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Synthesis and Properties of Poly(pyrazolyl)borate and Related Boron-Centered Scorpionate Ligands. Part A: Pyrazole-Based Systems

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Abstract: This review is intended to cover the developments in the chemistry of poly(azolyl)borates through the years 2000-2008, based on the main synthetic methods, coordination properties, spectroscopic and structural features of this important class of ligands. The subject matter is the chemistry of substituted bis-, tris- and tetrakis-(pyrazolyl)borate ligands. In this review we provide essential information to allow the reader to probe more deeply into the main aspects of the chemistry of these fascinating and flexible ligands. This review would also demonstrate the enormous potential of poly(pyrazolyl)borates chemistry, as also the future perspectives in this field.

1. INTRODUCTION

Since poly(pyrazolyl)borate ligands were discovered by Trofimenko forty-three years ago [1], their coordination chemistry has been extensively developed; it is likely that even Trofimenko could not have foreseen the true immensity of the field that was to spring from his pioneering discovery of the poly(pyrazolyl)borates or "scorpionates" ligands. In fact, tris(pyrazolyl)borates are a very useful class of monoanionic, nitrogen-based, auxiliary ligands in coordination, organometallic and bioinorganic chemistry. They readily coordinate, usually as face-capping tridentate ligands, to a wide variety of metal ions affording stable metal complexes. Furthermore, it is possible to modify the steric and electronic properties of these ligands quite easily by varying the number and nature of substituents on the pyrazolyl rings and on the boron atom, thereby providing a convenient avenue to finetune the properties at the tris(pyrazolyl)borate ligand bound metal center.

Actually, more than 3000 papers have appeared in the intervening years concerned with the coordination chemistry of this versatile class of ligands. After the first reviews in 1971 [2] and 1972 [3] on poly(pyrazolyl)borate chemistry and pyrazole-derived ligands, through the boron-pyrazole compounds described in 1986 [4] Trofimenko reported in 1986 [5] and in 1993 [6] a summary on the coordination chemistry of poly(pyrazolyl)borates. In 1999 Trofimenko described the coordination chemistry of scorpionate ligands in a book [7]. Apart from Trofimenko's reviews, a number of reviews and chapters were devoted to this subject.

In 1982 Shaver [8] wrote a chapter on poly(pyrazolyl)borate and related ligands; in 1983 McCleverty reviewed his work on chemistry of Tp* with Mo and W [9]; in 1988 Niedenzu reviewed the pyrazaboles [10] and in 1992 Canty *et al.* wrote about the simple tris(pyrazolyl)borate chemistry of Pd and Pt [11].

In 1993 the molecular structures and electronic spectra of a series of four-, five-, and six-coordinate complexes of cobalt, nickel, copper, and zinc, stabilized by tris(pyrazolyl)borate ligands, have been reported by Parkin *et al.* [12]. In 1994 Kitajima and Moro-Oka presented many copper-dioxygen complexes of tris(pyrazolyl)borate ligands [13].

In 1995 [14] and 2002 [15] Santos and Marques as well as Marques *et al.* wrote on coordination chemistry of tris(pyrazolyl) borate ligands in lanthanides and actinides complexes; in 1995 Parkin reported also metal hydroxides, hydrides and organometallics derived from hindered poly(pyrazolyl)borate ligands [16], while Tolman *et al.* reviewed the organometallic and bioinorganic chemistry of hindered hydrotris(pyrazolyl)borate ligands [17].

In 1996 Parkin discussed the effect of Tp^x-ligation on Grignard reagents [18]; in the same years Reger reviewed on pyrazolylborate complexes of gallium and indium [19], while Etienne devoted a review to coordination chemistry of Tp ligands with V, Nb and Ta [20].

In 1997 [21] and 1998 [22] Janiak has summarized the coordination chemistry of Tp^x toward Tl; in the same years the action of oxygen-atom transfer enzymes which contain Tp-based molybdenum and tungsten pterin enzyme models centres was discussed in a review of Young and Wedd [23].

In 1998 McCleverty *et al.* described the use of scorpionate ligands to form a variety of bridged polynuclear complexes of Mo [24]; the same authors reviewed their work on coordination and supramolecular chemistry of Tp^{Py}-based ligands in 2001 [25]. An overview on the coordination chemistry of Re with poly(pyrazolyl)borates has been presented by Santos *et al.*, including a variety of compounds like trioxo, dioxo, oxo, and hydrides with the metal in different oxidation states [26].

In 1999 Vahrenkamp reported the zinc pyrazolylborate chemistry related to zinc enzymes [27]. Ruthenium complexes of the hydrotris(pyrazolyl)borate ligands have been reported by Kirchner *et al.* [28]: particular emphasis was on complexes containing metal-carbon single and double bonds and on the synthesis of highly reactive vinylidene complexes and their involvement in stoichiometric C-C coupling reactions with activated alkanes and olefins. The structural features, acidity and chemical properties of some dihydrogen/hydride complexes of group VIII metals with poly(pyrazolyl)borate ligands were described by Jia *et al.* [29]. In a review on the π-bonding and the lone pair effect in multiple bonds between heavier main group elements, Power described the molecular gallium and indium species of formula $Tp(^tBu)_2EE'$ (E = Ga, E' = S, Se, or Te; E = In, E' = Se) with terminal bonds to chalogens and in particular the structure of $[Ga(Tp^{tBu2})S]$ [30].

In 2000 advances in the chemistry of cobalt-dioxygen and related complexes supported by hydrotris(pyrazolyl)borate ligands were reviewed by Hikichi *et al.* [31]. Bioinorganic zinc chemistry explored through synthetic analogs of zinc enzymes containing the 3-substituted hydrotris(pyrazolyl)borate ligands has been well reported by Parkin in a feature article [32]. In a chapter for *Metal Ions in Biological Systems* Parkin reviewed on synthetic analogs that mimic function and structure of active sites of zinc enzymes [33]. Templeton *et al.* summarized a number of transition-metal η^2-vinyl complexes and synthetic methods which yield η^2-vinyl complexes also containing Tp^x ligands [34].

In 2001 a review was given by Edelmann [35] on the coordination chemistry of pyrazolylborate ligands with topics including electronic effects, novel coordination modes and new ligands. Carmona *et al.* described the C-H activation and coordination chemistry of rhodium- and iridium-tris(pyrazolyl)borate complexes [36]. A general review on organometallic complexes of pyrazolylborates and related ligands spanning from nontransition metals to copper, silver, and gold species has been written by Sadimenko [37].

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In 2002 Akita and Hikichi reviewed some transition metal complexes containing hydrotris(pyrazolyl)borate ligands ranging from bioinorganic chemistry of dioxygen species to organometallic systems [38]. A review of the inorganic coordination complexes reactivity with NO, including poly(pyrazolyl)borates and their Cu-NO_x and Fe-NO_x redox chemistries, was described by Wasser *et al.* [39]. Tris(pyrazolyl)borates have been reported also in the book "*Metal Dihydrogen and sigma-Bond Complexes - Structure, Theory, and Reactivity*", authored by Kubas, in Chapter 13 on B-H [40] and in Chapter 11 on X-H [41] activation (X = Si, Ge, Sn). An overview of recent work on the chemistry of the divalent lanthanide hydride deals with the hydrotris(3-*tert*-butyl, 5-methyl-pyrazolyl)borate was reported by Ferrence and Takats [42].

In 2003 the scorpionate ligands and their father Trofimenko were guests of honor at a symposium to celebrate 35 years of chemistry with scorpionates and related ligands [43]. *Polyhedron* also dedicated the special issues 2-3 of volume number 23 to this topic, the first paper being presented by Trofimenko on development of scorpionate ligand system from its genesis [44]. A perspective study on double C–H bond activation reactions of ethers (cyclic and non-cyclic) and amines to give Fischer-type iridium carbenes, and subsequently the migratory insertion chemistry of highly electrophilic, cationic iridium carbenes containing Tp^x ligands was published by Carmona *et al.* [45]. DFT methods were applied by Hall and Webster to a variety of ligand systems and substrates (alkanes and silane) for the reactions in the C-H bond activation by Ir(III) complexes containing also the tris(pyrazolyl)borate ligands [46].

In 2004 a comprehensive review of the coordination chemistry of poly(pyrazolyl)borates and related scorpionate ligands has been reported by Pettinari and Santini [47]. A review by Mirica *et al.* [48] on copper-dioxygen complexes also focused on structure and spectroscopic properties of side-on superoxocopper(II) Tp^x complexes. Highly coordinatively unsaturated, tetrahedral hydrocarbyl and dinuclear complexes bearing a hydrotris(pyrazolyl)borate ligand, in particular $[M(Tp^x)R]$ and $[(Tp^x)MM'L]$ complexes (M = Fe, Co, Ni; M' = Ru, Co), were reviewed by Akita [49]. Parkin has highlighted recent studies that afforded an understanding of the bioinorganic chemistry of zinc by investigating synthetic analogs that mimic both the structure and function of the active sites of zinc enzymes, such as the tripodal ligands tris(pyrazolyl)borates [50]; in the same year copper and silver derivatives of scorpionates have been reviewed [51], while Santos and coworkers presented an overview of synthetic procedures, reactivity and structural data involving group 7 elements and actinides with scorpionate ligands; this includes oxides, polyhydrides and carbonyls of group 7 elements and any type of compounds of actinides(III) and (IV) [52]. A detailed discussion on spin-state changes in poly(pyrazolyl)borate iron(II) and cobalt(II) complexes has been reported by Long *et al.* [53].

In 2005 an overview on Ir(III) fragments stabilized by hydrotris(pyrazolyl)borate ligands was presented by Carmona *et al.* [54], concentrating on some aliphatic, non-cyclic ethers and on anisole. Copper, silver and gold-based catalysts containing tris(pyrazolyl) borates have been described by Diaz-Requejo and Pérez [55]. A new generation of dearomatizing π-bases having the general form TpM(L)(π-acid) (where Tp = hydrotris(pyrazolyl)borate, M = rhenium, molybdenum, tungsten, L = variable ligand, and π-acid CO, NO^+) has been developed [56]. The design and preparation of stable cyanide-bearing six-coordinate complexes of formula $[M(L)(CN)_x]^{(x+l-m)-}$ (M = transition metal ion, x = number of cyanide ligands, l = charge of L and m = charge of M) were extensively discussed by Julve *et al.* [57].

In 2006 Tolman described the use of copper(II) tris(pyrazolyl) borate systems to understand copper protein active-sites chemistry [58]. Sessler *et al.* reported a review focusing on uranium cation coordination complexes with multidentate nitrogen-containing ligands including also scorpionates family [59].

In 2007 an overview of fluorinated tris(pyrazolyl)borate ligands and their role in the development of silver adducts containing group 14 ligands has been reported by Dias and Fianchini [60].

In 2008 a book, dedicated to Swiatoslaw Trofimenko, about the coordination chemistry of poly(pyrazolyl)borates and related scorpionate ligands has been published by the Imperial College Press [61]. In the same year Dias and Lovely [62] reported a description of carbonyl and olefin adducts of coinage metals supported by poly(pyrazolyl)borate and poly(pyrazolyl)alkane ligands and related silver mediated atom transfer reactions. Rapenne *et al.* [63] described the synthesis of various pentaphenylcyclopentadienyl hydrotris(pyrazolyl)borate ligands and the peculiar reactivity of such hindered ligands in their coordination to a ruthenium(II) center. More recently the volume 56 of the Advances in Organometallic Chemistry has been devoted to "The Organotransition Metal Chemistry of Poly(pyrazolyl)borates" [64-67].

In 2009 Maseras *et al.* [68] reviewed on the agostic interactions in alkyl derivatives of sterically hindered tris(pyrazolyl)borate complexes of niobium and in particular described how the joint experimental and computational study of a series of niobium(tris(pyrazolyl))(chloride)(alkyne)(alkyl) complexes has unearthed a very rich chemistry involving a variety of agostic interactions between the alkyl chain and the niobium centre. More recently Spicer and Reglinski elegantly described the development of the anionic soft poly(methimazolyl)borate ligands [69].

This review is intended to cover the developments in the chemistry of substituted bis-, tris- and tetrakis-(pyrazolyl)borate ligands through the years 2000-2008. In this review we provide essential information about the main synthetic methods and spectroscopic and structural features of this important class of ligands, to allow the reader to probe more deeply into the main aspects of the chemistry of poly(pyrazolyl)borates.

The fundamental feature in all poly(pyrazolyl)borate complexes is the six-membered ring within a more general structure RR'B(μ-pz)$_2$M(L)$_n$, (Fig. **1**).

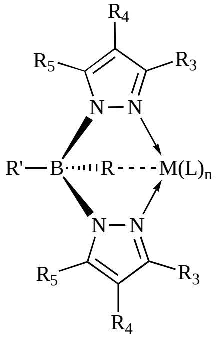


Fig. (1). General structure of poly(pyrazolyl)borate complexes.

Because of the bond angles and distances involved, the B(μ-pz)$_2$M ring has almost nearly a boat conformation. In Fig. (**1**) R and R' are different: the pseudoequatorial R' is pointing away from the metal roughly along the B-M axis, but the pseudoaxial R is directed towards the metal, and may bond to it, interact with it, or simply screen it towards other ligands. R may be H, alkyl, aryl, OR, SR, NMe_2 or another pyrazolyl group with unspecified substituents (pz^x). It was this feature that prompted Trofimenko to coin the term "scorpionates" for polypyrazolylborates, as the coordination behavior of the RR'B(μ-pz)$_2$ ligands closely resembles the hunting habits of a scorpion: this creature grabs its prey with two identical claws (coordination of M through the two 2-N atoms of the B(μ-pz)$_2$ groups), and then may, or may not, proceed to sting it with its overarching tail (the R' group).

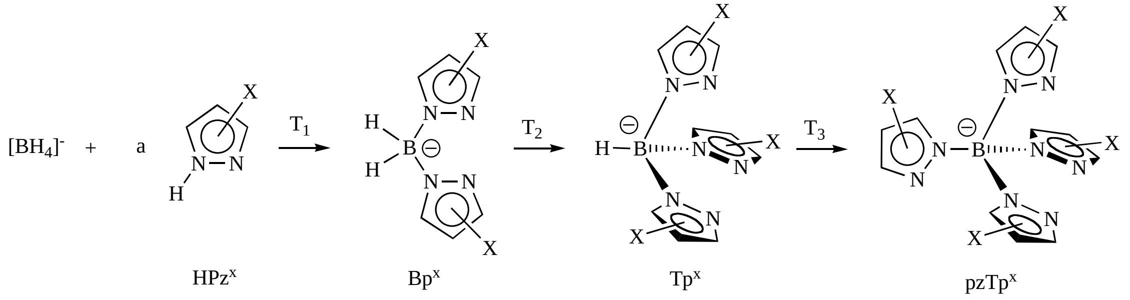


Fig. (2). Synthesis of poly(pyrazolyl)borates in molten pyrazole (a = 2.5 – 6) or in high boiling solvents.

Two families of scorpionate ligands may be distinguished. The first is *homoscorpionates*, where the pseudoaxial R group is another pyrazolyl group (pz^x) identical to the two bridging pz^x groups. In this case the ligand is tridentate and has a local C_{3v} symmetry. Homoscorpionates typically coordinate to the metal in tridentate fashion, a feature that prompted to compare the Tp ligands system to the cyclopentadienyls Cp or Cp^x. The second is *heteroscorpionates*, where the coordinating pseudoaxial R group is anything but pz^x. Heteroscorpionates also include ligands where R is another pyrazolyl group (pz^y) different from pz^x. Heteroscorpionate ligands may coordinate in tridentate fashion, not only in case where R is pz^y or a heteroatom, but even in cases where R is a hydrogen or an alkyl group (agostic bonding).

2. ABBREVIATION SYSTEMS

The systematic method of representing the tris(pyrazolyl)borate ligands proposed by Curtis [70, 71] is to use the abbreviation "Tp" for the hydrotris(pyrazol-1-yl)borate, also indicated as $HB(pz)_3$, and "Tp*" for hydrotris(3,5-dimethylpyrazol-1-yl)borate, also indicated as $HB(3,5\text{-}Me_2pz)_3$. For schematic convenience the generic poly(pyrazolyl)borate ligand with unspecified substituents will be denoted as follows: "Tp^x" for tris(pyrazolyl)borate, "Bp^x" for a general bis(pyrazolyl)borate ligand and "$pzTp^x$" will be used to denote a general tetrakis(pyrazolyl)borate ligand. As proposed by Trofimenko [6] other polypyrazolylborate ligands are identified on the basis of the "Tp" abbreviation system by using the following rules:

a) The basic $HB(pz)_3$ structure is denoted by Tp, and non-hydrogen substituent in the 3-position is denoted by a superscript. Thus, hydrotris(3-methylpyrazolyl)borate is denoted as Tp^{Me}. When there are four identical pyrazolyl groups bound to boron, as in tetrakis(3-methylpyrazol-1-yl)borate, the ligand will be denoted as $pzTp^R$. Boron substituents are written preceding "Tp": for instance, butyl[tris(pyrazolyl)]borate is BuTp.

b) The 5-substituent follows the 3-substituent as a superscript, separated by a comma. For instance, hydrotris(3-isopropyl-5-methylpyrazolyl)borate is denoted as $Tp^{iPr,Me}$. When both 3 and the 5 substituents are identical, the superscript R-substituent is followed by a 2: for instance hydrotris(3,5-diisopropylpyrazol-1-yl)borate is Tp^{iPr2}. In the case of the most commonly used ligand, hydrotris(3,5-dimethylpyrazol-1-yl)borate, the systematic abbreviation would be Tp^{Me2}, although Tp* is generally preferred due to the long historical use.

c) A substituent in the 4-position is denoted as a 4R superscript. Thus, hydrotris(3-methyl-4-bromopylpyrazol-1-yl)borate is $Tp^{Me,4Br}$ and hydrotris(4-chloropylpyrazolyl)borate is Tp^{4Cl}. Since Tp* defines uniquely the position of the two methyl substituents, a substituent in the 4-position follows the asterisk: for instance, the hydrotris(3,4,5-trimethylpylpyrazol-1-yl)borate ligand is Tp^{*Me}.

d) Polyindazolylborate ligands will be represented as benzopyrazolylborates, Tp^{Bo}, with the mode of fusion of the benzo ring to pz indicated by the superscript of 3 or 4 preceding "Bo" to indicate a 3,4- or 4,5- fusion of the benzo ring, and with the position numbering following the indazole numbering system.

e) Heteroscorpionate ligands will be abbreviated as "Bp", with the C-substituents denoted as defined above for Tp, and with the non-hydrogen substituents on the boron written before the abbreviation. For instance, diethyl[bis(pyrazolyl)]borate will be denoted as Et_2Bp, and dihydrobis(3-*tert*-butylpyrazolyl)borate as Bp^{tBu}.

3. SYNTHESIS OF POLY(PYRAZOLYL)BORATES

Poly(pyrazolyl)borate ligands can be prepared, through a more general reaction, by heating tetrahydroborate ion in a large excess of molten pyrazole or in high boiling solvents such as toluene, DMAC, kerosene, anisole, etc. (Fig. **2**).

This reaction can be stopped, through careful temperature control and emanating hydrogen measurement, to yield bis-, tris-, and in the case of 5-unsubstituted pyrazoles, tetrakis-(pyrazolyl)borates. Syntheses of the parent ligands $[H_2B(pz)_2]^-$, $[HB(pz)_3]^-$, and $[pzB(pz)_3]^-$ have been described in detail by Trofimenko [72]. A large variety of 1-H-pyrazoles may be employed to synthesize poly(pyrazolyl)borates by this route, with the exception of those containing functionalities incompatible with the borohydride salt. Tetrakis(pyrazolyl)borate ligands, $pzTp^x$, which are limited to 5-unsubstituted pyrazoles, are prepared by the reaction of Hpz^x with KBH_4 in a 5-6:1 mol ratio. After completion of the reaction, excess Hpz^x is either distilled off, or sublimed in vacuo, and the residue can be directly used for the synthesis of complexes or it can be converted to the Tl salt.

The known types of heteroscorpionate ligands are:

1) $H_2B(pz^x)_2$ (or Bp^x), including $R_2B(pz^x)_2$ (or R_2Bp^x), where R = alkyl, aryl, or halogen (Fig. **3**).

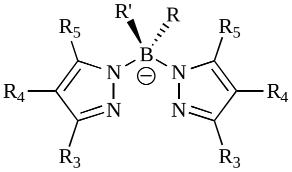


Fig. (3). General structure of heteroscorpionate $[RR'B(pz^x)_2]^-$ ligands.

2) $R(R'Z)B(pz^x)_2$ (= $R(R'Z)Bp^x$), where R = H, alkyl, aryl, and Z is a heteroatom (O, S, NR').

3) $H_2B(pz^x)(pz^y)$ where pz^x and pz^y are different pyrazolyl groups.

In general, the $H_2B(pz^x)_2$ ligands are prepared from reaction, in refluxed high boiling solvents, of substituted pyrazoles and MBH_4 (M = Li, Na or K) in a >2.0:1.0 mole ratio. The residue is boiled with organic solvents which should dissolve most of the un-reacted pyrazole. The crude $M[H_2B(pz^x)_2]$ is contaminated by only small amounts of Hpz^x and is usually suitable for complex formation. Additional purification can be achieved by converting the crude M salt to the Tl salt which shows no tendency to retain Hpz^x.

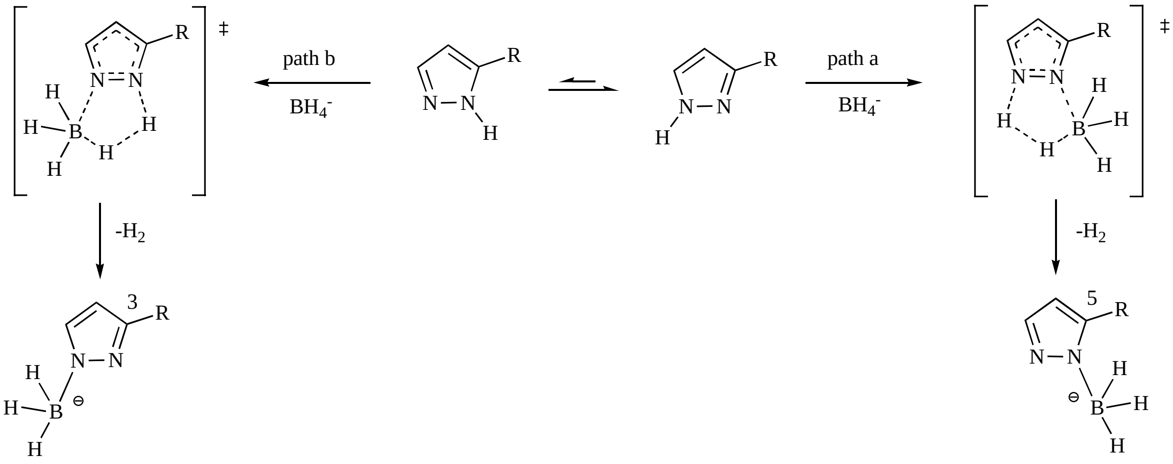


Fig. (4). Regiochemistry of the B-N bond formation.

The $[H_2B(pz^x)_2]^-$ ligands are characterized by the presence of the BH_2 group which although renders the Bp^x ligands more hydrolytically labile than their $[HB(pz^x)_3]^-$ counterparts, permits elaboration of the Bp^x ligand through the addition of various unsaturated systems to the B-H bond. Moreover the Bp^x ligands are able to establish an agostic B-H-M bond with many metals. In 1982 the first Bp^x ligand containing two different pyrazolyl groups, $Li[H_2B(pz)(3,5\text{-}Me_2pz)]$, was synthesized [73]; reaction of the boronium iodide $[H_2B(3,5\text{-}Me_2pzH)(Hpz)]^+I^-$ with NaH produces the analogous sodium salt $Na[H_2B(3,5\text{-}Me_2pz)(pz)]$ [74]. Unsymmetrical ligands, $Li[H_2B(pz)(3,5\text{-}{}^tBu_2pz)]$, $Li[H_2B(3,5\text{-}Me_2pz)(3,5\text{-}{}^tBu_2pz)]$ and $Li[H_2B(3\text{-}(trip)pz)(3,5\text{-}{}^tBu_2pz)]$, have been obtained also by the use of $LiBH_4$ with a 1:1 mixture of two different pyrazoles [75].

In general, the procedure for the synthesis of Tp^x ligands involves thermolysis of a mixture of the suitable pyrazole and a borohydride salt, MBH_4 (M = K or Na), in a 4:1 ratio, either as a melt or in a high-boiling solvent. The reaction is monitored by hydrogen evolution. When the pyrazole is a liquid or a low-melting solid, the excess pyrazole is distilled out keeping the temperature as low as possible, in order to prevent the formation of the tetrasubstituted $pzTp^x$ ligand. The residual $M[Tp^x]$ salt can be converted to the Tl(I) salt and purified by recrystallization. If the pyrazole is 3-substituted and high-melting, the best method is to reflux a mixture in 3.5:1 pyrazole to MBH_4 ratio in high-boiling solvent such as toluene, dimethylacetamide, anisole, methylanisole or kerosene. As with pyrazole itself, the reactions affording Tp^x ligands proceed via the dihydrobis(pyrazolyl)borate anion, which in some instances has been isolated [76]. If the temperature is too high the $pzTp^x$ anion also can be isolated [72]. With large R groups in 3-position the formation of the more highly boron-substituted product is relatively disfavored, facilitating the preparation of the desired Tp^x in most cases. With 3,5-disubstituted pyrazoles the melt method is preferred, since tetrasubstitution does not take place, and high temperatures can be employed. It would be better to use a large excess of pyrazole.

Thallium(I) derivatives of Tp^x ligands have frequently been used as mild and efficient reagents for the transfer of ligands to a variety of transition metals because of their lower reducing ability than that of the corresponding alkali metal salts. Furthermore, the stability and crystallinity of the Tl complexes facilitate the isolation and structural characterization of new Tp^x ligands. The thallium complexes are generally prepared in two steps: (i) MTp^x is synthesized from MBH_4 (M = Na or K) and the corresponding pyrazole derivatives (HPz^x); (ii) the potassium salt reacts with $TlNO_3$ to give $TlTp^x$. The process is simple, but the requirement of excess HPz^x sometimes causes a problem in the isolation of MTp^x. Furthermore, the removal of the by-product MNO_3 in the second step decreases the efficiency of the process. These disadvantages should become much more significant in the case where HPz^x is hard to obtain. Recently Kitamura *et al.* have established a highly reliable and safe procedure for the preparation of $TlBH_4$ and related $TlTp^x$ complexes [77].

A critical issue in the synthesis of poly(pyrazolyl)borate ligands obtained from pyrazoles whose anions are not of C_{2v} symmetry, is the regiochemistry of the B-N bond formation. Usually, the larger substituents end up at the pyrazolyl ring 3-position (more distant from the boron center). This tendency is most pronounced when the size difference between the substituents at 3- and 5-positions is large. This regioselectivity was first demonstrated in the reaction of 3(5)-methylpyrazole, leading to $[H_2B(3\text{-}(Me)pz)_2]^-$ [78] and to $[HB(3\text{-}(Me)pz)_3]^-$ [79] as well as in the regiospecific synthesis of $[HB(3\text{-}(Ph)pz)_3]^-$ [80] and $[HB(3\text{-}({}^tBu)pz)_3]^-$ [76]. A mixture containing 3,3,5-substituted tris(pyrazolyl)borates, where two substituents are at the 3-position and the other one at the 5-position, is obtained when the steric differences between the pyrazolyl ring substituents in the 3- and in the 5-position are less substantial [81]. However, a few exceptions like the formation of $[HB(3\text{-}(Mes)pz)_2(5\text{-}(Mes)pz)]$ ligand [82, 83] or the rearrangement of a 3,3,3-substituted ligand during the formation of metal adducts (e.g., octahedral $[HB(3\text{-}({}^iPr)pz)_2(5\text{-}({}^iPr)pz)]_2M)$ [84] are also known. The probable reason for 3,3,3-regioselectivity is that the B-N bond formation, involving a concerted loss of hydrogen, proceeds through a less sterically encumbered transition state, when bonding occurs to the less hindered nitrogen (Fig. **4**, path b).

Electronic effects may also control the regiochemical course of the ligand syntheses, with electron-withdrawing groups preferring the 3-position. This tendency is most clearly manifested in ligands like $[HB(3\text{-}(CF_3)\text{-}5\text{-}(Me)pz)_3]^-$ [85] and $[HB(3\text{-}(CF_3)\text{-}5\text{-}(thionyl)pz)_3]^-$ [86] in which electronically quite different substituents are present. The syntheses of these ligands are highly regioselective with the more electron withdrawing CF_3 group residing exclusively in the 3-position of the final product. However in these molecules, the steric factors may also contribute to the formation of the 3,3,3-isomer because the CF_3 is also the larger substituent. The electronic control is more clearly manifested when benzopyrazole (or indazole) and its derivatives containing alkyl or aryl substituents in the 3-, 4-, 5-, or 6-positions [87, 88], or 3-(Ar)-4,5-dibromopyrazoles [89] are used as azole precursors in the scorpionate ligand synthesis. They afford scorpionates in which the boron is bonded to the more hindered nitrogen (Fig. **4**, path a). This happens, presumably, because electronic effects outweigh steric ones. The preference of an electron-withdrawing group for the 3-position in tris(pyrazolyl)borate ligands can be explained via an argument analogous to that invoked to rationalize the equilibrium between the pyrazole tautomers [3-(CF_3)pz]H and [5-(CF_3)pz]H. The inductive electron-withdrawing effect of the CF_3 group makes the distal nitrogen more basic, favoring the tautomer with the CF_3 group in the 3 position, [3-(CF_3)pz]H [90].

It has been suggested that the B-N bond preference is kinetic in origin, the less favored tautomer [5-(CF_3)pz]H leading to the more favorable transition state during the course of its reaction with BH_4^-. In view of the facility of borotropic rearrangements and the ease of pyrazole exchange processes under the thermolytic synthetic conditions used; however, one must also consider that the isomeric preference derives from the greater thermodynamic stability of the system when the boron binds to the more basic nitrogen atom [17]. Under non thermolytic conditions we can suggest that the more favored tautomer [3-(CF_3)pz]H leads to the transition state with the boron bonded to the less basic nitrogen azole atom (Fig. **4**, path a).

Despite the impressive chemistry based on bis-, tris- and tetrakis-(azolyl)borates, very few studies have been done on the syntheses of poly(pyrazolyl)borate systems under non thermolytic condition [91]. In these conditions the interplay of steric and electronic influence coupled with the kinetic B-N bond preference and the thermodynamic stability of the product seem to favor the 5-substituted pyrazolylborate $[H_3B(5\text{-}(CF_3)pz)]^-$. On the basis of these observations Santini and Dias evaluated the possibility of preparing trihydro(pyrazolyl)borates starting from 3-trifuoromethyl-pyrazole [3-(CF_3)pz]H, under non thermolytic condition (Fig. **5**).

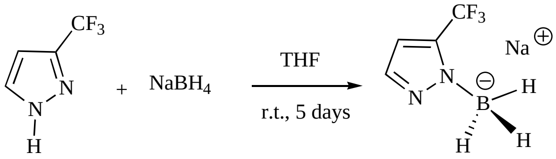


Fig. (5). Synthesis of the 5-substituted pyrazolylborate $Na[H_3B(5\text{-}(CF_3)pz)]$.

This novel class of scorpionates, if acting as κ^3-H,H,N or κ^2-H,N chelators, will allow for the synthesis of complexes with new or uncommon coordinating features. The X-ray structures of $[H_3B(5\text{-}(CF_3)pz)]Ag[P(C_6H_5)_3]_2$ and $[H_3B(5\text{-}(CF_3)pz)]Ag[P(p\text{-}C_6H_4CH_3)_3]_2$ show uncommon κ^2-N,H poly(pyrazolyl)borate ligand coordination modes and rare $Ag\cdots HB$ contacts [91].

In 2008 we described a synthetic pathway to an unsymmetrical 3- and 5-substituted bis(pyrazolyl)borate system. In fact the $Na[H_2B(3\text{-}(CF_3)pz)(5\text{-}(CF_3)pz)]$ has been synthesized by treating 3-(trifluoromethyl)-1H-pyrazole with sodium trihydro(5-trifluoromethyl-pyrazol-1-yl)borate in 1:1 molar ratio, in toluene solution at 70°C (Fig. **6**) [92].

Considering the interest, and the variety of effects induced by these electron withdrawing ligands, we decided to develop a new class of poly(azolyl)borates, using nitro-substituted heterocyclic compounds [93, 94]. No poly(azolyl)borates containing a $-NO_2$ function have been previously prepared, presumably due to difficulties in the synthesis of ligands having both a hydride and a nitro group. However, a poly(azolyl)borate containing a $-NO_2$ substituent could be of interest due to its high coordinative flexibility from κ^2- to κ^4-N_2O_2 coordination ability. We recently reported the first successful synthesis of a such heteroscorpionate ligand, dihydrobis(3-nitro-pyrazolyl)borate, $[H_2B(3\text{-}(NO_2)pz)_2]^-$, and its silver(I) complexes [95].

The boron-substituted anionic ligands $[RB(pz^x)_3]^-$, where R is alkyl or aryl, are generally prepared from the reaction of RBX_2 or $ArBX_2$ [96] (X = halogen or leaving groups) with the pyrazolate ion and excess pyrazole. The reaction of (dibromoboryl)ferrocene with 3 equivalents of pyrazole (Hpz) and 2 equivalents of NEt_3 in toluene at 0°C gave the ferrocenyltris(pyrazolyl)borate ligand (Fig. **7**); the thallium(I) derivative provides the first example of a polymeric structure with bridging tris(pyrazolyl)borate units in the solid state [97].

The bifunctional ligand (Fig. **8**, (**a**)) may be obtained by slowly adding a toluene solution of 1,1'-bis(dibromoboryl)ferrocene to an ethereal solution of 6 equiv. of lithium pyrazolide, Lipz, at -78°C (Fig. **8**, (i)). The synthesis of the lithium salt according to method (i) is severely hampered by the formation of side product **(b)**, which is inert toward further attack of Lipz, while the yield of the thallium salt according to method (ii) is about 80% [97].

Alternatively, the $[RB(pz^x)_3]^-$ ligands may be prepared from reaction of alkyl- or aryl-boronic acids [96, 98] or $RB(OR)_2$ esters [99, 100] with the pyrazolate ion and excess pyrazole (Fig. **9**).

A different route employs organoborohydrides RBH_2 or $LiRBH_3$ [101], obtained from reaction of the corresponding boronic acids $RB(OH)_2$ with $LiAlH_4$ [102], in the reaction with pyrazolate ion and excess pyrazole [103]. It is noteworthy that the lithium and thallium salts of the *tert*-butyl-tris(3-hydrocarbylpyrazol-1-yl)borate ligands, $[^tBu\text{-}B(3\text{-}R\text{-}Pz)_3]^-$ (R = H, Me, ^{i}Pr, ^{t}Bu, Ph), have been prepared and characterized; because of steric congestion at the boron center, the reaction between $Li[^tBuBH_3]\cdot 5Et_2O$ and excess 3,5-dimethylpyrazole afforded the derivative $Tl[^tBuBH(3,5\text{-}(CH_3)_2pz)_2]$ after metathesis with $TlNO_3$ [104].

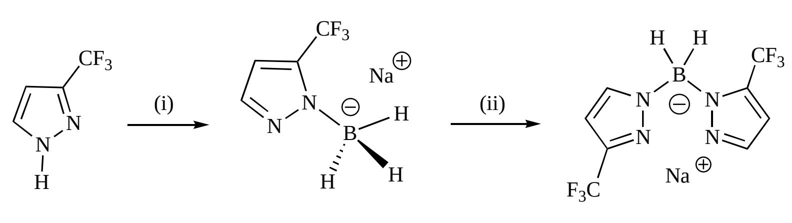


Fig. (6). (i) $NaBH_4$, THF, room temp.; (ii) 3-(trifluoromethyl)pyrazole, toluene, 70°C.

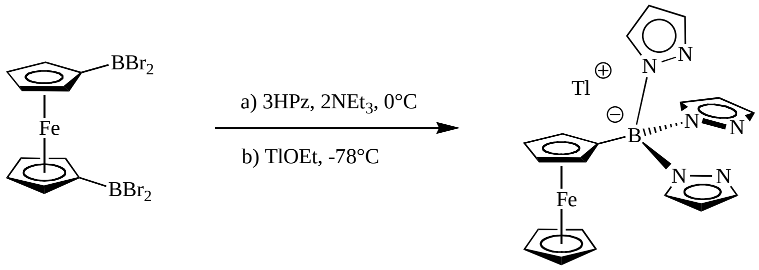


Fig. (7). Synthesis of $Tl[FcB(pz)_3]$.

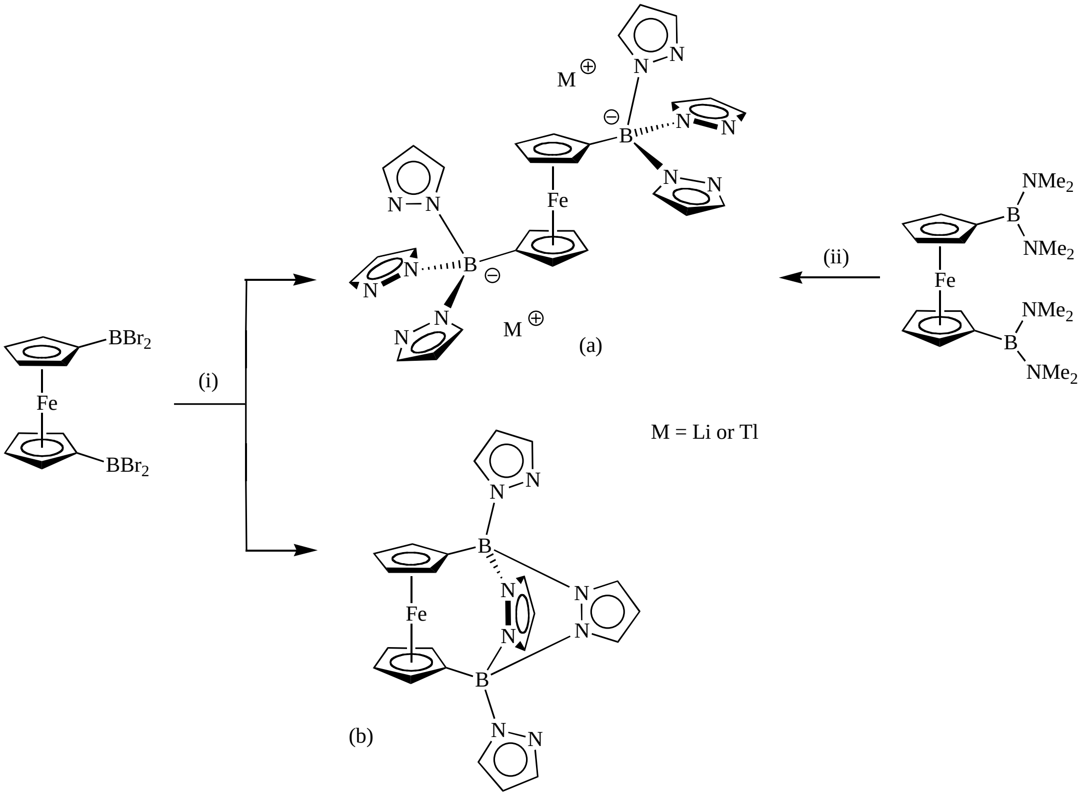


Fig. (8). (i) 6 LiPz, -78°C; (ii) 2 LiPz, 4 HPz, toluene/THF, reflux, exc. $TlNO_3$.

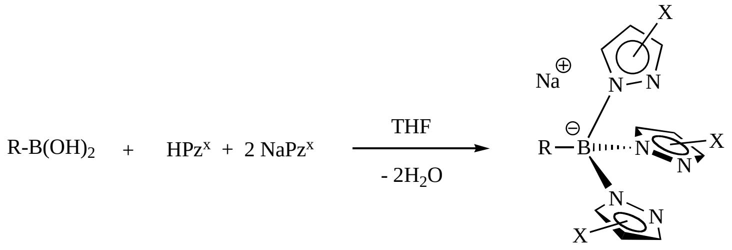


Fig. (9). Synthesis of $Na[RB(pz^x)_3]$ ligands.

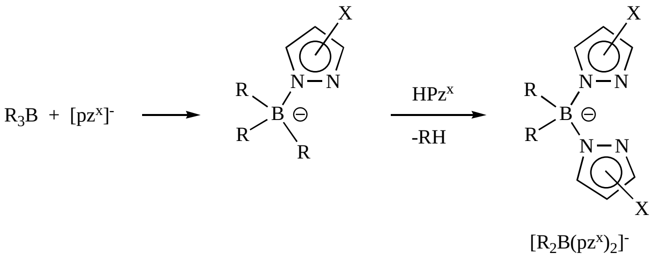


Fig. (10). Synthesis of $[R_2B(pz^x)_2]^-$ ligands.

Bis(pyrazolyl)borate ligands type $[R_2B(pz^x)_2]^-$ may be prepared from trialkylboranes, triarylboranes, or tetraphenylborate ion. A typical reaction of an Ar_3B or R_3B species with pyrazole has to be preceded by the formation of an anionic species $[R_3B(pz^x)]^-$, through the reaction of R_3B with a pyrazolate ion, $[pz^x]^-$. The R groups in $[R_3B(pz^x)]^-$ can be replaced by pz^x groups upon reaction with excess pyrazole (Fig. **10**).

The reaction in Fig. (**10**) generally stops at the di-substitution stage. With high boiling substituted pyrazoles, it can be driven one step further to obtain the $[RB(pz^x)_3]^-$ species. As with the KBH_4 reaction, the pyrazole 3(5)-substituent ends up in the 3-position. It is necessary the presence of sufficient pyrazolate ion, $(pz)^-$, to convert quickly $[R_3B(pz^x)]^-$ to $[R_2B(pz^x)_2]^-$ species, otherwise the $[R_2B(pz^x)]^-$ species will dimerize to the stable pyrazabole $R_2B(\mu\text{-}pz^x)_2BR_2$ (Fig. **11**), which is not readily convertible to scorpionate ligands [105, 106].

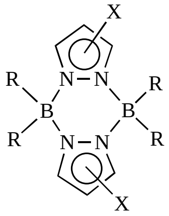


Fig. (11). General structure of pyrazaboles.

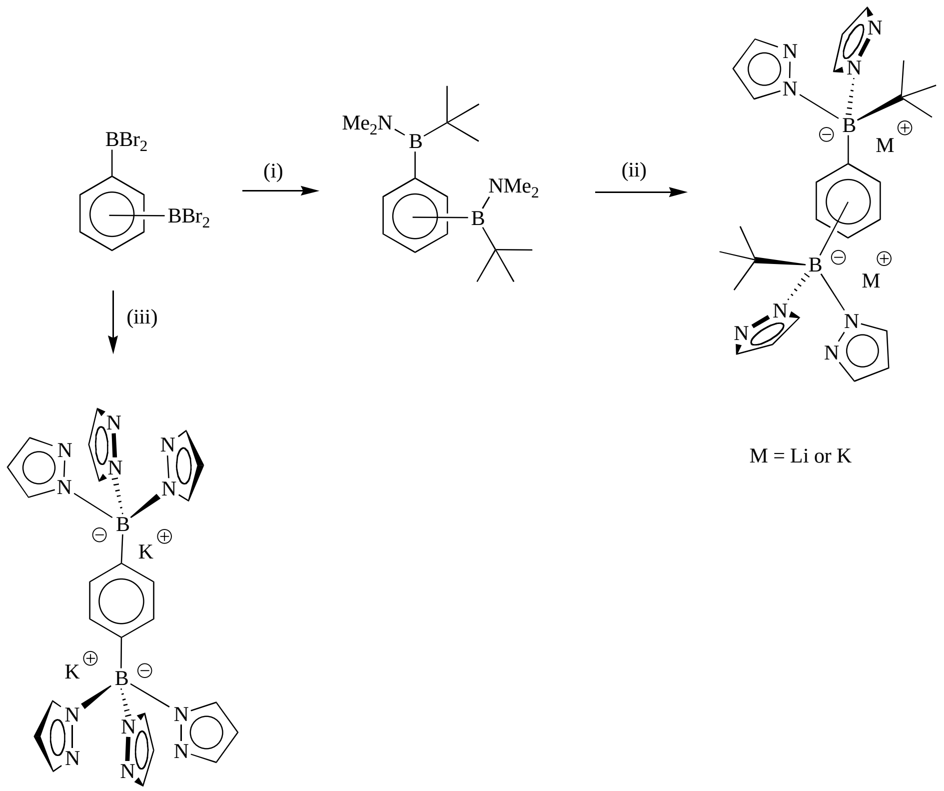


Fig. (12). (i) 10 equiv. of HNMe$_2$, toluene, -78°C to +80°C; + 2 equiv. of BCl$_3$, toluene/heptane, -78°C to r.t.; + 2 equiv. of ^{t}BuLi, toluene, -78°C to r.t. (ii) 2 equiv. of Mpz/2 equiv. of Hpz, toluene, reflux. (iii) 1,4-isomer + 10 equiv. of HNMe$_2$, toluene, -78 to +80°C; 2 equiv. of Kpz/4 equiv. of Hpz, toluene, reflux.

Polytopic poly(pyrazol-1-yl)borate ligands have shown great potential for the preparation of coordination polymers [107-109], multiple-decker sandwich complexes [110-113], metallomacrocycles [114], dinuclear complexes with cooperating metal ions [115-118], and metalloenzyme models [119]. The two ligating sites have been linked together by a direct B−B bond [120-122], the 1,1′-ferrocenylene moiety [97], and the *m*- or *p*-phenylene ring [115].

Starting from 1,4- and 1,3-diborylated benzene derivatives, ditopic poly(1-pyrazolyl)borates (K$_2$[1,4-(^{t}BuBpz$_2$)$_2$C$_6$H$_4$]; M$_2$[1,3-(^{t}BuBpz$_2$)$_2$C$_6$H$_4$] M = Li or K) and tris(1-pyrazolyl)borates (K$_2$[1,4-(Bpz$_3$)$_2$C$_6$H$_4$]) have been synthesized (Fig. **12**) [115, 117].

Recently Wagner *et al.* [118] described the synthesis and full characterization of the ditopic lithium bis(pyrazol-1-yl)borates Li$_2$[*p*-C$_6$H$_4$[B(Ph)(pz^R)$_2$]$_2$] (pz^R = 3-phenylpyrazol-1-yl or 3-*t*-butylpyrazol-1-yl) and they reported unexpected differences in the affinity of their lithium salts towards chloride ions (Fig. **13**).

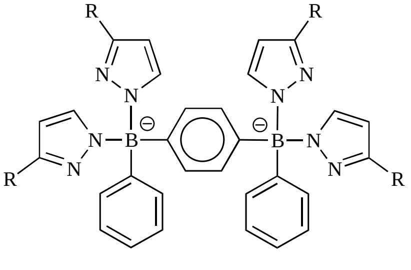


Fig. (13). General structure of ditopic bis(pyrazol-1-yl)borates.

In recent years, oligotopic poly(pyrazol-1-yl)borate ligands with polymeric or dendritic backbones have been prepared. Jäkle *et al.* [123] reported the syntheses of copolymers with different boron loadings by silicon/boron exchange, starting from poly(4-trimethylsilyl)styrene and BBr$_3$; in-situ treatment of the resulting BBr$_2$ functionalized copolymer with a slight excess of Me$_3$SiNMe$_2$ gave the B(NMe$_2$)$_2$-modified random copolymer. The product was converted to the oligotopic poly(pyrazol-1-yl)borate by treatment with pyrazole/sodium pyrazolide (Fig. **14**).

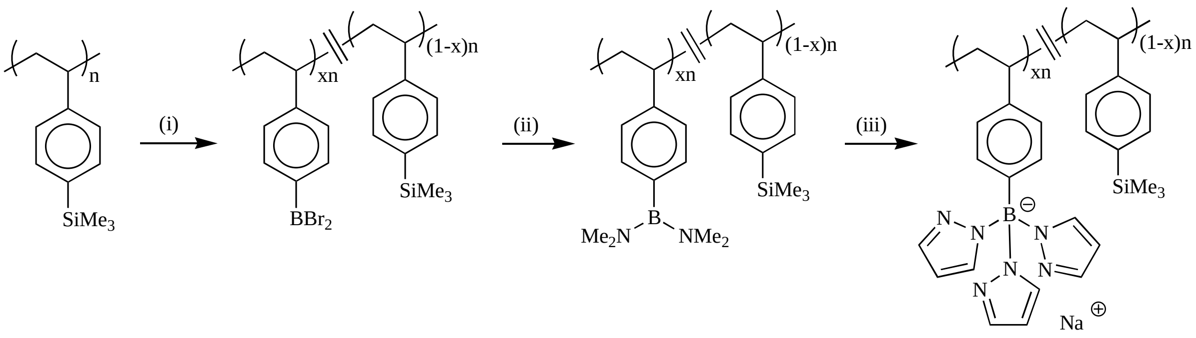


Fig. (14). Synthesis of Tp-functionalized polymers: (i) BBr$_3$, CH$_2$Cl$_2$; (ii) excess of Me$_3$SiNMe$_2$; (iii) 2 HPz, 1 NaPz, THF, 80°C.

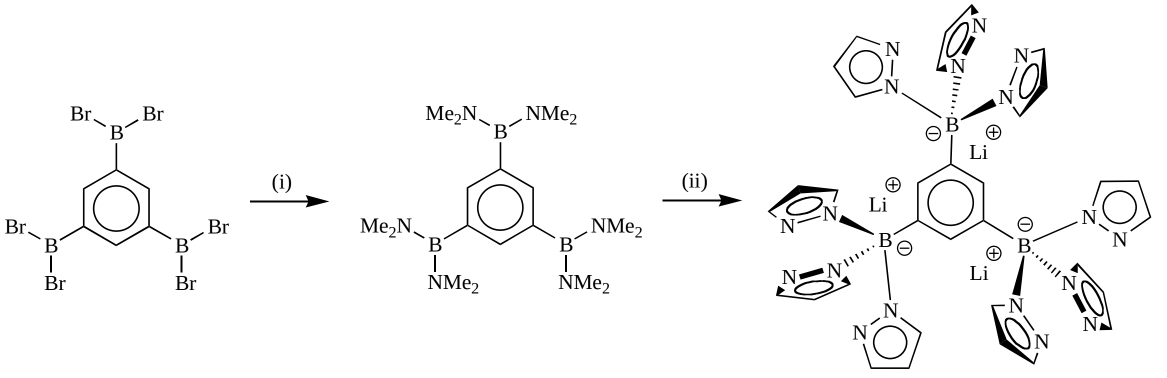


Fig. (15). Synthesis of the tritopic tris(pyrazol-1-yl)borates: (i) 6 Me_3SiNMe_2, toluene, 0°C; (ii) 3 LiPz / 6 HPz, toluene, reflux.

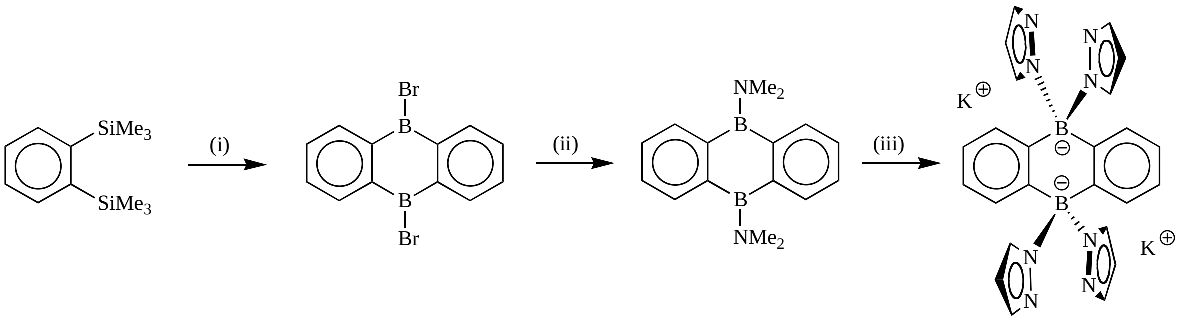


Fig. (16). (i) Excess of BBr_3, toluene, r.t.; (ii) 2 equiv. of Me_3SiNMe_2, toluene, -30°C to r.t.; (iii) 2 equiv. of Kpz/2 equiv. of Hpz, toluene, reflux.

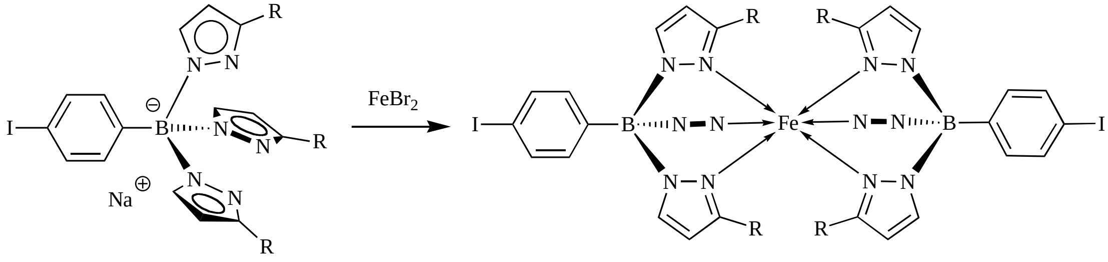


Fig. (17). Synthesis of $Fe[(p\text{-}IC_6H_4)B(pz)_3]_2$ and $Fe[(p\text{-}IC_6H_4)B(3\text{-}Mepz)_3]_2$.

The first tritopic tris(pyrazol-1-yl)borate has been reported by Morawitz *et al.* [124] which is a promising building block for the generation of two-dimensional transition metal aggregates (Fig. **15**).

Simultaneous introduction of $[RBpz_2]^-$ moieties (R = pz, ^{t}Bu) into the positions 1 and 2 of a benzene ring would result in severe steric congestion; overcrowding in hypothetical $[1,2\text{-}(RBpz_2)_2C_6H_4]_2^-$ ligands can, however, be avoided when the two substituents R are replaced by a second bridging 1,2-phenylene bridge as in the 9,10-dihydro-9,10-diboraanthracene-based system $K_2[(Bpz_2)_2(C_6H_4)_2]$ (Fig. **16**) [115].

The ligands $Na[(p\text{-}IC_6H_4)B(3\text{-}Rpz)_3]$ (R = H, Me) have been prepared by converting $I_2C_6H_4$ to $IC_6H_4SiMe_3$ with Li^{t}Bu and $SiMe_3Cl$, and then to $IC_6H_4BBr_2$ with BBr_3 and subsequent reaction with 3 equiv. of unsubstituted pyrazole and 1 equiv. of NaO^{t}Bu. The preparation of the bromophenylsubstituted Tp derivatives $M[p\text{-}BrC_6H_4B(pz)_3]$ (M = Et_3NH, Li) by the reaction of $p\text{-}BrC_6H_4BBr_2$ with pyrazole and a base follows the precedent synthetic procedure developed by Wagner *et al.* [97] and Reger and coworkers [125, 126]. A related method was used by Trofimenko and coworkers to make the transition metal sandwich complexes $[PhB(pz)_3]_2M$ (M = Mn, Fe, Co, Ni, Cu, Zn) from $PhBCl_2$, excess pyrazole and a divalent metal salt [96]. Also, $[p\text{-}BrC_6H_4Tp]Na$ was made by reacting $p\text{-}BrC_6H_4B(OH)_2$ with pyrazole and sodiumpyrazolide [127]. The ligands $Na[(p\text{-}IC_6H_4)B(pz^R)_3]$ react with $FeBr_2$ to give either purple, low-spin $Fe[(p\text{-}IC_6H_4)B(pz)_3]_2$ or colorless, high-spin $Fe[(p\text{-}IC_6H_4)B(3\text{-}Mepz)_3]_2$ derivatives (Fig. **17**) [128].

The compound $Fe[(p\text{-}IC_6H_4)B(pz)_3]_2$ was smoothly converted to the dialkynylated bitopic $Fe[(pz)_3CCH_2OCH_2\text{-}C_2\text{-}C_6H_4B(\kappa^3\text{-}N,N',N''\text{-}pz)_3]_2$ by reaction with $HC_2CCH_2OCH_2C(pz)_3$ (Fig. **18**, (i)) and a similar reaction with $3,5\text{-}[(pz)_3CCH_2OCH_2]_2C_6H_3(C_2H)$ yields the tetratopic metalloligand $Fe[\{3,5\text{-}[(pz)_3CCH_2OCH_2]_2 C_6H_3C_2\}C_6H_4B(\kappa^3\text{-}N,N',N''\text{-}pz)_3]_2$ (Fig. **18**, (ii)) by using Sonogashira coupling reactions [128].

The platinum trimethyl complex of a benzoic acid-functionalized hydrotris(pyrazolyl)borate ligand $[p\text{-}(HO_2C)C_6H_4B(pz)_3]PtMe_3$ has been synthesized from the corresponding p-bromo complex $[p\text{-}BrC_6H_4B(pz)_3]PtMe_3$. The complex $[p\text{-}(HO_2C)C_6H_4B(pz)_3]PtMe_3$ may be readily coupled to biomolecules such as amino acids as exemplified by coupling to L-phenylalanine-*tert*-butyl ester to provide $[p\text{-}(^tBuO\text{–}Phe\text{–}CO)C_6H_4B(pz)_3]PtMe_3$ (Fig. **19**) [129]. As an extension of these studies Metzer-Nolte *et al.* reported the coupling between transition metal $[p\text{-}(HO_2C)C_6H_4B(pz)_3]$ complexes and biomolecules and also reported the solid-phase synthesis, isolation, and characterization of the la-

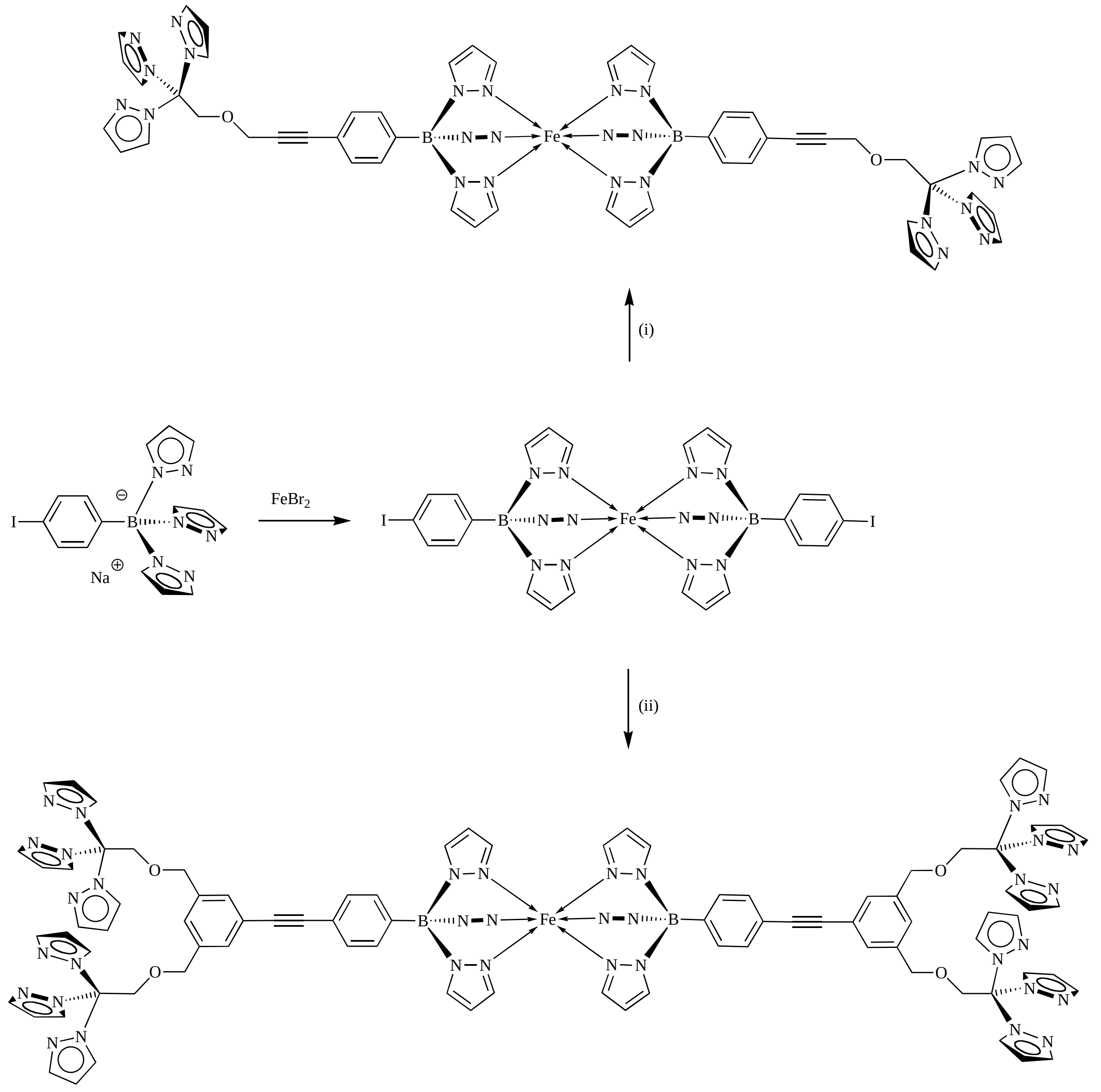


Fig. (18). (i) $HC_2CH_2OCH_2C(pz)_3$, $Pd(PPh_3)_2Cl_2$ (5 mol%), CuI (8 mol%), THF/piperidine; (ii) 3,5-$[(pz)_3CCH_2OCH_2]_2C_6H_3(C_2H)$, $Pd(PPh_3)_2Cl_2$ (5 mol%), CuI (9 mol%), THF/piperidine.

beled Enkephalin (Enk = -Tyr-Gly-Gly-Phe-Leu-) derivatives, [p-(Enk-OH)$COC_6H_4B(pz)_3$]$PtMe_3$ and [p-(Enk-OH)COC_6H_4B(3-Mepz)$_3$]$Re(CO)_3$ [130]. More recently several differently substituted mixed ligand sandwich complexes CpRu[(p-BrC_6H_4)$B(pz)_3$], CpRu[(p-BrC_6H_4)B(3-Mepz)$_3$], Cp*Ru[(p-BrC_6H_4)$B(pz)_3$], Cp^{iPr}Ru [(p-BrC_6H_4)B(3-Mepz)$_3$], incorporating cyclopentadienyl (Cp) and functionalized tris(pyrazolyl)borate ligands, have been synthesized and characterized. Air-stable Cp^{iPr}Ru[p-$BrC_6H_4B(pz)_3$] has been converted to benzoic acid-functionalized Cp^{iPr}Ru[p-$(CO_2H)C_6H_4$)B (pz)$_3$] and it has been coupled to the pentapeptide Enkephalin, to provide Cp^{iPr}Ru[p-(CO-Tyr-Gly-Gly-Phe-Leu-OH)$C_6H_4B(pz)_3$] as the first example of a mixed ligand sandwich ruthenium bioconjugate [131]. These studies are the first examples of Tp bioconjugates made using solid-phase peptide synthesis (SPPS).

Casado *et al.* reported a synthetic strategy leading to an allyl-bis(pyrazolyl)borate ligand, Li(TMED)[$CH_2{=}CHCH_2B(pz)_2$], bi-functionalized with a phosphine group [132] and an allyl-tris(pyrazolyl)borate K[$CH_2{=}CHCH_2B(pz)_3$] (Fig. **20**) [133].

The boron compound $CH_2{=}CHCH_2B(O^iPr)_2$ [99] is a highly versatile reagent, whose allyl group provides the linking to carbosilane dendrimers through a platinum-catalyzed hydrosilylation process; it has been linked to the periphery of a carbosilane dendrimer, resulting in the polyanionic dendrimer $[Li(TMED)]_4[Si\{(CH_2)_3SiMe_2(CH_2)_3B(CH_2PPh_2)(pz)_2\}_4]$ (Fig. **21**) [132].

The extension of this approach to the chemistry of tris(pyrazolyl)borate systems has allowed the preparation of stable dendritic polyanionic assemblies up to the third generation. The procedure

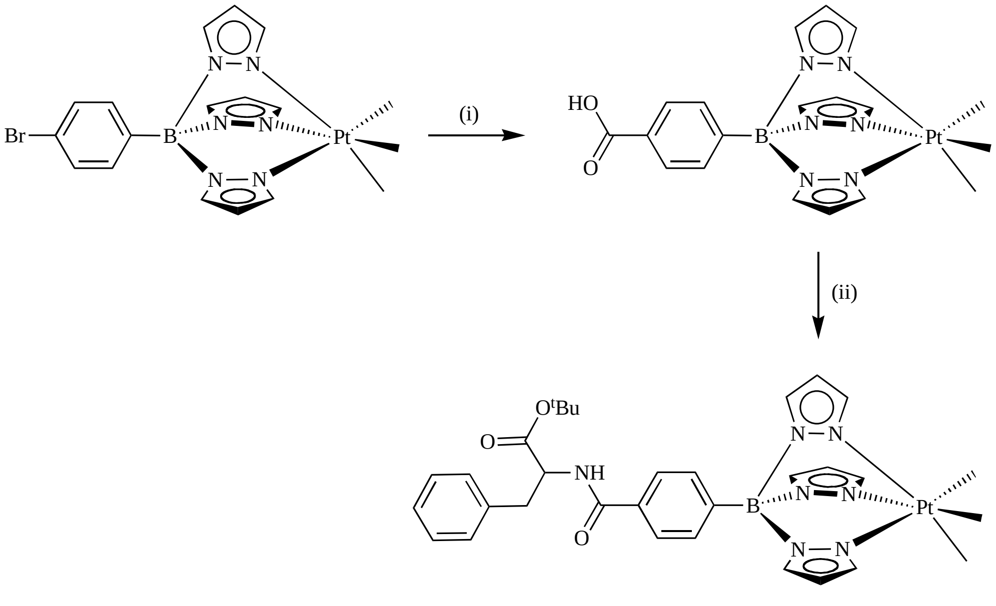


Fig. (19). (i) ^{n}BuLi, -78°C in THF, CO_2 (s), HCl (aq); (ii) N,N'-diisopropylethylamine, O-(1H-benzotriazo-1-yl)-N,N,N',N''-tetramethyluronium tetrafluoroborate (TBTU), L-phenylalanine-*tert*-butyl ester hydrochloride in CH_2Cl_2 at r.t.

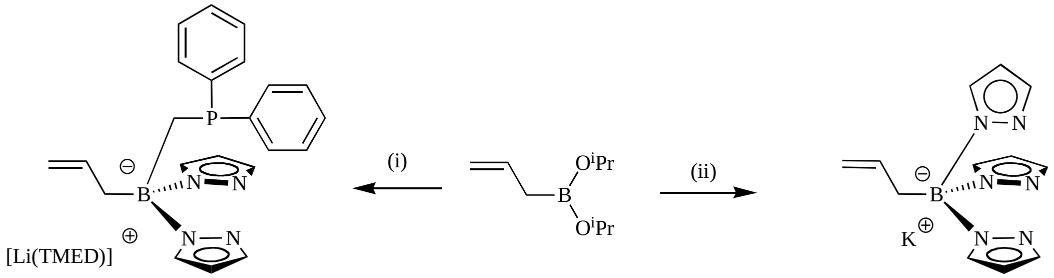


Fig. (20). (i) [Li(TMED)][CH_2PPh_2], 2 HPz, toluene; (ii) Kpz + 2 Hpz, refluxing toluene.

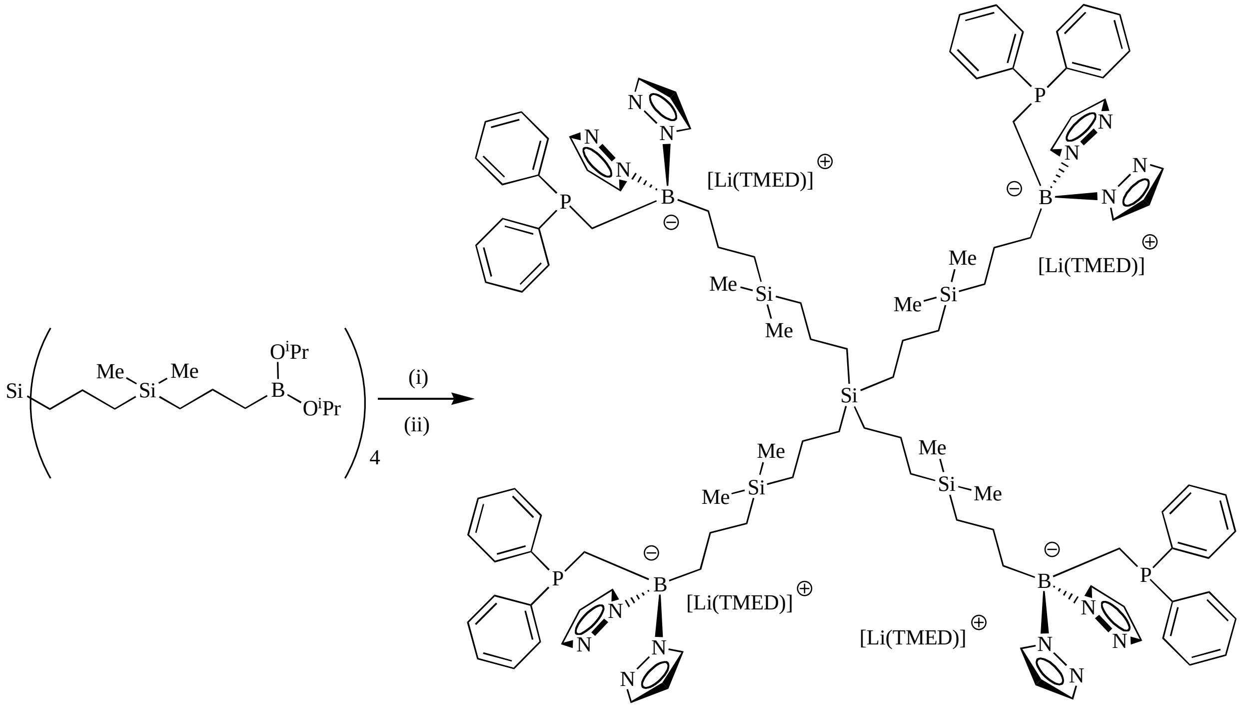
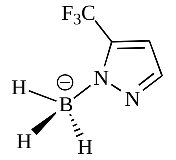
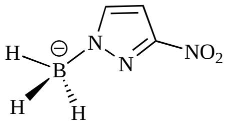
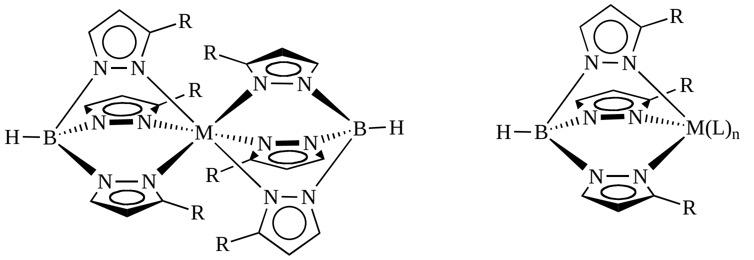


Fig. (21). (i) [Li(TMED)][CH_2PPh_2], toluene; (ii) Hpz, refluxing toluene.

Table 1. $[H_3B(pz^x)]^-$

No.	Abbreviation and References	Structure
1	$[H_3B(5\text{-}(CF_3)pz)]^-$ [91]	
2	$[H_3B(3\text{-}(NO_2)pz)]^-$ [192]	



(a) (b)

Fig. (22). General structure of $Tp^x{}_2M$ and $Tp^xM(L)_n$ complexes.

consists of platinum catalyzed hydrosilylation reactions involving the borate compound $CH_2{=}CHCH_2B(O^iPr)_2$ and carbosilane dendritic cores adapted with terminal Si–H functionalities [134, 135] using the Karstedts catalyst, $[O(SiMe_2CH{=}CH_2)_2]_3Pt_2$ to give selectively the anti-Markovnikov addition products. Then, the dendritic intermediate $Si[(CH_2)_3SiMe_2(CH_2)_3B(O^iPr)_2]_4$ was reacted with four molar equiv. of potassium pyrazolate and pyrazole in excess in refluxing toluene to give the tetraanionic dendrimer $K_4[Si\{(CH_2)_3SiMe_2(CH_2)_3B(pz)_3\}_4]$, peripherally functionalised with four tris(pyrazolyl)borate groups. Following this synthetic protocol, the anionic dendrimers $K_8[Si[(CH_2)_3SiMe\{(CH_2)_3SiMe_2(CH_2)_3B(pz)_3)\}_2]_4]$ and $K_{16}[Si[(CH_2)_3SiMe\{(CH_2)_3SiMe[(CH_2)_3SiMe_2(CH_2)_3B(pz)_3]_2\}_2]_4]$ containing tris(pyrazolyl)borates on their peripheries were straightforwardly obtained by reaction of the dendritic borates with potassium pyrazolate and pyrazole under the appropriate molar ratio [133].

Procedures for the synthesis of specific and differently substituted poly(pyrazolyl)borates are given in the references in Tables **1-16**.

4. PROPERTIES OF POLY(PYRAZOLYL)BORATES

In a $M[Tp^x]$ fragment the x substituents protrude in space past the metal, enveloping it, and forming a protective pocket of varying size and shape. Then, evaluation of the size of the variously substituted Tp^x ligands is more important for developing and understanding of the influence of pyrazolyl ring substituents on the chemistry of their metal complexes. Ligand size can be evaluated by the concept of *cone angle* (θ). Refinements to the original method of cone angle determination, which was originally introduced for phosphine ligands [136], which attempt to take into account steric demand changes accompanying orientational variations have been introduced. The smaller the cone angle, and the larger the wedge angle, the easier it is for other ligands coordination to the metal. Because of this feature, the proper choice of 3-R substituents does adjust the steric accessibility of the coordinated metal, in this fashion controlling the coordination chemistry of the Tp^xM species [6, 137-140]. All of the Tp ligands have a cone angle (θ) larger then 180°, and the trends in the values of these angles were consistent with the trends in the coordination chemistry of the Tp^x ligands. Indeed, the ligands of small cone angle (i.e. $[HB(pz)_3]$, $[HB(3\text{-}Mepz)_3]$, etc.) are characterized by a strong tendency to form $Tp^x{}_2M$ (Fig. **22**, (**a**)) complexes with divalent first row transition metals, and the inability to form stable $Tp^xM(L)_n$ species (Fig. **22**, (**b**)) [6, 12, 14, 16, 17, 19, 21, 22].

Ligands having an intermediate cone angle (i.e. $[HB(3\text{-}^iPrpz)_3]$, $[HB(3\text{-}Phpz)_3]$, etc.) are capable of forming both $Tp^x{}_2M$ and Tp^xMX species. Indeed, coordination of a solvent (sol) molecule or stronger binding of an additional TpM unit to form five-coordinate $(Tp^x)MX(sol)$ or $(Tp^x)M(\mu\text{-}L)_nM(Tp^x)$ dimers, respectively, are possible [141-143]. The most sterically demanding ligands (i.e., $[HB(3\text{-}^tBupz)_3]$, $[HB(3\text{-}Mspz)_3]$, etc.) inhibit formation of $(Tp^x)_2M$ and heavily favour four-coordinate compounds $(Tp^x)MX$ with C_{3v}-distorted tetrahedral geometries [144]. The cone angles depend not only on the ligand itself, but also on the length of the N-M bond. The choice of thallium complexes $(Tp^x)Tl$, the structures of which have been established by X-ray crystallography as “standard” systems for calculating the cone angles, seemed to be the best choice. These specifications can be used to establish a relative steric hierarchy for the various Tp^x ligands [21]. The combined results from experimental studies in which the structures, spectroscopic properties, and reactivity of a number of metal complexes were examined and in some cases directly compared, can be summarized by the following series according to effective steric bulk at a complexed metal center [17]:

$$Tp^{Cy} > Tp^{4Bo,3Me} > Tp^{Cy,4Br} > Tp^{Cpe} > Tp^{tBu} > Tp^{tBu,Me} \approx Tp^{iPr,4Br} > Tp^* > Tp^{(CF3)2} > Tp^{4Bo,3Me} > Tp^{Br3} \approx Tp^{Cbu} > Tp^{Cpr} > Tp$$

Comparison of the structure, physical and spectroscopic properties of similar compounds with homologous ligands provides insight into the relative electron-donating or electron-withdrawing capabilities of Tp^x ligands. Much of these experimental data has been collected during efforts to compare tris(pyrazolyl)borate ligands with their formally iso-electronic analogues cyclopentadienyls [145-150]. In particular $M(Cp^x)(CO)_3$ and $M(Tp^x)(CO)_3$ radicals and anions (M = Cr, Mo, and W), have been employed to derive a series of electrodonating ability. Tp^x ligands seem stronger electron donors and the following trend in ligand electronreleasing

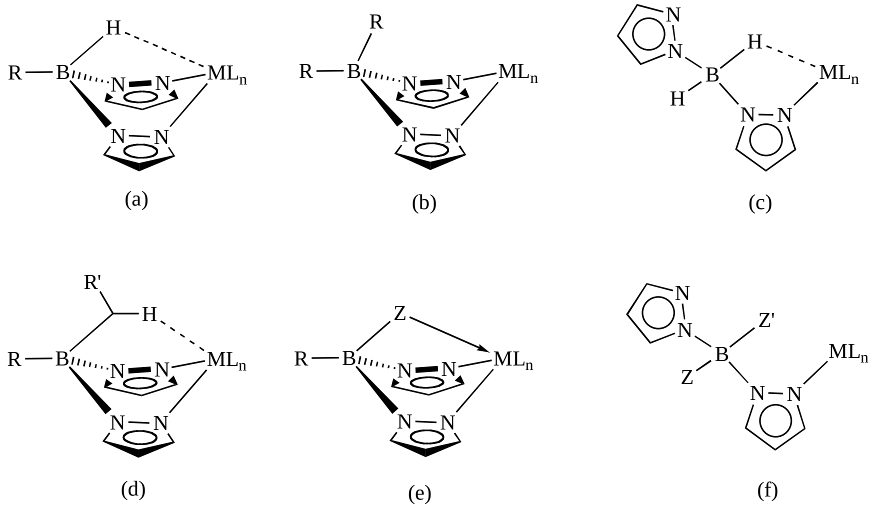


Fig. (23). Coordination modes in poly(pyrazolyl)borate complexes.

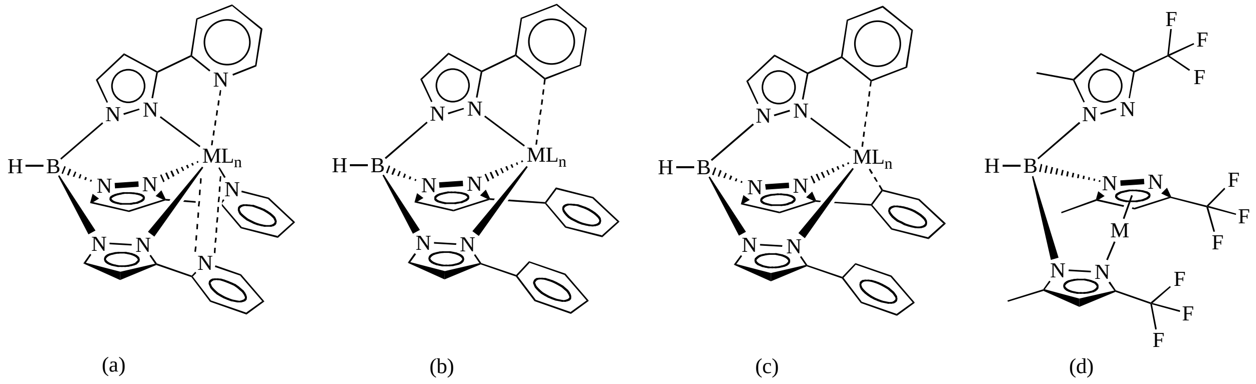


Fig. (24). Coordination modes of 3-substituted tris(pyrazolyl)borate complexes.

capability: [HB(3,5-Me$_2$pz)$_3$] > [HB(pz)$_3$] ≈ Cp* > Cp has been proposed. However, conflicting reports can be found in the literature on the electron-donating properties of [HB(3,5-Me$_2$pz)$_3$] and [HB(pz)$_3$] in comparison to Cp and Cp* [151]. Tellers and coworkers [152] have summarized data useful in comparing the electron-density at Tp^x- and Cp^x-bearing metal centers. A consistent trend across the periodic table in the relative electrondonating abilities of these two important ligand classes is clearly lacking. Instead, the electron donor ability varies with the identity of the metal, its oxidation state, and the other ligands of the complex. These differences are undoubtedly the result of differences in the bonding nature of Tp^x and Cp^x: Tp^x is a weak-field ligand possessing relatively hard nitrogen σ-donors, while Cp^x is relatively soft and capable of re-donation. Tp^x also strictly enforces an octahedral geometry about the metal center, in contrast to Cp^x. As reported by Kitajima and Tolman [17] the relative electron-donating or electron-releasing properties of the more hindered Tp^x ligands can be gained by comparing ν(CO) data for sets of like metal carbonyl complexes [Tp^x]M(CO)$_n$, that differ only in their pyrazolyl ring substituents: Tp^{x}Cu(CO) [153-155], η^2-Tp^{x}Rh(CO)$_2$ [138], η^3-Tp^{x}Rh(CO)$_2$ [82], (NEt$_4$)[TpW(CO)$_3$] [148, 156] and Tp^{x}Mo(CO)$_2$(NO) [157]. Higher values for the carbonyl stretching frequencies reflect less electron density at the metal center and decreased electron donation by the Tp^x ligand for compounds within each set.

Poly(pyrazolyl)borate ligands are so popular due to their reliability and accountability as spectator ligands, which normally do not interfere with the reaction scenarios occurring at the metal centers. Tris(pyrazolyl)borates, Tp^x, generally coordinate as tridentate ligands κ^3-N,N’,N” (Fig. **22**, (**b**)), through three nitrogen atoms of the pyrazole rings thereby providing effective steric shielding of the metal center. Besides the very common κ^3-N,N’,N” coordination mode, the tridentate κ^3-N,N’,B-H type (Fig. **23**, (**a**)) [158], the bidentate κ^2-N,N’ (Fig. **23**, (**b**)) [159] and κ^2-N,B-H coordination (Fig. **23**, (**c**)) [160-162] are also known; Santini and coworkers have recently reported the synthesis of a new class of trihydro(5-trifluoromethyl-pyrazolyl)borates able to coordinate to metals in κ^2-N,B-H fashion [91].

In contrast to the relatively easy formation of agostic B-H-M bonds with Bp^x ligands, the formation of agostic B-C-H-M (Fig. **23**, (**d**)) bonds does not occur very frequently [163]. The [R(Z)H$_2$B(pz^x)]$^-$ ligands are generally tridentate, due to the presence of a heteroatom Z which can, and does, coordinate to the metal (Fig. **23**, (**e**)). The [R(Z)H$_2$B(pz^x)]$^-$ ligands also include those where Z is a pyrazolyl group, provided it is different from pz^x, and is not its regioisomer. Lower denticity, such as κ^1-*N*, has been also reported (Fig. **23**, (**f**)) [164, 165]. Recently, Carmona *et al.* were able to prove a denticity changes in a rhodium pyrazolylborate system and thereby isolate the first ionic complex containing a κ^0-Tp^x ligand as an uncoordinated counter ion [166]. It was possible to interconvert Tp^x-κ^3*N*, κ^2*N*, κ^1*N*, and κ^0 complexes; the stepwise change in the denticity of pyrazolylborate ligands from κ^3 to κ^0 may have important implications in catalytic uses of Tp^x metal complexes. Expansion of Tp^x denticity beyond κ^3 can occur by way of the 3-R substituent containing donor atoms, as in the demonstrably hexadentate tris[3-(2-pyridyl)pyrazolyl]borate lanthanoids and actinoids complexes (Fig. **24**, (**a**)) [167, 168], or in the potentially hexadentate ligands tris[3-(2-methoxyphenyl)pyrazolyl]borate, [HB(3-(An)pz)$_3$]$^-$ [169] or tris[(dimethoxyphenyl)pyrazolyl]borate,

$[HB((2,4\text{-}(OMe)_2Ph)pz)_3]^-$ [170]. On the other hand, tetradenticity has been reported in Tp^x ligands where R doesn't contain donor atoms, either by way of agostic bonding [171], or through cyclometalation taking place at one of the aliphatic R groups per ligand (Fig. **24**, (**b**)) [172]. Recently Slugovc *et al.* [173] have reported an example of unusual κ^5 coordination of hydrotris(3-phenylpyrazolyl)borate ligands ($[HB(3\text{-}Phpz)_3]^-$) (Fig. **24**, (**c**)). Yet another entirely new aspect of scorpionate coordination chemistry is the η^5 coordination of a pyrazole ring. Despite the formal similarities with the cyclopentadienyl ligands a π interaction between a pyrazolylborate ligand and a metal center has been recently reported only in a complex of composition $[\{K[HB((3\text{-}CF_3\text{-}5\text{-}Me)pz)_3]\}_2(CuCO_3)]_2$ (Fig. **24**, (**d**)) [174].

5. OPTICALLY ACTIVE LIGANDS

The well-established ability of tris(pyrazolyl)borate ligands to strongly bind metal combined with the pronounced steric effects of substituents at the 3-position of the pyrazolyl rings on the properties of the resulting metal complexes, has led to target novel optically active variants of generalized structure Tp^{R*} (Fig. **25**) for synthetic studies [175, 176].

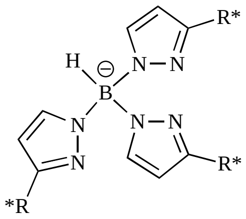


Fig. (25). General structure of optically active Tp^{R*} ligands.

The C_3-symmetric array of stereogenic centers in Tp^{R*} is designed to afford an unusual chiral "fence" about a coordinated metal ion that may induce interesting and potentially useful stereoselective metal-mediated reactivity [177] and chiral recognition [178]. Chiral derivatives of tris(pyrazolyl)borates have been studied principally by Tolman and co-workers, who have investigated the synthesis and coordination behaviour of several chiral tris(pyrazolyl)borate ligands [175, 176, 179] and the use of their complexes in asymmetric catalysis [180, 181]. All of the known chiral Tp^{R*} ligands are potentially tridentate, with a chiral unit such as camphoryl or menthyl fused to two sites of the pyrazolyl ring, such that the coordination behaviour of the ligand is basically that of a conventional but sterically hindered Tp^x ligand [17].

The synthesis and structural characterization of several metal complexes of a relatively small class of such ligands derived via standard synthetic methods from (+)/(-)-camphor ($[HB(camphpz)_3]^-$ [182] and $[(BBN)Bp^{+/-camph}]^-$ [183]), (2*S*,5*R*)-(-)-menthone ($[Tp^{Menth}]^-$) or (*R*)-(+)-pulegone ($[Tp^{Mementh}]^-$) [171, 175, 179] were reported (see Table **16**): they are specific examples of ligands that have the particular advantages of being accessible from readily available precursors and of having stereogenic centers of fixed orientation resulting from their incorporation into fused ring systems [175]. Ligands analogous to $[Tp^{Menth}]^-$ and $[Tp^{Mementh}]^-$ but with aryl instead of simple branched alkyl substituents proximal to the metal binding site are particularly attractive; in particular they could more thoroughly modulate the nature of the chiral cavity provided by the strongly binding Tp^x unit and could give edgeface and/or face-face aromatic interactions in substrate recognition processes [184]. In this context, the (4*R*,7*R*)-4-methyl-7-phenyl-4,5,6,7-tetrahydro-2*H*-indazole, with a phenyl substituent, was employed in the synthesis of enantiopure, multidentate C_1-symmetric bis(pyrazolyl)diphenylborate (Tl[*cis*-Ph_2Bp^{pm}]) and C_3-symmetric tris(pyrazolyl)borate (K[*trans*-Tp^{pm}]) ligands (see Table **16**) [180]. Interestingly, epimerization of the benzylic stereogenic center occurred during the synthesis of K[*trans*-Tp^{pm}]. Comparison of the abilities of copper complexes of the [*cis*-$Ph_2Bp^{pm}]^-$ and [*trans*-$Tp^{pm}]^-$ ligands to catalyze the cyclopropanation of styrene by ethyldiazoacetate revealed significantly enhanced enantioselectivity for the [*trans*-$Tp^{pm}]^-$ system. This result represents the first example of a high degree of enantiocontrol in a catalytic reaction of any complex of a Tp^x ligand and provides experimental support for the possible efficacy of higher order rotational symmetry in metal-mediated stereoselective reactions [180].

Table 2. $[H_2B(pz^x)_2]^-$

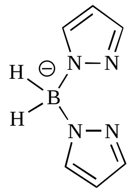
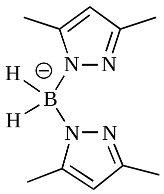
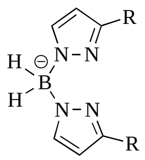
No.	Abbreviation and References	Structure
3	Bp or $[H_2B(pz)_2]^-$ [193]	
4	Bp* or $[H_2B(3,5\text{-}Me_2pz)_2]^-$ [96]	
5	R = Me: $[H_2B(3\text{-}Mepz)_2]^-$ [78]	
6	R = ^{i}Pr: $[H_2B(3\text{-}^iPrpz)_2]^-$ [84]	
7	R = ^{t}Bu: $[H_2B(3\text{-}^tBupz)_2]^-$ [76]	
8	R = Ph: $[H_2B(3\text{-}Phpz)_2]^-$ [76]	
9	R = Ferrocenyl: $[H_2B(3\text{-}Fcpz)_2]^-$ [194]	
10	R = CF_3: $[H_2B(3\text{-}(CF_3)pz)_2]^-$ [95]	
11	R = NO_2: $[H_2B(3\text{-}(NO_2)pz)_2]^-$ [95]	
12	R = 2-Pyridyl: Bp^{2Py} [195]	
13	R = 3-Pyridyl: Bp^{3Py} [196]	
14	R = 4-Pyridyl: Bp^{4Py} [196]	
15	R = Bipyridyl: Bp^{Bipy} [197]	

Table 2. contd…

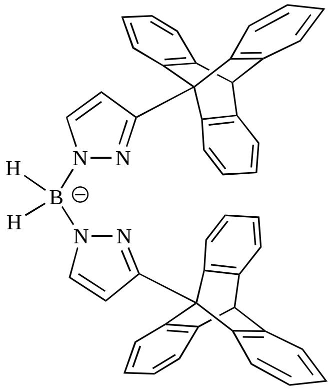
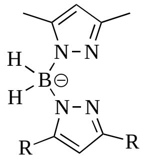
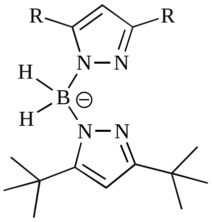
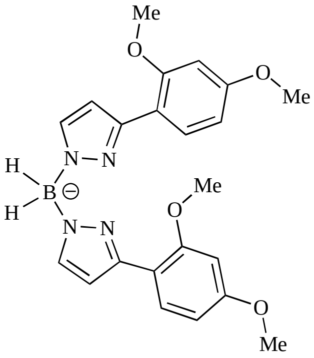
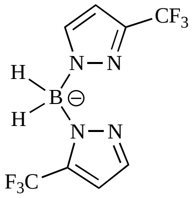
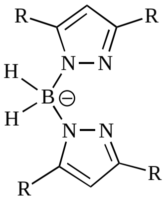
No.	Abbreviation and References	Structure
16	Bp^{trip} [198]	
17 18	R =H: [$H_2B(pz)(3,5\text{-}Me_2pz)]^-$ [74] R = Ph: [$H_2B(3,5\text{-}Me_2pz)(3,5\text{-}Ph_2pz)]^-$ [74]	
19 20 21	R = H: [$H_2B(pz)(pz^{tBu2})]^-$ [75] R = Me: [$H_2B(pz^{Me2})(pz^{tBu2})]^-$ [75] R = Tripticyl: [$H_2B(pz^{trip})(pz^{tBu2})]^-$ [75]	
22	$Bp^{[2,4(OMe)2Ph]}$ [170]	
23	[$H_2B(3\text{-}(CF_3)pz)(5\text{-}(CF_3)pz)]^-$ [92]	
24 25	R = CF_3: [$H_2B(3,5\text{-}(CF_3)_2pz)_2]^-$ [199] R = Et: [$H_2B(3,5\text{-}Et_2pz)_2]^-$ [200]	

Table 2. contd…

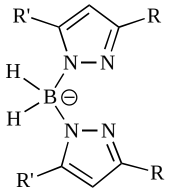
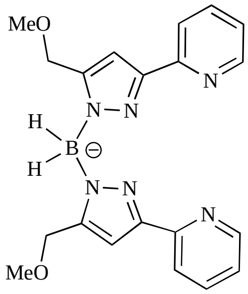
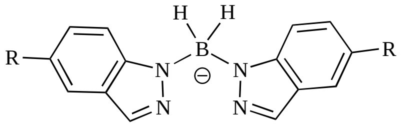
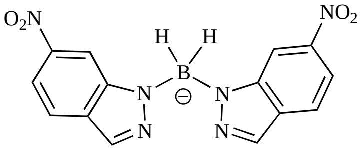
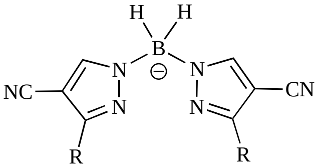
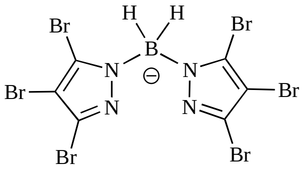
No.	Abbreviation and References	Structure
26 27	R = COOEt, R' = CH_3: $\mathrm{Bp}^{\mathrm{COOET,Me}}$ [201] R = ^{t}Bu, R' = ^{i}Pr: $\mathrm{Bp}^{\mathrm{tBu,iPr}}$ [202]	
28	$\mathrm{Bp}^{\mathrm{(COC)Py}}$ [203]	
29 30 31	R = H: $\mathrm{Bp}^{\mathrm{4Bo}}$ [204] R = NO_2: $\mathrm{Bp}^{\mathrm{4Bo,5NO2}}$ [205] R = NH_2: $\mathrm{Bp}^{\mathrm{4Bo,5NH2}}$ [206]	
32	$\mathrm{Bp}^{\mathrm{4Bo,6NO2}}$ [207]	
33 34	R = H: $\mathrm{Bp}^{\mathrm{4CN}}$ [208] R = Ph: $\mathrm{Bp}^{\mathrm{Ph,4CN}}$ [209]	
35	$\mathrm{Bp}^{\mathrm{Br3}}$ [210]	

Table 3. $[(R)HB(pz^{x})_2]^{-}$

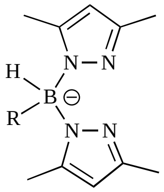
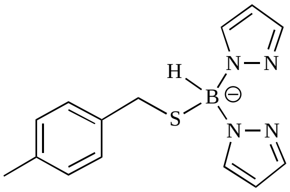
No.	Abbreviation and References	Structure
36 37	R = Cp: $[(C_5H_4)HB(3,5\text{-}Me_2pz)_2]^{-}$ [211] R = p-Tol-S: (p-TolS)Bp* [212]	
38	(MeBzS)Bp [213]	

Table 3. contd…

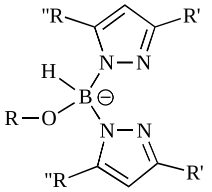
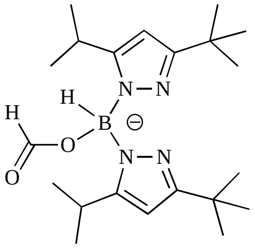
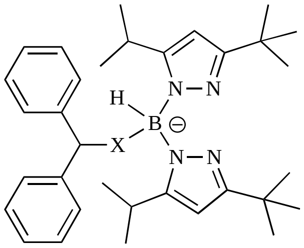
No.	Abbreviation and References	Structure
39	R = Me, R’ = R” = H: [(MeO)HB(pz)$_2$]$^-$ [214]	
40	R = Me, R’ = R” = Me: [(MeO)HB(3,5-Me$_2$pz)$_2$]$^-$ [214]	
41	R = Me, R’ = ^{t}Bu, R” = ^{i}Pr: (MeO)Bp^{tBu,iPr} [202]	
42	R = Et, R’ = R” = H: [(EtO)HB(pz)$_2$]$^-$ [214]	
43	R = Et, R’ = R” = Me: [(EtO)HB(3,5-Me$_2$pz)$_2$]$^-$ [214]	
44	R = Me, R’ = ^{t}Bu, R” = H: [HB(MeO)(3-^{t}Bupz)$_2$]$^-$ [215]	
45	R = Et, R’ = ^{t}Bu, R” = H: [HB(EtO)(3-^{t}Bupz)$_2$]$^-$ [215]	
46	R = ^{i}Pr, R’ = ^{t}Bu, R” = H: [HB(^{i}PrO)(3-^{t}Bupz)$_2$]$^-$ [215]	
47	R = ^{i}Pr, R’ = ^{i}Pr, R” = Me: [HB(^{i}PrO)(3-^{i}Pr-5-Mepz)$_2$]$^-$ [216]	
48	(HCOO)Bp^{tBu,iPr} [217]	
49	X = O: (Ph$_2$CHO)Bp^{tBu,iPr} [218]	
50	X = S: (Ph$_2$CHS)Bp^{tBu,iPr} [218]	

Table 4. [R$_2$B(pz^x)$_2$]$^-$

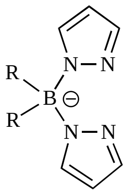
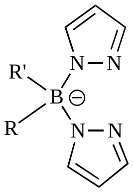
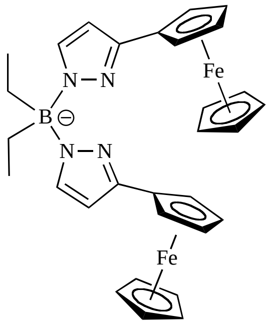
No.	Abbreviation and References	Structure
51	R = Me: Me$_2$Bp [219]	
52	R = Et: Et$_2$Bp [96]	
53	R = Pr: Pr$_2$Bp [220]	
54	R = Bu: Bu$_2$Bp [96]	
55	R = Ph: Ph$_2$Bp [96]	
56	R = MeO: (MeO)$_2$Bp [214]	
57	R = EtO: (EtO)$_2$Bp [214]	
58	R = Ferrocenyl: [Fc$_2$B(pz)$_2$]$^-$ [112]	
59	R = Ph, R’ = NMe$_2$: [(Me$_2$N)PhB(pz)$_2$]$^-$ [221]	
60	R = Ferrocenyl, R’ = Me: [Fc(Me)Bpz$_2$]$^-$ [112]	
61	[(C$_2$H$_5$)$_2$B(3-Fcpz)$_2$]$^-$ [194]	

Table 4. contd…

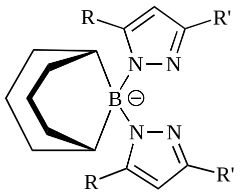
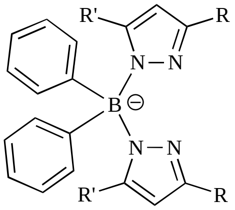
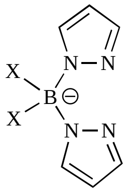
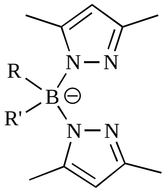
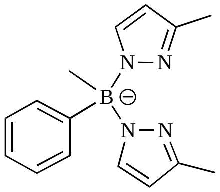
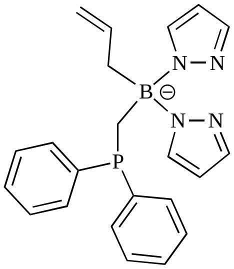
No.	Abbreviation and References	Structure
62	R = R’ = H: (BBN)Bp [222]	
63	R = H, R’ = Me: (BBN)Bp^{Me} [223]	
64	R = H, R’ = Ph: (BBN)Bp^{Ph} [224]	
65	R = H, R’ = Ferrocenyl: (BBN)Bp^{Fc} [194]	
66	R = R’ = Me: (BBN)Bp* [224]	
67	R = Me, R’ = Ph: (BBN)Bp^{Ph,Me} [224]	
68	R = R’ = Ph: (BBN)Bp^{Ph2} [224]	
69	R = Ph, R’ = H: Ph$_2$Bp^{Ph} [225]	
70	R = ^{t}Bu, R’ = H: Ph$_2$Bp^{tBu} [225]	
71	R = Ph, R’ = Me: Ph$_2$Bp^{Ph,Me} [225]	
72	X = Cl: Cl$_2$Bp [226]	
73	X = Br: Br$_2$Bp [226]	
74	X = I: I$_2$Bp [226]	
75	R = R’ = F: F$_2$Bp* [96]	
76	R = ^{t}Bu, R’ = H: ^{t}BuBp* [104]	
77	(Me)(Ph)Bp^{Me} [99]	
78	[(CH$_2$=CHCH$_2$)(CH$_2$PPh$_2$)B(pz)$_2$]$^-$ [132]	

Table 5. $[HB(3\text{-}Rpz)_3]^-$

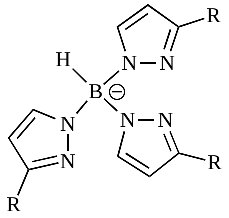
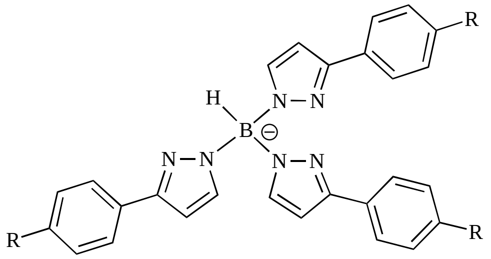
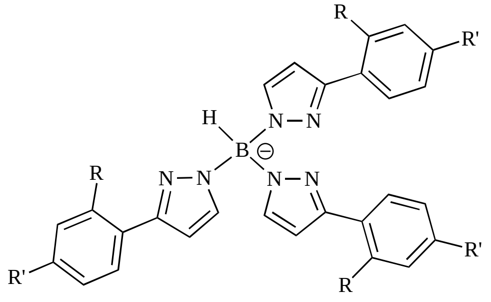
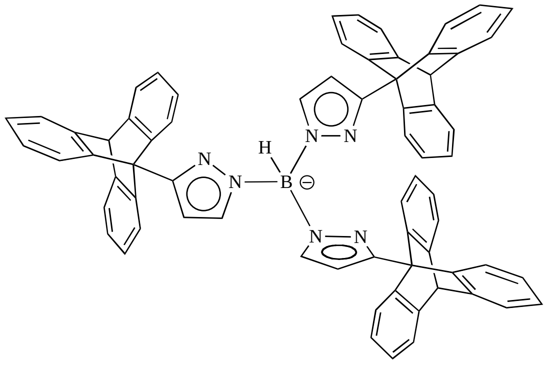
No.	Abbreviation and References	Structure
79	R= H: Tp or $[HB(pz)_3]^-$ [72, 193]	
80	R = Me: $[HB(3\text{-}Mepz)_3]^-$ [79]	
81	R = ^{i}Pr: $[HB(3\text{-}^iPrpz)_3]^-$ [84]	
82	R = ^{t}Bu: $[HB(3\text{-}^tBupz)_3]^-$ [76]	
83	R = Ph: $[HB(3\text{-}Phpz)_3]^-$ [76]	
84	R = $CHPh_2$: Tp^{CHPh2} [227]	
85	R = Neopentyl: $[HB(3\text{-}nppz)_3]^-$ [228]	
86	R = Cyclopropyl: Tp^{Cpr} [140]	
87	R = Cyclobutyl: Tp^{Cbu} [229]	
88	R = Cyclopentyl: Tp^{Cpe} [229]	
89	R = Ciclohexyl: $[HB(3\text{-}Cypz)_3]^-$ [230, 231]	
90	R = Mesityl: Tp^{Ms} [82]	
91	R = CF_3: $[HB(3\text{-}(CF_3)pz)_3]^-$ [232, 233]	
92	R = C_2F_5: $[HB(3\text{-}(C_2F_5)pz)_3]^-$ [234]	
93	R = C_3F_7: $[HB(3\text{-}(C_3F_7)pz)_3]^-$ [234]	
94	R = 2-thienyl: $[HB(3\text{-}(2'\text{-thienyl})pz)_3]^-$ [137]	
95	R = 3-Pyridyl: Tp^{3Py} [196]	
96	R = 4-Pyridyl: Tp^{4Py} [196]	
97	R = ^{t}BuPy, R' = H: Tp^{tBuPy} [203]	
98	R = 4-benzonitrile: Tp^{4Bz} [235]	
99	R = Carboxypyrrolidido: Tp^{cpd} [236]	
100	R = $C(CH_3)_2CH_2OCH_3$: $Tp^{C(Me2)CH2OMe}$ [237]	
101	R = Me: $[HB(3\text{-}(4\text{-}Tol)pz)_3]^-$ [144, 238]	
102	R = F: $[HB(3\text{-}(4\text{-}FC_6H_4)pz)_3]^-$ [239]	
103	R = OMe: Tp^{pAn} [144, 239]	
104	R = OMe, R' = H: Tp^{An} [169, 240]	
105	R = R' = OMe: $Tp^{[2,4(OMe)2Ph]}$ [170]	
106	R = SMe, R' = H: $[HB(3\text{-}(2\text{-}MeSPh)pz)_3]^-$ [241]	
107	Tp^{Trip} [198]	

Table 5. contd…

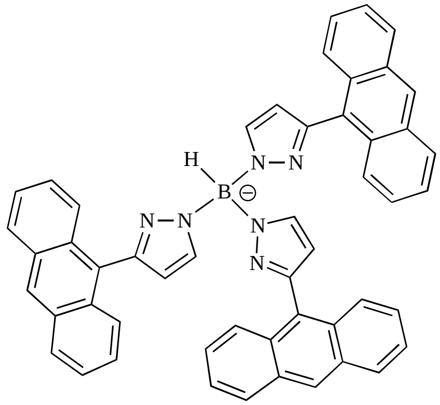
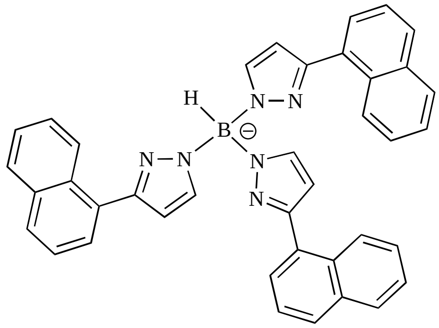
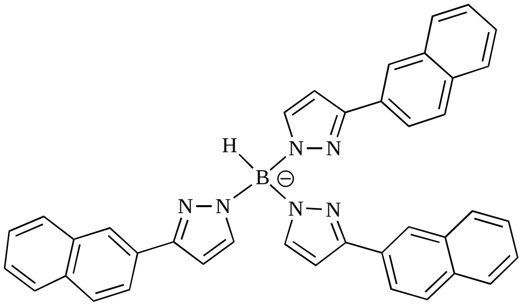
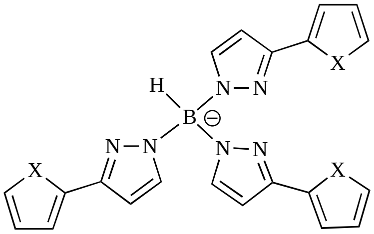
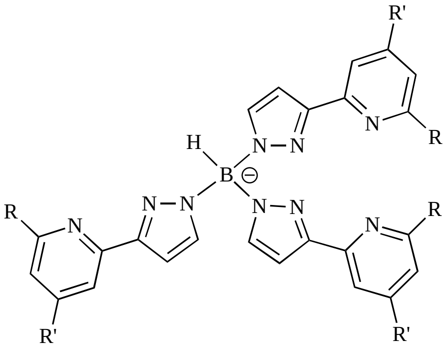
No.	Abbreviation and References	Structure
108	Tp^{Ant} [242]	
109	Tp$^{\alpha Nt}$ [243, 244]	
110	Tp$^{\beta Nt}$ [243, 244]	
111 112	X = O: [HB(3-(2-furyl)pz)$_3$]$^-$ [239] X = S: [HB(3-(2-thienyl)pz)$_3$]$^-$ [137]	
113 114 115	R' = H, R = H: [HB(3-(2'-pyridyl)pz)$_3$]$^-$ [167, 241] R' = H, R = Me: [HB(3-(6-Mepy)pz)$_3$]$^-$ [241, 245] R' = ^{t}Bu, R =H: Tp^{BuPy} [203]	

Table 6. [HB(4-Rpz)$_3$]$^-$

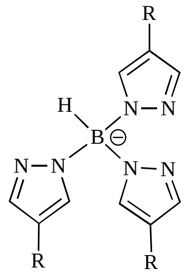
No.	Abbreviation and References	Structure
116	R = Me: [HB(4-Mepz)$_3$]$^-$ [246]	
117	R = ^{i}Pr: [HB(4-^{i}Prpz)$_3$]$^-$ [96]	
118	R = ^{t}Bu: Tp^{4tBu} [247]	
119	R = Cl: [HB(4-Clpz)$_3$]$^-$ [96]	
120	R = Br: [HB(4-Brpz)$_3$]$^-$ [248]	

Table 7. [HB(3R,4R'-pz)$_3$]$^-$

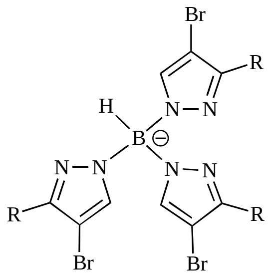
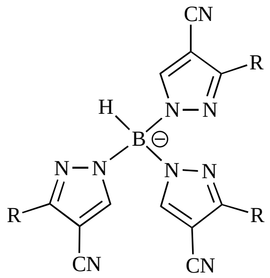
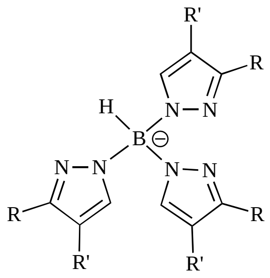
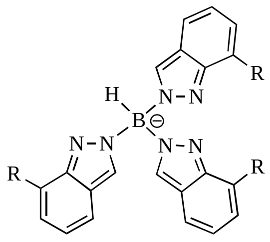
No.	Abbreviation and References	Structure
121	R = ^{i}Pr: Tp^{iPr,4Br} or [HB(3-^{i}Pr-4-Br-pz)$_3$]$^-$ [84]	
122	R = Cy: Tp^{Cy,4Br} [231]	
123	R = p-ClPh: Tp$^{p\text{-}ClPh,4Br}$ [89]	
124	R = Ph: Tp^{Ph,4CN} [249]	
125	R = ^{t}Bu: Tp^{tBu,4CN} [250]	
126	R = Bz, R' = Ph: Tp^{Bz,4Ph} [251]	
127	R = ^{i}Pr, R' = ^{t}Bu: Tp^{iPr,4tBu} [247]	
128	R = p-Tolyl, R' = ^{t}Bu: Tp^{Tol,4tBu} [247]	
129	R = Me: Tp^{3Bo,7Me} [88]	
130	R = ^{t}Bu: Tp^{3Bo,7tBu} [88, 252]	

Table 7. contd…

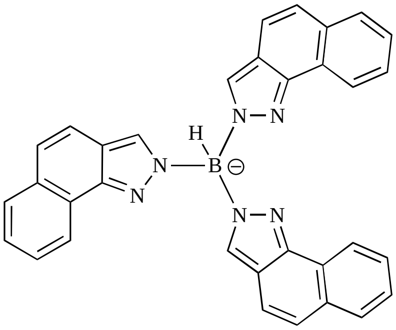
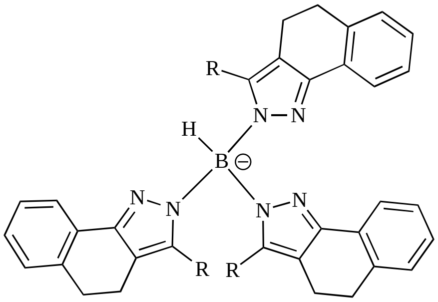
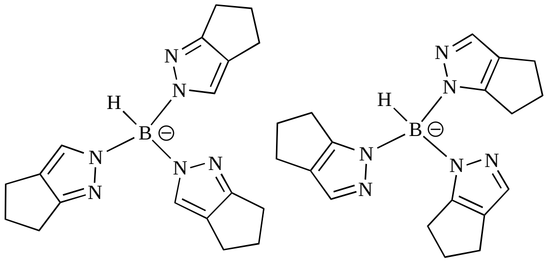
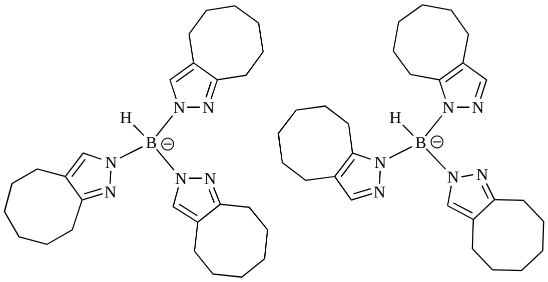
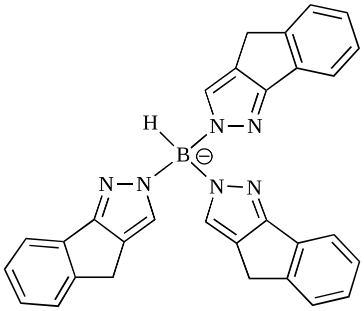
No.	Abbreviation and References	Structure
131	Tp^{a}* [88]	
132 133	R = H: Tp^{a} [138] R = Me: Tp^{a,Me} [138]	
134	Tp$^{(3(5),4\text{-}(CH2)3)}$ [253]	
135	Tp$^{(3(5),4\text{-}(CH2)6)}$ [253]	
136	Tp^{b} [138]	

Table 8. $[HB(3R,5R\text{-}pz)_3]^-$

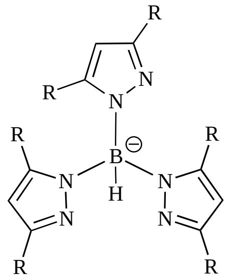
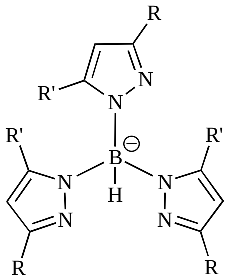
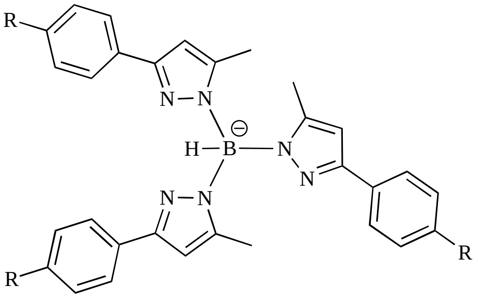
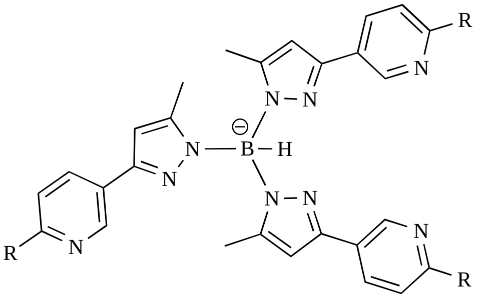
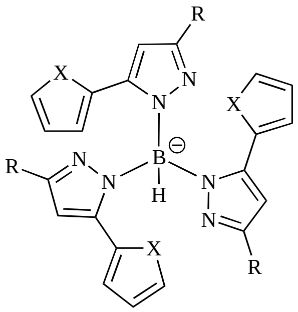
No.	Abbreviation and References	Structure
137	R= Me: Tp* [96]	
138	R= Et: Tp^{Et2} [96]	
139	R = ^{i}Pr: $[HB(3,5\text{-}{}^{i}Pr_2pz)_3]^-$ [254]	
140	R = ^{t}Bu: Tp^{tBu2} [255]	
141	R = CF_3: $[HB(3,5\text{-}(CF_3)_2pz)_3]^-$ [256, 257]	
142	R = Ph: $[HB(3,5\text{-}Ph_2pz)_3]^-$ [254]	
143	R = p-^{t}BuPh: $[HB(3,5\text{-}({}^{t}BuPh)_2pz)_3]^-$ [258]	
144	R = ^{i}Pr, R’ = Me: $[HB(3\text{-}{}^{i}Pr\text{-}5\text{-}Mepz)]^-$ [157]	
145	R = ^{t}Bu, R’ = Me: $Tp^{tBu,Me}$ [144]	
146	R = ^{t}Bu, R’ = ^{i}Pr: $Tp^{tBu,iPr}$ [244]	
147	R = p-Tolyl, R’ = Me: $Tp^{p\text{-}Tol,Me}$ [259]	
148	R = CF_3, R’ = Me: $Tp^{CF3,Me}$ [260]	
149	R = C_2F_5, R’ = Me: $Tp^{C2F5,CH3}$ [261]	
150	R = Ph, R’ = Me: $Tp^{Ph,Me}$ [138]	
151	R = CO_2Et, R’ = Me: $Tp^{CO2Et,Me}$ [262]	
152	R = Mes, R’ = Me: $Tp^{Mes,Me}$ [263]	
153	R = Benzyl, R’ = Me: $Tp^{Bz,Me}$ [251]	
154	R = $(CH_3)_2CC_6H_5$, R’ = Me: $Tp^{Me2Bz,Me}$ [264]	
155	R = Adamantyl, R’ = ^{i}Pr: $Tp^{Ad,iPr}$ [265]	
156	R = ^{i}Pr: $Tp^{Cum,Me}$ [266]	
157	R = ^{t}Bu: $Tp^{(p\text{-}tBuPh,Me)}$ [267]	
158	R = H: $Tp^{3Py,Me}$ [268]	
159	R = Me: $Tp^{3Pic,Me}$ [268]	
160	X = S, R = CF_3: $Tp^{CF3,Tn}$ [86]	
161	X = S, R = Ph: $HB(3\text{-}Ph\text{-}5\text{-}(2’\text{-}thie)pz)_3]^-$ [269]	

Table 8. contd…

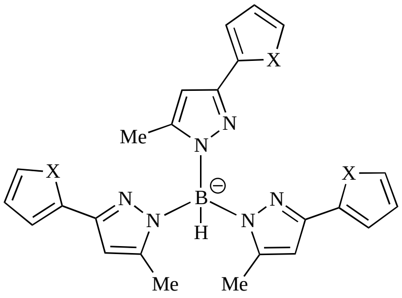
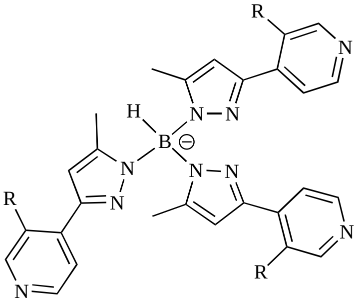
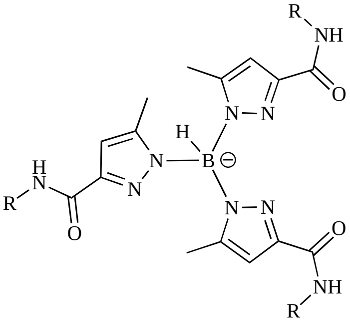
No.	Abbreviation and References	Structure
162 163	X = S: Tp^{Th,Me} [270] X = O: Tp^{Fu,Me} [271]	
164 165	R = H: Tp$^{(4Py),Me}$ [272] R = Me: Tp$^{(4-(2-MePy),Me}$ [272]	
166 167	R = ^{t}Bu: [HB(3-CONH^{t}Bu-5-Mepz)$_3$]$^-$ [272] R = Ph: [HB(3-CONHPh-5-Mepz)$_3$]$^-$ [272]	

Table 9. [HB(4R,5R-pz)$_3$]$^-$

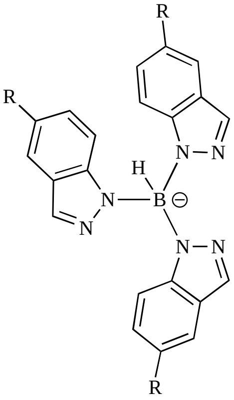
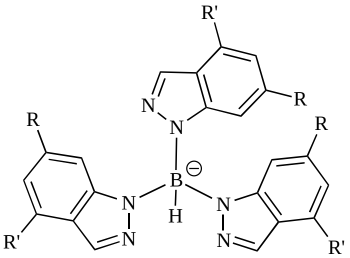
No.	Abbreviation and References	Structure
168 169 170 171 172 173 174	R = H: Tp^{4Bo} [87, 88] R = Me: Tp^{4Bo,5Me} [88] R = Et: Tp^{4Bo,5Et} [88] R = ^{t}Bu: Tp^{4Bo,5tBu} [88] R = Ph: Tp^{4Bo,5Ph} [88] R = NH$_2$: Tp^{4Bo,5NH2} [206] R = NO$_2$: Tp^{4Bo,5NO2} [273]	
175 176 177 178	R = R' = Me: Tp^{4Bo,4,6Me2} [88] R = NO$_2$, R' = H: Tp^{4Bo,6NO2} [207] R = COOEt, R' = H: Tp$^{4Bo,6-COOEt}$ [189] R = CH$_2$SEt, R' = H: Tp$^{4Bo,6-CH2SEt}$ [189]	

Table 10. [HB(3R,4R’,5R”-pz)$_3$]$^-$

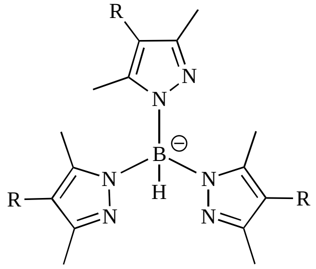
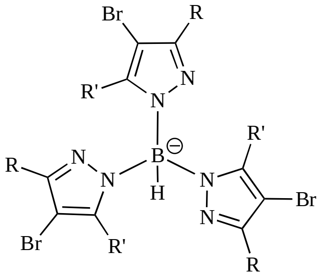
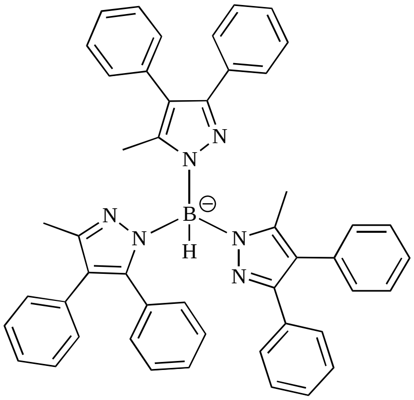
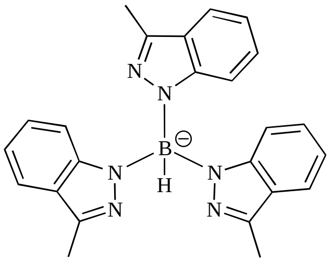
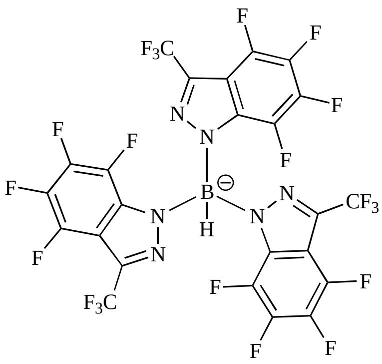
No.	Abbreviation and References	Structure
179	R = Me: Tp*^{Me} [96]	
180	R = Et: Tp*^{Et} [274]	
181	R = ^{n}Bu: Tp*^{Bu} [96, 274]	
182	R = Amyl: Tp*^{Am} [274]	
183	R = Cl: Tp*^{Cl} [275]	
184	R = Br: Tp*^{Br} [276]	
185	R = Benzyl: Tp*^{Bz} [274, 277]	
186	R = R’ = ^{i}Pr: Tp^{iPr2,Br} [278]	
187	R = R’ = Br: Tp^{Br3} [210]	
188	R = Br, R’ = Ph: Tp^{Br,Ph,Br} [89]	
189	R = Br, R’ = p-Tolyl: Tp$^{Br,p\text{-}Tol,Br}$ [89]	
190	R = Br, R’ = p-ClPh: Tp$^{Br,p\text{-}ClPh,Br}$ [89]	
191	R = Ph, R’ = Me: Tp^{Ph,Me,Br} [89]	
192	Tp^{Ph,Me,Ph} [279]	
193	Tp^{4Bo,3Me} [88]	
194	F$_{21}$-Tp^{4Bo,3CF3} [280]	

Table 10. contd…

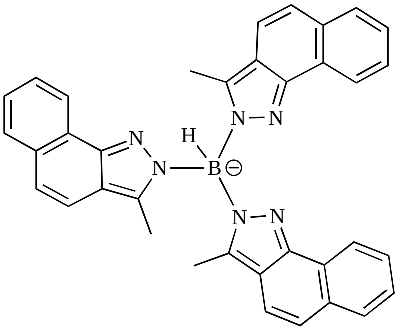
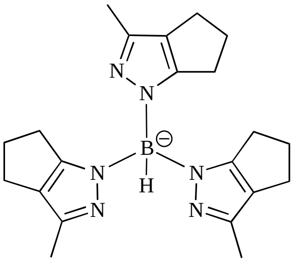
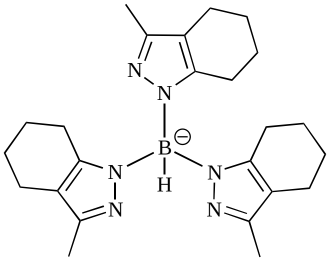
No.	Abbreviation and References	Structure
195	Tp^{a*,3Me} [88]	
196	Tp^{Me,mt3} [281]	
197	Tp^{Me,mt4} [281]	

Table 11. [HB(pz^{x})(pz^{y})$_2$]$^-$

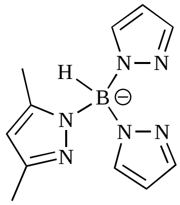
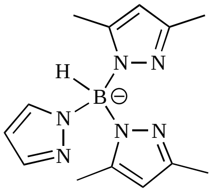
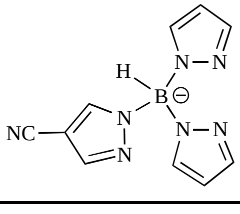
No.	Abbreviation and References	Structure
198	[HB(pz)$_2$(dmpz)]$^-$ [282]	
199	[HB(pz)(dmpz)$_2$]$^-$ [282]	
200	(pz^{4CN})Bp [2]	

Table 11. contd…

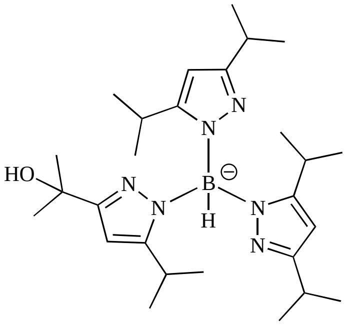
No.	Abbreviation and References	Structure
201	$[HB(3\text{-}Me_2C(OH)\text{-}5\text{-}^iPrpz)(3,5\text{-}^iPr_2pz)_2]^-$ [283]	

Table 12. $[(R)B(pz^x)_3]^-$

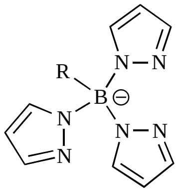
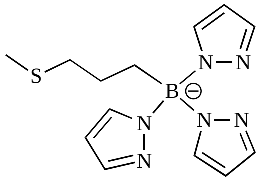
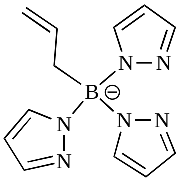
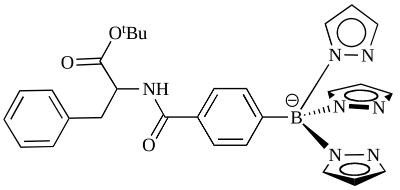
No.	Abbreviation and References	Structure
202	R = Me: MeTp [284]	
203	R = ^{i}Bu: ^{i}BuTp [284]	
204	R = ^{n}Bu: $[BuB(pz)_3]^-$ [96]	
205	R = ^{t}Bu: ^{t}BuTp [104]	
206	R = Ph: $[C_6H_5B(pz)_3]^-$ [96]	
207	R = ^{i}Pr: ^{i}PrTp [98]	
208	R = p-IC_6H_4: $[(p\text{-}IC_6H_4)B(pz)_3]^-$ [125]	
209	R = p-BrC_6H_4: $[(p\text{-}BrC_6H_4)B(pz)_3]^-$ [127]	
210	R = p-$(COOH)C_6H_4$: $[p\text{-}(COOH)C_6H_4B(pz)_3]^-$ [129]	
211	R = p-$Me_3SiC_2C_6H_4$: p-$Me_3SiC_2C_6H_4$Tp [126]	
212	R = p-$PhC_2C_6H_4$: p-$PhC_2C_6H_4$Tp [126]	
213	R = p-$HC_2C_6H_4$: p-$HC_2C_6H_4$Tp [126]	
214	R = C_6D_5: C_6D_5Tp [285]	
215	R = p-Tolyl: p-TolTp [286]	
216	R = m-Tolyl: m-TolTp [286]	
217	R = Ferrocenyl: FcTp [97, 107]	
218	R = Me_2N: $[Me_2NB(pz)_3]^-$ [221, 287, 288]	
219	$CH_3S(CH_2)_3$Tp [103]	
220	$[CH_2{=}CHCH_2B(pz)_3]^-$ [133]	
221	$[p\text{-}(^tBuO\text{–}Phe\text{–}CO)C_6H_4B(pz)_3]^-$ [129]	

Table 12. contd…

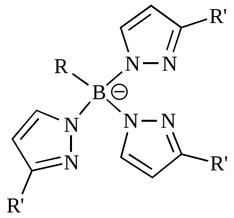
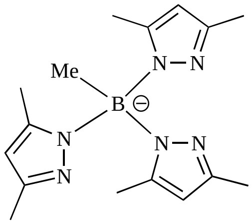
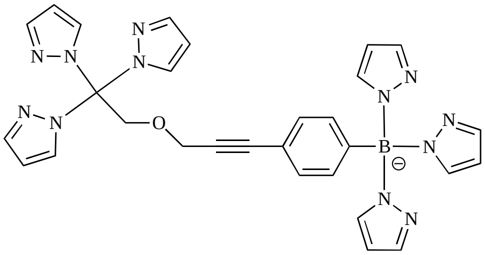
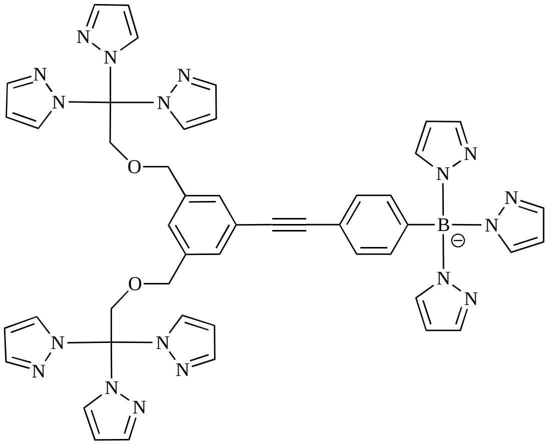
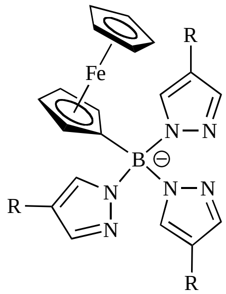
No.	Abbreviation and References	Structure
222	R = R' = Me: MeTp^{Me} [99]	
223	R = Me, R' = CF$_3$: MeTp^{CF3} [289]	
224	R = Me, R' = C$_2$F$_5$: MeTp^{C2F5} [290]	
225	R = Me, R' = mesityl: MeTp^{Ms} [291]	
226	R = Me, R' = ^{t}Bu: MeTp^{tBu} [291]	
227	R = Ph, R' = CF$_3$: PhTp^{CF3} [292]	
228	R = Ph, R' = ^{t}Bu: PhTp^{tBu} [293]	
229	R = ^{t}Bu, R' = Me: ^{t}BuTp^{Me} [104]	
230	R = ^{t}Bu, R' = ^{i}Pr: ^{t}BuTp^{iPr} [104]	
231	R = ^{t}Bu, R' = ^{t}Bu: ^{t}BuTp^{tBu} [104]	
232	R = ^{t}Bu, R' = Ph: ^{t}BuTp^{Ph} [104]	
233	R = p-IC$_6$H$_4$, R' = Me: [(p-IC$_6$H$_4$)B(3-Mepz)$_3$]$^-$ [125]	
234	R = p-Me$_3$SiC$_2$C$_6$H$_4$, R' = Me: [(p-Me$_3$SiC$_2$C$_6$H$_4$)B(3-Mepz)$_3$]$^-$ [126]	
235	R = p-HC$_2$C$_6$H$_4$, R' = H or Me: p-HC$_2$C$_6$H$_4$Tp or p-HC$_2$C$_6$H$_4$Tp^{Me} [126]	
236	R = Ferrocenyl, R' = Me: FcTp^{Me} [294]	
237	R = Ferrocenyl, R' = Ph: FcTp^{Ph} [294]	
238	R = Tetramethylcyclopentadienyl, R' = Me: C$_5$Me$_4$Tp^{Me} [295]	
239	MeTp* [296]	
240	[{(pz)$_3$CCH$_2$OCH$_2$C$_2$}C$_6$H$_4$B(pz)$_3$]$^-$ [128]	
241	[{3,5-[(pz)$_3$CCH$_2$OCH$_2$]$_2$C$_6$H$_3$C$_2$}C$_6$H$_4$B(pz)$_3$]$^-$ [128]	
242	R = Cy: [FcB(pz$^{4\text{-}Cy}$)$_3$]$^-$ [108]	
243	R = CH$_2$Cy: [FcB(pz$^{4\text{-}CH2Cy}$)$_3$]$^-$ [108]	
244	R = SiMe$_3$: [FcB(pz$^{4\text{-}SiMe3}$)$_3$]$^-$ [108]	
245	R = Ph: [FcB(pz$^{4\text{-}Ph}$)$_3$]$^-$ [108]	

Table 12. contd…

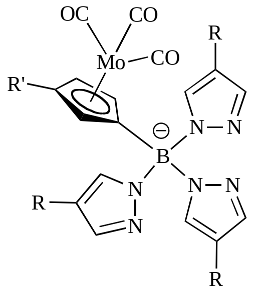
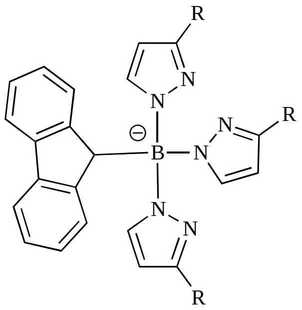
No.	Abbreviation and References	Structure
246	R = R’ = H: [(Cym)B(pz)$_3$]$^-$ [297]	
247	R = H, R’ = Me: [(Cym’)B(pz)$_3$]$^-$ [297]	
248	R = Br, R’ = Me: [(Cym’)B(pz$^{4\text{-Br}}$)$_3$]$^-$ [297]	
249	R = CH$_2$Cy, R’ = Me: [(Cym’)B(pz$^{4\text{-CH2Cy}}$)$_3$]$^-$ [297]	
250	R = H: FlTp [298]	
251	R = ^{t}Bu: FlTp^{tBu} [298]	

Table 13. Unsymmetrical Tp^{x}*

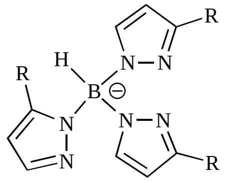
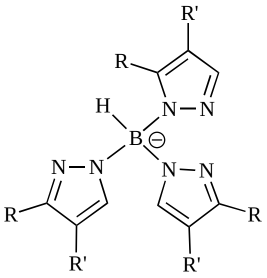
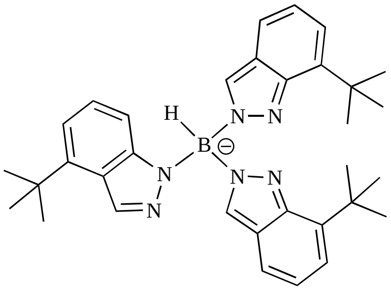
No.	Abbreviation and References	Structure
252	R = Neopentyl: [HB(3-Nppz)$_2$(5-Nppz)]$^-$ [228]	
253	R = Ph: [HB(3-Phpz)$_2$(5-Phpz)]$^-$ [299]	
254	R = Cyclohexyl: Tp^{Cy}* [231]	
255	R = Mesityl: Tp^{Ms}* [82]	
256	R = Cy, R’ = Br: Tp$^{(Cy,4Br)}$* [231]	
257	R = Ph, R’ = CN: Tp$^{(Ph,4CN)}$* [249]	
258	R = ^{i}Pr, R’ = Br: Tp$^{(iPr,4Br)}$* [84]	
259	Tp$^{(3Bo,7tBu)}$* [88]	

Table 13. contd…

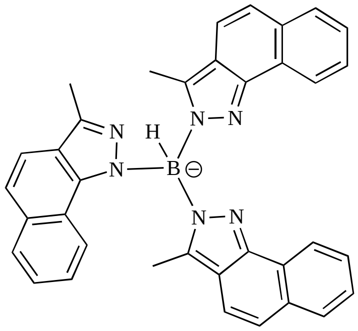
No.	Abbreviation and References	Structure
260	$\mathrm{Tp}^{(a*,3Me)*}$ [88]	

Table 14. $[(pz^x)B(pz^x)_3]^-$

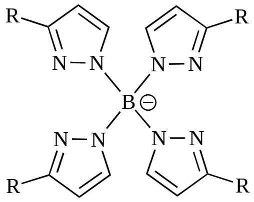
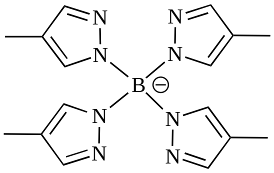
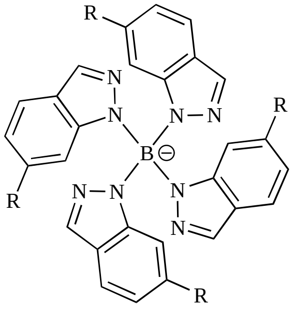
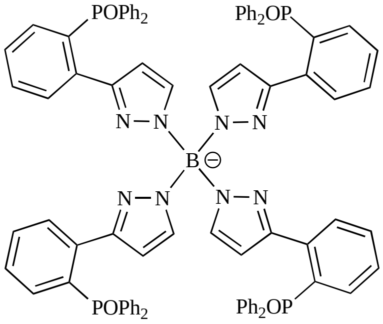
No.	Abbreviation and References	Structure
261	R = H: pzTp [72, 193]	
262	R = Me: $[B(pzMe)_4]^-$ [79]	
263	R = p-Tolyl: $[HB(3\text{-}(4\text{-}Tol)pz)_4]^-$ [144, 238]	
264	R = ^{i}Pr: $[B(3\text{-}^iPrpz)_4]^-$ [84]	
265	R = ^{t}Bu: $[(3\text{-}^tBupz)_4]^-$ [76]	
266	R = Cyclopropyl: pz°Tp^{Cpr} [300]	
267	R = Cyclobutyl: pz°Tp^{Cbu} [229]	
268	R = Cyclopentyl: pz°Tp^{Cpe} [229]	
269	R = Cyclohexyl: pz°Tp^{Cy} [231, 301]	
270	R = p-anisyl: pz°Tp^{An} [301]	
271	R = 3-Pyridyl: pz°Tp^{3Py} [196]	
272	R = 4-Pyridyl: pz°Tp^{4Py} [196]	
273	Pz°Tp^{4Me} [246]	
274	R = H: pz°Tp^{4Bo} [302]	
275	R = NO$_2$: pz°Tp^{4Bo,6NO2} [207]	
276	$[\mathrm{T_kp}^{phos(O)}]^-$ [303]	

Table 15. $[(pz^x)_nR'_zB_m(R)]^{-m}$

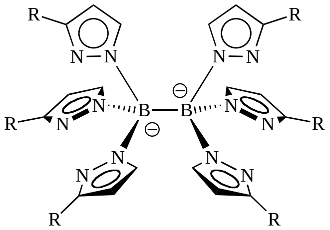
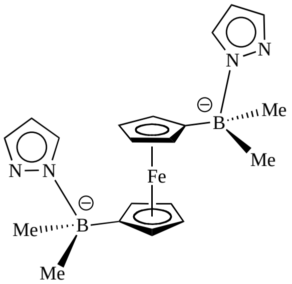
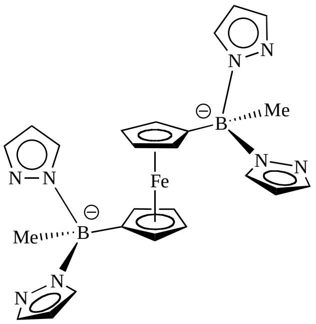
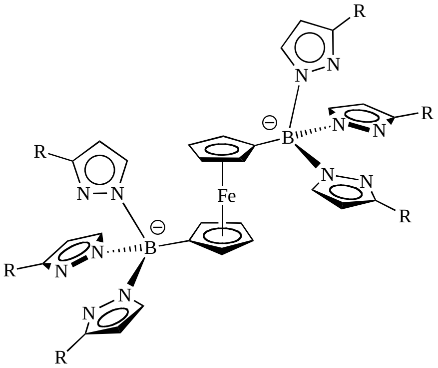
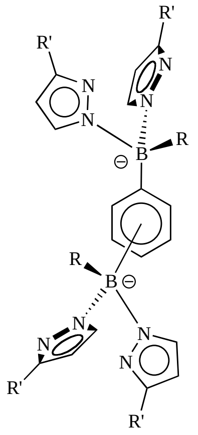
No.	Abbreviation and References	Structure
277 278 279	R = H: $[(pz)_3B\text{-}B(pz)_3]^{2-}$ [120] R = Me: $[(pz^{Me})_3B\text{-}B(pz^{Me})_3]^{2-}$ [121] R = 2-Py: $[(pz^{2\text{-}py})_3B\text{-}B(pz^{2\text{-}py})_3]^{2-}$ [121]	
280	1,1'-fc$[B(Me)_2pz]_2^{2-}$ [111, 113]	
281	1,1'-fc$[B(Me)pz_2]_2^{2-}$ [112]	
282 283 284	R = H: $Fc(Tp)_2$ [108] R = Me: $Fc(Tp^{Me})_2$ [294] R = Ph: $Fc(Tp^{Ph})_2$ [294]	
285 286 287 288	R = ${}^tBu$, R' = H: $[1,4\text{-}({}^tBuBpz_2)_2C_6H_4]^{2-}$ [115] R = ${}^tBu$, R' = H: $[1,3\text{-}({}^tBuBpz_2)_2C_6H_4]^{2-}$ [115] R = Ph, R' = Ph: $[1,4\text{-}(PhBpz^{Ph}{}_2)_2C_6H_4]^{2-}$ [118] R = Ph, R' = ${}^tBu$: $[1,4\text{-}(PhBpz^{tBu}{}_2)_2C_6H_4]^{2-}$ [118]	

Table 15. contd…

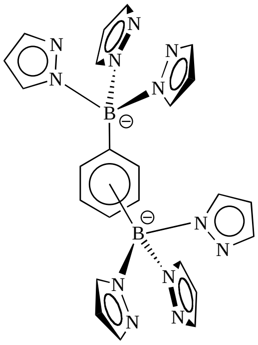
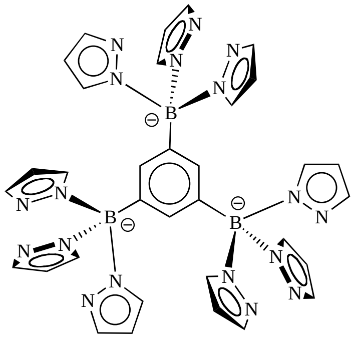
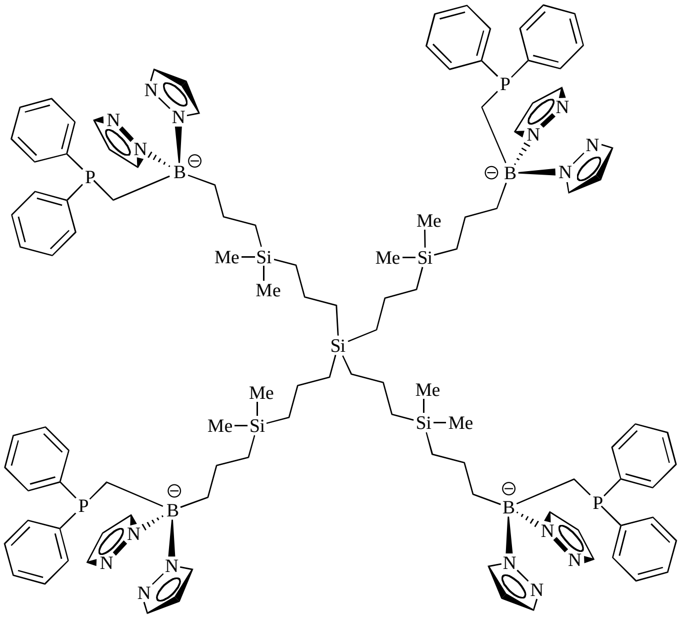
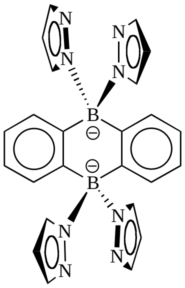
No.	Abbreviation and References	Structure
289 290	$[1,4\text{-}(Bpz_3)_2C_6H_4]^{2-}$ [115] $[1,3\text{-}(Bpz_3)_2C_6H_4]^{2-}$ [124]	
291	$[1,3,5\text{-}(Bpz_3)_3C_6H_3]^{3-}$ [124]	
292	$[Si[(CH_2)_3SiMe_2(CH_2)_3B(CH_2PPh_2)pz_2]_4]^{4-}$ [132]	
293	$[(Bpz_2)_2(C_6H_4)_2]^{2-}$ [115]	

Table 16. Optically Active Tp^{R}*-Type Ligands

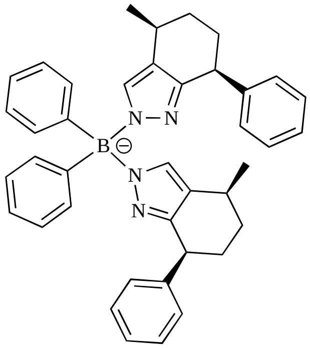
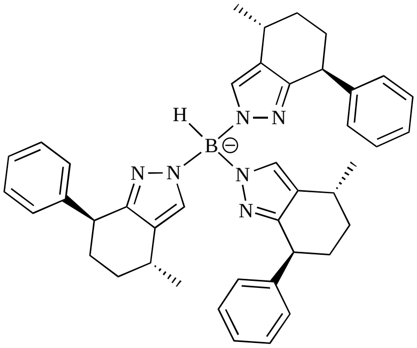
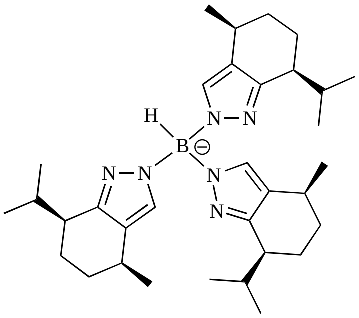
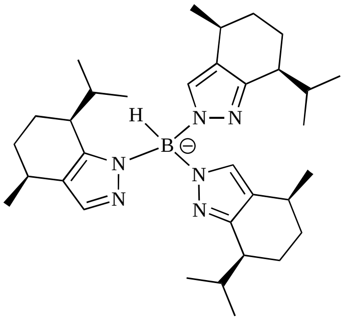
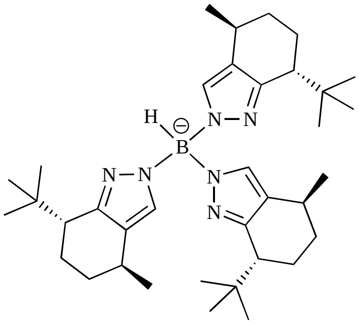
No.	Abbreviation and References	Structure
294	[*cis*-Ph_2Bp^{pm}] [180]	
295	[*trans*-Tp^{pm}] [180]	
296	Tp^{Menth} [179]	
297	Tp^{Menth}* [179]	
298	$Tp^{Mementh}$ [179]	

Table 16. contd…

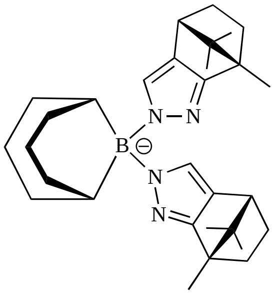
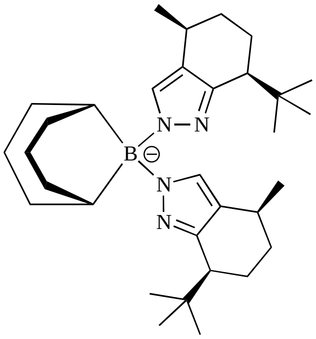
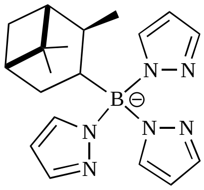
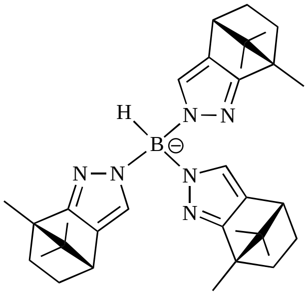
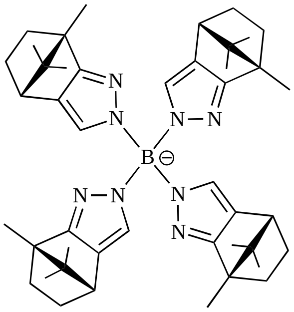
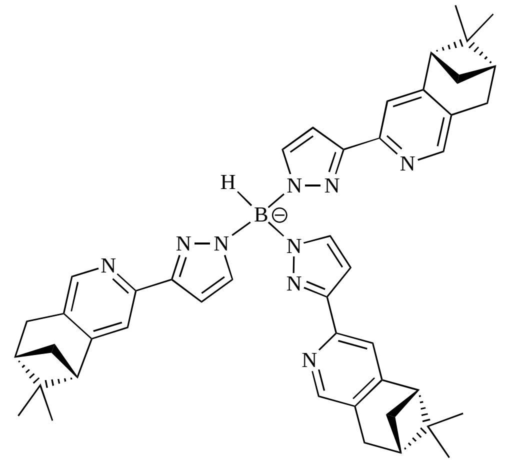
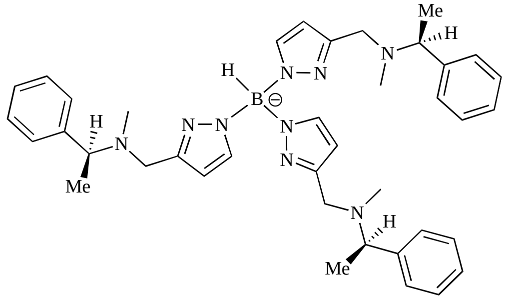
No.	Abbreviation and References	Structure
299	(BBN)Bp$^{+/- \text{ camph}}$ [183]	
300	(BBN)Bp$^{+\text{menth}}$ [183]	
301	IpcTp [304]	
302	[HB(camphpz)$_3$]$^-$ [182]	
303	[B(camphpz)$_4$]$^-$ [182]	

Table 16. contd…

No.	Abbreviation and References	Structure
304	$Tp^{Py}*$ [185]	
305	$[HB(P1)_3]^-$ or $Tp^{CH2N(Me)EtPh}$ [188]	

The first example of a C_3-symmetric *hexadentate* tripodal ligand, tris[3-{2-(pinene[4,5]pyridyl)}pyrazolyl]hydroborate ($[Tp^{Py}*]^-$), based on a tris(pyrazolyl)borate core has been reported by McCleverty and co-workers [185]. The achiral hexadentate parent ligand $[Tp^{Py}]^-$ has been extensively studied [25, 186, 187] and the addition of 2-pyridyl substituents to the C_3 position of the pyrazolyl rings, such that each arm of the ligand is now a bidentate chelate, results in completely different coordination behaviour from the simpler terdentate Tp^x ligands.

Optically active sodium salt of hydrotris((-)-3(5)-methyl-1-phenylethylaminomethylpyrazolyl)borate, $Na[HB(P1)_3]$, was prepared by Singh *et al.* [188] starting from (-)-3(5)-methyl-1-phenylethylaminomethylpyrazole. Its use in various metal-catalysed enantioselective cyclopropanation reactions of styrene and several diazoacetates gave the corresponding *trans*- and *cis*-phenylcyclopropane-1-carboxylates with moderate to reasonably good enantioselectivities [188].

Chiral and C_3-symmetrical hydrotris(indazolyl)borate ligands [189] have also a potential interest in the design of molecular machines, to prepare organometallic molecular turnstiles [190] or as building blocks in the synthesis of a family of surface-mounted electrically-driven molecular motors [63]. In order to conceive an unidirectional rotation in a molecular machine, which is still a challenge nowadays, a strong dissymmetrization of the two directions of rotation is required. In this context, Rapenne *et al.* [191] studied the synthesis of enantiopure chiral pyrazoles for the preparation of C_3-symmetrical hydrotris(pyrazolyl)borate ligands focusing on pyrazoles derived from (5R)-dihydrocarvone.

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TABLES

Structure of ligands and related references. For schematic convenience the ligands are identified with the name originally reported from the authors and the counterions are omitted [6, 70, 71].

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