

Chapter 1

Introduction

1.1. General Considerations

In 1966 Swiatoslaw Trofimenko, while at the Central Research Department of the DuPont Company, began working on boron-pyrazole chemistry. He reported a new class of ligands, the poly(pyrazolyl)borates, of general structure $[\text{RR}'\text{B}(\text{pz}^x)_2]^-$ (Fig. 1.1) ($\text{pz}^x = \text{pyrazol-1-yl}$; R, R' = H, alkyl, aryl or pz^x) which he later named as scorpionates.

These molecules, combining some features of the cyclopentadienyl and β -diketonate ligands, are extremely versatile because the number of pyrazolyl groups and the substituents thereon or at the B center can be easily modified in order to obtain ligands with different steric and electronic profiles. They have been extensively used to prepare complexes of main and transition group metals and are particularly useful for the synthesis of monomeric derivatives in which the coordination sphere about the metal can be carefully controlled. Since their discovery,¹ a very large number of publications²⁻⁵ has appeared describing also the possible application of the poly(pyrazolyl)borates, or Trofimenko's ligands, in an extraordinarily wide range of chemistry, from modeling the active site of metalloenzymes, through analytical chemistry and organic synthesis, to catalysis and material science.

The poly(pyrazolyl)borates are often defined as spectator ligands, generally not interfering with the reaction scenarios occurring at the

2 Scorpionates II: Chelating Borate Ligands

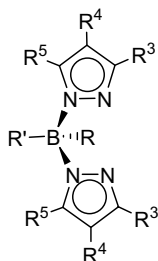


Fig. 1.1. General structure of poly(pyrazolyl)borates.

metal centers. However, it has been demonstrated that several different coordination modes of poly(pyrazolyl)borate ligands are possible, being responsible for the diverse chemical behavior of their compound and a number of examples are known in which they may have a noninnocent participation through hapticity changes. In fact, the term scorpionate has been used to describe the interchange between bidentate and tridentate coordination modes of these ligands. Like the pincers of a scorpion (Fig. 1.2), these versatile tripodal ligands introduced by Trofimenko (Fig. 1.3) bind a metal with nitrogen heteroatoms from two pyrazole rings attached to a central boron atom. The third pyrazole ring (or the R group), attached to the boron, rotates forward like a scorpion's tail to "sting" the metal.

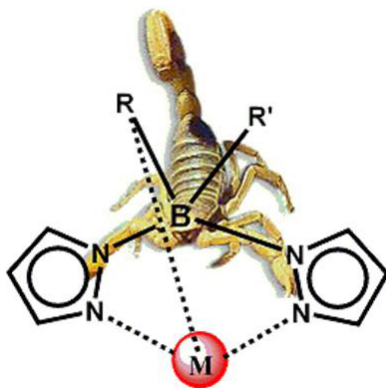


Fig. 1.2. The "scorpion" image used to visualize the poly(pyrazolyl)borates binding.



Fig. 1.3. Trofimenko and Pettinari at Camerino University (September 2004).

The development of the “second generation” of scorpionates,^{6,7} bearing bulky substituents (R) such as ^tBu, Ph or Cum on the 3-position of the pyrazoles and also of the “nonpyrazolyl scorpionate” ligands,⁸ containing a boron core but a different donor atom from N, resulted in large increase of the articles (>2800) on the chemistry of these ligands, over 200 different scorpionates being known and complexes with *ca.* 70 elements of the periodic table being reported.

In 2003, Trofimenko and his “scorpionate” ligands were guests of honor (Fig. 1.4) at an ACS symposium to celebrate 35 years of chemistry accomplished with the pyrazolylborate and related tripodal ligands.

In 2005, in a mail directed to me, Trofimenko said:

... when I wrote the book “Scorpionates” I had in mind to follow, after some years, with another book “Scorpionates-2”, which would continue where the first book stopped, i.e. it would contain materials from references beyond the book (which has 1568 references). It would also be an all-inclusive reference work, following the organization of the original book. And so I continued to collect references beyond the book’s range, and have now about 500 of them, including



Fig. 1.4. The ACS symposium held in new orleans (March 2003).

all papers cited in those references. I am sure that I did not catch a number of the newer ones, but I did what I could....

Unfortunately, my health is not the best these days, and I came to the conclusion that planning to write the second book is for me unrealistic...Would you consider writing something like the “Scorpionates-2” book or, perhaps, a large article (since 500 is too few references for a book) in the style of the original book?⁹

I have accepted his proposal and this book would absolve this very difficult task by providing a “full” coverage of the scorpionate chemistry from 1999 to date, so that it could be used as reference source in addition to the first book on “Scorpionates”, and also could provide information on the areas more recently investigated and developed (as that of mercaptoimidazolylborates). After a careful analysis of the literature data, I have found more than 1300 papers that reported on scorpionates in the last 8 years and for this reason a book seems the more valid and useful instrument to describe advances in the area. In memory of Trofimenko, I wanted to use the scheme adopted in the first edition, so that the first chapter covers the general features of the ligands, their coordination modes, general and new procedures adopted for their synthesis, the abbreviation system, the reviews published on these molecules describing synthesis, uses and applications of scorpionate derivatives, as well as a list of the new

poly(pyrazolyl)borate ligands (also third generation), their synthesis and related metal derivatives. In the second chapter, I will describe the first generation homoscorpionates, i.e. complexes of Tp and Tp* grouped according to metal, whereas in the third chapter I will extend my discussion to more complicated homoscorpionate (second generation) ligands, grouped by ligand.

The fourth chapter deals with heteroscorpionate chemistry, whereas Chaps. 5, 6 and 7 have been dedicated to the chemistry of nonpyrazole based ligands, i.e. scorpionates based on thioimidazolones, thioethers, and diaryl- and dialkyl-phosphines as donors, respectively.

Specific applications of scorpionate ligands are dealt with in Chap. 8 which describes catalytic, enzyme modeling, C–H bond activation and metal extraction studies. Chapter 9 will briefly indicate some emerging areas and possible further developments and perspectives.

1.2. Scorpionate Ligands: Abbreviation System

Following the system proposed by Curtis *et al.*,^{10,11} the abbreviation Tp is used for the simplest member of this family, i.e. the hydrotris(pyrazol-1-yl)borate (also indicated as $[\text{HB}(\text{pz})_3]^-$) and Tp* for hydrotris(3,5-dimethylpyrazol-1-yl)borate (also indicated as $[\text{HB}(3,5\text{-Me}_2\text{pz})_3]^-$), the two most frequently used ligands. Tp^R denotes a substituted tris(pyrazolyl-1-yl)borate. The following rules have been generally employed:

- (a) any nonhydrogen substituent in the 3-position of the pz ring is denoted by a superscript. Hydrotris(3-methylpyrazol-1-yl)borate is denoted as Tp^{Me} and hydrotris(3-*t*-butyl-pyrazol-1-yl)borate is written as Tp^{*t*Bu}. When rearrangement of the 3-substituted ligand has taken place and Tp^R transformed in $[\text{HB}(3\text{-Rpz})_2(5\text{-Rpz})]^-$, the ligand is denoted as Tp^{R*}. Analogously, if a double rearrangement occurs yielding a $[\text{HB}(3\text{-Rpz})(5\text{-Rpz})_2]^-$, the ligand is denoted with a double asterisk: Tp^{R**}, i.e. the $[\text{HB}(3\text{-Mspz})(5\text{-Mspz})_2]^-$ is abbreviated Tp^{M_s**};

- (b) when there are four identical pyrazolyl groups bound to boron, the ligand will be denoted as $\text{pz}^0\text{Tp}^{\text{R}}$, i.e. $(3\text{-Mepz})_4\text{B}$ is also indicated $\text{pz}^0\text{Tp}^{\text{Me}}$. The not substituted tetrakis ligand is denoted pzTp ;
- (c) boron substituents are written preceding “Tp”: for instance, phenyltris(pyrazol-1-yl)borate is PhTp ;
- (d) the 5-substituent follows the 3-substituent as a superscript, separated by a comma; for instance, $\text{HB}(3\text{-Ph-5-Mepz})_3$ is denoted as $\text{Tp}^{\text{Ph,Me}}$. When the 3 and the 5 substituents are identical, the superscript R-substituent is followed by 2: for instance hydrotris(3,5-diisopropylpyrazol-1-yl)borate is Tp^{iPr_2} . In the case of $\text{HB}(3,5\text{-Me}_2\text{pz})_3$ the systematic abbreviation would be Tp^{Me_2} although Tp^* continues to be the most used notation;
- (e) when the ligand exhibits substituents in the 4-position a 4R superscript is present. $\text{HB}(4\text{-CF}_3\text{pz})_3$ is Tp^{4CF_3} , $\text{HB}(3\text{-Me-4-Brpz})_3$ is $\text{Tp}^{\text{Me,4Br}}$. The only exception is when the ligand has both 3 and 5 position already indicated, so that $\text{HB}(3,4,5\text{-Me}_3\text{pz})$ ligand is Tp^*Me ;
- (f) poly(indazolyl)borates are represented as benzopyrazolylborates, Tp^{Bo} , and the fusion of the benzo ring to pz (3,4- or 4,5) is denoted by a superscript of 3 or 4 preceding “Bo”;
- (g) heteroscorpionate ligands will be abbreviated as “Bp”. In the case of the C- and B-substituted ligands the same rules above indicated must be used. Ph_2Bp , means diphenylbis(pyrazol-1-yl)borate, whereas $\text{Bp}^{t\text{Bu}}$ is bis(3-*tert*-butylpyrazol-1-yl)borate;
- (h) a general homoscorpionate ligand with unspecified substituents will be denoted as Tp^{x} , and a general pyrazolyl group will be pz^{x} ; Bp^{x} and $\text{pz}^0\text{Tp}^{\text{x}}$ are general bis- and tetrakis-pyrazolylborate, respectively;
- (i) bis- and tris(thioimidazolyl)borates are generally denoted as Bm^{x} and Tm^{x} , respectively. Bm^{R} and Tm^{R} denote substituted ligands at the 1-positions of the imidazole rings. A methyl substituent in the 1-position can be omitted, so Tm denotes the hydrotris(methimazolyl)borate ligand. In the case of the C- and B-substituted ligands the same rules adopted for Tp ligands must

be used, so PhTm^{Ph} indicates the ligand phenyltris(1-phenyl-2-thioxoimidazolyl)borate;

- (l) hydrotris(thioxotriazolyl)borate and dihydrobis(thioxotriazolyl)borate will be indicated in this book as Tr^{x} and Br^{x} , respectively, in accordance with the author's use; hydrotris(mercaptothiazolyl)borate and hydrotris(mercaptobenzothiazolyl)borate will be indicated as Tz and Tbz , respectively; whereas $\text{HB}(\text{tz})_3$ and $\text{H}_2\text{B}(\text{tz})_2$ will be employed for tris and bis(triazol-yl)borate, respectively.

1.3. Scorpionate (poly(pyrazolyl)borate) Features

Two families of scorpionate ligands (pyrazole-based) may be distinguished:

- (a) homoscorpionates, in which the pseudo-axial R group in Fig. 1.1 is another pyrazolyl group (pz^{x}) identical to the two bridging pz^{x} groups. These ligands typically coordinate the metal as tripodal N_3 -donors, exhibiting a $\text{C}_{3\text{v}}$ symmetry. If both R and R' are pz^{x} , we have still a homoscorpionate;
- (b) heteroscorpionates, where the coordinating pseudo-axial R group is anything but pz^{x} . Heteroscorpionates also include ligands where R is another pyrazolyl group (pz^{y}) different from pz^{x} . They can act in either bidentate or tridentate manner, depending on the type of the R and R' substituents on boron.

Most of poly(pyrazolyl)borate complexes $\text{RR}'\text{B}(\text{pz}^{\text{R}})_2\text{M}(\text{L})_y$ have a well-defined feature: a six-membered ring $\text{B}(\mu\text{-pz}^{\text{R}})_2\text{M}$, generally in the boat form, with the pseudo-equatorial R' pointing away from the metal roughly along the B–M axis, and the pseudo-axial R group being directed toward the metal (Fig. 1.5), to interact with it, or simply screen it from other ligands. The R substituent protrudes in space past the metal, enveloping it, and forming a protective pocket of varying size and shape.

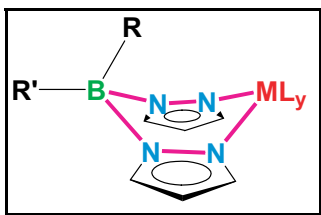


Fig. 1.5. The six-membered ring in poly(pyrazolyl)borate complexes.

The steric effects of the Tp^x ligand, relevant to understanding the metal complexes structure and properties, can be evaluated and quantified by the ligand cone angle (Θ), i.e. the “cone” swept out by the ligand at the metal center. However, this parameter, as also the wedge angle, depends not only on the ligand substituents but also on the length of the N–M bond.

All the Tp^x ligands have a cone angle larger than 180° . The ligands of small cone angle are characterized by a strong tendency to form $[\text{M}(\text{Tp}^x)_2]$ complexes with divalent first row transition metals, and the inability to form stable $[\text{MX}(\text{Tp}^x)]$ species ($\text{X} = \text{halide or R}$). Ancillary ligands can easily coordinate the metal as the Tp^x cone angle becomes smaller and the wedge angle larger.

Cone angles for several Tp^x ligands (averaged) have been calculated using X-ray crystallography data of selected complexes (a compilation based on first row transition metals),^{12,13} connecting the center of the metal atom to the outermost point of the R-group in the 3-position and taking into account its van der Waals radii for all hydrogen atoms.¹⁴ However, the choice of thallium complexes $[\text{Tl}(\text{Tp}^x)]$, the structures of which have been established by X-ray crystallography,^{15–18} as “standard” systems for calculating the cone angles seemed to be the best choice. The values found can be used to establish a relative steric hierarchy for the various Tp^x ligands (selected relevant values are reported in Table 1.1).¹⁹

A progressive increase in the steric hindrance of Tp^x ligands influences the depth of the hydrophobic pocket around the metal as shown in Fig. 1.6.

Table 1.1. Cone and Wedge angles of the common Tp^x ligands.

Complex	Cone angle	Wedge angle
Tp	183	70
Tp^{CPr}	223	68
Tp^{CBu}	234	51
Tp^{Br_3}	234	60
$\text{Tp}^{\text{4Bo, 3Me}}$	235	68
$\text{Tp}^{\text{(CF}_3)_2}$	237	49
Tp^*	239	67
$\text{Tp}^{\text{iPr, 4Br}}$	243	28
$\text{Tp}^{\text{tBu, Me}}$	243	31
Tp^{tBu}	251	29
Tp^{Cpe}	253	46
$\text{Tp}^{\text{Cy, 4Br}}$	273	46
$\text{Tp}^{\text{3Bo, 7tBu}}$	277	33
Tp^{Cy}	281	53

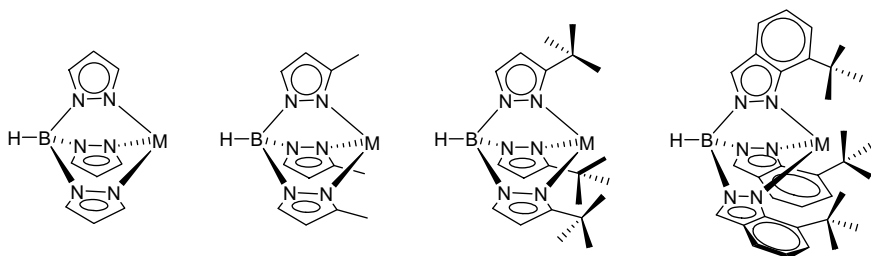


Fig. 1.6. The depth of the hydrophobic pocket around the metal increases with increasing in steric hindrance of Tp^x .

Some ligands exhibit unique features: for example Tp^{Ms} , having a phenyl group essentially orthogonal to the pyrazolyl plane and a minimal amount of rotational freedom, presents the smallest wedge angle between the Tp^x ligands. This creates a differently shaped pocket around the coordinated metal, compared with hitherto known Tp^{Ar} ligands (Fig. 1.7).²⁰

On the other hand, the tethering of the 3-phenyl group leads to an increase or decrease of the cone angle of the ligand, depending on

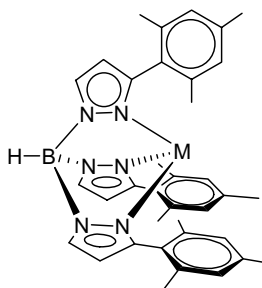


Fig. 1.7. Tp^{Ms} creates a shaped pocket around the metal.

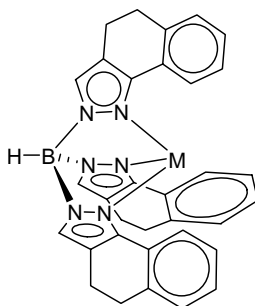


Fig. 1.8. The tethering of the 3-phenyl group with the CH_2CH_2 chain leads to a significant increase of the cone angle.

the length of the tether, and to an increase of the wedge angle, as compared with an untethered 3-phenyl group. In the case of the short tether, $-\text{CH}_2-$, the wedge angle is 82.4° close to that of the parent ligand Tp. With the longer zig-zagging tether, $-\text{CH}_2\text{CH}_2-$ (Fig. 1.8), the cone angle is very large, especially when a 5-Me group is present on the pyrazolyl ring, approaching that of the 3-*t*Bu group, the wedge angle still being relatively open ($\sim 44^\circ$). The coordination chemistry of these ligands reflects such spatial restrictions. All the tethered ligands display significant tendency to form octahedral $[\text{M}(\text{Tp}^{\text{x}})_2]$ complexes, while the formation and stability of half-sandwich complexes is inverse to the tightness of the tether.²¹

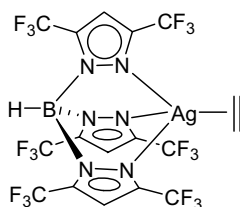


Fig. 1.9. $\text{Tp}^{(\text{CF}_3)_2}$ is a protective “Teflon coated” container for the $\text{Ag}(\text{C}_2\text{H}_4)$ fragment.

The highly fluorinated $\text{Tp}^{(\text{CF}_3)_2}$ ligand (Fig. 1.9) essentially serves as a protective “Teflon coated” container for $\text{M}(\text{I})\text{-L}$ ($\text{L} = \text{CO}, \text{C}_2\text{H}_4$) fragments.^{22,23}

Some Bp and Tp ligands with expanded denticity via potential oxygen donors on the 3-phenyl substituent were able to coordinate through the *o*-methoxy substituent. These ligands may be particularly useful in lanthanide and actinide coordination chemistry.²⁴

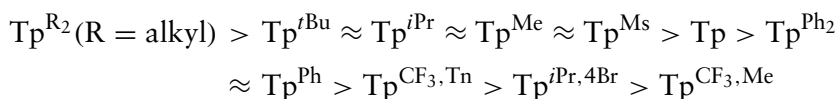
The ligand hydrotris[3-(2'-thienyl)pyrazol-1-yl]borate (= Tp^{Tn}) is reported to have the second-lowest steric hindrance among the known poly(pyrazolyl)borates, also if *a priori* tris(pyrazolyl)borates with the 3-(2'-thienyl) substituent were expected to fit between those with 3-phenyl and those with 3-methyl substituents in terms of steric hindrance. Tp^{Tn} forms octahedral $[\text{M}(\text{Tp}^{\text{Tn}})_2]$ complexes with first-row transition-metal ions, but fails to yield stable $[\text{MX}(\text{Tp}^{\text{Tn}})]$ species, except with $\text{Zn}(\text{II})$.¹²

Comparison of the structural, physical, and spectroscopic properties of similar compounds with homologous ligands allowed to assign the relative electron-donating or -withdrawing capabilities of Tp^x ligands. Tp and Tp^* ligands have been compared with their formally iso-electronic analogous Cp and Cp^* . In particular $\text{M}(\text{Cp}^x)(\text{CO})_3$ and $\text{M}(\text{Tp}^x)(\text{CO})_3$ radicals and anions, where M is Cr, Mo, and W, have been employed to derive a series of electrodonating ability.^{25–27} Stereoelectronic effect differences have been inferred from IR $\nu(\text{CO})$ values and oxidation potentials for the carbonyl anions.²⁸ Tp^x ligands seems stronger electron donors and the following trend in ligand electron-releasing capability: $\text{Tp}^* > \text{Tp} \approx \text{Cp}^* > \text{Cp}$ has been proposed.

However, conflicting reports can be found in the literature on the electron-donating properties of Tp and Tp* in comparison to Cp and Cp*. An investigation on C–H activation reactions by [Ir(Tp*)] complexes suggest that [Ir(Tp*)] derivatives are less electron-rich than the corresponding [Ir(Cp*)] complexes.²⁹

A report by Tellers and coworkers³⁰ has 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 electron-donating 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 π donation. Tp^x also strictly enforces an octahedral geometry about the metal center, in contrast to Cp^x.

Kitajima and Tolman³¹ found that the relative electron-donating or electron-releasing properties of the more hindered Tp^x ligands can be gained by comparing $\nu(\text{CO})$ data for sets of metal–carbonyl complexes that differ only in their pyrazolyl ring substituents as [Cu(Tp^x)(CO)],^{32–35} [Rh(η^2 -Tp^x)(CO)₂],²¹ and [Mo(Tp^x)(CO)₂(NO)].^{7,36,37} Higher values for the carbonyl stretching frequencies reflect lower electron density at the metal center and decreased electron donation by the Tp^x ligand for compounds within each set. The following trend of electron-donating ability of Tp^x ligands has been derived:



in which the order is generally expected on the basis of the electronic effects due to the substituents.

Database analysis and molecular mechanics were used to determine the conformational flexibility of tridentate scorpionate ligands. It has been reported that tris(pyrazolyl)borate ligands act like molecular vises, opening their tripodal structure for larger metals and closing around smaller metal ions. The Tp^x ligand conformation

flexibility has been compared with that of the isosteric and isoelectronic neutral tris(pyrazolyl)methanes. Tris(pyrazolyl)methanes and tris(pyrazolyl)borates have similar conformational flexibilities. It has been found that placing sterically hindered groups on the central carbon or boron has only a minor effect on the geometry of the tris(pyrazolyl)methanes and tris(pyrazolyl)borates. However, it does influence the flexibility of the ligands (Table 1.2), particularly when they have to open far from their ideal geometry.³⁸

Some ligands, such as 1,5-cyclooctanediylbis(pyrazol-1-yl)borate (Fig. 1.10), are very suitable for the study of C–H–M interaction, due

Table 1.2. Selected parameters (A, deg) defining the flexibility of all RTp ligands in a data set of RB(pz)₃ complexes with any group at positions 3, 4 and 5 of the pyrazolyl ligands, including hydrogen (RTp^x) or only hydrogen (RTp) (adapted from Ref. 38).

Data	Shortest values in RTp ^x ³⁹	Longest value in RTp ^x ⁴⁰	Average value in RTp ^x
M–N	1.89	2.80	2.22
Bite size	2.73	2.97	2.90
N–M–N	94.3	66.5	82.2

	Shortest values in RTp ⁴¹	Longest value in RTp ⁴²	Average value in RTp
M–N	1.78	2.93	2.22
Bite size	2.73	3.17	2.95
N–M–N	100	67.3	84.0

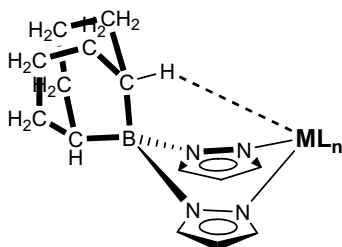


Fig. 1.10. The 1,5-cyclooctanediylbis(pyrazol-1-yl)borate ligand gives complexes showing C–H···M interactions.

to the presence of a single bridgehead hydrogen well-directed at the coordinated metal.⁴³

1.4. Scorpionate Coordination Modes

Tris(pyrazolyl)borates, Tp^x , generally coordinate as tridentate κ^3 - N,N',N'' -ligands through three nitrogen atoms of the pyrazole rings (Fig. 1.11(a)), 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. 1.11(b)),¹⁸ the bidentate κ^2 - N,N' (Fig. 1.11(c))⁴⁴ and κ^2 - $N,B-H$ coordination (Fig. 1.11(d))^{45,46} have been also reported. In contrast to the relatively easy formation of

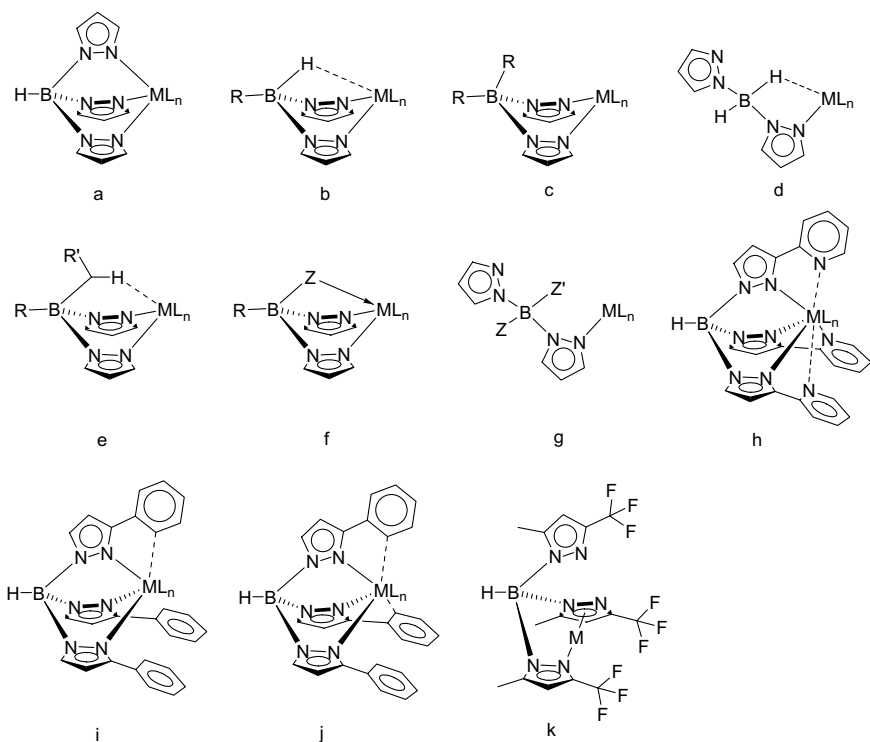


Fig. 1.11. Selected coordination modes of scorpionates.

agostic B–H···M bonds with Bp^x ligands, the formation of agostic B–C–H···M (Fig. 1.11(e)) bonds occurs only in limited cases. Ligands of type R(Z)Bp^x are generally tridentate, due to the presence of a heteroatom Z which can coordinate to the metal (Fig. 1.11(f)). Lower denticity, such as κ^1 -N, has been also reported (Fig. 1.11(g)).^{46–48} The first ionic complex containing a κ^0 -Tp^x ligand was reported by Carmona and coworkers.⁴⁹ The stepwise change in the denticity of poly(pyrazolyl)borate ligands from κ^3 to κ^0 may have important implications in catalytic uses of Tp metal complexes. Expansion of Tp^x denticity beyond κ^3 can occur by way of the 3-R substituent containing additional donor atoms, as in the hexadentate Tp^{py} (Fig. 1.11(h)).^{50,51} On the other hand, tetradenticity has been reported in Tp^x ligands where R does not contain donor atoms, either by way of agostic bonding,⁵² or through cyclometalation taking place at one of the aliphatic R groups per ligand (Fig. 1.11(i)).⁵³ Tp^{ph} can also coordinate in a κ^5 -fashion (Fig. 1.11(j)).⁵⁴ A π interaction between a poly(pyrazolyl)borate ligand and a metal center (η^5 -pz) has been reported in the complex $[(\text{KTp}^{\text{CF}_3, \text{Me}})_2(\text{CuCO}_3)]_2$ (Fig. 1.11(k))⁵⁵ in which one of the coordination hemispheres of the potassium ion is occupied by two carbonate oxygen atoms, one N atom of the Tp^{CF₃,Me} ligand, and three fluorine atoms. On the opposite side, the potassium ion is located directly above the center of a pyrazole ring, thus allowing a comparison with the η^5 -cyclopentadienyl coordination in polymeric K(Cp).⁵⁶

1.5. Reviews

Trofimenko reviewed his work on poly(pyrazolyl)borate chemistry and pyrazole-derived ligands in 1971⁵⁷ and 1972.⁵⁸ In the 1972 contribution Tp^x ligands were contained as a separate category. In 1986⁵⁹ Trofimenko reported a summary on the coordination chemistry of poly(pyrazolyl)borates. Its review in 1993² covers the 1984–1993 period and contains the systematic abbreviation system that we employed in this book and which could be adapted to most types of substitution on the Tp ligand, greatly facilitating writing chemical formulas for Tp^x complexes. Shaver also commented the Tp^x

coordination chemistry.⁶⁰ McCleverty, who carved out large specialty research areas involving Tp^* complexes of low-valent Mo and W, presented an overview of his work in 1983.⁶¹

In 1988, Niedenzu reviewed the pyrazaboles,⁶² whereas in 1992, Cauty and coworkers described the Pd- and Pt- Tp^x coordination chemistry.⁶³ In 1994, Kitajima and Moro-oka presented many copper-dioxygen complexes of Tp^x ,⁶⁴ whereas the lanthanides and actinides complexes were exhaustively investigated and described by Santos and Marques.⁶⁵ Parkin, author of a review of Tp -based models for carbonic anhydrase⁶⁶ and of a discussion on the effect of Tp^x -ligation on Grignard reagents,⁶⁷ reported also metal hydroxides, hydrides, and organometallics derived from hindered poly(pyrazolyl)borate ligands.⁶⁸ The organometallic and bioinorganic chemistry of hindered Tp^x ligands, developed by Kitajima and Tolman, was reviewed in 1995.³¹ A year later Etienne presented a review on the coordination chemistry of Tp ligands with V, Nb, and Ta,⁶⁹ whereas Reger reported Ga and In derivatives of Bp^x and Tp^x .⁷⁰ In 1997¹⁹ and 1998,⁷¹ Janiak reviewed Tp^x -Tl derivatives. In 1998 McCleverty and Ward described the use of scorpionate ligands to form a variety of bridged polynuclear complexes of Mo.⁷² Some Tp -based Mo and W pterine enzyme models were discussed in a review of Young and Wedd.⁷³ Cobalt scorpionate complexes were reviewed by Theopold *et al.*⁷⁴

The book *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*, organized according to the ligand type and to the coordinated metal, is the reference work for the papers published on poly(pyrazolyl)borates until April 1999.⁷⁵ A review on this book by Templeton appeared in *Journal of American Chemical Society* in 2000.⁷⁶ More recently, Trofimenko described also the most important features of poly(pyrazolyl)borates, from their synthesis and naming to their main applications.⁷⁷

The scorpionate ligands and their father were guests of honor at a symposium to celebrate 35 years of chemistry with Tp^x and related ligands.⁷⁸ *Polyhedron* also dedicated a special issue to this topic, the first paper being presented by Trofimenko on development of Tp^x ligand system from its inception.⁷⁹

A general review on organometallic complexes of Tp^x spanning from nontransition metals to copper, silver, and gold species has been written by Sadimenko.⁸⁰ A chapter dealing with the coordination chemistry of poly(pyrazolyl)borate and scorpionate ligands has been inserted in both editions of *Comprehensive Coordination Chemistry*.^{81,82} An overview of progress reached with scorpionate ligands was given by Pettinari in 2004.⁸³ Gold, silver, and copper Tp^x complexes, catalysts for carbene and insertion reactions have been described by Pérez.^{84,85} Non-Cp ancillaries in organogroup III metal chemistry including Tp^x have been reviewed by Piers and Emslie.⁸⁶ Studies on transition-metal complexes supported by Tp^x are reviewed, with emphasis on dioxygen complexes, by Akita *et al.*⁸⁷ who indicated in a subsequent paper the perspectives opened by Tp^x in Co–O₂ chemistry.⁸⁸ A review on copper–dioxygen complexes also focuses on structure and spectroscopic properties of Cu(Tp^x)/O₂ species.⁸⁹ In a subsequent review Akita and Hikichi examined not only the inorganic but also the organometallic chemistry of oxo, hydroxo, peroxy, alkylperoxy, and hydroperoxy species of Mn, Co, Fe, Ni, and Pd.⁹⁰

Coordinatively unsaturated organometallic systems based on Tp^x ligands, in particular $[\text{M}(\text{Tp}^x)\text{R}]$ and $[(\text{Tp}^x)\text{MM}'\text{L}]$ complexes ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}$; $\text{M}' = \text{Ru}, \text{Co}$), have been fully analyzed by Akita.⁹¹

Fe/Cu metalloenzymes, also based on Tp and their NO_x redox chemistry, is described by Wasser *et al.*⁹² Information on zinc poly(pyrazolyl)borate chemistry related to zinc enzymes is provided by Vahrenkamp in 1999.⁹³ Bioinorganic zinc chemistry explored through synthetic analogs of zinc enzymes containing tripodal Tp^x ligands is well condensed in a feature article⁹⁴ of Parkin that in 2001 in a chapter for *Metal Ions in Biological Systems* reported a detailed investigation on synthetic analogs that mimic function and structure of active sites of zinc enzymes.⁹⁵ The same author summarized in 2004 all synthetic analogs relevant to the structure and function of zinc enzymes.⁹⁶ In the same year Edelmann⁹⁷ pointed out new developments in the coordination chemistry of Tp^x , showing that these ligands can be more versatile than reported by several authors. More recently

some $[\text{Cu}^{\text{II}}(\text{Tp}^{\text{x}})]$ complexes have been reported as models for dioxygen activation in dopamine β -monooxygenase and peptidylglycine α -hydroxylating monooxygenase.⁹⁸ A personal perspective describing the use of $[\text{Cu}^{\text{II}}(\text{Tp}^{\text{x}})]$ systems to understand copper protein active sites has been presented by Tolman.⁹⁹ Copper and silver derivatives of scorpionates were also reviewed by Pettinari *et al.* in 2004.¹⁰⁰

An overview of fluorinated tris(pyrazolyl)borate ligands and their use in the synthesis of silver adducts containing group 14 ligands has been presented by Dias and Fianchini.¹⁰¹

Carmona along with other researchers reported rhodium and iridium tris(pyrazoyl)borate chemistry giving great emphasis to C–H activation.¹⁰² A perspective study on the generation and reactivity of sterically hindered iridium carbene containing Tp^{x} ligands based on a presentation given at Dalton Discussion was published by the Carmona's group in 2003.¹⁰³ Iridium carboxycarbene complexes were fully presented in 2005.¹⁰⁴ Ru complexes containing Tp^{x} have been reviewed by Kirchner in 1999,¹⁰⁵ in a paper referred to as being in print in the Trofimenko *Scorpionates* book. The structural features, acidity, and chemical properties of dihydrogen/dihydride complexes of group VIII metals were described by Jia and Lau.¹⁰⁶

In a review on non-Cp type homogeneous catalytic systems for olefin polymerization, complexes based on $\text{Tp}^{\text{x}}\text{-Sc, -Hf, -Ti, -Zr, -Y}$ have been also described.¹⁰⁷

The lanthanides chemistry using Tp^{x} ligands has been reviewed by Takats and coworkers.¹⁰⁸ Uranium complexes containing multidentate ligands, including also scorpionates family have been reported by Sessler *et al.*¹⁰⁹

A general review on rhenium complexes containing poly(pyrazolyl)borates appeared in 1998.¹¹⁰ In 2004, an overview of the progress involving group VII elements and actinide was presented by Santos and coworkers,¹¹¹ who very recently described also rhenium and technetium complexes anchored by scorpionates prepared for radiopharmaceutical application.¹¹² Keane and Harman described exhaustively the coordination chemistry of a new generation of π -basic dearomatization agents $\{\text{M}(\text{Tp})(\text{L})(\pi\text{-acid})\}$.¹¹³ Jones *et al.*¹¹⁴ reported a review on the role of unstable alkane

transition-metal complexes, including also Tp^x derivatives, in the processes of catalytic C–H activation, whereas Norris and Templeton more specifically described the hydrocarbon C–H activation with $[\text{Pt}(\text{Tp}^x)]$ complexes.¹¹⁵

In a review on the π -bonding and the lone pair effect in multiple bonds between heavier main group elements, Power described the structure of $[\text{Ga}(\text{Tp}^t\text{Bu}_2)\text{S}]$.¹¹⁶

$[\text{M}(\text{Tp})(\text{CN})_x]$ complexes were extensively discussed in a report on the design of single chain magnets through cyanide bearing six-coordinate complexes.¹¹⁷

Bp^{PY} and Tp^{PY} , multinucleating ligands, and their coordination and supramolecular chemistry have been reported by Ward *et al.*¹¹⁸

A detailed discussion on spin crossover in poly(pyrazolyl)borate iron and cobalt complexes has been performed by Long *et al.*¹¹⁹

Tris(pyrazolyl)borates have been reported also in two chapters on B–H¹²⁰ and X–H¹²¹ activation ($X = \text{Si}, \text{Ge}, \text{Sn}$) in the book *Metal Dihydrogen and σ -Bond Complexes*, edited by Kubas.

Metric parameters for the $[\text{X}]^+[\text{Mo}(\text{Tp}^x)(\text{CO})_3]$ and $[\text{Mo}(\text{Tp}^x)(\text{allyl})(\text{CO})_3]$ complexes have been reviewed by Wołowicz and coworkers.¹²²

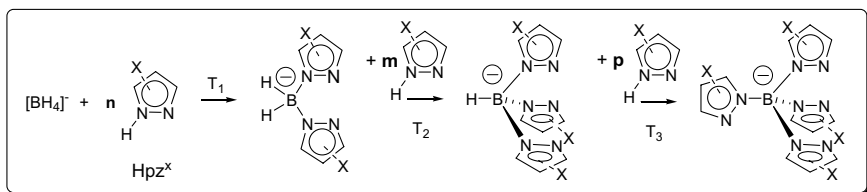
An overview of the chemistry of the divalent lanthanide hydride $[\text{Yb}(\mu\text{-H})(\text{Tp}^t\text{Bu}, \text{Me})_2]$ is reported by Ferrence and Takats.¹²³

Templeton reviewed a number of transition-metal η^2 -vinyl complexes also containing Tp^x ligands,¹²⁴ whereas Hall reported DFT calculations suitable for designing and testing alternative ligand schemes for transition iridium organometallic complexes, one chapter of the review being dedicated to Tp^x ligands.¹²⁵ Pettinari contributed also some chapters dedicated to Tp^x -organotin chemistry in two reviews on organotin compounds.^{126,127}

A brief description of the third generation of Tp^x is given by Fujisawa and Okamoto.¹²⁸

1.6. Synthesis of Scorpionate Ligands

Poly(pyrazolyl)borate ligands can be prepared, through a more general reaction, by heating BH_4^- in molten Hpz^x (Scheme 1.1). A large



Ligand	Conditions	$n + m + p$	T
Bp ^x	Reaction of substituted pz ^x and MBH ₄ in refluxed anhydrous DMF (M = Li, Na or K). Recrystallization from aromatic high-boiling solvents.	2.3	120–130°C
Tp ^x	Hpz ^x liquid: Neat-reaction with distillation of the excess pyrazole to prevent pzTp ^x formation. Required emanating hydrogen measurement.	4	170–190°C
Tp ^{3R}	Hpz ^{3R} : reflux, with rapid stirring in 3 or 4-methylanisole.	3.5	Boiling T
Tp ^{3R,5R}	Hpz ^{3R,5R} : Neat reaction with sublimation of the excess pyrazole. No pzTp ^x formation.	6–8	180–220°C
pzTp ^x	Limited to 5-unsusbstituted Hpz ^x : No solvent required, distillation or sublimation of Hpz ^x . Possible decomposition.	6	>180°C

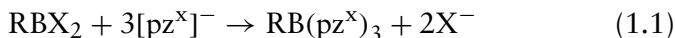
Scheme 1.1. Synthesis of poly(pyrazol-1-yl)borates.

variety of 1-H pyrazoles may be employed to synthesize the ligands by this route, with the exception of those containing functionalities incompatible with the borohydride ion. With asymmetric pyrazoles, such as 3-R-pyrazoles, this reaction proceeds with boron being bonded to the least hindered nitrogen atom. The only exceptions are indazole (benzopyrazole) and indazoles with substituents at

positions other than 7, which bond through the more hindered nitrogen atom.^{129,130}

The reaction of MBH_4 with Hpz^x can be used, through careful temperature control, to yield bis-, tris-, and in the case of 5-unsubstituted pyrazoles, tetrakis(pyrazolyl)borates. Synthesis of the parent ligands Bp , Tp , and pzTp has been detailed by Trofimenko.¹³¹

Boron halides, hydrides, arylboronic acids and corresponding esters can be employed as boron sources, when specific R on the boron atoms are requested. For example, the boron-substituted RTp^x ($\text{RB}(\text{pz}^x)_3$) may be synthesized according to the following reaction (1.1) by using pyrazolate ion and excess pyrazole:



Janiak *et al.* found that dibromo(methyl)borane MeBBr_2 reacts with Hpz^x at room temperature in the presence of NEt_3 and $\text{Tl}(\text{OEt})$ to form $[\text{Tl}(\text{MeTp}^x)]$ in high yield.¹³² For the synthesis of $\text{R}_2\text{B}(\text{pz}^x)$ species, sufficient pyrazolate ion is required to be present to convert $[\text{R}_3\text{B}(\text{pz}^x)]$ quickly to $[\text{R}_2\text{B}(\text{pz}^x)_2]$, otherwise the $\text{R}_2\text{B}(\text{pz}^x)$ species will dimerize to the stable pyrazabole $\text{R}_2\text{B}(\mu\text{-pz}^x)_2\text{BR}_2$.

1.7. Regiochemistry

In the synthesis of Tp^x ligands using 3(5)-monosubstituted pyrazoles or pyrazoles whose anions are not of C_{2v} symmetry, the following products can be formed: $\text{Tp}^{3\text{R}}$, $\text{Tp}^{5\text{R}}$, and $[\text{HB}(\text{pz}^{3\text{R}})_n(\text{pz}^{5\text{R}})_{3-n}]$. Usually, larger substituents end up in the pyrazolyl ring 3-position, relatively distant from the B–N bond. This tendency is pronounced when the steric differences between R(3) and R(5) are large. This regioselectivity is found in the reaction of 3(5)-Mepz with $[\text{BH}_4]^-$, leading to Bp^{Me} ,¹³³ and to Tp^{Me} ,¹³⁴ as well as in the regiospecific synthesis of Tp^{Ph} ,⁶ and $\text{Tp}^{t\text{Bu}}$.⁷ On the other hand, a mixture of Tp^{R} and $\text{Tp}^{5\text{R}}$ isomers can be obtained when the steric differences between the pyrazolyl rings substituent in the 3-position and in the 5-position are less substantial. Reaction of $\text{Hpz}^{i\text{Pr},\text{Me}}$ with $[\text{BH}_4]^-$ resulted in the formation of $\text{Tp}^{i\text{Pr},\text{Me}}$ and its isomer $[\text{HB}(\text{pz}^{i\text{Pr},\text{Me}})_2(\text{pz}^{\text{Me},i\text{Pr}})]$ ($= \text{Tp}^{i\text{Pr},\text{Me}^*}$; an asterisk (*) indicates an isomeric species) in an approximate 4:1 ratio.¹³⁵ The regioselectivity

can be explained with the fact that boron–nitrogen bond formation, involving a concerted loss of hydrogen, proceeds through a less sterically encumbered transition state, when bonding occurs to the less hindered N(1) rather than to N(2). The regiochemistry of homoscorpionate ligands prepared from indazoles can be summarized as follows:

1. Indazole itself and indazoles containing alkyl or aryl substituents in positions 3, 4, 5, and 6 form ligands where boron is bonded to the more hindered N-1 which represent a special class of homoscorpionate ligands containing a protective pocket.
2. Indazoles containing both 3- and 7-substituents (including a fused 6,7-benzo ring) do not yield regiochemically pure ligands, although bonding to the less hindered N-2 is still preferred.

The electronic effects can also play an important role: the syntheses of $\text{Tp}^{\text{CF}_3, \text{Me}}$,¹³⁶ and $\text{Tp}^{\text{CF}_3, \text{Tn}}$,¹³⁷ in which electronically quite different substituents are present, are highly regioselective with the larger CF_3 group residing exclusively in the 3-position. The preference of an electron-withdrawing group for the 3-position in Tp^{x} ligands is likely due to the inductive electron-withdrawing effect of the CF_3 group, which makes the distal nitrogen more basic, favoring tautomer with the CF_3 group in the 3-position.¹³⁸ The relative influence of steric and electronic effect on the course of ligand synthesis is evident from the preparation of Tp^{Ms} ($\text{Hpz}^{\text{Ms}} = 3\text{-mesitylpyrazole}$)²⁰ in which the asymmetric isomer $[\text{HB}(3\text{-Rpz})_2(5\text{-Rpz})] (= \text{Tp}^{\text{Ms}*})$ ¹³⁹ was the major product. A similar situation occurs, for instance, in the synthesis of Tp^{Np140} and $\text{Tp}^{\text{Ant 15}}$.

Sometimes a regiochemically pure ligand Tp^{R} undergoes rearrangement to $\text{Tp}^{\text{R}*}$ during the course of complex formation. Tp^{iPr} and $\text{Tp}^{\text{iPr, 4Br}}$ having large substituent in the 3-position which prevent $[\text{M}(\text{Tp}^{\text{R}})_2]$ formation, yields octahedral cobalt(II) complexes containing, upon a borotropic migration of the original ligands, $\text{Tp}^{\text{iPr}*}$ and $\text{Tp}^{\text{iPr, 4Br}*}$, respectively.³⁶ $[\text{Ir}(\text{Tp}^{\text{Me}})(\text{COD})]$ has been found to rearrange in solution first to $[\text{Ir}(\text{Tp}^{\text{Me}*})(\text{COD})]$ and then, on heating, to $[\text{Ir}\{\text{HB}(\text{pz}^{\text{5Me}})_2(\text{pz}^{\text{3Me}})\}(\text{COD})]$.¹⁴¹

1.8. New Ligands

1.8.1. Tp^{CHPh_2}

The ligand hydrotris[3-(diphenylmethyl)pyrazol-1-yl]borate, Tp^{CHPh_2} , has been prepared by Trofimenko and coworkers¹² and its coordination chemistry compared with that of Tp^{iPr} . The complexes $[MX(Tp^{CHPh_2})]$ ($M = Co, Ni, Zn; X = Cl, NCO, NCS$), $[Pd(Tp^{CHPh_2})-(\eta^3\text{-methallyl})]$, $[Co(Tp^{CHPh_2})(acac)]$, and $[Co(Tp^{CHPh_2})(Tp^x)]$ have been synthesized and characterized. $[Tl(Tp^{CHPh_2})]$, $[CoCl(Tp^{CHPh_2})]$, $[Co(Tp^{CHPh_2})(NCS)(DMF)]$, $[Ni(Tp^{CHPh_2})(NCS)(DMF)_2]$, $[Co(Tp^{CHPh_2})(acac)]$, $[Co(Tp^{CHPh_2})(Ph_2Bp)]$, $[Co(Tp^{CHPh_2})(Bp^{Ph})]$, $[Co(Tp^{CHPh_2})(Tp)]$, and $[Ni(Tp^{CHPh_2})_2][C_2O_4](H_2O)_2$ were also structurally characterized.¹⁴²

1.8.2. Tp^{cpd}

Trofimenko and coworkers¹⁴³ also reported the ligand hydrotris[3-(carboxypyrrolidido)pyrazol-1-yl]borate Tp^{cpd} (the Tl salt has been investigated by X-ray single-crystal study), and its coordination chemistry toward La, Nd, and Sm salts. $[Sm(Tp^{cpd})_2]PF_6$, structurally characterized, contains a lanthanide ion in a 10-coordinate environment consisting of one N_3O_3 hexadentate Tp^{cpd} ligand (Fig. 1.12), and one N_2O_2 tetradentate Tp^{cpd} ligand.¹⁴³

1.8.3. Tp^{4tBu} , $Tp^{Tol,4tBu}$, and $Tp^{iPr,4tBu}$

Homoscorpionate ligands containing a *tert*-butyl group as substituent in the 4-position (Tp^{4tBu}), ($Tp^{Tol,4tBu}$), and ($Tp^{iPr,4tBu}$) were synthesized with the aim to investigate the restriction of rotation of the 3-R group through “remote control”. While the 4-*tert*-butyl group does not alter the coordination chemistry of Tp^{4tBu} and $Tp^{Tol,4tBu}$, the coordination chemistry of $Tp^{iPr,4tBu}$ is different with respect to that of Tp^{iPr} , $Tp^{iPr,4tBu}$ acting as a “tetrahedral enforcer” (Fig. 1.13). $[Co(Tp^{4tBu})(Tp^{Np})]$, $[Tl(Tp^{Tol,4tBu})]$,

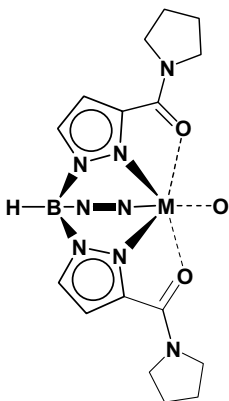


Fig. 1.12. The hexadentate N_3O_3 environment provided by the Tp^{cpd} ligand.

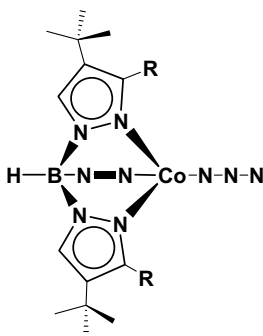


Fig. 1.13. $[Co(Tp^{iPr,4tBu})(N_3)]$.

$[Rh(Tp^{Tol,4tBu})(CO)_2]$, $[CoCl(Tp^{iPr,4tBu})]$, $[Co(Tp^{iPr,4tBu})(N_3)]$, and $[Co(Tp^{iPr,4tBu})(NCS)]$ have been structurally characterized.¹⁴⁴

1.8.4. $Tp^{(2,4(OMe)_2Ph)}$ and $Bp^{(2,4(OMe)_2Ph)}$

To expand the scorpionate ligand denticity beyond the number of pz rings, Trofimenko and coworkers²⁴ reported two ligands, hydrotris[3-(2,4-dimethoxyphenyl)pyrazol-1-yl]borate $Tp^{(2,4(OMe)_2Ph)}$ and dihydrobis [3-(2,4-dimethoxyphenyl)pyrazol-1-yl]borate $Bp^{(2,4(OMe)_2Ph)}$, able to coordinate through both pyrazolyl nitrogens and *o*-methoxy

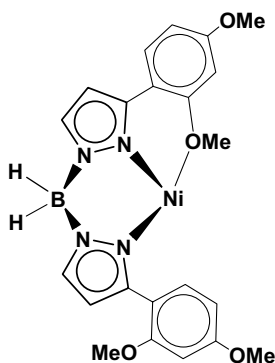


Fig. 1.14. $[\text{Ni}(\text{Bp}^{(2,4(\text{OMe})_2\text{Ph})})_2]$ (only one scorpionate ligand is shown).

groups on the phenyl rings and giving a secondary chelation occurring through a six-membered ring. $[\text{Ni}(\text{Bp}^{(2,4(\text{OMe})_2\text{Ph})})_2]$ (Fig. 1.14) and $[\text{Tl}(\text{Tp}^{(2,4(\text{OMe})_2\text{Ph})})]$ have been also structurally characterized.

1.8.5. $\text{Tp}^{\text{Me},\text{mt}3}$ and $\text{Tp}^{\text{Me},\text{mt}4}$

In a subsequent paper Trofimenko and others¹⁴⁵ reported the synthesis of the ligands hydrotris(3-methyl-4,5-propylenepyrazol-1-yl)borate $\text{Tp}^{\text{Me},\text{mt}3}$ and hydrotris(3-methyl-4,5-butylenepyrazol-1-yl)borate $\text{Tp}^{\text{Me},\text{mt}4}$, and the structures of their representative cobalt and rhodium complexes, $[\text{Co}(\text{Tp}^{\text{Me},3\text{mt}})(\text{Tp}^{\text{Np}})]$ and $[\text{Rh}(\kappa^2\text{-Tp}^{\text{Me},4\text{mt}})(\text{COD})]$.

1.8.6. $\text{Tp}^{\text{Fu},\text{Me}}$

The new ligand hydrotris(3-(2'-furyl)-5-methylpyrazolyl)borate $\text{Tp}^{\text{Fu},\text{Me}}$ reacts with zinc salts forming complexes $[\text{ZnX}(\text{Tp}^{\text{Fu},\text{Me}})]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}, \text{CH}_3\text{COO}, \text{CF}_3\text{COO}$). When zinc(II) perchlorate was employed, however, $[\text{Zn}(\text{Tp}^{\text{Fu},\text{Me}})_2]$ afforded preferably. Careful control of the reaction conditions allows the formation of the “enzyme model” $[\text{Zn}-\text{OH}(\text{Tp}^{\text{Fu},\text{Me}})]$, which mimics carbonic

anhydrase by inserting CO₂ and CS₂ in methanol, producing [Zn-OCOOMe(Tp^{Fu,Me})] and [Zn-SCSOMe(Tp^{Fu,Me})] able to deprotonate trifluoroacetamide, yielding thus [Zn-NHCOCF₃(Tp^{Fu,Me})].¹⁴⁶

1.8.7. *Tp^{Cy}, Tp^{Cy,4Br}, and pz⁰Tp^{Cy}*

Hydrotris(3-cyclohexylpyrazol-1-yl)borate Tp^{Cy}, tetrakis(3-cyclohexylpyrazol-1-yl)borate pz⁰Tp^{Cy}, and hydrotris(3-cyclohexyl-4-bromopyrazol-1-yl)borate Tp^{Cy,4Br} were prepared as Tl(I) salts and converted to tetrahedral [MX(Tp^x)] and octahedral [M(Tp^x)(Tp^y)] complexes, as well as to the dinuclear [Ni(Tp^{Cy})₂(CO₃)] and the mononuclear [Ni(Tp^{Cy,4Br})(pz^{Cy,4Br})₃H₂] (which may be regarded as the free acid of the novel dianionic ligand [Ni(Tp^{Cy,4Br})(pz^{Cy,4Br})₃]²⁻). [CoCl(Tp^{Cy})], [CoCl(Tp^{Cy,4Br})], [Co(Tp^{Cy,4Br})(NCS)], [Ni(Tp^{Cy})₂(CO₃)], [Ni(Tp^{Cy,4Br})(pz^{Cy,4Br})₃](H)₂, and [Mo(Tp^{Cy})(η³-methallyl)(CO)₂] were also structurally characterized. The paramagnetic heteroleptic complexes [Co(Tp^{Cy})(Tp)], [Co(Tp^{Cy})(Tp*)], [Co(Tp^{Cy,4Br})(Tp)], and [Co(Tp^{Cy,4Br})(Tp*)] were investigated by NMR. The homoleptic derivatives [Co(Tp^{Cy})₂] and [Co(Tp^{Cy,4Br})₂] rearrange thermally to [Co(Tp^{Cy*})₂] and [Co(Tp^{Cy,4Br*})₂], respectively.¹⁴⁷

1.8.8. *Tp^{Bn,Me} and Tp^{Bn,4Ph}*

In order to explore how the coordination chemistry of the Tp^{Ph} ligand changes with the introduction of a methylene spacer between the pyrazolyl 3-C and a phenyl group, Trofimenko developed the synthesis of the ligands hydrotris(3-benzyl-5-methylpyrazol-1-yl)borate Tp^{Bn,Me} and hydrotris(3-benzyl-4-phenylpyrazol-1-yl)borate Tp^{Bn,4Ph}. The dynamic behavior of a number of metal complexes containing these ligands was investigated by NMR. Structures of [Tl(Tp^{Bn,Me})], [Tl(Tp^{Bn,4Ph})], [Co(Tp^{Bn,Me})(Tp^{Np})], [Mo(Tp^{Bn,Me})(CO)₂NO], [Co(Tp^{Bn,4Ph})(Tp)], and [Mo(Tp^{Bn,Me})(η³-methallyl)(CO)₂] were determined by X-ray crystallography. While in Tp^{Bn,Me} the benzyl group is freely rotating and provides less steric hindrance to the coordinated metal than a neopentyl group, steric

hindrance is increased in the $\text{Tp}^{\text{Bn,4Ph}}$, where the rotation of the benzyl substituent is restricted by the 4-phenyl substituent.¹⁴⁸

1.8.9. $\text{Tp}^{(7\text{azain})}$

The ligand $\text{Tp}^{(7\text{azain})}$ has been obtained from the reaction of KBH_4 with 7-azaindole. It has been employed in the synthesis of $[\text{Zn}(\text{Cl})(\text{Tp}^{(7\text{azain})})]$ and $[\text{Cu}(\text{Tp}^{(7\text{azain})})(\text{PPh}_3)]$. $\text{K}(\text{Tp}^{(7\text{azain})})$ has a dimeric structure linked together by two K^+ ions, $[\text{Zn}(\text{Cl})(\text{Tp}^{(7\text{azain})})]$ a symmetric tripodal structure with all three 7-azaindolyl groups being coordinated to the Zn^{II} center, whereas $[\text{Cu}(\text{Tp}^{(7\text{azain})})(\text{PPh}_3)]$ has an asymmetric structure with two of the 7-azaindolyl groups being coordinated to the Cu^{I} center and the third 7-azaindolyl group uncoordinated.¹⁴⁹ The same ligand interacts with $[\text{RuCl}(\text{Cp}^*)]_4$ yielding $[\text{Ru}(\kappa^3\text{-H,N,N-Tp}^{(7\text{azain})})(\text{Cp}^*)]$ which upon interaction with CO forms $[\text{Ru}(\kappa^2\text{-H,N-Tp}^{(7\text{azain})})(\text{Cp}^*)(\text{CO})]$. Both Ru species have been structurally characterized.¹⁵⁰

1.8.10. $\text{Tp}^{(3,5\text{-(CH}_2)_3)}$ and $\text{Tp}^{(3,4\text{-(CH}_2)_6)}$

The structure of two thallium scorpionates derived from 3(5),4-trimethylene- and 3(5),4-hexamethylenepyrazole, $\text{Tp}^{(3,5\text{-(CH}_2)_3)}$ and $\text{Tp}^{(3,4\text{-(CH}_2)_6)}$, respectively, has been determined by multinuclear NMR, both in solution and in the solid state. As for the other 3-substituted pyrazolyl derivatives, these compounds can exist, in principle, in four isomeric forms (Fig. 1.15) depending on the substitution pattern. The isomeric distribution has been found the same in both phases suggesting a kinetic origin.¹⁵¹

1.8.11. Tp^{Br_3}

The synthesis of hydrotris(3,4,5-tribromopyrazol-1-yl)borate, $(\text{Tp}^{\text{Br}_3})$, described also in the first edition, has been reported by Trofimenko and coworkers in detail in 2002.¹⁵² $[\text{Mo}(\text{Tp}^{\text{Br}_3})(\eta^3\text{-methallyl})(\text{CO})_2]$, $[\text{Pd}(\text{Tp}^{\text{Br}_3})(\eta^3\text{-methallyl})]$, and $[\text{Rh}(\text{Tp}^{\text{Br}_3})(\text{CO})_2]$ have been structurally characterized and compared with $[\text{Mo}(\text{Tp}^*)\text{-}$

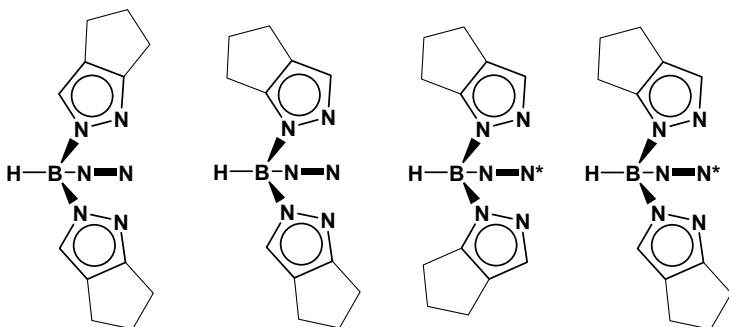


Fig. 1.15. Possible isomeric forms for $\text{Tp}^{(3,5-(\text{CH}_2)_3)}$ (the asterisk indicates a 3-substituted pyrazolyl ring).

(η^3 -methallyl)(CO) $_2$], and [Pd(Tp*)(η^3 -methallyl)]. Tp^{Br_3} has a unique feature among scorpionates of containing no C–H bonds, thus making its organometallic derivatives more suitable for spectroscopic (IR, NMR) studies with respect to other Tp^x ligands.

The complex [Cu(Tp^{Br₃})(NCMe)] reported by Pérez's group has been demonstrated an excellent catalyst for the regioselective carbene-transfer reaction to tertiary C–H bonds of hydrocarbons.¹⁵³ The choice of the scorpionate was dictated by the hypothesis that the existence of electron-withdrawing groups on ligands in the coordination sphere could favor insertion reaction, due to the enhancement in the electrophilicity of the metal–carbene intermediate. [Cu(Tp^{Br₃})(NCMe)] catalyzes the insertion of a nitrene group into the carbon–hydrogen bond of cyclohexane and benzene, as well as into the primary C–H bonds of the methyl groups of toluene and mesitylene, in moderate to high yield, respectively.¹⁵⁴ It catalyzes the transfer of the nitrene unit and its subsequent insertion into the sp^3 C–H bonds of alkyl aromatic and cyclic ethers or the sp^2 C–H bonds of benzene,¹⁵⁵ and catalyzes the addition of the :CHCO₂Et unit (derived from EDA) to benzene forming a cycloheptatriene ring,¹⁵⁶ in analogy with the Büchner reaction. The same copper complex, dissolved in the perfluoropolyether FOMBLIN[®] has been also employed as a catalyst for the styrene cyclopropanation reaction with ethyl diazoacetate.¹⁵⁷ [Ag(Tp^{Br₃}) $_2$ ·CH₃COCH₃] and [Ag(Tp^{Br₃})(THF)] also catalyze the

insertion of the :CHCO₂Et group from EDA into the saturated C–H bonds of several C5, C6, and C8 linear and branched alkanes.¹⁵⁸

[Ir(C₂H₄)₂(Tp^{Br₃})] photochemically activates the C–H bonds of *n*-pentane. The process consists of two steps, the first one being the formation of the isolable alkyl-hydride intermediate [IrH(C₂H₄)(C₅H₁₁)(Tp^{Br₃})], the second a β-hydride elimination generating a terminal olefin complex [IrH₂(C₅H₁₀)(Tp^{Br₃})]. This reaction can be extended to diethyl ether, the reaction proceeding by the activation of one of the β-CH bonds with formation of the alkyl-hydride [IrH(C₂H₄)(CH₂CH₂OCH₂CH₃)(Tp^{Br₃})] and then yielding [IrH₂(CH₂=CHOCH₂CH₃)(Tp^{Br₃})]. These processes compete with the intramolecular C–H activation of one of the coordinated ethylene ligand by the Ir center in [Ir(C₂H₄)₂(Tp^{Br₃})] affording the hydride-vinyl complex [Ir(CH=CH₂)(C₂H₄)(Tp^{Br₃})]. When the same reactions was carried out at high-temperature, the hydride-α,ω-butenyl complex [Ir(H)(CH₂CH₂CH=CH₂)(Tp^{Br₃})] and the hydride-crotyl derivative [IrH(C₄H₇)(Tp^{Br₃})] have been obtained.¹⁵⁹

1.8.12. *Bp*^{Br₃}

The ligand dihydrobis(3,4,5-tribromopyrazol-1-yl)borate, (Bp^{Br₃}), and its derivative [Mo(Bp^{Br₃})(η³-methallyl)(CO)₂] have been prepared and characterized by Trofimenko and coworkers who compared the structure of the Mo complex with that of [Mo(Bp^{*})(η³-methallyl)(CO)₂].¹⁵²

1.8.13. *Tp*^{Br,Ph,Br}, *Tp*^{Br,p-Tol,Br}, *Tp*^{Br,p-ClPh,Br}, *Tp*^{p-ClPh,4Br}, and *Tp*^{Ph,Me,Br}

The new ligands *Tp*^{Br,Ph,Br}, *Tp*^{Br,p-Tol,Br}, and *Tp*^{Br,p-ClPh,Br}, first examples of an “atypical” B–N bond to the most sterically hindered pyrazole nitrogen, exhibit all aryl substituents in the 5-position of the ligand, forming a protective pocket around the B–H bond. These complexes display a rather high B–H stretch frequency in the IR region. On the other hand *Tp*^{p-ClPh,4Br} and *Tp*^{Ph,Me,Br}, containing no outer bromine substituents, show normal B–N bonding to the least-hindered

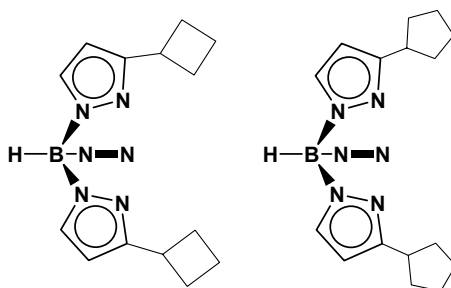


Fig. 1.16. Tp^{Cpe} (left) and Tp^{Cbu} (right).

nitrogen. These ligands, isolated as their Tl salts, have been employed to form $[\text{Cu}(\text{NCMe})(\text{Tp}^{\text{x}})]$, also tested as catalysts in carbene and nitrene transfer reactions.¹⁶⁰

1.8.14. Tp^{Cpe} and Tp^{Cbu}

The Tl derivatives of the new ligands Tp^{Cpe} and Tp^{Cbu} (Fig. 1.16) have been prepared and structurally characterized. The cone and wedge angles of these two compounds have been compared with those of $[\text{Tl}(\text{Tp}^{\text{Cpr}})]$ and $[\text{Tl}(\text{Tp}^{\text{Cy}})]$ and it has been reported that the cone angle of $[\text{Tl}(\text{Tp}^{\text{Cbu}})]$ is relatively similar to $[\text{Tl}(\text{Tp}^{\text{Cpr}})]$, whereas the cone angle of $[\text{Tl}(\text{Tp}^{\text{Cpe}})]$ is roughly midway between those of $[\text{Tl}(\text{Tp}^{\text{Cpr}})]$ and $[\text{Tl}(\text{Tp}^{\text{Cy}})]$.¹⁶¹

1.8.15. $\text{Tp}^{\alpha\text{Nt}}$ and $\text{Tp}^{\beta\text{Nt}}$

The homoscorpionate ligands $\text{Tp}^{\alpha\text{Nt}}$ and $\text{Tp}^{\beta\text{Nt}}$ (Fig. 1.17) were synthesized by using 3-(α -naphthyl)pyrazole and 3-(β -naphthyl)pyrazole, respectively, bonded either through the 1-position $\text{Tp}^{\alpha\text{Nt}}$ or through the 2-position $\text{Tp}^{\beta\text{Nt}}$. $\text{Tp}^{\beta\text{Nt}}$ resembles other Tp^{Ar} ligands, where Ar is a *para*-substituted phenyl group, although the 2-naphthyl substituent provided a substantially deeper pocket around the coordinated metal while retaining rotational freedom. By contrast, rotation of the 1-naphthyl substituent in $\text{Tp}^{\alpha\text{Nt}}$ was restricted, which led to complexes of lower symmetry than those of the $\text{Tp}^{\beta\text{Nt}}$ ligand and, at times, as in the case of $[\text{Co}(\text{Tp}^{\alpha\text{Nt}})(\text{Tp}^{\text{*}})]$, to a structure devoid of any symmetry

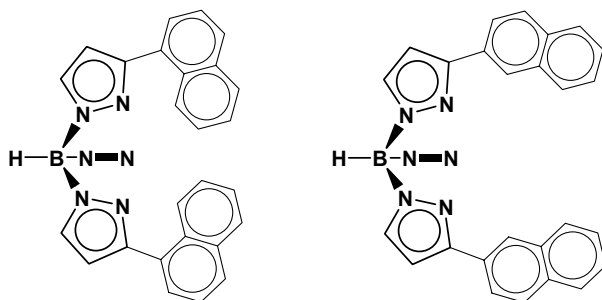


Fig. 1.17. $Tp^{\alpha Nt}$ (left) and $Tp^{\beta Nt}$ (right).

elements. $Tp^{\alpha Nt}$ could find some use in the preparation of asymmetric catalysts.¹⁶²

1.8.16. $Tp^{Me_2Bn,Me}$

$[K(Tp^{Me_2Bn,Me})]$ and $[Ti(Tp^{Me_2Bn,Me})]$ have been reported by Biagini *et al.* (Fig. 1.18). The reaction of $Tp^{Me_2Bn,Me}$ with $TiCl_4$ gave, after rearrangement of the ligand (a double 1,2-borotropic shift), $[TiCl_3\{HB(pz^{Me_2Bn,Me})(pz^{Me,Me_2Bn})_2\}]$.¹⁶³

1.8.17. Tp^{4py} , Bp^{4py} , pz^0Tp^{4py} , Bp^{3py} , Tp^{3py} , and pz^0Tp^{3py}

The hydro-tris[3-(4-pyridyl)pyrazol-1-yl]borate, (Tp^{4py}), has been isolated as its Tl(I) complex which shows an infinite one-dimensional polymeric chain, in which the Tl(I) center is connected to a pendant

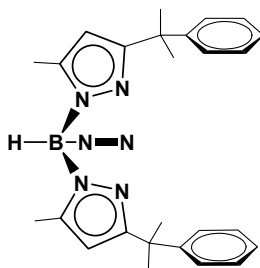


Fig. 1.18. $Tp^{Me_2Bn,Me}$.

4-pyridyl residue from an adjacent complex unit to build up the chain. The $\text{Bp}^{4\text{py}}$ and its Tl derivative has been also described.¹⁶⁴ $[\text{Tl}(\text{Bp}^{3\text{py}})]$, $[\text{Tl}(\text{Bp}^{4\text{py}})]$, and $[\text{Tl}(\text{Tp}^{4\text{py}})]$ are one-dimensional polymeric chains via coordination of one of their pendant pyridyl units to the Tl(I) center of an adjacent complex fragment; $[\text{Tl}(\text{Tp}^{3\text{py}})]$ contains the three pendant pyridyl units coordinated to separate Tl(I) neighbors and yielding two-dimensional polymeric sheet. In $[\text{Tl}(\text{pz}^0\text{Tp}^{3\text{py}})]$, and $[\text{Tl}(\text{pz}^0\text{Tp}^{4\text{py}})]$ the Tl(I) is coordinated by two or three of the four pyrazolyl arms, respectively; bridging interactions of pendant 4-pyridyl groups with adjacent Tl(I) centers result in a two-dimensional sheet. In $[\text{Ag}(\text{pz}^0\text{Tp}^{4\text{py}})]$ the silver ion is coordinated by two pyrazolyl rings, and two bridging pyridyl ligands from other complex units, resulting in a one-dimensional chain consisting of pairs of cross-linked zigzag chains. $[\text{Cu}(\text{Tp}^{4\text{py}})]$ and $[\text{Cd}(\text{OAc})(\text{Tp}^{3\text{py}})]$ are dimers, stabilized by π - π stacking interactions between sections of the two ligands. $[\text{Ni}(\text{Tp}^{3\text{py}})_2]$ is monomeric, with an octahedral coordination geometry. $[\text{Re}(\text{CO})_3(\text{Tp}^{4\text{py}})]$ is also monomeric.¹⁶⁵

1.8.18. Tp^{BuPy}

The potassium salt of the hexadentate tris[3-((4-*t*butyl)-pyrid-2-yl)-pyrazol-1-yl]hydroborate (Tp^{BuPy}) has been described together with the crystal structure of $[\text{La}(\text{NO}_3)_2(\text{Tp}^{\text{BuPy}})]$.¹⁶⁶

1.8.19. $\text{Bp}^{(\text{COC})\text{py}}$

The potassium salt of the tetradentate bis[3-(2-pyridyl)-5-(methoxymethyl)pyrazol-1-yl]-dihydroborate ($\text{Bp}^{(\text{COC})\text{py}}$) has been described together with the crystal structures of $[\text{La}(\text{X})(\text{Bp}^{(\text{COC})\text{py}})_2]$ ($\text{X} = \text{NO}_3$ or OTf).¹⁶⁶

1.8.20. $\text{Bp}^{2\text{pyr}}$

$\text{Bp}^{2\text{pyr}}$, in which each pyrazolyl ring is functionalized with a pyrazin-2-yl group at the C2 position, is a potentially chelating tetradentate ligand with two externally directed N atoms available for additional

metal-ion binding. The crystal structure of $[\text{Tl}(\text{Bp}^{2\text{pyr}})]$ indicates it as a simple mononuclear complex with the Tl ion coordinated in the N_4 binding pocket of the ligand and the externally directed N atoms involved only in intermolecular $\text{N} \cdots \text{H}-\text{C}$ hydrogen bonding interactions. $[\text{Pb}(\text{Bp}^{2\text{pyr}})_2] \cdot \text{Et}_2\text{O}$ contains a Pb center nine-coordinate by two tetradentate chelating ligands and the ninth donor being a pyrazinyl N_4 atom from an adjacent molecule.¹⁶⁷

1.8.21. $\text{Tp}^{(4\text{py}),\text{Me}}$, $\text{Tp}^{(4-(2-\text{Mepy}),\text{Me})}$, $\text{Tp}^{(\text{CONHPh}),\text{Me}}$,
and $\text{Tp}^{(\text{CONHC}(\text{Me}_3),\text{Me})}$

Four new Tp^x ligands, bearing pyridyl and carboxamide substituents at the 3-positions of the pyrazole rings, were prepared by Vahrenkamp group (Fig. 1.19).¹⁶⁸ Structure determination of their K salts was also carried out (Fig. 1.20). Their coordinative properties were explored by preparing $[\text{Zn}(\text{X})(\text{Tp}^x)]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NO}_3, \text{OAc}$, phenolate, thiophenolate, and diorganophosphate) and the cationic complexes $[\text{Zn}(\text{Tp}^x)(\text{L})]^+$ ($\text{L} = \text{MeOH}$ or Hpz). Polar Tp^x ligands favor coordination numbers higher than four for zinc, either by inducing bidentate coordination of the coligands X and L, using the carboxamide oxygen atoms for coordination, or by linking two $[\text{Zn}(\text{X})(\text{Tp}^x)]$ units through

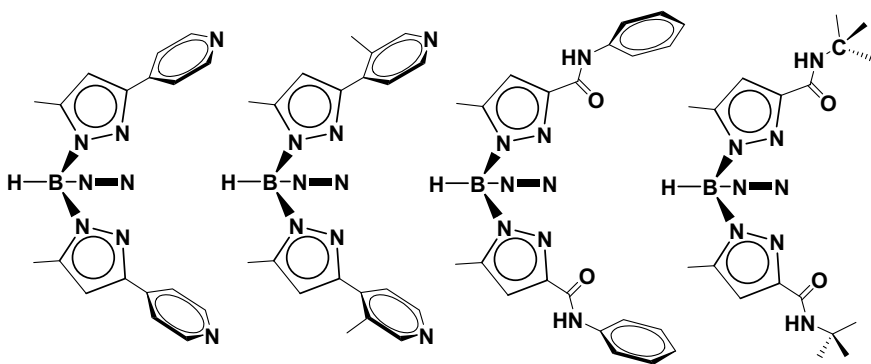


Fig. 1.19. The four new ligands recently reported by Vahrenkamp group.¹⁶⁸ From left to right, respectively: $\text{Tp}^{(4\text{py}),\text{Me}}$, $\text{Tp}^{(4-(2-\text{Mepy}),\text{Me})}$, $\text{Tp}^{(\text{CONHPh}),\text{Me}}$, and $\text{Tp}^{(\text{CONHC}(\text{Me}_3),\text{Me})}$.

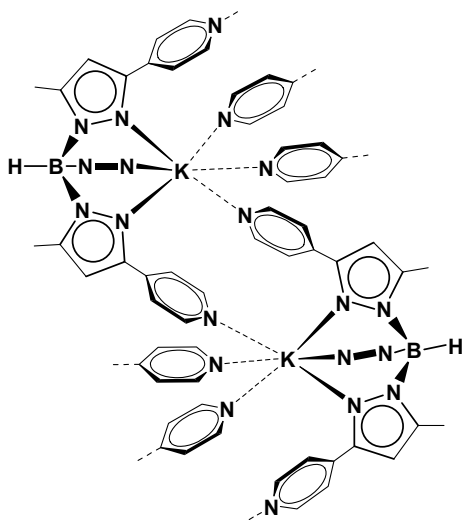


Fig. 1.20. Coordination of K^+ ion in $K(Tp^{(4py)})\cdot Me$.

the pyridyl nitrogen atoms. Coordination dimers and polymers were reported.¹⁶⁸ The same ligands were employed for the synthesis of mono and dinuclear Zn–hydroxo species. The Zn–OH₂, Zn–OH, Zn–OH–Zn, and Zn–O₂H₃–Zn coordination motifs were found.¹⁶⁹ The same authors investigated the reactivity of selected species toward hydrolyzable substrates. $[ZnOH(Tp^{4-py,Me})]$ inserted CO₂ and CS₂ yielding $[Zn(OCOOMe)(Tp^{4-py,Me})]$ and $[Zn(SCSOMe)Tp^{4-py,Me}]$, respectively.¹⁷⁰

1.8.22. $Tp^{2(6Me)py}$

The new podand ligand hydrotris[3-(6-methyl)pyridin-2-ylpyrazol-1-yl]borate, ($Tp^{2(6Me)py}$), has been reported by McCleverty and Ward.¹⁷¹ It possesses a methyl group attached to the C6 positions of the pyridyl rings, which interferes when the ligand is coordinated in a fully hexadentate manner. In fact, $[M(Tp^{2(6Me)py})(NO_3)_2(H_2O)]$ ($M = Eu, Tb$ or Gd) (Fig. 1.21) showed partial dissociation of the podand occurring to relieve potential steric problems: either one or two of the pyridyl groups are not coordinated, such that $Tp^{2(6Me)py}$

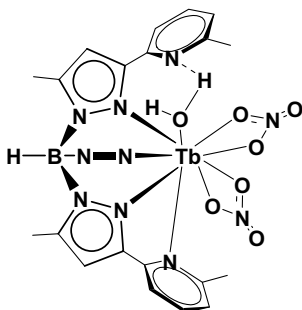


Fig. 1.21. The structure of $[\text{Tb}(\text{Tp}^{2(6\text{Me})\text{py}})(\text{NO}_3)_2(\text{H}_2\text{O})]$.

is penta- or tetra-dentate. Both structural forms are present in single crystals of the Gd and Eu complexes, suggesting facile interconversion between them in solution. Luminescence and NMR studies for these complexes have been reported and compared with those of $[\text{M}(\text{Tp}^{2\text{py}})(\text{NO}_3)_2]$.¹⁷¹

1.8.23. $\text{Tp}^{\text{Ad},i\text{Pr}}$

$\text{Tp}^{\text{Ad},i\text{Pr}}$, the most hindered hydrotris(pyrazolyl)borate ligand, has been reported by Fujisawa *et al.*¹⁷² $[\text{CuCl}(\text{Tp}^{\text{Ad},i\text{Pr}})]$ has been also prepared and characterized by X-ray diffraction.¹⁷²

1.8.24. $\text{Bp}^{4\text{CN}}$ and $\text{Bp}^{\text{Ph},4\text{CN}}$

$[\text{Co}(\text{Bp}^{4\text{CN}})(\text{Tp}^{\text{Np}})]$, $[\text{Co}(\text{Bp}^{4\text{CN}})(\text{Tp}^{\text{Cy}})]$, and $[\text{Co}(\text{Bp}^{4\text{CN}})_2(\text{DMF})_2]$ contain the heretoscorpionate $\text{Bp}^{4\text{CN}}$, a new ligand able to lead oligomeric or polymeric structures. It has been shown that when sterically hindered Tp^x or DMF solvent is employed, the CN group in $\text{Bp}^{4\text{CN}}$ cannot coordinate to the metal ion of a neighboring molecule. $[\text{Co}(\text{Bp}^{4\text{CN}})(\text{Tp}^{\text{Np}})]$ contains a five-coordinate Co center both in the solid and solution state.¹⁷³

The synthesis of $\text{Bp}^{\text{Ph},4\text{CN}}$ has been reported by Eichhorn and coworkers.¹⁷⁴ The monomeric homoleptic square-planar copper complex $[\text{Cu}(\text{Bp}^{\text{Ph},4\text{CN}})_2]$ has been prepared by the reaction of

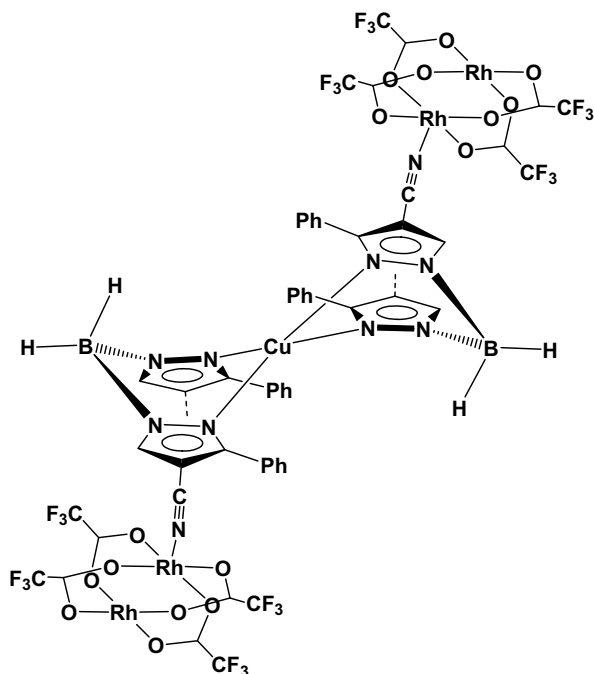


Fig. 1.22. Structure hypothesized for the coordination polymer formed by $[\text{Cu}(\text{Bp}^{\text{Ph},4\text{CN}})_2]$ with $\text{Rh}_2(\text{CF}_3\text{COO})_4$.

$\text{Bp}^{\text{Ph},4\text{CN}}$ with $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$. Protection of a substituent in the 3-position inhibits polymerization reactions,¹⁷⁴ however, when $[\text{Cu}(\text{Bp}^{\text{Ph},4\text{CN}})_2]$ reacts with $\text{Rh}_2(\text{CF}_3\text{COO})_4$, a coordination polymer forms for which a structure has been proposed consisting of $\text{Rh}_2(\text{CF}_3\text{COO})_4$ moieties linked to $[\text{Cu}(\text{Bp}^{\text{Ph},4\text{CN}})_2]$ through the CN groups (Fig. 1.22). This compound has been characterized by IR, EPR, and ESI MS spectroscopy.¹⁷⁵

1.8.25. $\text{Tp}^{4\text{Bo},6-\text{COOEt}}$ and $\text{Tp}^{4\text{Bo},6-\text{CH}_2\text{SEt}}$

Two new tripodal ligands, able to anchor complexes onto surfaces, have been synthesized by Rapenne's group.¹⁷⁶ They integrate ester or thioether functions at the 6-position of the indazoles. Potassium

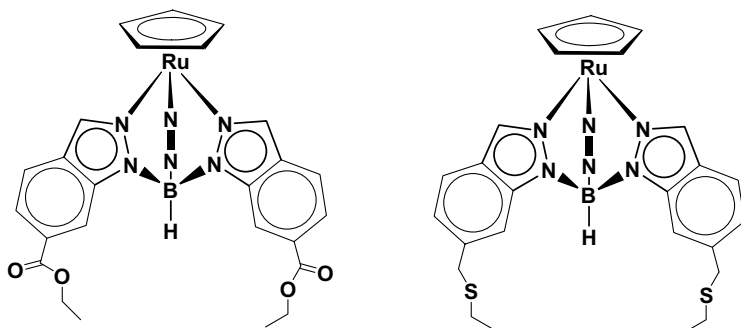
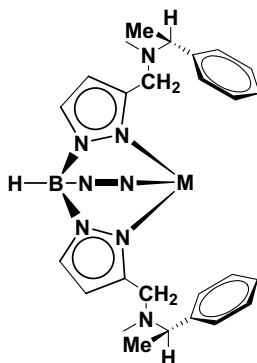


Fig. 1.23. The two piano-stool-shaped $[\text{Ru}(\text{Cp})-(\text{Tp}^{4\text{Bo},6}\text{-COOEt})]$ and $[\text{Ru}(\text{Cp})-(\text{Tp}^{4\text{Bo},6}\text{-CH}_2\text{SEt})]$.

hydrotris[6-(ethoxycarbonyl)indazolyl]borate $\text{K}(\text{Tp}^{4\text{Bo},6}\text{-COOEt})$ and potassium hydrotris[6-[(ethylsulfanyl)methyl]indazolyl]borate $\text{K}(\text{Tp}^{4\text{Bo},6}\text{-CH}_2\text{SEt})$ react with $[\text{Ru}(\text{Cp})(\text{MeCN})_3]\text{PF}_6$ yielding two piano-stool-shaped complexes that were characterized by X-ray diffraction (Fig. 1.23). Comparison with the synthesized unfunctionalized analog showed that the three 6-substituted functions do not interfere with the coordination site and are particularly well oriented for surface deposition.¹⁷⁶

1.8.26. $pz\text{Tp}^{\text{caph}}$, $\text{Tp}^{\text{CH}_2\text{N}(\text{Me})\text{EtPh}}$, $(\text{BBN})\text{Bp}^{+/-\text{caph}}$, and $(\text{BBN})\text{Bp}^{+\text{menthone}}$

The sodium salt of the optically active tetrakis(4,5,6,7-tetrahydro-7,8,8-trimethyl-2*H*-4,7 methanoindazolyl)borate, $\text{Na}(pz\text{-Tp}^{\text{caph}})$ was prepared by the reaction of 4,5,6,7-tetrahydro-7,8,8-trimethyl-2*H*-4,7-methanoindazole with NaBH_4 . Analogously the sodium salt of hydrotris((-)-3(5)-methyl-1-phenylethylaminomethylpyrazolyl)borate, $\text{Na}(\text{Tp}^{\text{CH}_2\text{N}(\text{Me})\text{EtPh}})$ (Fig. 1.24) was obtained by the reaction of (-)-3(5)-methyl-1-phenylethylaminomethylpyrazole with NaBH_4 . These ligands were used in metal-catalyzed (Cu and Rh) enantioselective cyclopropanation reactions of styrene and several diazoacetates.¹⁷⁷

Fig. 1.24. $Tp^{CH_2N(Me)EtPh}$.

Chisholm *et al.*¹⁷⁸ reported the synthesis and the structure of chiral C2 and C1 symmetric $M\{(cyclooctane-1,5\text{-diyl})bis[(4S,7R)\text{-}7,8,8\text{-}trimethyl\text{-}4,5,6,7\text{-}tetrahydro\text{-}4,7\text{-}methano\text{-}2H\text{-}indazol\text{-}2\text{-}yl]borato-\kappa N^1, \kappa N^1\}$ $M(BBNBp^{+camph})$ ($M = K$ or Tl), $K(cyclooctane-1,5\text{-diyl})[(4S,7R)\text{-}7,8,8\text{-}trimethyl\text{-}4,5,6,7\text{-}tetrahydro\text{-}4,7\text{-}methano\text{-}2H\text{-}indazol\text{-}2\text{-}yl][(4S,7R)\text{-}7,8,8\text{-}trimethyl\text{-}4,5,6,7\text{-}tetrahydro\text{-}4,7\text{-}methano\text{-}2H\text{-}indazol\text{-}2\text{-}yl]borato-\kappa N^1, \kappa N^1\} \cdot 3THF$, $K(BBNBp^{+/-camph})$, and $K\{(cyclooctane-1,5\text{-diyl})bis[(4R,7R)\text{-}7\text{-}isopropyl\text{-}4\text{-}methyl\text{-}4,5,6,7\text{-}tetrahydro\text{-}2H\text{-}indazol\text{-}2\text{-}yl]borato-\kappa N^1, \kappa N^1\} \cdot 4THF$, $K(BBNBp^{+menthone})$.¹⁷⁸

1.8.27. Tp^{4Bz}

Hydrotris[3-(4-benzonitrile)-pyrazol-1-yl]borate Tp^{4Bz} , reported by Batten *et al.*¹⁷⁹ and structurally characterized as potassium salt, reacts with MX_2 salts yielding octahedral monomeric $[M(Tp^{4Bz})_2]$ (solv) species ($M = Mn, Co, Ni,$ and Cd). The nitrile groups do not coordinate.¹⁷⁹

1.8.28. $Tp^{CO_2Et, Me}$

$Tp^{CO_2Et, Me}$, a hydrogen-bond accepting ligand, was synthesized by Carrano and coworkers who also reported stable penta- or hexa-coordinate metal aquo complexes $[M(Tp^{CO_2Et, Me})(H_2O)_x]$ ($x = 2$ or

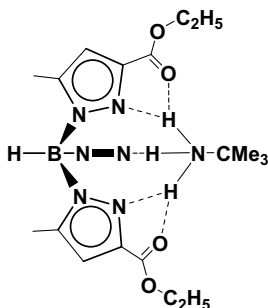


Fig. 1.25. $[\text{Tp}^{\text{CO}_2\text{Et, Me}}][\text{NH}_3\text{R}]$, a rare example of host-guest complex.

3) ($\text{M} = \text{Ni}, \text{Co}, \text{Mn}, \text{and Cu}$) which are unprecedented for the alkyl substituted Tp analogs.¹⁸⁰

$[\text{Tp}^{\text{CO}_2\text{Et, Me}}][\text{NH}_3\text{R}]$, a host-guest complex, as revealed by an X-ray crystal structure of the *tert*-butylammonium analog (Fig. 1.25) has been isolated during the transamidation reactions to convert 3-ester-substituted $\text{Tp}^{\text{CO}_2\text{Et, Me}}$ into 3-amido-substituted ligands.¹⁸¹

The water molecules in $[\text{M}(\text{Tp}^{\text{CO}_2\text{Et, Me}})(\text{H}_2\text{O})_3]$ ($\text{M} = \text{Ni}, \text{Co}, \text{Mn}, \text{or Cu}$) have been displaced by neutral bidentate ligands L giving $[\text{M}(\text{Tp}^{\text{CO}_2\text{Et, Me}})(\text{L})\text{H}_2\text{O}]$.¹⁸²

$[\text{Zn}(\text{NO}_3)(\text{Tp}^{\text{CO}_2\text{Et, Me}})]$, $[\text{Zn}(\text{OAc})(\text{Tp}^{\text{CO}_2\text{Et, Me}})(\text{H}_2\text{O})]$, $[\{\text{Zn}(\text{Tp}^{\text{CO}_2\text{Et, Me}})_2(\text{OH})\}(\text{ClO}_4)]$, and $[\text{Zn}(\text{Tp}^{\text{CO}_2\text{Et, Me}})(\text{H}_2\text{O})_3](\text{ClO}_4)$ have been isolated and structurally characterized. These derivatives are stabilized by internal H-bonding between the water or hydroxide and the ester carbonyls of the donor. $[\{\text{Zn}(\text{Tp}^{\text{CO}_2\text{Et, Me}})_2(\text{OH})\}(\text{ClO}_4)]$ appears to catalyze self-transesterification reaction in alcoholic solvents. The expansion of the coordination sphere from four to five in $[\text{Zn}(\text{OAc})(\text{Tp}^{\text{CO}_2\text{Et, Me}})(\text{H}_2\text{O})]$ or the dimerization in $[\{\text{Zn}(\text{Tp}^{\text{CO}_2\text{Et, Me}})_2(\text{OH})\}(\text{ClO}_4)]$ suggests that a more sterically restrictive ester substituted ligand is needed to enforce the desired mononuclear four-coordinate pseudo-tetrahedral geometry characteristic of zinc metalloenzyme active sites.¹⁸³

1.8.29. $\text{Bp}^{\text{CO}_2\text{Et, Me}}$

The ligand $\text{Bp}^{\text{CO}_2\text{Et, Me}}$, prepared as potassium salt in kerosene solution using ethyl 3-methylpyrazole-5-carboxylate and KBH_4 , reacts

with CuCl and PPh_3 yielding $[\text{Cu}(\text{Bp}^{\text{CO}_2\text{Et,Me}})(\text{PPh}_3)]$. $\text{Bp}^{\text{CO}_2\text{Et,Me}}$ and $[\text{Cu}(\text{Bp}^{\text{CO}_2\text{Et,Me}})(\text{PPh}_3)]$ have been fully characterized by elemental analyses and FT-IR in the solid state and by NMR (^1H , ^{13}C , and ^{31}P) spectroscopy and electrospray ionization mass spectrometry in solution. A single-crystal structural characterization is reported for $[\text{Cu}(\text{Bp}^{\text{CO}_2\text{Et,Me}})(\text{PPh}_3)]$.¹⁸⁴

$\text{Bp}^{\text{CO}_2\text{Et,Me}}$ reacts also with divalent metals giving $[\text{M}(\text{Bp}^{\text{CO}_2\text{Et,Me}})_2]$ ($\text{M} = \text{Mn, Fe, Co, Ni, Zn, Cu, Pb, and Cd}$). All complexes have been fully characterized by elemental analyses and FT-IR in the solid state and by NMR spectroscopy and electrospray ionization mass spectrometry in solution. In $[\text{Cu}(\text{Bp}^{\text{CO}_2\text{Et,Me}})_2]$ and $[\text{Zn}(\text{Bp}^{\text{CO}_2\text{Et,Me}})_2]$ the metals are four-coordinated and only bound to the nitrogen atoms of $\text{Bp}^{\text{CO}_2\text{Et,Me}}$.¹⁸⁵

1.8.30. $\text{Tp}^{\text{C}(\text{Me}_2)\text{CH}_2\text{OMe}}$

A potential hemilabile tris(pyrazolyl)borate ligand bearing ether appendages (Fig. 1.26), $\text{Tp}^{\text{C}(\text{Me}_2)\text{CH}_2\text{OMe}}$, is reported by Chisholm's group.¹⁸⁶ Structural characterization of its Li^+ , Na^+ , K^+ , Tl^+ , and Ca^{2+} complexes evidenced its η^3 , η^5 , η^6 , and μ -binding modes.

1.8.31. PhTp^{tBu}

$[\text{PhTp}^{\text{tBu}}]\text{H}$ is one of the rare $[\text{Tp}^{\text{x}}]\text{H}$ structurally characterized: its pyrazolyl groups are not symmetrical disposed with $\text{C}_{3\text{v}}$ symmetry.

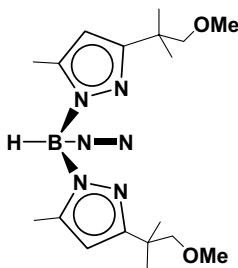
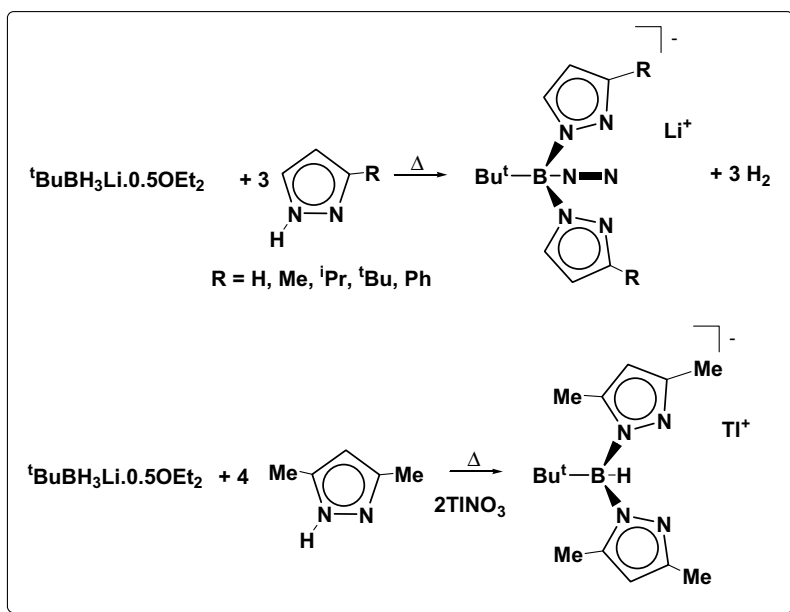


Fig. 1.26. The hemilabile ligand $\text{Tp}^{\text{C}(\text{Me}_2)\text{CH}_2\text{OMe}}$.

$\text{Tl}(\text{PhTp}^{\text{tBu}})$ shows an unprecedented structure in which one of *tert*-butylpyrazolyl groups is rotated by *ca.* 90° and the Tl interacts with the nitrogen attached directly to the boron via a π -orbital component of the aromatic π -system of the pyrazolyl nucleus. $[\text{Tl}(\text{PhTp}^{\text{tBu}})]$ is stereochemically nonrigid on the NMR spectroscopic timescale in solution at room temperature.¹⁸⁷

1.8.32. ${}^t\text{BuTp}^{\text{R}}$ ($\text{R} = \text{H}, \text{Me}, {}^i\text{Pr}, {}^t\text{Bu}, \text{Ph}$) and ${}^t\text{BuBp}^*$

The lithium and thallium salts of ${}^t\text{BuTp}^{\text{R}}$ ($\text{R} = \text{H}, \text{Me}, {}^i\text{Pr}, {}^t\text{Bu}, \text{Ph}$) have been prepared and characterized. It is noteworthy that the reaction between ${}^t\text{BuBH}_3\text{Li} \cdot 5\text{Et}_2\text{O}$ and excess Hpz^* afforded ${}^t\text{BuBp}^*$ due to steric congestion at B (Scheme 1.2). The solid-state ${}^7\text{Li}$ and ${}^{11}\text{B}$ NMR spectra of $[\text{Li}({}^t\text{BuTp}^{\text{iPr}})]$ suggest that this salt exists as a mixture of axial and equatorial isomers. The partial hydrolysis of $[\text{Li}({}^t\text{BuTp}^{\text{tBu}})]$ afforded the dimeric $[\text{Li}({}^t\text{BuB}(\text{pz}^{\text{tBu}})_2)_2-$



Scheme 1.2. Synthesis of ${}^t\text{BuTp}^{\text{R}}$ and ${}^t\text{BuBp}^*$.

$(\mu\text{-OH})\}_2$ containing two Li cations encapsulated by the heteroscorpionate $[\text{tBuB}(\text{pz}^{\text{tBu}})_2(\mu\text{-OH})]$ ligands. The homoleptic, paramagnetic low-spin iron(III) complexes $[\text{Fe}(\text{tBuTp})_2]\text{PF}_6$ and $[\text{Fe}(\text{tBuTp}^{\text{Me}})_2]\text{PF}_6$ have been also reported and characterized.¹⁸⁸

When $\text{FeCl}_2(\text{THF})_{1.5}$ reacts with the sterically hindered thallium salt of $(\text{tBuTp}^{\text{tBu}})$, the complex *trans*- $\text{FeCl}_2(\text{Hpz}^{\text{tBu}})_4$ is formed, the only isolable product appearing to be the first example of a *trans*-dichloro pseudo-octahedral iron(II) complex bearing four neutral pyrazole ligands.¹⁸⁹

1.8.33. *FlTp and FlTp^{tBu}*

Two hybrid Tp^x ligands, FlTp and FlTp^{tBu} have been synthesized as Li salts and characterized by X-ray. The reaction of $[\text{Li}(\text{FlTp})]$ and ZnCl_2 afforded $[(\text{THF})_3\text{Li}(\text{FlTp})\text{ZnCl}_2]$ in which a ZnCl_2 moiety is chelated by two pyrazolyl ligands while the third pz ring coordinates to a $\text{Li}(\text{THF})_3$ fragment. $[(\text{THF})_3\text{Li}(\text{FlTp})\text{ZnCl}_2]$ gradually decomposes into the mononuclear species $[\text{Zn}(\text{FlTp})_2]$. In the compounds described by Wagner and coworkers,¹⁹⁰ the hybrid ligands FlTp and FlTp^{tBu} adopt a conformation with only two pyrazolyl rings bonded to the central metal, the third pyrazolyl acting as dangling substituent. The fluorenyl substituent of $[\text{Li}(\text{FlTp})]$ may be deprotonated with KH .¹⁹⁰ Degradation reactions of these scorpionates were observed in the presence of transition-metal salts MX_2 to give transition-metal adducts containing neutral pyrazoles.¹⁹¹

1.8.34. *MeTp^x (Tp^x = Tp, Tp* or Tp^{Me})*

Reaction of MeBBr_2 with pyrazoles in the presence of TlOEt and NEt_3 yields the tris(pyrazolyl)borate thallium salts $[\text{Tl}(\text{MeTp}^x)]$ ($\text{Tp}^x = \text{Tp}$, Tp^* or Tp^{Me}). In $[\text{Tl}(\text{MeTp}^*)]$ a bridging bidentate coordination of MeTp^* is found, which has been explained as sterically enforced, on the basis of a comparison between the structure of $[\text{Tl}(\text{MeTp}^*)]$ and $[\text{Tl}(\text{MeTp}^{\text{Me}})]$.¹³²

1.8.35. $Fc(Tp^{Ph})$

A series of ferrocene-based mono and bifunctional tris(pyrazolyl)-borates bearing either methyl or phenyl substituents at the 3-position has been prepared via a *trans*-amination reaction. The lithium salts have been converted in the analogous Tl species and $[Tl(Fc(Tp^{Ph}))]$ has been also structurally characterized. These compounds feature monomeric units with tridentate $Fc(Tp^{Ph})$ in striking contrast to the sterically less congested $[Tl(Fc(Tp))]$ that forms polymeric rods in the solid state. In the same paper the authors reported the structure of $Tl(Tp)$ for purpose of comparison.¹⁹²

1.8.36. $CymTp$, $Cym'Tp$, and $Cym'Tp^R$ Tl ($R = CH_2(C_6H_{11})$)

Reaction of $CymBBr_2$ and $Cym'BBr_2$ with Hpz in the presence of triethylamine gave new cymanthrene based ligands as their Tl salts. The structure of $[Tl(CymTp)]$, and $[Tl(Cym'Tp)]$ is similar to that of $[Tl(FcTp)]$. $[Tl(CymTp)]$ features a polymeric structure with bridging Tp fragments whereas $[Tl(Cym'Tp)]$ shows an oligomeric structure. $[Tl(Cym'Tp^R)]$ ($R = CH_2(C_6H_{11})$), ligand of high solubility in non-polar solvents, has been also reported.¹⁹³

The di- and trinuclear complexes $[Mn(CO)_3(CymTp)]$ (Fig. 1.27), $[Mn(CO)_3(CymBp(OH))]$, and $[Zn(CymTp)_2]$ have been also reported.¹⁹⁴ The structure of $[Mn(CO)_3(CymTp)]$, exhibiting a cyclopentadienyl ring together with a scorpionate moiety in the same molecule, indicates that both ligand types (Cp and Tp) exert a very similar electronic influence on the respective $Mn(CO)_3$ fragment. $[Mn(CO)_3(CymBp(OH))]$ is obtained when the reaction between

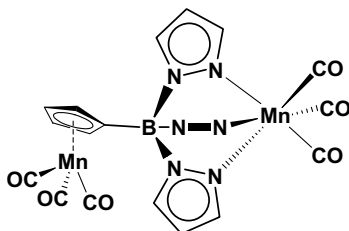


Fig. 1.27. The dinuclear $[Mn(CO)_3(CymTp)]$.

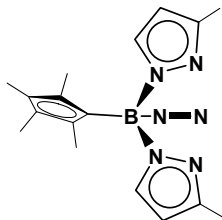


Fig. 1.28. The dianionic ligand $(C_5Me_4Tp^{Me})^{2-}$.

[Tl(CymTp)] and $Mn(CO)_5Br$ is performed without exclusion of air and moisture.¹⁹⁴

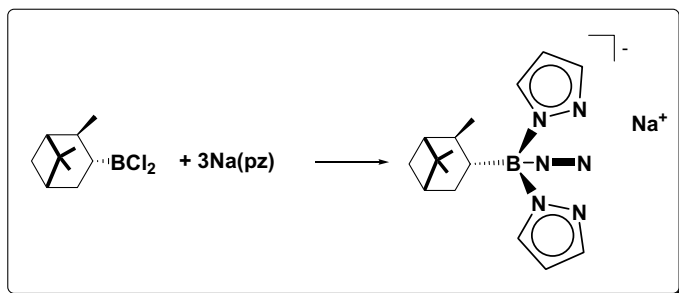
Wagner and coworkers¹⁹⁵ reported also some rare examples of complexes featuring a chelating Cp/scorpionate hybrid ligand and obtained by photolytic decarbonilation of $K[(CymTp)]$ which leads to the constrained geometry complex $K[(OC)_2Mn(C_5H_4-B((\mu-pz)(pz)_2))]$.

1.8.37. $C_5Me_4Tp^{Me}$

Marques and coworkers¹⁹⁶ reported the new dianionic ligand $(C_5Me_4Tp^{Me})^{2-}$ (Fig. 1.28) and characterized it as lithium and potassium salt. In the solid state $[Li_2(C_5Me_4Tp^{Me})(THF)_3]$ is monomeric, one lithium being tetracoordinate by two nitrogen atoms of the Tp^x ligand and two oxygen atoms from THF, the second lithium being η^5 -coordinated to the C_5Me_4 ring, one N from Tp^x and one O from the third THF molecule. $[K_2(C_5Me_4Tp^{Me})(THF)_2]_\infty$ consists of infinite puckered chains, one K atom being described as distorted square-pyramidal, the other in a triangular-pyramidal coordination environment. These derivatives have been prepared by the reaction of $B(NMe_2)_2(C_5Me_4H)$ with 2 equiv. of Hpz^{Me} and 1 equiv. of $M(pz^{Me})$ ($M = Li, K$) followed by the deprotonation with $nBuLi$ or K . The crystal structure of the intermediate monoanion $[Li\{C_5Me_4HTp^{Me}\}(THF)_2]$ has been also reported.¹⁹⁶

1.8.38. *IpcTp*

$Na[(Ipc)Tp]$, prepared by a new general synthetic method (Scheme 1.3), has been used to synthesize $[Mn\{(Ipc)Tp\}(CO)_3]$.¹⁹⁷



Scheme 1.3. Synthesis of Na[(Ipc)Tp].

1.8.39. *MeTp*^{CF₃}

The thallium derivative of *MeTp*^{CF₃} has been synthesized via a two-step process using the corresponding pyrazole, Li[MeBH₃], and thallium(I) acetate. Reaction of [Tl(MeTp^{CF₃})] with CuBr in the presence of ethylene gave [Cu(MeTp^{CF₃})(C₂H₄)] which reacts with [(Bn)₂ATI]SnCl to yield [(MeTp^{CF₃})Cu]←Sn(Cl)[(Bn)₂ATI], containing an unsupported Cu(I)–Sn(II) bond.¹⁹⁸ [Ag(MeTp^{CF₃})(C₂H₄)] has been also prepared and characterized.¹⁹⁹

1.8.40. *PhTp*^{CF₃}

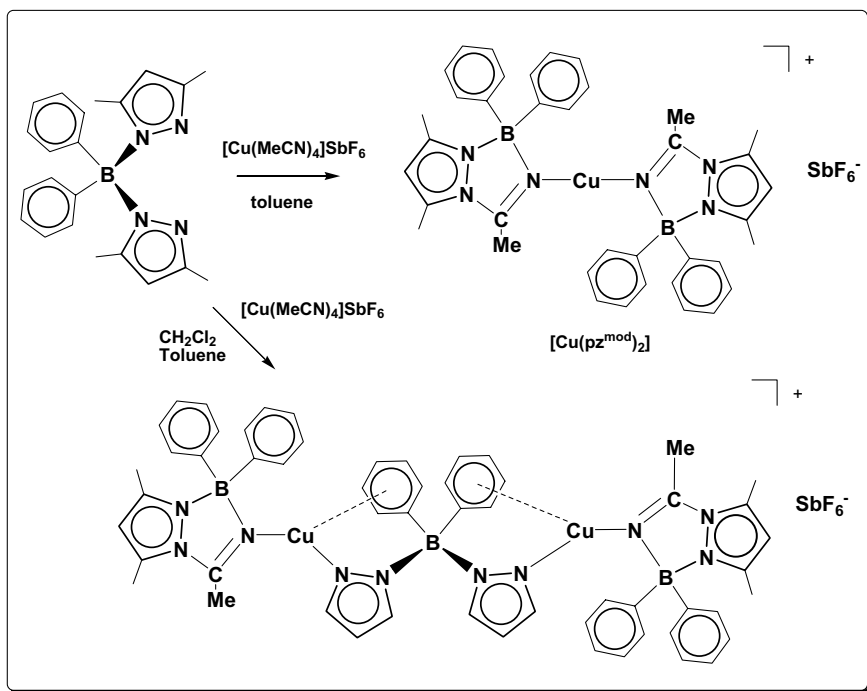
[Ag(PhTp^{CF₃})(C₂H₄)] obtained from the lithium poly(pyrazolyl)-borate salt, AgOTf and ethylene, has a planar three-coordinate silver center; whereas the ethylene-free [Ag(PhTp^{CF₃})]_n adopts a helical structure with a hexagonal pore.¹⁹⁹

1.8.41. *MeTp*^{(C₂F₅)₃}

The new B-methylated ligand [MeTp^{(C₂F₅)₃], reported by Rasika Dias and Wang,²⁰⁰ enables the isolation of the lithium adduct [Li(MeTp^{(C₂F₅)₃)] exhibiting a *fac*-N₃F₃ coordination, and the formation of two stable silver species [Ag(MeTp^{(C₂F₅)₃)CO] and [Ag(MeTp^{(C₂F₅)₃)(C₂H₄)].²⁰⁰}}}}

1.8.42. $Ph_2Bp^{R,R'}$

The ligands $Ph_2Bp^{R,R'}$ ($R = Ph$, $R' = H$, and $R = R' = CH_3$) were synthesized by heating $pz^{R,R'}$ and $NaBPh_4$, a method similar to that reported for the preparation of the parent $Na(Ph_2Bp)$. Treatment of $Na(Ph_2Bp^{Ph})$ with $[Cu(MeCN)_4]SbF_6$ afforded $[Cu(Ph_2Bp^{Ph})(Hpz^{Ph})]$. Reaction of $Na(Ph_2Bp^*)$ with $[Cu(MeCN)]SbF_6$ yields as major product, a compound containing two new N-donor ligands bound to a single Cu(I) ion that adopts a linear coordination geometry (Scheme 1.4). In the new ligand (pz^{mod}), one pyrazolyl ring is missing from each boron center. The second product contains both pz^{mod} and a bridging Ph_2Bp^* ligand coordinated also through the aromatic Ph rings.²⁰¹

Scheme 1.4. Reaction of Ph_2Bp^* with $[Cu(MeCN)_4]SbF_6$.

1.8.43. MeTp^{Ms} and MeTp^{tBu}

MeTp^{Ms} has been synthesized by Dias and Wang as Tl salt.²⁰² The copper complex $[\text{CuCl}(\text{MeTp}^{\text{Ms}})]$ has been employed to polymerize cleanly the aniline dimer, *N*-(4-aminophenyl)aniline under mild conditions to obtain polyaniline.²⁰³ $[\text{Ag}(\text{CO})(\text{MeTp}^{\text{Ms}})]$, $[\text{Ag}(\text{C}_2\text{H}_4)(\text{MeTp}^{\text{Ms}})]$ and $[\text{Tl}(\text{MeTp}^{\text{tBu}})]$ have been also described and characterized.²⁰⁴

1.8.44. “Third generation” scorpionates

Daniel Reger introduce the term “third generation” poly(pyrazolyl)borate ligands to designate ligands that are specifically functionalized at the noncoordinating “back” position (Fig. 1.29).

1.8.44.1. $(p\text{-IC}_6\text{H}_4)\text{Tp}^{\text{R}}$ ($\text{R} = \text{H}$ or Me)

$(p\text{-IC}_6\text{H}_4)\text{Tp}^{\text{x}}$ ($\text{Tp}^{\text{x}} = \text{Tp}$ or Tp^{Me}), prepared according to Scheme 1.5, reacts with FeBr_2 giving the low-spin $\text{Fe}[(p\text{-IC}_6\text{H}_4)\text{Tp}]_2$

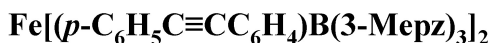
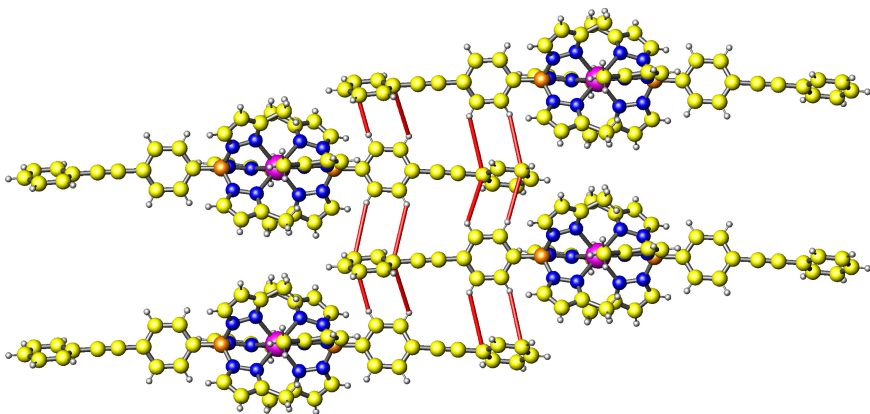
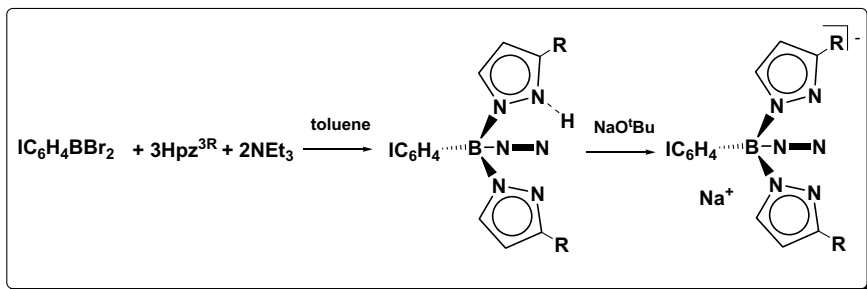


Fig. 1.29. “Third generation” scorpionates.

Scheme 1.5. Synthesis of $[(p\text{-IC}_6\text{H}_4)\text{Tp}]^*$.

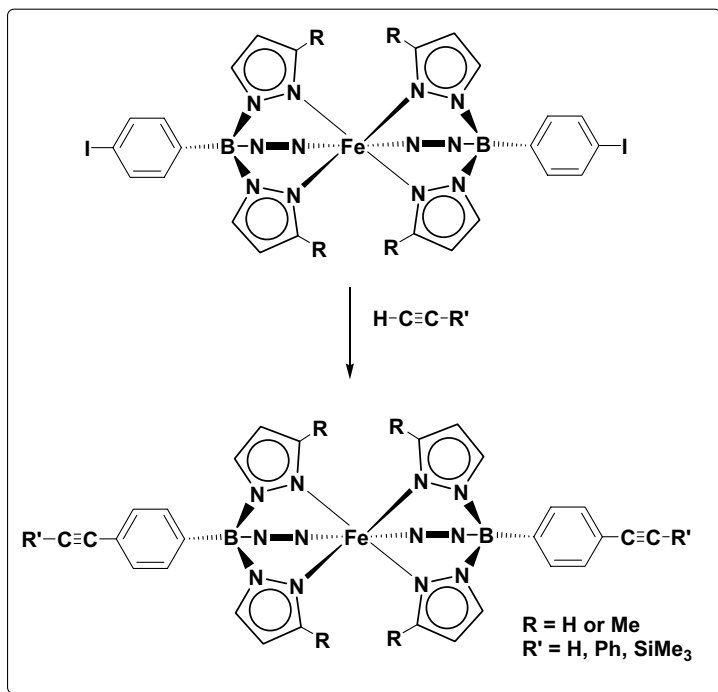
and the high-spin $\text{Fe}[(p\text{-IC}_6\text{H}_4)\text{Tp}^{\text{Me}}]_2$. The latter, can exist as two polymorphs.²⁰⁵

1.8.44.2. $(p\text{-PhC}_2\text{C}_6\text{H}_4)\text{Tp}^{\text{Me}}$, $(p\text{-Me}_3\text{SiC}_2\text{C}_6\text{H}_4)\text{Tp}^{\text{R}}$,
and $(p\text{-HC}_2\text{C}_6\text{H}_4)\text{Tp}^{\text{R}}$ ($\text{R} = \text{H}$ or Me)

Sonogashira coupling reactions (Scheme 1.6) of terminal alkynes with $[\text{Fe}\{(p\text{-IC}_6\text{H}_4)\text{Tp}^{\text{Me}}\}_2]$ yielded $[\text{Fe}\{(p\text{-PhC}_2\text{C}_6\text{H}_4)\text{Tp}^{\text{Me}}\}_2]$, $[\text{Fe}\{(p\text{-Me}_3\text{SiC}_2\text{C}_6\text{H}_4)\text{Tp}^{\text{R}}\}_2]$ ($\text{R} = \text{H}, \text{Me}$), and $[\text{Fe}\{(p\text{-HC}_2\text{C}_6\text{H}_4)\text{Tp}^{\text{R}}\}_2]$ ($\text{R} = \text{H}, \text{Me}$). The crystal structures of $[\text{Fe}\{(p\text{-PhC}_2\text{C}_6\text{H}_4)\text{Tp}^{\text{Me}}\}_2]$ obtained for each of the three distinct electronic spin states, reveal two crystallographically different iron(II) sites. Analysis of the molecular/supramolecular structures indicates that the difference in the degree of pyrazolyl ring tilting in the ligands between the two sites, rather than the strength of the intermolecular forces, plays a prominent role in determining the temperature of the spin-state crossover.²⁰⁶

1.8.44.3. $p\text{-BrC}_6\text{H}_4\text{Tp}$, $p\text{-(HO}_2\text{C)C}_6\text{H}_4\text{Tp}$, and
 $p\text{-}(^t\text{BuO-Phe-CO)C}_6\text{H}_4\text{Tp}$

Kuchta and coworkers²⁰⁷ reported the synthesis of $p\text{-BrC}_6\text{H}_4\text{Tp}$ and $[\text{PtMe}_3\{p\text{-(HO}_2\text{C)C}_6\text{H}_4\text{Tp}\}]$ from $[\text{PtMe}_3\{p\text{-BrC}_6\text{H}_4\text{Tp}\}]$. $[\text{PtMe}_3\{p\text{-(HO}_2\text{C)C}_6\text{H}_4\text{Tp}\}]$ can be readily coupled to biomolecules such as amino acids, as *L*-phenylalanine-*tert*-butylester, to provide species

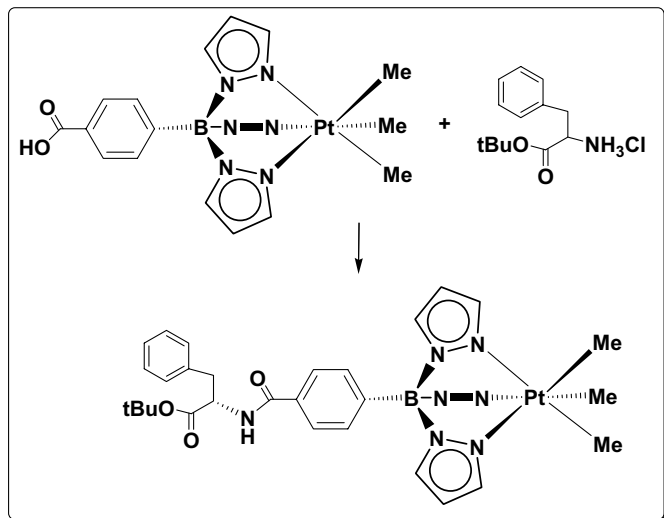


Scheme 1.6. Sonogashira coupling reactions for the synthesis of new scorpionates.

as $[\text{PtMe}_3\{p\text{-}(t\text{BuO-Phe-CO})\text{C}_6\text{H}_4\text{Tp}\}]$ (Scheme 1.7) which has been structurally characterized in the solid state by X-ray diffraction. This compound constitutes the first example of a tris(pyrazolyl)borate bioconjugate.²⁰⁷

1.8.44.4. $(pz)_3\text{CCH}_2\text{OCH}_2\text{-C}_2\text{-C}_6\text{H}_4\text{Tp}$ and $\{3,5\text{-}[(pz)_3\text{CCH}_2\text{OCH}_2]_2\text{C}_6\text{H}_3\text{C}_2\}\text{C}_6\text{H}_4\text{Tp}$

The reaction of $\text{HC}_2\text{CH}_2\text{OCH}_2\text{C}(pz)_3$ with $[\text{Fe}\{(p\text{-IC}_6\text{H}_4)\text{Tp}\}_2]$ yields the bitopic, metalloligand $\text{Fe}\{(pz)_3\text{CCH}_2\text{OCH}_2\text{-C}_2\text{-C}_6\text{H}_4\text{Tp}\}_2$, structurally characterized. The analogous reaction with $3,5\text{-}[(pz)_3\text{CCH}_2\text{OCH}_2]_2\text{C}_6\text{H}_3(\text{C}_2\text{H})$ yields the tetratopic metalloligand $\text{Fe}\{\{3,5\text{-}[(pz)_3\text{CCH}_2\text{OCH}_2]_2\text{C}_6\text{H}_3\text{C}_2\}\text{C}_6\text{H}_4\text{Tp}\}_2$ (Fig. 1.30).²⁰⁸



Scheme 1.7. Synthesis of tris(pyrazolyl)borate bioconjugate.

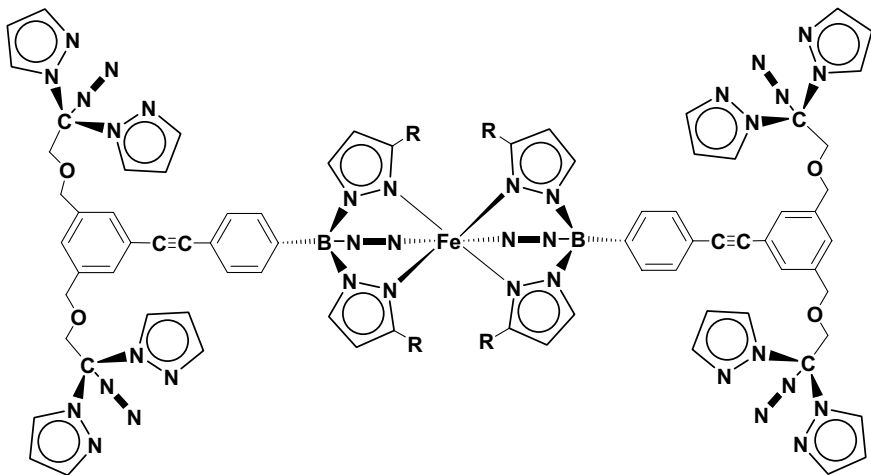


Fig. 1.30. The tetratopic metalloligand Fe[{3,5-[(pz)₃CCH₂OCH₂]₂C₆H₃C₂}C₆-H₄Tp]₂.

1.8.45. Me_2NTp

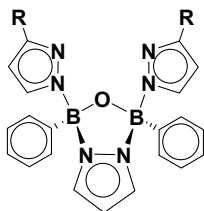
Bieller *et al.*²⁰⁹ reported the syntheses and structures of the $M(Me_2NTp)$ ($M = Na, K$), consisting of polymeric chains containing subunits where Me_2NTp acts as tridentate ligand toward Na^+ and K^+ .

1.8.46. $Fc(Me)Bp$, Fc_2Bp , and $1,1'-fc[(Me)Bp]_2$

Reaction of $FcB(Me)NMe_2$, Fc_2BNMe_2 , and $1,1'-fc[B(Me)NMe_2]_2$ with 1:1 mixtures of pyrazole and $K(pz)$ in refluxing THF gave $K[Fc(Me)Bp]$, $K[Fc_2Bp]$, and $K_2\{1,1'-fc[(Me)Bp]_2\}$. $K[Fc(Me)Bp]$ and $K[Fc_2Bp]$ are centrosymmetric dimers with short $K \cdots Cp$ contacts suggesting an η^5 -coordination mode of the potassium ion. The crystal lattice of the ditopic ligand $K_2\{1,1'-fc[(Me)Bp]_2\}$ consists of coordination polymer strands featuring essentially the same structural motif that has been observed for the monotopic derivatives. These scorpionate ligands are promising building blocks for the preparation of ferrocene-containing multiple-decker sandwich complexes.²¹⁰

1.8.47. $1,1'-fc(BMe_2pz)_2$

Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ salts of the ditopic $\{1,1'-fc(BMe_2pz)_2\}^{2-}$ are multiple-decker sandwich complexes with the M^+ ions bound to the π faces of the ferrocene cyclopentadienyl rings in an η^5 manner. The lithium complex reveals discrete trimetallic entities with each lithium ion being coordinated by only one cyclopentadienyl ring. The sodium salt consists of polyanionic zig-zag chains where each Na^+ ion bridges the Cp of two ferrocene moieties. $[-CpR-Fe-CpR-M^+-CpR-Fe-CpR-M^+-]_{\infty}$ ($R = [-BMe_2pz]^-$, $M = K, Rb$, and Cs) exist as linear columns in the solid state.²¹¹ In $[Li_2\{1,1'-fc(BMe_2pz)_2\}]$ the lithium ions are coordinated by two solvent molecules (Et_2O), the pyrazolyl side-arm and the cyclopentadienyl ring. $[Li_2\{1,1'-fc(BMe_2pz)_2\}]$ can be regarded as a trinuclear segment of the polymeric structure $[-(C_5H_4R)Li(C_5H_4R)Fe-]_{\infty}$ ($R = BMe_2pz$).²¹²

Fig. 1.31. $[\text{pz}^{\text{R}}(\text{Ph})\text{B}(\mu\text{-pz})(\mu\text{-O})\text{B}(\text{Ph})\text{pz}^{\text{R}}]$.

1.8.48. $[\text{pz}(\text{Ph})\text{B}(\mu\text{-pz})(\mu\text{-O})\text{B}(\text{Ph})\text{pz}]$ and
 $[\text{pz}^{\text{Ph}}(\text{Ph})\text{B}(\mu\text{-pz})(\mu\text{-O})\text{B}(\text{Ph})\text{pz}^{\text{Ph}}]$

Trans-coordinating tridentate poly(pyrazolyl)borate ligands have been reported by Wagner and coworkers who describe the synthesis of $[\text{pz}(\text{Ph})\text{B}(\mu\text{-pz})(\mu\text{-O})\text{B}(\text{Ph})\text{pz}]$ (Fig. 1.31) and of $[\text{pz}^{\text{Ph}}(\text{Ph})\text{B}(\mu\text{-pz})(\mu\text{-O})\text{B}(\text{Ph})\text{pz}^{\text{Ph}}]$ as well as the synthesis and the structural properties of $[\text{FeCl}_2\{\text{pz}(\text{Ph})\text{B}(\mu\text{-pz})(\mu\text{-O})\text{B}(\text{Ph})\text{pz}\}]$, $[\text{CuCl}\{\text{pz}(\text{Ph})\text{B}(\mu\text{-pz})(\mu\text{-O})\text{B}(\text{Ph})\text{pz}\}]$, and $[\text{FeCl}\{\text{pz}(\text{Ph})\text{B}(\mu\text{-pz})(\mu\text{-O})\text{B}(\text{Ph})\text{pz}\}(\text{py})]$.²¹³

1.8.49. $[1,n\text{-}(\text{tBuBp})_2\text{C}_6\text{H}_4]$, $[1,4\text{-}(\text{Tp})_2\text{C}_6\text{H}_4]$,
 and $[(\text{Bp})_2(\text{C}_6\text{H}_4)_2]$

The Wagner research group reported the synthesis and crystal structure analysis of the lithium salt of the ditopic *p*-phenylene-bridged bis(pyrazol-1-yl)borate $[\text{Li}_2\{p\text{-C}_6\text{H}_4\text{-}(\text{tBuBp})_2\}]$. The dinuclear complex $[\text{Mn}_2(\text{THF})_2(\mu\text{-Cl})_2\{p\text{-C}_6\text{H}_4\text{-}(\text{tBuBp})_2\}]$ has been obtained through a salt metathesis. Reaction of $[\text{Li}_2\{p\text{-C}_6\text{H}_4\text{-}(\text{tBuBp})_2\}]$ with 2 equiv. of $[\text{Ti}(\text{NMe}_2)_3\text{Cl}]$ gave the dinuclear titanium compound $[\text{Ti}_2(\text{NMe}_2)_6\{p\text{-C}_6\text{H}_4\text{-}(\text{tBuBp})_2\}]$, whereas reaction with $[\text{Ti}(\text{NMe}_2)_2\text{Cl}_2]$ and water afforded $[[\text{Ti}_2(\text{NMe}_2)_2\text{Cl}_2]_2(\mu\text{-O})\{p\text{-C}_6\text{H}_4\text{-}(\text{tBuBp})_2\}]$.²¹⁴

$[\text{K}_2\{1,4\text{-}(\text{tBuBp})_2\text{C}_6\text{H}_4\}]$, $[(\text{Li},\text{K})_2\{1,3\text{-}(\text{tBuBp})_2\text{C}_6\text{H}_4\}]$, and $[\text{K}_2\{1,4\text{-}(\text{Tp})_2\text{C}_6\text{H}_4\}]$ have been prepared by using 1,4- and 1,3-diborylated benzene derivatives. $[\text{K}_2\{1,3\text{-}(\text{tBuBp})_2\text{C}_6\text{H}_4\}]$ possesses a

polymeric structure in the solid state. The unsymmetrically substituted hydrolysis product $[\text{Li}_2\{1,3-(t\text{BuBp})_2(t\text{BuB}(\text{OH})\text{pz})\text{C}_6\text{H}_4\}]$ contains discrete dimers formed by four lithium cations encapsulated by the organic ligands. The 9,10-dihydro-9,10-diboraanthracene derivative $[\text{K}_2\{(\text{Bp})_2(\text{C}_6\text{H}_4)_2\}]$ (Fig. 1.32) bears two pyrazolyl substituents at each of its boron atoms and stands out due to its stereorigidity.²¹⁵

$[\text{Tl}_2\{1,3-\text{C}_6\text{H}_4(t\text{BuBp})_2\}]$, $[(\text{PPh}_3)\text{Cu}\{1,3-\text{C}_6\text{H}_4(t\text{BuBp})_2\} \text{Cu}(\text{PPh}_3)]$, and $[\text{Ag}(\text{PPh}_3)\{1,3-\text{C}_6\text{H}_4(t\text{BuBp})_2\}\text{Ag}(\text{PPh}_3)]$ containing the ditopic 1,3-phenylene-bridged heteroscorpionate (Fig. 1.33) have been prepared and investigated by ^1H , ^{13}C , ^{11}B , and ^{31}P NMR spectroscopy.²¹⁶

1.8.50. $\{\text{CH}_2=\text{CHCH}_2\text{Bp}(\text{CH}_2\text{PPh}_2)\}$, $\{\text{CH}_2=\text{CHCH}_2\text{Tp}\}$, and their carborane dendrimer

Oro and coworkers described the synthesis of a novel hybrid pyrazolate/phosphine anionic ligand $\{\text{CH}_2=\text{CHCH}_2\text{Bp}(\text{CH}_2\text{PPh}_2)\}$

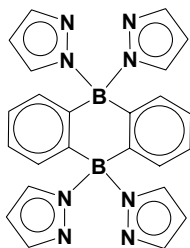


Fig. 1.32. The 9,10-dihydro-9,10-diboraanthracene $[\text{K}_2\{(\text{Bp})_2(\text{C}_6\text{H}_4)_2\}]$.

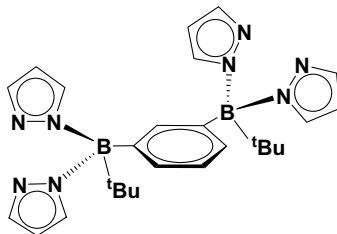
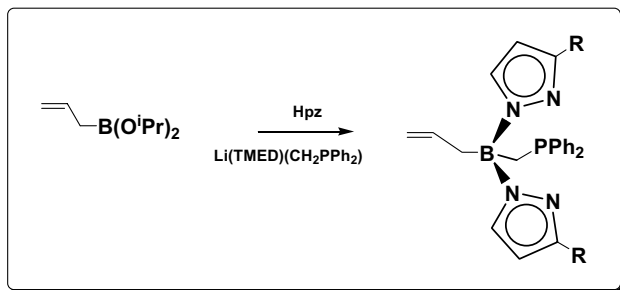


Fig. 1.33. The ditopic 1,3-phenylene-bridged $1,3-\text{C}_6\text{H}_4(t\text{BuBp})_2$.



Scheme 1.8. Formation of a hybrid pyrazolate/phosphine ligand.

(Scheme 1.8). Coordination of this ligand in a *fac* tridentate fashion occurs in the complexes $[M(\text{COD})\{\text{CH}_2=\text{CHCH}_2\text{Bp}(\text{CH}_2\text{PPh}_2)\}]$ ($M = \text{Rh}, \text{Ir}$). The ligand has been linked to the periphery of a carborasilane dendrimer, resulting in the polyanionic dendrimer $[\text{Li}(\text{TMED})]_4[\text{Si}\{(\text{CH}_2)_3\text{SiMe}_2(\text{CH}_2)_3\text{Bp}(\text{CH}_2\text{PPh}_2)\}_4]$ (Fig. 1.34), which gave the corresponding metallodendrimer with four rhodium atoms.²¹⁷

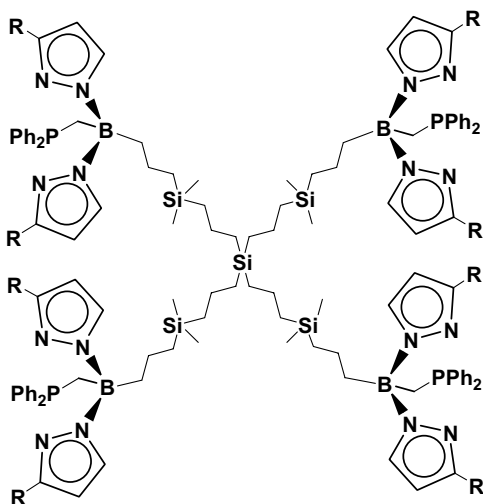


Fig. 1.34. The polyanionic dendrimer able to form a metallodendrimer with four Rh(I) olefin moieties.

A modified tris(pyrazolyl)borate ligand has been prepared analogously by reaction of $\text{CH}_2=\text{CHCH}_2\text{B}(\text{O}^i\text{Pr})_2$ with potassium pyrazolate and pyrazole to give $\text{K}[\text{CH}_2=\text{CHCH}_2\text{Tp}]$ which acts as a bi or tridentate ligand in its mononuclear complexes $[\text{CH}_2=\text{CHCH}_2\text{-TpM}(\text{LL})]$ ($\text{M} = \text{Rh}$, $\text{LL} = \text{NBD}$; TFB ; $(\text{CO})(\text{PPh}_3)$; $\text{M} = \text{Ir}$, $\text{LL} = \text{COD}$). The borate-containing dendrimers $\text{Si}[(\text{CH}_2)_3\text{SiMe}_2(\text{CH}_2)_3\text{B}(\text{O}^i\text{Pr})_2]_4$, $\text{Si}[(\text{CH}_2)_3\text{SiMe}\{(\text{CH}_2)_3\text{SiMe}_2(\text{CH}_2)_3\text{B}(\text{O}^i\text{Pr})_2\}_2]_4$, and $\text{Si}[(\text{CH}_2)_3\text{SiMe}\{(\text{CH}_2)_3\text{SiMe}\{(\text{CH}_2)_3\text{SiMe}_2(\text{CH}_2)_3\text{B}(\text{O}^i\text{Pr})_2\}_2\}_2]_4$ react with Kpz and Hpz yielding the corresponding polyanionic dendrimers which contain 4, 8, and 16 Tp groups symmetrically located around the dendritic peripheries. These unusual polyanionic dendrimers are excellent scaffolds to support metal centers, as shown by their reactions with $[\{\text{Rh}(\mu\text{-Cl})(\text{NBD})\}_2]$.²¹⁸

1.8.51. $\text{HB}(\text{tz}^t\text{Bu,Me})_3$

3-*tert*-butyl-5-methyl-1,2,4-triazole reacted with KBH_4 to give tris(3-*tert*-butyl-5-methyl-1,2,4-triazolyl)borate, $(\text{HB}(\text{tz}^t\text{Bu,Me})_3)$. $\text{HB}(\text{tz}^t\text{Bu,Me})_3$ gave the four-coordinate $[\text{CoCl}(\text{HB}(\text{tz}^t\text{Bu,Me})_3)]$ and the five-coordinate $[\text{CoNO}_3(\text{HB}(\text{tz}^t\text{Bu,Me})_3)]$ and $[\text{Zn}(\text{OAc})(\text{HB}(\text{tz}^t\text{Bu,Me})_3)]$ complexes. $\text{K}(\text{HB}(\text{tz}^t\text{Bu,Me})_3)$, more water soluble than $\text{K}(\text{Tp}^t\text{Bu,Me})$, can lead to functional models for enzyme active sites in an aqueous environment and yields water-soluble analogs of Tp catalysts.²¹⁹

1.8.52. $\text{H}_2\text{B}(\text{tz}^*)_2$

$\text{K}[\text{H}_2\text{B}(\text{tz}^*)_2]$ ($\text{tz}^* = 3,5$ -dimethyl-1,2,4-triazolyl) has been prepared and its reaction with copper and zinc salt investigated. The complexes $[\text{Cu}\{\text{H}_2\text{B}(\text{tz}^*)_2\}_2(\text{H}_2\text{O})]$ and $[\text{Zn}\{\text{H}_2\text{B}(\text{tz}^*)_2\}_2(\text{H}_2\text{O})]$ have been investigated by single-crystal X-ray, both being five-coordinated with four nitrogen atoms from triazolyl and one oxygen atom from the water molecule. In both compounds, the hydrogen atoms of H_2O are connected by hydrogen bonding with N atoms of two adjacent complex molecules to form 2-D planes.²²⁰

1.8.53. $\{H_2B(tz^{NO_2})_2\}$

$\{H_2B(tz^{NO_2})_2\}$ has been prepared in DMAC and characterized as potassium salt. $[MCl\{H_2B(tz^{NO_2})_2\}(H_2O)_2]$ ($M = Zn$ or Cd) have been obtained by metathesis of $K\{H_2B(tz^{NO_2})_2\}$ with $ZnCl_2$ and $CdCl_2$, respectively. The complexes likely contain a metal core in which the ligand is coordinated in the κ^2-N,N' - or κ^4-N,N',O,O' -fashion. A single-crystal structural characterization is reported for $K\{H_2B(tz^{NO_2})_2\}$, polymeric showing $K \cdots N$ and $K \cdots O$ interactions.²²¹

$[Cu\{H_2B(tz^{NO_2})_2\}(PR_3)_2]$, $[Cu\{H_2B(tz^{NO_2})_2\}(dppe)]$ and $[Cu\{H_2B(tz^{NO_2})_2\}(PR_3)]$ have been synthesized from the reaction of $CuCl$ with $K\{H_2B(tz^{NO_2})_2\}$, and mono or bidentate tertiary phosphines. Selected complexes have also been tested against a panel of several human tumor cell lines.²²²

$[Ag\{H_2B(tz^{NO_2})_2\}(PR_3)_x]$ have been also synthesized and characterized. $[Ag\{H_2B(tz^{NO_2})_2\}(P(m-Tol)_3)_2]$, in which the borate ligand acts as monodentate donor, has been also structurally characterized.²²³

1.8.54. $mt^R Bp$ ($R = tBu$ or iPr)

The anionic bis(pyrazolyl)(thioimidazolyl)borate ligands $mt^R Bp$ ($R = tBu$ or iPr) were prepared by reaction of $K(Tp)$ with the corresponding thioimidazoles (Hmt^R) in the melt at $150^\circ C$. They were used in the synthesis of zinc complexes such as $[ZnCl(mt^{tBu}Bp)]$ and $[Zn(SC_6H_4-p-Cl)(mt^{iPr}Bp)]$, structurally characterized.²²⁴ The same ligands react with zinc nitrate or zinc chloride and several thiolates, yielding $mt^R Bp$ zinc–thiolate complexes. Structure determinations have been carried out, that evidenced tetrahedral ZnN_2S_2 coordination. Upon reaction with MeI , $[ZnI(L)]$ ($L = H_2B(pz)(mt^{Bu})$, $H_2B(mt^{iPr})_2$) is formed.²²⁵

1.8.55. $\{HB(pz^{Ph,Me})(mt^{(2,6-Me_2Ph)})_2\}$

$\{HB(pz^{Ph,Me})(mt^{(2,6-Me_2Ph)})_2\}$ (Fig. 1.35) reacts with $Zn(ClO_4)_2$ giving $[Zn(OCLO_3)\{HB(pz^{Ph,Me})(mt^{(2,6-Me_2Ph)})_2\}]$, which partly

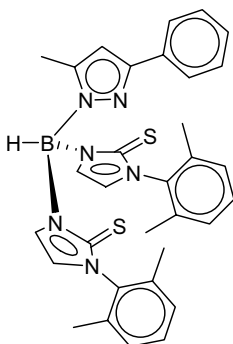


Fig. 1.35. $\{\text{HB}(\text{pz}^{\text{Ph,Me}})(\text{mt}^{(2,6\text{-Me}_2\text{Ph})})_2\}$.

decomposes in CH_2Cl_2 upon attempts to replace the perchlorate ion by *p*-nitrophenolate. Two equivalents of the released $\text{mt}^{(2,6\text{-Me}_2\text{Ph})}$ react with CH_2Cl_2 to form a dithioacetal able to coordinate two zinc moiety.²²⁶

1.8.56. $[\text{MeB}(\text{Im}^{\text{N-Me}})_2(\text{pz}^{\text{x}})]$

The monoanionic tripodal ligands $[\text{MeB}(\text{Im}^{\text{N-Me}})_2(\text{pz}^{\text{x}})]$ ($\text{Im}^{\text{N-Me}} = 1\text{-methylimidazol-2-yl}$, $\text{pz}^{\text{x}} = \text{pz}^{\text{Me}}$, pz^{Ph} or pz^{Me_3}) have been synthesized and their reactivity toward Ni tested. It has been reported that the coordination mode (κ^3 vs κ^2) to the metal centers depends on the steric congestion around the boron center. The replacement of the B-bonded pz^{Me_3} by acetate anion (Fig. 1.36) occurred

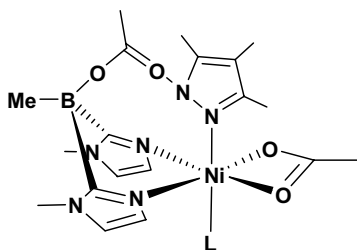


Fig. 1.36. The Ni complex containing the $[\text{MeB}(\text{Im}^{\text{N-Me}})_2(\text{OAc})]$ ligand obtained upon replacement of pz^{Me_3} by the acetate anion.

during the metathesis reaction of $[\text{MeB}(\text{Im}^{\text{N-Me}})_2(\text{pz}^{\text{Me3}})]$ with $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in $\text{MeOH}/\text{CH}_2\text{Cl}_2$.²²⁷

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