal ions. This bridge can be of several different geometries, depending on the donor atoms of the ligands and the properties of the metal.

Since the pairs or clusters of metal ions appear to mediate certain chemical reactions differently from complexes of isolated metal centers, in nature, many metalloproteinase appear to have active sites comprising pairs of metal ions in close proximity. Much research is devoted to mimicking these enzymatic reactions by functionalized models or using such complexes in reactions other than the enzymatic ones. The fact that 1,2,4-triazoles are quite similar in geometry to imidazoles, which occur overwhelmingly in nature, is the second property that has made the triazoles and triazole complexes much sought after compounds to mimic such processes. They are also used to mimic imidazoles in model compounds for such processes (Bucher *et al.*, 1995). Also, the substitution of pyrazole ligands by triazoles is being investigated and offers many exciting possibilities, for instance in the research of tripyrazoylborates (Sirianni *et al.*, 2014; Canty *et al.*, 1986).

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