

Synthesis and Properties of Poly(pyrazolyl)borate and Related Boron-Centered Scorpionate Ligands. Part B: Imidazole-, Triazole- and Other Heterocycle-Based Systems

Maura Pellei*, Giancarlo Gioia Lobbia, Grazia Papini and Carlo Santini

Dipartimento di Scienze Chimiche, Università degli Studi di Camerino, Via S. Agostino 1, 62032, Camerino, Italy

Abstract: This review is intended to cover the developments in the chemistry of poly(azolyl)borates, derived from triazoles, imidazoles, oxazolines, thioimidazoles and related systems, based on the main synthetic methods, coordination properties, spectroscopic and structural features of this important class of ligands. The subject matter has been divided into the main categories: (i) N-donor boron-centered ligands, (ii) soft S-donor boron-centered ligands and (iii) hybrid scorpionate ligands. In this review we provide essential information to allow the reader to probe more deeply into the main aspects of the chemistry of these fascinating and flexible ligands. This review would also demonstrate the enormous potential of poly(azolyl)borates chemistry by discussing the future perspectives in this field.

Keywords: Scorpionates, poly(azolyl)borates, triazoles, tetrazoles, oxazoles, imidazoles, thioimidazoles, boratranes, poly(thioalkyl)borates, poly(phosphinomethyl)borates, hybrid systems, synthesis, coordination properties.

1. INTRODUCTION

Poly(azolyl)borate systems or scorpionates [1], based on the central anchoring B-R unit (R = hydrogen, alkyl or aryl), are unsurpassed in their value as tridentate ligands in coordination chemistry [2-7], organometallic chemistry [8-11], catalysis [12-15], bioinorganic chemistry [16-25] and enzyme modeling [26-34]. The success of poly(pyrazolyl)borates has inspired the development of new scorpionate ligands that are based on other donor groups. These include borate ligands with heterocyclic moieties such as imidazoles, oxazoles, triazoles, tetrazoles, thioimidazoles, together with boratranes, poly(thioalkyl)- and poly(phosphinomethyl)-borates, Se-donor and hybrid systems. Despite the design similarities to poly(pyrazolyl)borates, these scorpionates differ in their topology and flexibility, donor properties and reactivity pathways.

This review is intended to cover the developments in the chemistry of substituted bis-, tris- and tetrakis(azolyl)borate ligands, from the origins until the early 2009. In this review we provide essential information about the main synthetic methods and spectroscopic and structural features of this important class of ligands. We deeply analyzed the fundamental aspects of the chemistry of N-donor boron-centered, soft S-donor boron-centered and hybrid scorpionate ligands to complete the overview of these fascinating and flexible ligands.

2. ABBREVIATION SYSTEMS

As there is no consistent nomenclature for these ligands and their constituents, we prefer to adopt a scheme derived from that of the tris(pyrazolyl)borate ligands, first proposed by Curtis and co-workers [35, 36] and subsequently extended by Trofimenko [37]. In particular to avoid confusions, we adopt an extensive nomenclature based on the abbreviation RB(az^x)₃, R₂B(az^x)₂ or R₃B(az^x) (R = H, alkyl or aryl substituents, az = azole, X = substituent on the azole ring) to denote the tris-, bis- or mono-(azolyl)borate. For schematic convenience the generic bis(azol-1-yl)borate ligands (with azole different from pyrazole) with unspecified substituents on the azole rings, will be denoted [RR'B(az^x)₂], the generic tris- and tetrakis(azol-1-yl)borate ligands will be denoted as [RB(az^x)₃] and [B(az^x)₄], respectively (R or R' = hydrogen, alkyl or aryl).

We reserve the following abbreviations for the azoles:

- a) pz for the pyrazol-1-yl;
- b) im for imidazol-1-yl;

- c) bzim for benzoimidazol-1-yl;
- d) imc for imidazol-2-yl;
- e) ozc for oxazol-2-yl;
- f) tz for 1,2,4-triazol-1-yl;
- g) bztz for 1,2,3-benzotriazol-1-yl;
- h) tet for tetrazol-1-yl;
- i) 7-azn for 7-azaindol-1-yl
- j) tim for thioimidazol-1-yl;
- k) Seim for selenoimidazol-1-yl;
- l) thi for 2-thienyl;
- m) ttz for 5-thioxo-1,2,4-triazol-1-yl;
- n) mtdz for 2-thioxo-1,3,4-thiadiazol-3-yl.

The non-hydrogen substituents in the different positions on the azoles are denoted by superscripts in a numerical order corresponding to the ring positions starting from the substituents at the N-position of the azole ring without numbering. Thus, we call the dihydrobis(imidazol-1-yl)borate [H₂B(im^x)₂] and the hydrotris(thioimidazolyl)hydroborate [HB(tim^x)₃] with x naming the substituent at the N-positions of the imidazole rings. In addition, we call HB(tim^{R,4R',5R''}) to indicate substitution at the 4- and 5-position of the imidazole ring. For example we indicate the potassium tris(3-*tert*-butyl-5-methyl-1,2,4-triazolyl)borate ligand K[HB(tz^{3tBu,5Me})₃] and we call the lithium isopropoxy(methyl)bis(1-methyl-1H-imidazol-2-yl)borate Li[Me(OⁱPr)B(imc^{Me})₂]. The hydro- and dihydro-prefixes are omitted.

3. N-DONOR BORON-CENTERED SCORPIONATE LIGANDS

3.1. Poly(imidazol-1-yl)borates

Poly(imidazolyl)borates, H_nB(im)_{4-n} (Fig. 1), can be prepared in analogy with that reported for poly(pyrazolyl)borates [38]. Unlike poly(pyrazolyl)borates, the H_nB(im)_{4-n} ligands cannot chelate a metal center but have to bridge between metal ions.

H_nB(im)_{4-n} complexes have been widely described [39], but only a few metal derivatives are structurally authenticated: the lithium salt of tetrakis(imidazolyl)borate, Li[B(im)₄], [40]; the thallium(I) tris(imidazolyl)borate, Tl[HB(im)₃], in which each imidazolyl ring coordinates a different thallium ion to form a one-dimensional twisted ladder-like strand [41] and two silver(I) compounds in which the metal atoms are bridged by [H₂B(im)₂] and [B(im)₄] ligands [42] (Table 1).

Ziegler *et al.* investigated the coordinating anion tetrakis(imidazolyl)borate as a component of coordination solids

*Address correspondence to this author at the Dipartimento di Scienze Chimiche, Università degli Studi di Camerino, Via S. Agostino 1, 62032, Camerino, Italy; Tel/Fax: +39 (0)737 402213; E-mail: maura.pellei@unicam.it

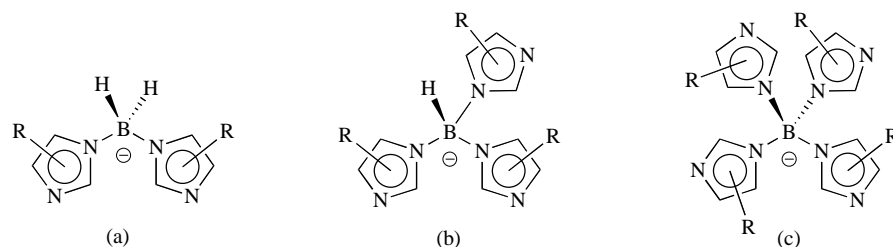


Fig. (1). Structure of bis-, tris- and tetrakis-(imidazolyl)borates.

and they reported that the reaction of the $\text{Pb}(\text{NO}_3)_2$ salt with the ligand leads to the formation of a layered coordination polymer, with a formula of $\text{Pb}[\text{B}(\text{im})_4](\text{NO}_3)_n\text{H}_2\text{O}$, able to incorporate anionic organic guest molecules into the interlayer spacing of the material [43, 44]. Several anionic organic guests have been incorporated into $\text{Pb}[\text{B}(\text{Im})_4]\text{X}$ based materials (where X is the anionic guest) and Hamilton *et al.* [45] have reported the nanoscale organization of carboxylate modified TEMPO and PROXYL: $\text{Pb}[\text{B}(\text{im})_4](4\text{-carboxy-TEMPO})$ and $\text{Pb}[\text{B}(\text{im})_4](3\text{-carboxy-PROXYL})(\text{H}_2\text{O})$ (4-carboxy-TEMPO = 4-carboxy-2,2,6,6-tetramethylpiperidinyloxy; 3-carboxy-PROXYL = 3-carboxy-2,2,5,5-tetramethylpyrrolidinyloxy). This coordination polymer could be used as a host material for generating conducting polymers where the polymer is grown in the interlayer spacing. In particular Cetin *et al.* [46] reported the enclathration of three different aniline derivatives between the layers of this lead-borate material and an investigation into the polymerization of these preorganized monomers. The metal in the compound $\text{Pb}[\text{B}(\text{im})_4](\text{NO}_3)_n(\text{H}_2\text{O})$ can be replaced with isoelectronic $\text{Tl}(\text{I})$, affording $\text{Tl}[\text{B}(\text{im})_4]$, and the borate can be modified by using 4-methylimidazole, resulting in $\text{Pb}[\text{B}(\text{Im}^{4\text{Me}})_4](\text{NO}_3)$ and $\text{Tl}[\text{B}(\text{im}^{4\text{Me}})_4]$. Like the parent $\text{Pb}[\text{B}(\text{im})_4](\text{NO}_3)_n(\text{H}_2\text{O})$, $\text{Tl}[\text{B}(\text{im})_4]$ and $\text{Tl}[\text{B}(\text{im}^{4\text{Me}})_4]$ are layered network structures but both lack anions or solvent molecules in the interlayer spacing [47]. The synthesis and structures of group II metal cation incorporating the $[\text{B}(\text{im})_4]^-$ ligand, of empirical formula $\text{M}[\text{B}(\text{im})_4](\text{H}_2\text{O})_2$ (where M = Mg, Ca, and Sr), have also been reported by Hamilton *et al.* [48]. In the same paper the authors present the structure of the protonated anion $\text{B}(\text{Him})(\text{im})_3$ as a model for the default structure of this anion and discuss how the conformation of tetrakis(imidazolyl)borate can affect the structure of network solids.

Lanthanide complexes with bis(benzimidazolyl)borate, $[\text{H}_2\text{B}(\text{bzim})_2]^-$ (Table 1), for which a seven-coordinate polymeric structure has been proposed have been described by Khan and co-workers [49].

A series of macrocyclic imidazolylboranes $[\text{R}_2\text{Bim}]_n$ ($n = 4$ or 5), where selected carbon atoms of imidazolyl rings may bear substituents other than hydrogen, have been obtained by Siebert *et al.* [50] by reaction of 1-trimethylsilylimidazoles with haloboranes under high dilution (Fig. 2). Depending on the nature of the substituents at the imidazole ring and at the boron atom, the formation of different ring sizes was observed.

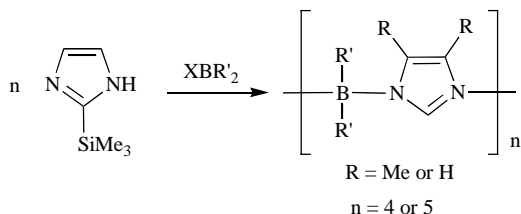


Fig. (2). Synthesis of macrocyclic imidazolylboranes.

The presence of a bromine atom should increase the reactivity towards bases to give anionic carbenes, useful for host-guest chemistry via the formation of metal-carbene complexes. In particular,

several macrocycles have been obtained by reaction from 1-trimethylsilylimidazoles [51] and haloboranes R_2BX by boron/silicon exchange using 2-bromoimidazole or benzimidazole [52] (Fig. 3).

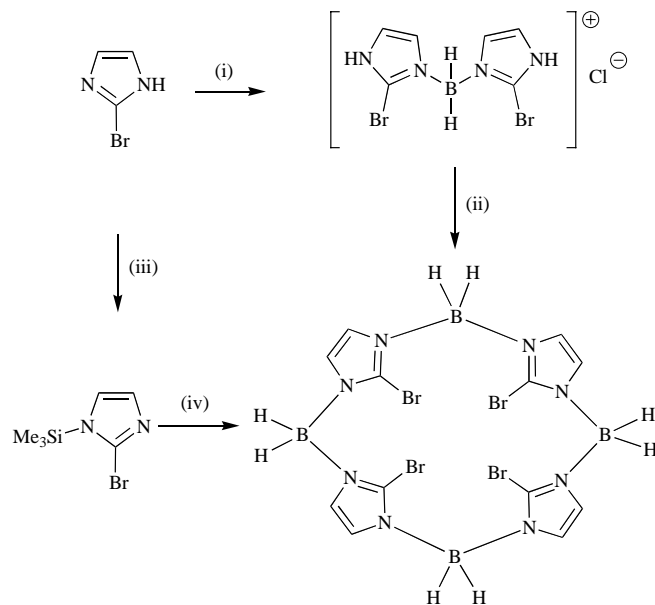


Fig. (3). (i) $2 \text{H}_2\text{BBr}$; (ii) $4 \text{BH}_3 \cdot \text{THF}$; (iii) $4 \text{HN}(\text{SiMe}_3)_2$, saccharine; (iv) $4 \text{H}_2\text{BCl} \cdot \text{THF}$.

These macrocycles are formally zwitterionic and contain imidazolyl rings linked through their nitrogen atoms by BH_2 , BR_2 or BRX units.

3.2. Poly(imidazol-2-yl)borates

Moro-Oka *et al.* [53] have developed a brand-new monoanionic ligand systems, poly(imidazol-2-yl)borates (Table 2), on the basis of the $\text{B}-\text{C}_{\text{alkyl}}$ linkage which should be resistant to nucleophilic attack on the boron atom leading to decomposition of the ligands. In fact they reported the synthesis and characterization of a new class of borate compounds containing a methylbis(1-methyl-2-imidazolyl)borate framework $[\text{Me}(\text{X})\text{B}(\text{Im}^{\text{Me}})_2]^-$ (X = O^iPr , Cl, Pz or Ph). In particular, the reaction of di(isopropoxy)methylborane with 2 equivalents of 2-lithio-1-methylimidazole yielded the lithium isopropoxy(methyl)bis(1-methyl-1H-imidazol-2-yl)borate $\text{Li}[\text{Me}(\text{O}^i\text{Pr})\text{B}(\text{imc}^{\text{Me}})_2]$. The chloro(methyl)bis(1-methyl-1H-imidazol-2-yl)borate $\{\text{H}[\text{Me}(\text{Cl})\text{B}(\text{imc}^{\text{Me}})_2]\}_2(\text{HCl})_2$, which was obtained by treatment of $\text{Li}[\text{Me}(\text{O}^i\text{Pr})\text{B}(\text{imc}^{\text{Me}})_2]$ with HCl, could be transformed to the pyrazolyl and phenyl derivatives $\text{H}[\text{Me}(\text{Ph})\text{B}(\text{imc}^{\text{Me}})_2]$ and $\text{H}[\text{Me}(\text{pz})\text{B}(\text{imc}^{\text{Me}})_2]$, by nucleophilic substitution of the B-bound chlorine atom. Protonation of the imidazolyl groups results in delocalization of the positive charge over the imidazole ring and strong interaction with the negatively charged boron atom, and such electronic effect as well as interaction via inter- and intra-molecular hydrogen bonds result in stabilization of the protonated form (Fig. 4).

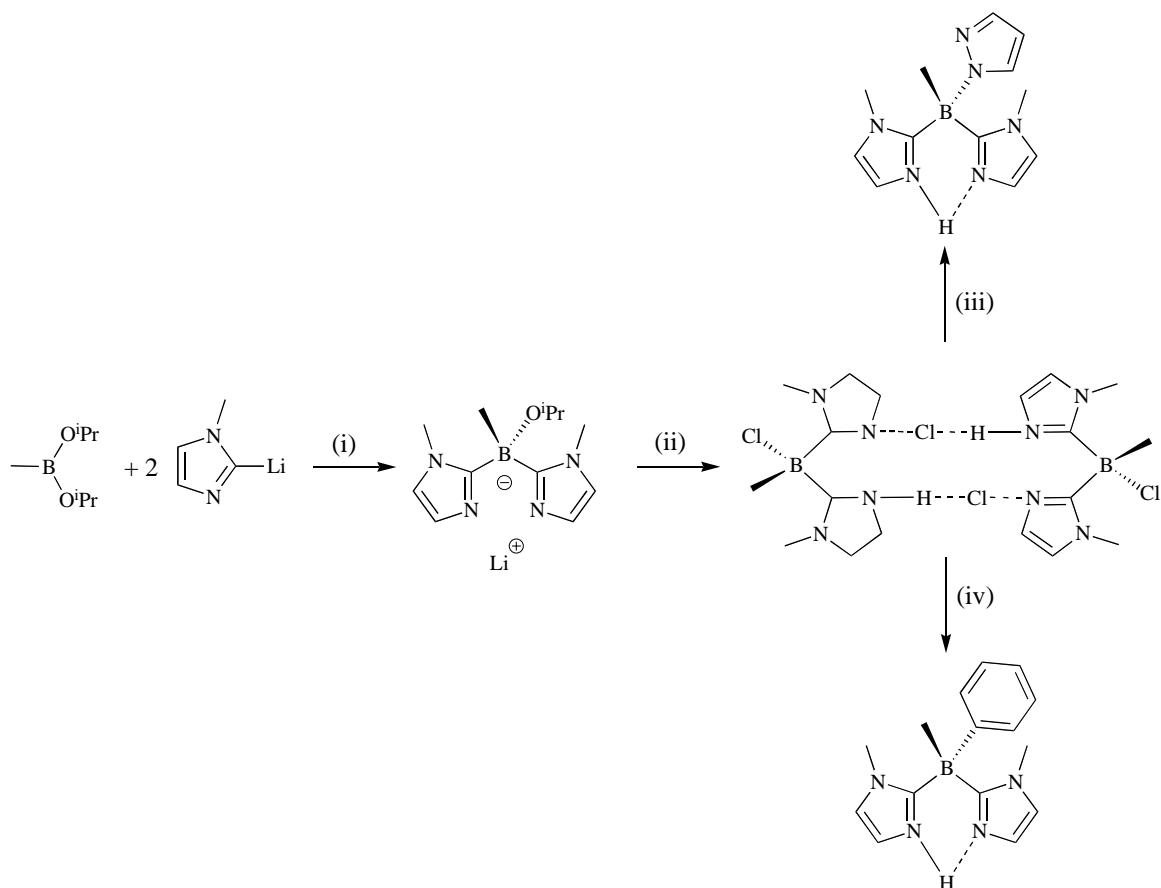


Fig. (4). (i) Reflux THF/hexane; (ii) anhydrous HCl (3 eq.); (iii) a) NaH (2 eq.), b) NaPz (1 eq.), c) H₂O; (iv) a) PhLi (3 eq.), b) H₂O.

3.3. Poly(oxazol-2-yl)borates

Poly(oxazolyl)borate scorpionate ligands (Table 3) that contain B–C linkages have been proposed to have greater resistance to cleavage and isomerization processes. In fact, although metal-mediated B–C bond cleavages are known, these reactions are less facile than B–N bond cleavage [54]. The synthesis of lithium tris(4,4-dimethyl-4,5-dihydrooxazol-2-yl)(phenyl)borate (Fig. 5), Li[PhB(ozc^{4Me₂})₃] the first example of this new ligand class, and its coordination chemistry in new zirconium(IV) complexes have been reported by Sadow *et al.* [55].

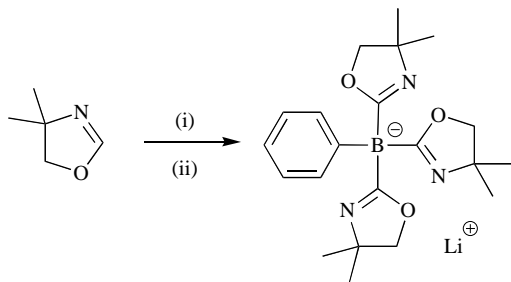


Fig. (5). (i) ⁿBuLi, THF, -78°C; (ii) PhBCl₂, -78°C.

This strategy, which differs from known synthetic approaches to bisoxazolines, is attractive because simple and readily accessible oxazolines can be used as precursors. Lithiation of oxazolines following the procedure of Meyers and Novachek [56] and subsequent treatment with haloborane at low temperature led to the lithium salts of bis- and tris-(oxazolin-2-yl)borates. Following this synthetic strategy Pfaltz and co-workers have prepared the bis(oxazolin-2-yl)borate ligands, named borabox (Fig. 6), and the zwitterionic

catalysts containing these ligands have improved enantioselectivities versus cationic bisoxazoline catalysts in copper(II)-catalyzed cyclopropanation [57].

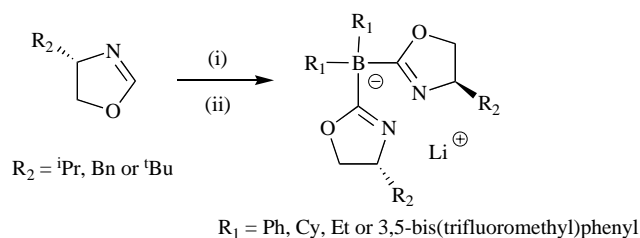


Fig. (6). (i) ⁿBuLi, -78°C, THF; (ii) (R¹)₂BX (X = Cl, Br), toluene, -78°C.

The lithium salts can be converted into the protonated ligands by chromatographic work-up on silica gel using hexane/ethyl acetate/triethylamine as the eluent. Regeneration of related compounds was readily accomplished by treatment of related compounds with one molar equivalent of *n*-butyllithium in diethyl ether at room temperature. A wide variety of sterically and electronically different ligands can be prepared by structural variation of the haloborane and the oxazolines. The borabox ligands readily form stable complexes with transition-metal ions, such as Cu(II), Zn(II), Pd(II), Rh(I), and Ir(I) ions, starting from the lithium salts or the protonated precursors in the presence of a base such as K₂CO₃ [57].

Recently Sadow *et al.* [58] prepared the lithium tris(4*S*-isopropyl-2-oxazolyl)phenylborate, Li[PhB(ozc^{4iPr})₃], an optically active tris(oxazolyl)borate as a chiral surrogate for cyclopentadienyl and tris(pyrazolyl)borate, by deprotonation of 4*S*-isopropylloxazoline to give 2-lithio-4*S*-isopropyl-2-oxazolidine, followed by reaction with PhBCl₂ in a second step (Fig. 7).

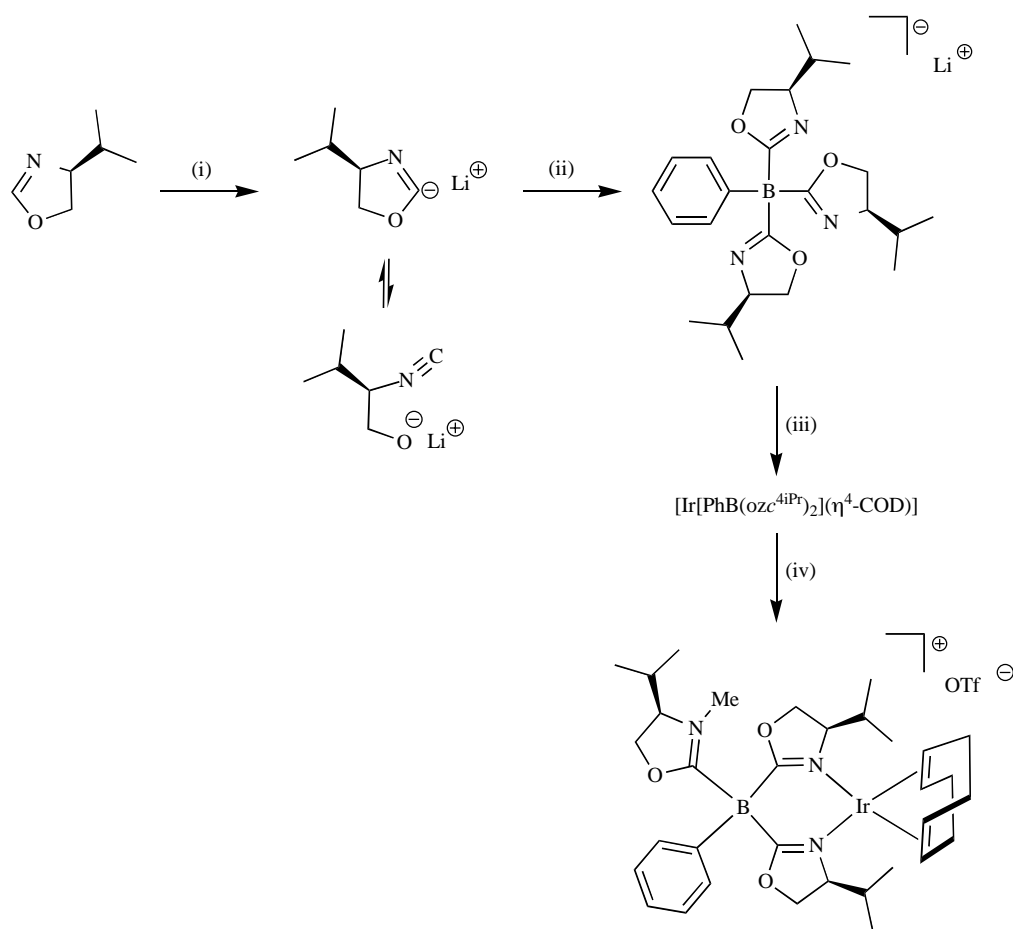


Fig. (7). (i) $\text{LiN}(\text{SiMe}_3)_2$, THF, -78°C ; (ii) PhBCl_2 , THF, -78°C ; (iii) $0.5 [\text{Ir}(\mu\text{-Cl})(\eta^4\text{-COD})_2]$, benzene, 80°C ; (iv) MeOTf , benzene, r.t.

Interestingly, the ligand $\text{Li}[\text{PhB}(\text{ozc}^{4i\text{Pr}})_3]$ reacts with $[\text{Ir}(\mu\text{-Cl})(\eta^4\text{-COD})_2]$ to give the complex $\{\text{Ir}[\text{PhB}(\text{ozc}^{4i\text{Pr}})_3](\eta^4\text{-COD})\}$. Given the ubiquity of oxazolines as ligands in catalytic processes involving electrophiles such as allylic substitution, this oxazoline alkylation may represent an important route for catalyst deactivation [59-61].

3.4. Poly(triazol-1-yl)borates

Although in 1967 Trofimenko reported the synthesis of the tris(1,2,4-triazolyl)borate (Table 4) and related cobalt(II) complexes [62], the chemistry of triazolylborate ligands has remained undeveloped for many decades. In 1991 a convenient preparation of the potassium salt $\text{K}[\text{HB}(\text{tz})_3]$ has been reported by Gioia Lobbia and coworkers [63], whereas the synthesis of the corresponding salt of $\text{K}[\text{H}_2\text{B}(\text{tz})_2]$ has been reported by Janiak *et al.* [64].

Two features of poly(1,2,4-triazolyl)borates (Table 4), $[\text{H}_n\text{B}(\text{tz})_{4-n}]^-$, made them attractive candidates for further examination: a) they should be electron-withdrawing relative to their pyrazolyl-based counterparts and the properties of metal complexes should differ accordingly; b) the exo ring-nitrogen atoms of the triazolyl-based ligands can bridge between metal centers, thereby creating coordination polymers with interesting solid-state structures and optical properties, as shown by Janiak and coworkers [64]. An unprecedented coordination mode has been found in a silver compound where $[\text{HB}(\text{tz})_3]^-$ bis-chelates the metal center with two endodontate nitrogen and also bridges to two other silver atoms through two of the three exodontate nitrogen atoms [65]. In a copper(II) complex $[\text{HB}(\text{tz})_3]^-$ utilizes all six nitrogen atoms in metal coordination, thereby bridging four copper centres and yielding a

three-dimensional coordination polymer [66]. The ligand $[\text{HB}(\text{tz})_3]^-$ has also been used to synthesize novel metalloligands $[\text{Fe}^{\text{III}}[\text{HB}(\text{tz})_3]_2]\text{ClO}_4 \cdot 2\text{MeCN}$ as molecular building blocks and for subsequent incorporation into new functional coordination polymers [67]. The non-interpenetrating 3D coordination polymer framework of $[\text{Fe}^{\text{II}}(\text{L})_2][\text{Rh}_2(\text{OAc})_4]_3 \cdot x\text{S}$ (L = hydrotris(1,2,4-triazolyl)borate anion, S = solvent) was characterized by single-crystal X-ray structure analysis.

The ligand $\text{K}[\text{H}_2\text{B}(\text{tz}^{3\text{Me},5\text{Me}})_2]$ ($\text{tz}^{3\text{Me},5\text{Me}}$ = 3,5-dimethyl-1,2,4-triazolyl) (Fig. 8a) has been synthesized by Wei-Zheng Shen *et al.* [68] and the reactions of two different metal salts (copper and zinc) with the ligand in agar gave two similar crystalline polymorphic forms. A dioxomolibdenum compound containing the methyl substituted $[\text{HB}(\text{tz}^{3\text{Me},5\text{Me}})_3]^-$ (Fig. 8b) was first reported by Xiao *et al.* [69].

The analogous sterically demanding triazolylborate ligand, the tris(3-*tert*-butyl-5-methyl-1,2,4-triazolyl)borate ligand, $\text{K}[\text{HB}(\text{tz}^{3\text{tBu},5\text{Me}})_3]$ has been synthesized by Jernigan *et al.* [70] from the reaction of KBH_4 in molten 3-*tert*-butyl-5-methyl-1,2,4-triazole (Fig. 8d). This ligand forms a four coordinate $[\text{HB}(\text{tz}^{3\text{tBu},5\text{Me}})_3]\text{CoCl}$ complex and five-coordinate $[\text{HB}(\text{tz}^{3\text{tBu},5\text{Me}})_3]\text{CoNO}_3$ and $[\text{HB}(\text{tz}^{3\text{tBu},5\text{Me}})_3]\text{ZnOAc}$ complexes. When these complexes were compared to the tris(pyrazolyl)borate analogues, with the tris(3-*tert*-butyl-5-methyl-pyrazolyl)borate ligand $\text{K}[\text{Tp}^{\text{tBu},\text{Me}}]$, it was found that triazolyl derivatives resulted in negligible steric differences. $\text{K}[\text{HB}(\text{tz}^{3\text{tBu},5\text{Me}})_3]$ is more water-soluble than $\text{K}[\text{Tp}^{\text{tBu},\text{Me}}]$, so bulky tris(triazolyl)borate ligands should lead to functional models for enzyme active sites in an aqueous environment and the creation of water-soluble analogues of Tp catalysts. The copper carbonyl

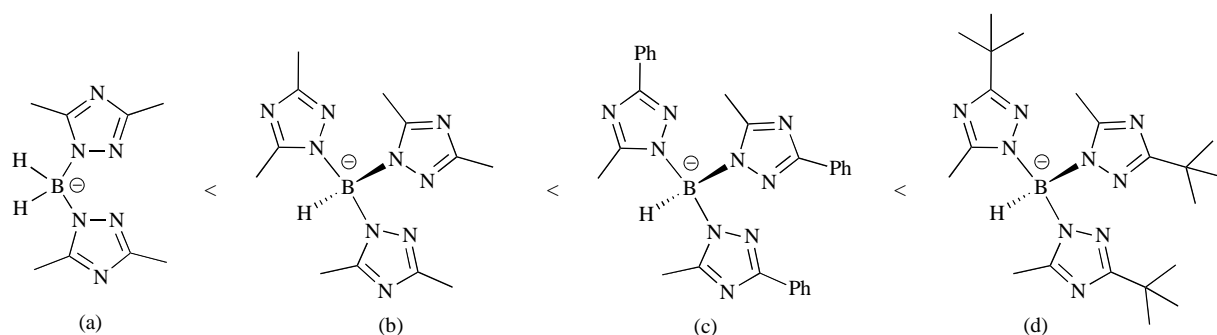


Fig. (8). Sterically demanding order in triazolylborate ligands.

complex $[\text{HB}(\text{tz}^{3\text{tBu},5\text{Me}})_3]\text{CuCO}$ was prepared and fully characterized by Papish *et al.* [71] to test whether the $[\text{HB}(\text{tz}^{3\text{tBu},5\text{Me}})_3]^-$ ligand, which is sterically similar to $[\text{Tp}^{3\text{tBu},5\text{Me}}]^-$, is electronically different; in fact, $[\text{HB}(\text{tz}^{3\text{tBu},5\text{Me}})_3]^-$ is a weaker electron donor and $[\text{HB}(\text{tz}^{3\text{tBu},5\text{Me}})_3]\text{CuCO}$ is water stable and has a propensity to form hydrogen bonds. A tris(triazolyl)borate ligand of intermediate steric bulk, the potassium tris(3-phenyl-5-methyl-1,2,4-triazolyl)borate, $[\text{KB}(\text{tz}^{3\text{Ph},5\text{Me}})_3]$, (Fig. 8c), was synthesized by Papish *et al.* [72] to investigate its potential for hydrogen bonding and improved solubility in hydrophilic solvents as applied to biomimetic chemistry.

In 2005 Pellei *et al.* [73] reported the first nitro-substituted scorpionate ligand, namely potassium bis(3-nitro-1,2,4-triazolyl)borate ligand, $[\text{K}(\text{H}_2\text{B}(\text{tz}^{3\text{NO}_2})_2)]$ (Fig. 9a), by reaction of 3-nitro-1,2,4-triazole and KBH_4 in dimethylacetamide solution, using careful temperature control. The potassium salt is polymeric and shows several $\text{K}\cdots\text{N}$ and $\text{K}\cdots\text{O}$ interactions. This ligand is the first synthesized poly(azolyl)borate containing a $-\text{NO}_2$ function, due to difficulties in the synthesis of ligands having both a hydride and a nitro group. Silver(I)-organophosphane complexes of the bis(3-nitro-1,2,4-triazolyl)borate ligand have been also synthesized and characterized by Santini *et al.* [74]. In the complexes $\text{Ag}[\text{H}_2\text{B}(\text{tz}^{3\text{NO}_2})_2](\text{PR}_3)_2$ the borate ligand acts as monodentate donor. Copper(I) complexes of the type $[\text{H}_2\text{B}(\text{tz}^{3\text{NO}_2})_2]\text{Cu}[\text{PR}_3]_2$, $[\text{H}_2\text{B}(\text{tz}^{3\text{NO}_2})_2]\text{Cu}[\text{dppe}]$ and $[\text{H}_2\text{B}(\text{tz}^{3\text{NO}_2})_2]\text{Cu}[\text{PR}_3]$ have been synthesized by Santini and coworkers [75] from the reaction of CuCl , $[\text{K}(\text{H}_2\text{B}(\text{tz}^{3\text{NO}_2})_2)]$, and mono- or bi-dentate tertiary phosphines. Some of these complexes have also been tested against a panel of several human tumor cell lines in order to evaluate their cytotoxic activity and they showed IC_{50} values appreciably lower than those exhibited by cisplatin, the most used metal-based antitumor drug. It is worth noting that all the tested $\text{Cu}(\text{I})$ complexes appear to be particularly effective against A549 carcinoma cells that are resistant to cisplatin treatment.

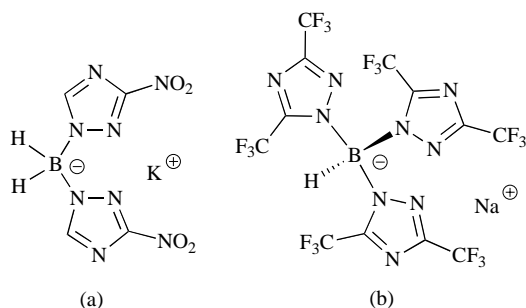


Fig. (9). Electron-withdrawing tris(triazolyl)borate species.

Recently Dias *et al.* [76] described the first fluorinated tris(triazolyl)borate species, bearing six trifluoromethyl substituents. The sodium derivative $[\text{Na}(\text{HB}(\text{tz}^{3\text{CF}_3,5\text{CF}_3})_3)]$ (Fig. 9b) has been readily synthesized by the reaction of NaBH_4 with 3,5-bis(trifluoromethyl-1,2,4-triazole) [77] at *ca.* 210°C. The copper

complex $[\text{HB}(\text{tz}^{3\text{CF}_3,5\text{CF}_3})_3]\text{CuCO}$ has also been synthesized and it represents a rare copper carbonyl that belongs to the classical-nonclassical border [78].

Density functional calculations results reported by Casarin *et al.* [79] provide a theoretical support to the use of hydrotris(1,2,4-triazolyl)borate ligands as a proper alternative to the hydrotris(pyrazolyl)borate ones, corroborating the suggestion [70, 71] that hydrotris(1,2,4-triazolyl)borate ligands could be useful in model studies of the catalytic activity of metal centers in biological systems.

A large number of salts that are triazole derivatives have been reported to be energetic materials [80-83]. Some features of triazole-based borates that make them attractive candidates for investigation as energetic materials include: (a) 1,2,4-triazole has a positive heat of formation (109 kJ/mol), which suggests that poly(1,2,4-triazolyl)borates could be energetic materials, (b) greater electron-withdrawing properties relative to those of imidazole- and pyrazole-based borates give characteristics that should differ accordingly, and (c) the bis(1,2,4-triazolyl)borate and tris-(1,2,4-triazolyl)borate anions are asymmetric bulky organic anions, which may result in lower melting points. Since many ionic liquids arise because of the asymmetry of their bulky organic cations such as 1,3-dialkylimidazolium, it is useful to study the properties of organic salts based on the asymmetric bulky borate anion. On this end Shreeve *et al.* [84] synthesized the tris(1,2,4-triazolyl)borate organic salts in high yields by metathesis reactions of $[\text{Ag}(\text{HB}(\text{tz}_3)]$ with substituted imidazolium, triazolium (Fig. 10), and tetrazolium iodides. These new borate salts melt at relatively low temperatures to give thermally stable ionic liquids.

3.5. Poly(benzotriazol-1-yl)borates

In 1988 Lalor *et al.* [85] reported the synthesis of a series of poly(benzotriazolyl)borate anions $[\text{H}_n\text{B}(\text{bztz})_{4-n}]^-$ ($n = 0-2$) by reaction of KBH_4 with molten benzotriazole, characterizing the bis(benzotriazolyl)borate, $[\text{K}(\text{H}_2\text{B}(\text{bztz})_2)]$ (Fig. 11a), and tris(benzotriazolyl)borate, $[\text{K}(\text{HB}(\text{bztz})_3)]$ ligands (Fig. 11b) (Table 5). The regioselectivity of the process differs from that of pyrazole/ BH_4^- reactions; the B-N bond formation takes place at the triazole N(1) atoms, in a manner that maximizes steric crowding at boron.

In 1989 Shiu *et al.* [86] described some new group VI metal carbonyls of $[\text{HB}(\text{bztz})_3]^-$. The synthesis and spectroscopic characterization of some bis(benzotriazolyl)borate and first-row transition metals and some Groups 12 and 14 elements have been reported by Cecchi *et al.* [87], whereas Hill and coworkers described some $\text{Rh}(\text{I})$ [88] and $\text{Ru}(\text{II})$ [89] carbonyl and isonitrile complexes of the bis(benzotriazolyl)borate. The formation of isonitrile derivatives has been hypothesized to proceed through an associative mechanism involving an intermediate complex containing a κ^1 -unidentate $[\text{H}_2\text{B}(\text{bztz})_2]^-$ ligand [90]. Two different coordination modes for this family of ligands have been recently structurally authenticated by

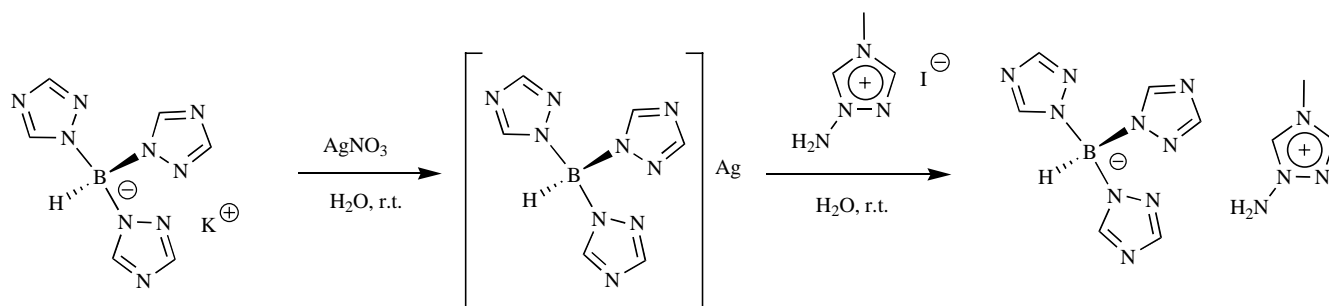


Fig. (10). Synthesis of hydrotris(1,2,4-triazolyl)borate organic salts.

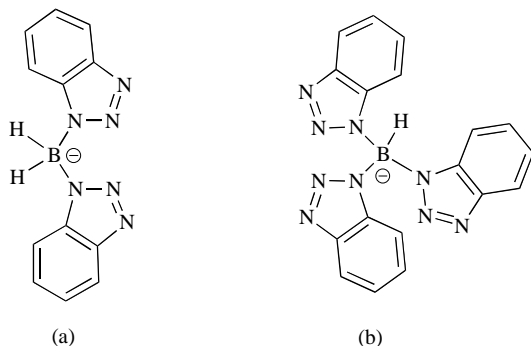


Fig. (11). Structure of bis- and tris-(benzotriazolyl)borates.

Santini and coworkers in a series of copper(I) complexes containing mono- and bi-dentate phosphine coligands [91, 92].

3.6. Tetrazole- and 7-azaindole-containing poly(azol-1-yl)borates

In 1993 the synthesis and structure of the first tetrazolylborate $[\text{H}_2\text{B}(\text{tet})_2]$ (Table 5) have been reported by Janiak *et al.* [93], which also employed it in the construction of infinite two-dimensional metal-ligand frameworks and one-dimensional water substructures [94].

Supramolecular C-H \cdots O and C-H \cdots N hydrogen bonding interactions in metal complexes with poly(1,2,4-triazolyl)borate and bis(tetrazolyl)borate ligands have been analyzed statistically and with respect to their role in determining the crystal packing arrangement by Janiak and Scharmann [95]. The additional ring nitrogen atoms in these modified, multitopic poly(azolyl)borate ligands are the origin of manifold C-H \cdots O and C-H \cdots N hydrogen bonds in this group of compounds. The additional nitrogen atoms play a dual role in enhancing the acidity of the ring hydrogen atoms and serving as hydrogen-bond acceptors.

The incorporation of the 7-azaindole anions with a single electron-deficient boron atom through N-B bonds results in the formation of a stable blue luminescent scorpionate ligand $\text{K}[\text{HB}(7\text{-azn})_3]$ [96] (Table 5). Bidentate and tridentate chelation modes have been

observed in copper(I) and zinc(II) complexes of this ligand. In addition, these complexes display blue luminescence and fluxional behavior.

4. SOFT DONOR SCORPIONATE LIGANDS

Chelating ligands belonging to the poly(pyrazolyl)borates, or Tp^x family, can be regarded as relatively *hard* donor ligands having two or three azole nitrogen atoms that can be involved in metal coordination. The analogous poly(methimazolyl)borate anions (methimazole = 1-methyl-1*H*-imidazole-2-(3*H*)-thione) have recently been reviewed by Reglinski and Spicer [97] (see below) in order to explore the properties of a softer coordination environment in an anionic ligand, provided in this case by thione sulfur atoms of the methimazole rings. The two ligand systems also differ fundamentally in the number of atoms linking the central boron atom to the donor atoms. The structural consequences of this difference are displayed in the dimensions of the chelate rings formed upon metal complex formation and the molecular symmetry generated as a consequence of the conformations adopted by these rings. Thus, complexes of the tris(pyrazolyl)borates family contain three six-membered chelate rings and the resulting complexes exhibit a local coordination environment of C_{3v} symmetry, while poly(methimazolyl)borates complexes contain three eight-membered chelate rings, thus generating a more flexible twisted or propeller-like ligand conformation and local C_3 symmetry.

4.1. Poly(thioimidazolyl)borates

The synthesis of the poly(pyrazolyl)borate anions is driven by the elimination of dihydrogen from the reaction of the tetrahydroborate anion with the acidic proton commonly found in pyrazoles. In 1996 Reglinski and coworkers [98] extended this synthetic route to the preparation of a softer species analogues of Tp^x [1]; particularly they attempted the reaction of methimazole with sodium borohydride in a solvent-free melt reaction to obtain the S_3 -donor $\text{Na}[\text{HB}(\text{tim}^{\text{Me}})_3]$ [99] (Table 6).

Both lithium [100] and potassium [101-103] borohydride have also been used in the synthesis of these ligands (Fig. 12). The extension of Trofimenko's synthetic route to the preparation of softer species became possible once it was realized that many 1,2-imine thiols such as 1-methyl-1*H*-imidazole-2-thiol are better formulated

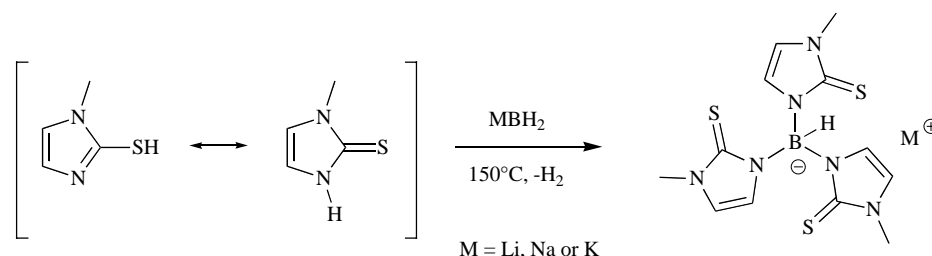


Fig. (12). Synthesis of tris(methimazolyl)borates.

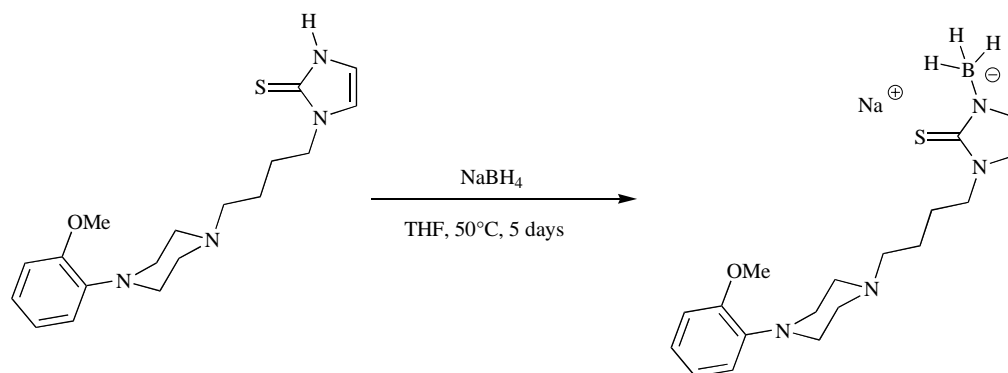


Fig. (13). Synthesis of Na[H₃B(tim^{Bupip})].

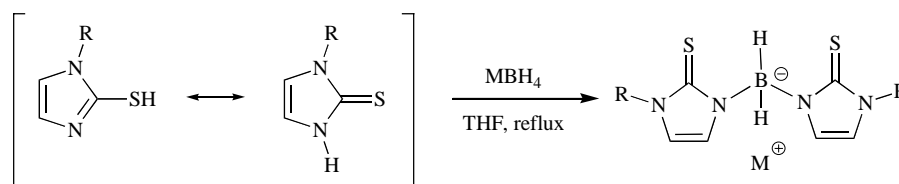


Fig. (14). Synthesis of bis(methimazolyl)borates.

as their thione tautomer 1-methyl-1H-imidazole-2(3H)-thione (or methimazole) [104, 105] (Fig. 12). The acidic hydrogen on the amine group should allow species such as methimazole to react in an analogous manner to pyrazole yielding species in which soft sulfur donors will be available for metal co-ordination. From the location of the acidic hydrogen the binding of methimazole to boron is expected to be *via* a B–N linkage. However, it is possible that thiol–thione tautomerisation (Fig. 12) [106, 107], while not dominant at room temperature, could occur in the melt prior to coupling. Alternatively a 1–3 shift might occur after the initial coupling reaction. Consequently, concern existed that under the prevailing reaction conditions the boron might migrate from the nitrogen to the sulfur.

The higher melting point of methimazole (ca. 147°C) renders formation of the bis(methimazolyl)borate anion, [H₂B(tim^{Me})₂][−], not viable by this method, because at the melting point the reaction generally proceeds directly to the trisubstituted species, [HB(tim^{Me})₃][−]. In addition, decomposition occurs at temperatures above ca. 180°C. Consequently, the tetrakis(methimazolyl)borate species remains as yet unknown.

The synthesis of the 1-alkyl- or 1-aryl-imidazole-2-thiones is reasonably straightforward and most of the resulting [HB(tim^x)₃][−] ligands are prepared by reaction with an alkali metal borohydride using the solution method described in Fig. (12).

The *N*-methyl group can be readily replaced by a wide range of alkyl groups, such as Et [108], ^tBu [109], Cy [110], Bz [111], Ph [100], *o*-Tol [110], *p*-Tol [111], Mes [100], Cum [109], 2,6-xylyl [110] and 2,6-ⁱPr₂C₆H₃ [112].

Very recently, Santos *et al.* have prepared the first member of the series Na[H₃B(tim^{Me})], reacting methimazole with sodium borohydride in THF at 50°C to form the sodium trihydro(methimazolyl)borate [113]. The analogous ligand functionalized with a small biomolecule 1-(4-(2-methoxyphenyl)piperazin-1-yl)butyl-1H-imidazole-2(3H)-thione (Htim^{Bupip}) was also prepared in the same conditions [113] (Fig. 13).

The bidentate S₂-donor bis(methimazolyl)borate species, M[H₂B(tim^{Me})₂] (M = Li, Tl), have been obtained by Parkin *et al.* by reaction of MBH₄ with 2 equivalents of methimazole in toluene at 50°C [114, 115].

The sodium salts Na[H₂B(tim^R)₂] (R = Bz, ^tBu, *p*-Tol) were also obtained in high yield starting from the appropriate 1-alkyl- or 1-aryl-imidazole-2-thiones, in refluxing tetrahydrofuran [116] (Fig. 14).

Substitution at C4 or C5 of the ring is also possible, although the only example of such substitution has been reported by Santos and coworkers, who placed biologically active groups in the 5-position [117]. In particular, the symmetric ligands Na[H₂B(tim^{Me,4pip})₂] [117] (Fig. 15a) and Na[H₂B(tim^{Me,4(CH₂-pip)})₂] [117] (Fig. 15b) were synthesized by reaction of sodium borohydride with (4-(2-methoxyphenyl)piperazin-1-yl)(3-methyl-2-thioxo-2,3-dihydro-1H-imidazol-4-yl)methanone (Htim^{Me,4pip}) and 5-((4-(2-methoxyphenyl)piperazin-1-yl)methyl)-1-methyl-1H-imidazole-2(3H)-thione (Htim^{Me,4(CH₂-pip)}) (Fig. 15). The Htim^{Me,4pip} can be obtained by reaction of the activated ester 2,5-dioxopyrrolidin-1-yl-3-methyl-2-thioxo-2,3-dihydro-1H-imidazole-4-carboxylate with 1-(2-methoxyphenyl)piperazine, as indicated in Fig. (15). The species Htim^{Me,4(CH₂-pip)} was reduced to the respective tertiary amine Htim^{Me,4(CH₂-pip)} by reaction with BH₃SMe₂ [118] (Fig. 15).

Following Reglinski's approach [98], Santos and coworkers [119] prepared bis(3-methyl-2-thioxoimidazol-1-yl)(organyl)borates ligands, [H(R)B(tim^{Me})₂][−], starting from the organoborohydrides Li[RBH₃] (R = Me, Ph), which were prepared by reaction of the corresponding boronic acids RB(OH)₂ with LiAlH₄, according to procedures described by Singaram *et al.* [120]. In fact, Li[RBH₃] species react readily, in THF, with two equivalents of 2-mercapto-1-methylimidazole, giving Li[(R)HB(tim^{Me})₂] (R = Me, Ph). The kinetics of the reaction depends on the nature of the substituent attached to the boron. Indeed, the species Li[(CH₃)HB(tim^{Me})₂] (Table 6) was easily prepared at r.t. while the preparation of Li[(Ph)HB(tim^{Me})₂] requires reflux in THF. Obviously, this difference reflects the higher basicity of the hydrides in [MeBH₃][−] in comparison with [PhBH₃][−], as a consequence of the electronic withdrawing properties of the phenyl group. Their coordination chemistry towards U(III) [121] and Re(I) [119] salts were also reported.

Recently Owen *et al.* [122] reported the formation of the species [(Bz)HB(tim^{Me})₂][−] as a consequence of a 'sting' on the benzylidene fragment of Grubbs' catalyst leading to formation and transfer of the benzyl fragment to boron (Fig. 16).

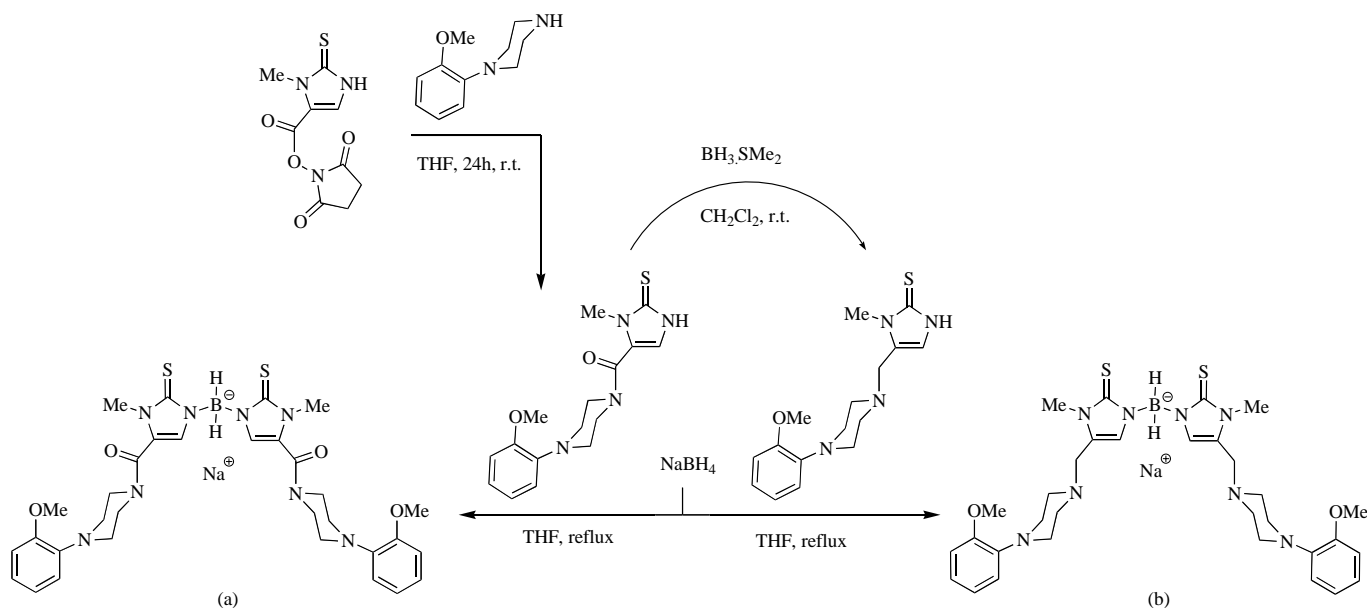


Fig. (15). Synthesis of $\text{Na}[\text{H}_2\text{B}(\text{tim}^{\text{Me},4\text{piP}})_2]$ (a) and $\text{Na}[\text{H}_2\text{B}(\text{tim}^{\text{Me},4(\text{CH}_2\text{-pip})})_2]$ (b).

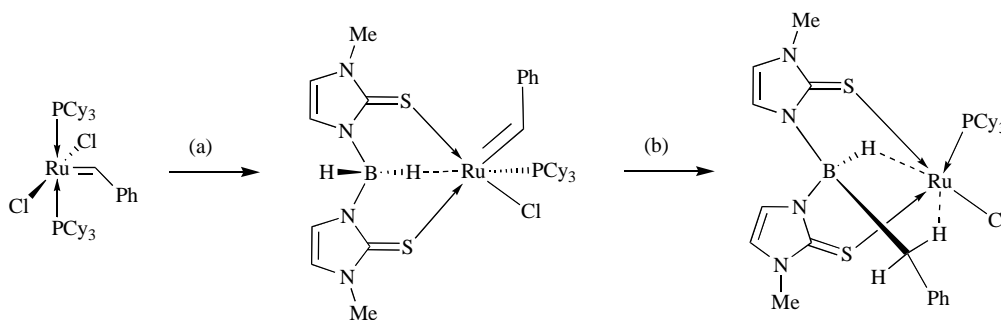


Fig. (16). (a) $\text{Na}[\text{H}_2\text{B}(\text{tim}^{\text{Me}})_2]$, THF, r.t., $-\text{NaCl}$, $-\text{PCy}_3$. (b) THF, r.t., transfer of benzyl fragment to boron.

The structure reveals that the 'hydride' maintains an interaction with the boron atom. An unprecedented coordination mode for the poly(thioimidazolyl)borate ligand results in which the two sulfur donors are mutually trans. The ruthenium atom adopts a distorted octahedral geometry and is coordinated by chlorine, tricyclohexylphosphine, the two sulfur atoms and interactions with the BH and benzyl methylene groups (Fig. 16). The agostic interaction with the benzyl group is trans to the phosphine. The Ru–Cl bond is trans to the BH unit and is longer than is usual for a six coordinate ruthenium complex [122].

Asymmetric bis(thioimidazolyl)borates $\text{Na}[(\text{Ph})\text{HB}(\text{tim}^{\text{Me}})(\text{tim}^{\text{Me},4\text{piP}})]$ and $\text{Na}[(\text{Ph})\text{HB}(\text{tim}^{\text{Me}})(\text{tim}^{\text{Me},4(\text{CH}_2\text{-pip})})]$ [117] (Table 6) with organoboryl moieties have been synthesized by Santos *et al.* [117] devising a strategy which lies on the formation of an intermediary mono(thioimidazolyl)borate, containing a methimazolyl ring, which is further reacted with a thioimidazole bearing a piperazine moiety. As indicated in Fig. (17), the preparation of the mono(methimazolyl)borate intermediate involved the reaction of $\text{Li}(\text{PhBH}_3)$ with methimazole in THF, at room temperature. The species $\text{Li}[\text{H}_2(\text{Ph})\text{B}(\text{tim}^{\text{Me}})]$ was generated *in situ* and then reacted with the functionalized thioimidazoles $\text{Htim}^{\text{Me},4\text{piP}}$ or $\text{Htim}^{\text{Me},4(\text{CH}_2\text{-pip})}$ (Fig. 17).

Parkin *et al.* has recently reported complexes which have B–Cl and B–OAc groups, derived by oxidative reaction of boratranes [123].

The tris(methimazolyl)borate ligands $\text{Li}[\text{RB}(\text{tim}^{\text{Me}})_3]$ (R = Me, Ph) (Table 6) have been synthesized by reaction, in refluxing tolu-

ene, of methimazole with lithium methylborohydride or phenylborohydride, respectively [124]. These ligands are the first examples of tris(thioimidazolyl)borates bearing alkyl or aryl substituents directly attached to the boron atom. They were used to prepare the Re(I) tris(carbonyl) complexes $[\text{Re}\{\text{tim}^{\text{Me}}\}_3\text{-}\kappa^3\text{S}_3\text{S}_3\text{CO}_3]$ (R = Me, Ph), which are quite resistant toward hydrolysis and aerial oxidation and can be seen as valuable models for the development of specific radiopharmaceuticals [124].

An improved synthesis (Fig. 18) of lithium phenyltris(methimazolyl)borate, $\text{Li}[\text{PhB}(\text{tim}^{\text{Me}})_3]$, was described by Reglinski *et al.* [125], and the structure of the methanol-solvated species $\text{Li}(\text{MeOH})_4[\text{PhB}(\text{tim}^{\text{Me}})_3]$ has been determined.

Poly(thioimidazolyl)borate ligands have found widespread applications and examples of metal complexes are known for a number of *p*-block and transition elements [97]. In particular the S_3 -donor hydrotris(methimazolyl)borate $[\text{HB}(\text{tim}^{\text{Me}})_3]$ has allowed stable scorpionate complexes of the lower main group to be synthesized and a number of authors, such as Reglinski *et al.* [98, 99], Parkin *et al.* [100], Vahrenkamp *et al.* [109] and Rheingold *et al.* [111], showed that this family of ligands is indeed suitable for a biomimetic zinc complex chemistry [126].

While the coordination chemistry of the poly(thioimidazolyl) borate family of ligands is extensive, they are subject to relatively facile degradation reactions in oxidising conditions. For instance, reaction of $[\text{HB}(\text{tim}^{\text{Me}})_3]$ with Cu(II) or Fe(III) ions results in the

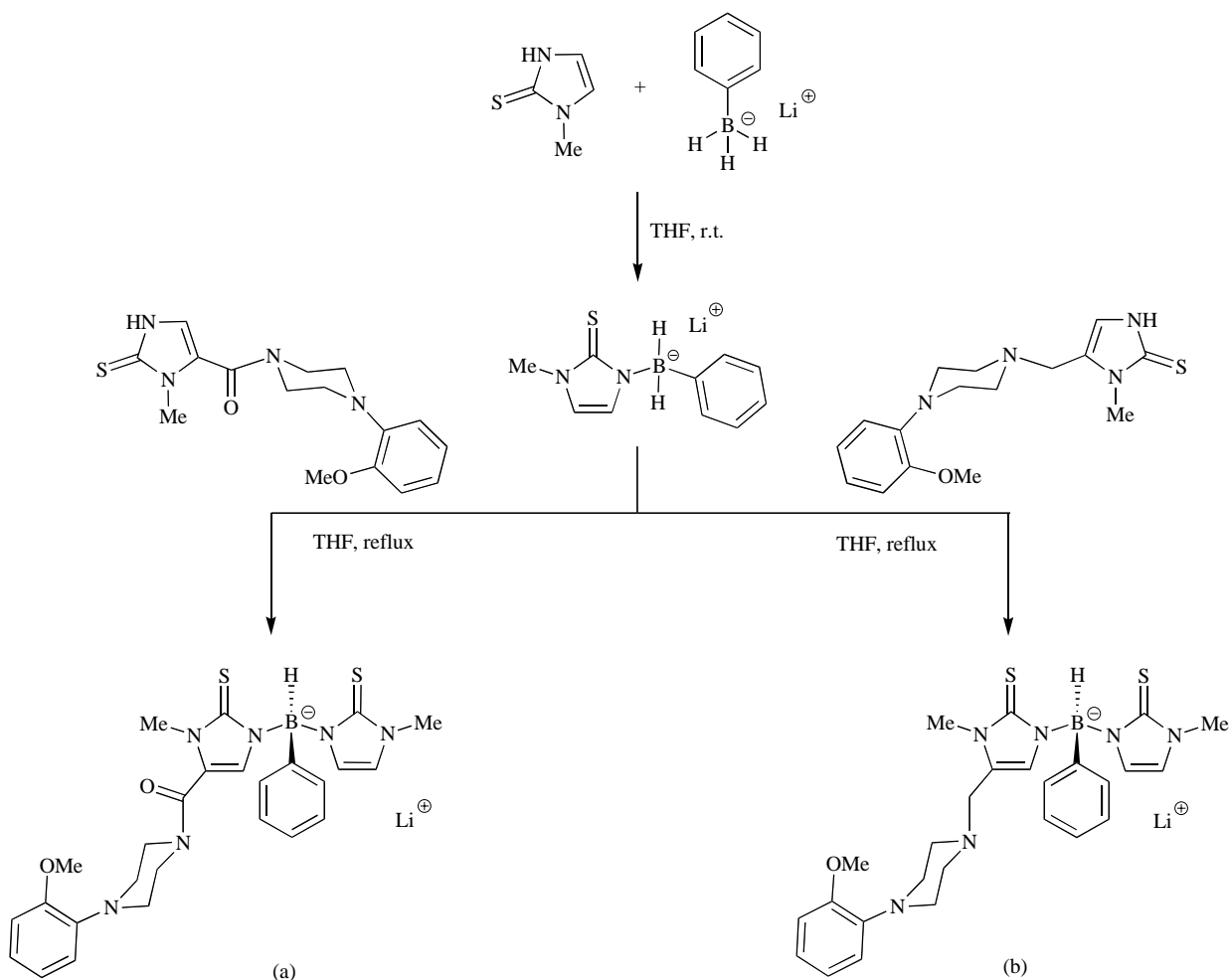


Fig. (17). Synthesis of $\text{Na}[(\text{Ph})\text{HB}(\text{tim}^{\text{Me}})(\text{tim}^{\text{Me},4\text{pip}})]$ (a) and $\text{Na}[(\text{Ph})\text{HB}(\text{tim}^{\text{Me}})(\text{tim}^{\text{Me},4(\text{CH}_2)_2\text{pip}})]$ (b).

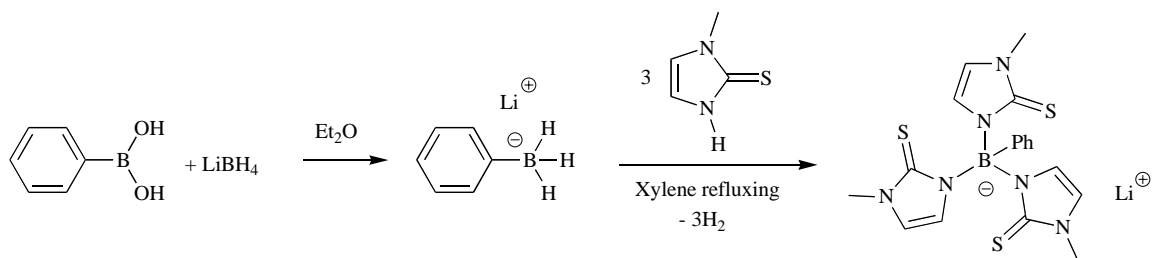


Fig. (18). Synthesis of the lithium phenyltris(methimazolyl)borate.

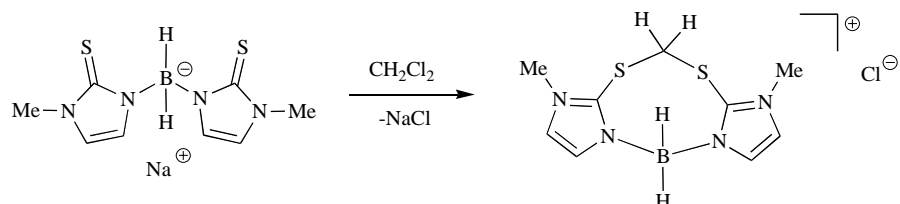


Fig. (19). Synthesis of $[\text{H}_2\text{C}(\text{tim}^{\text{Me}})_2\text{BH}_2]\text{Cl}$.

ligand cleavage. However, Hill *et al.* have shown that dichloromethane reacts slowly with the free ligand, leading to formation of the heterocyclic salt $[\text{H}_2\text{C}(\text{tim}^{\text{Me}})_2\text{BH}_2]\text{Cl}$ (Fig. 19) [127].

Similar products have been isolated from reaction of $\text{Na}[\text{HB}(\text{tim}^{\text{Me}})_3]$ or $\text{Na}[(\text{tim})_2\text{BBN}]$ (BBN = 9-borabicyclononyl) in dichloromethane to provide the species $[\text{H}_2\text{C}(\text{tim}^{\text{Me}})_2\text{BH}(\text{tim}^{\text{Me}})]\text{Cl}$

and $[\text{H}_2\text{C}(\text{tim}^{\text{Me}})_2\text{BBN}]\text{Cl}$ [127], respectively, characterized by the presence of an eight-membered heterocycle $\text{B}(\text{NCS})_2\text{C}$ (Table 6).

A side reaction of the B–H moiety of the $[\text{HB}(\text{tim}^{\text{Me}})_3]^-$ anion with nitronium cation (NO^+) results in the isolation of the dimethylformamide adduct of tris(methimazolyl)borane, $(\text{Me}_2\text{NCHO})\text{B}(\text{tim}^{\text{Me}})_3$, [128] (Fig. 20).

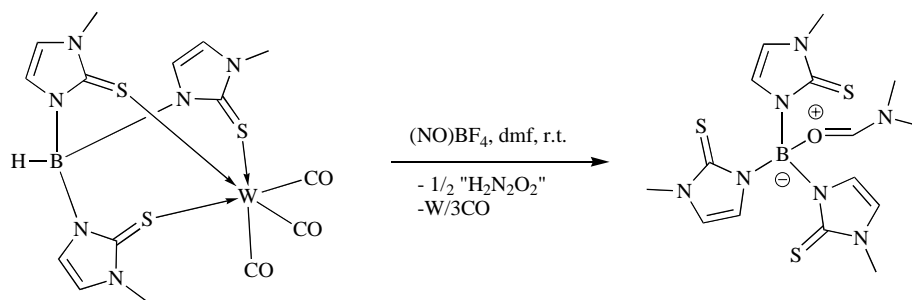


Fig. (20). Synthesis of $(\text{Me}_2\text{NCHO})\text{B}(\text{tim}^{\text{Me}})_3$.

The boron-centred molecule $(\text{Me}_2\text{NCHO})\text{B}(\text{tim}^{\text{Me}})_3$ maintains many of the structural features of the poly(thioimidazolyl)borate anions. These data provide further evidence that the reaction pathways of the poly(thioimidazolyl)borate ligands are more varied and less passive than the chemistry of the nitrogen-based scorpionates [128]. In particular, while the B–H moiety rarely reacts in poly(pyrazolyl)borates chemistry, it is not uncommon for it to do so in poly(thioimidazolyl)borate chemistry. These data support the view that $[\text{HB}(\text{tim}^{\text{Me}})]$ is a strong π -donor and that its character (i.e. its softness) is tempered by the nature of the bonding in the complex. This observation sets it apart from the anionic tripodal tris(phosphinomethyl)borates (*vide infra*) [129-131] and tris(thioalkyl)borates (*vide infra*) [132-135] and as such we can expect to continue seeing greater diversity within this sub grouping of the scorpionate species. In fact, Hill and coworkers have identified two related products which stem from the same reaction profile, namely a cyclic species [127] (Fig. 19) and an elegant series of metal boratranes (*vide infra*) [136, 137].

4.2. Boratranes

In their initial attempts to prepare classical chelate complexes containing the ligand $[\text{HB}(\text{tim}^{\text{Me}})_3]$, Hill and coworkers [136] have encountered an unprecedented class of reaction for tris(azolyl)borates, namely the intramolecular activation of the bridgehead B–H bond which provides the first example of metallaboratranes (Fig. 21), examples of which are known for the late transition metals Fe [123], Ru [136, 138], Os [139], Co [140], Rh [137, 141, 142], Ir [142, 143], Ni [112, 144], Pd [145] and Pt [146-148].

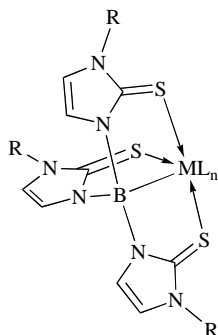


Fig. (21). General structure of metallaboratranes.

The elucidation of the metallaboratrane structural motif ($M \rightarrow B$), in the compounds $[\text{M}(\text{CO})(\text{PPh}_3)\{\text{B}(\text{tim}^{\text{Me}})_3\}]$ (Fig. 22) ($M = \text{Ru}$ [136, 149], Os [139]), afforded the first unequivocal evidence for long mooted dative metal \rightarrow boron interactions [150].

The mechanism of formation has not yet been elucidated unequivocally, but it seems likely that in the first instance a $M \cdots \text{H}-\text{B}$ interaction occurs, which is followed by a metal mediated activation of the B–H bond, which can be likened to an oxidative addition (Fig. 23).

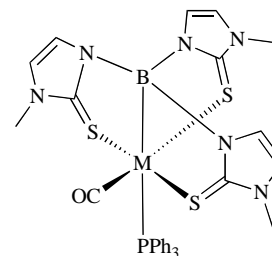


Fig. (22). Structure of $[\text{M}(\text{CO})(\text{PPh}_3)\{\text{B}(\text{tim}^{\text{Me}})_3\}]$ ($M = \text{Ru}$ or Os).

If no hydrogen acceptor group (R) is present, the resulting metal hydride can on occasions be isolated [149], but more normally this reacts rapidly, most typically by reductive elimination with an alkyl or aryl group leading to metallaboratrane formation (Fig. 23). Alternatively, one could envisage a concerted process in which the borohydride activation leads to a cyclic transition state from which elimination of R–H occurs with concurrent M–B bond formation (Fig. 23). In at least one case solvent has been clearly implicated in the process, with generation of CH_2Cl_2 from chloroform and the coordination of a chloride ligand being observed [141]. For example, the formation of the metallaboratrane of the type $[\text{M}(\text{R})\text{Cl}(\text{L})(\text{PPh}_3)_3]$ ($\text{ML} = \text{RuCO}$, OsCO , RhCl ; $\text{R} = \text{aryl}$, vinyl), obtained by the reaction of $\text{Na}[\text{HB}(\text{tim})_3]$ with d^6 transition-metal organyls, is a process which involves activation of an agostic B–H–M linkage and subsequent reductive elimination of R–H: the σ -organyl acts as a hydrogen acceptor. However, the platinaboratrane $[\text{PtH}(\text{PPh}_3)\{\kappa^4\text{B,S,S',S''-B}(\text{tim})_3\}]\text{Cl}$ [148] and iridaboratrane $[\text{IrH}(\text{CO})(\text{PPh}_3)\{\kappa^3\text{B,S,S'-B}(\text{tim})_2\text{R}\}]$, have been obtained directly from reaction of low-valent non-organometallic precursors, *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ [148] or the Vaska's complex $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ [143] and $\text{Na}[\text{HB}(\text{tim})_3]$.

The driving force for assembly of the metallaboratrane motif, and hence the dative interaction, may thus be considered a function of several factors, including d occupancy, geometric constraints, and metal σ -basicity. The subject of bonding in these compounds has been discussed in greater detail by Parkin *et al.* [142].

4.3. Se-donor Scorpionate Ligands

Whereas S_3 -donor tripodal ligands are ubiquitous [98-101, 109, 111, 151-154], analogous ligands that feature an Se_3 -donor array are uncommon, and the only examples we are aware of belong to the neutral triselenoethers $\text{MeC}(\text{CH}_2\text{SeMe})_3$ and $\text{MeC}(\text{CH}_2\text{SePh})_3$ [155-157]. Since the tris(thioimidazolyl)borate ligands introduced by Reglinski and coworkers [98] have proven to be versatile [158], with a large variety of $[\text{HB}(\text{tim}^{\text{R}})_3]$ derivatives having been prepared, Parkin *et al.* envisioned that a similar series of tripodal ligands that features an Se_3 -donor array should be accessible and thereby provide a set of ligands with modified electronic properties [159]. Indeed, the tris(3-mesityl-2-selenoxo-imidazol-1-yl)borate ligand (Table 7) has been obtained as its potassium derivative $\text{K}[\text{HB}(\text{Seim}^{\text{Mes}})_3]$ via the reaction of KBH_4 with 1-mesityl-

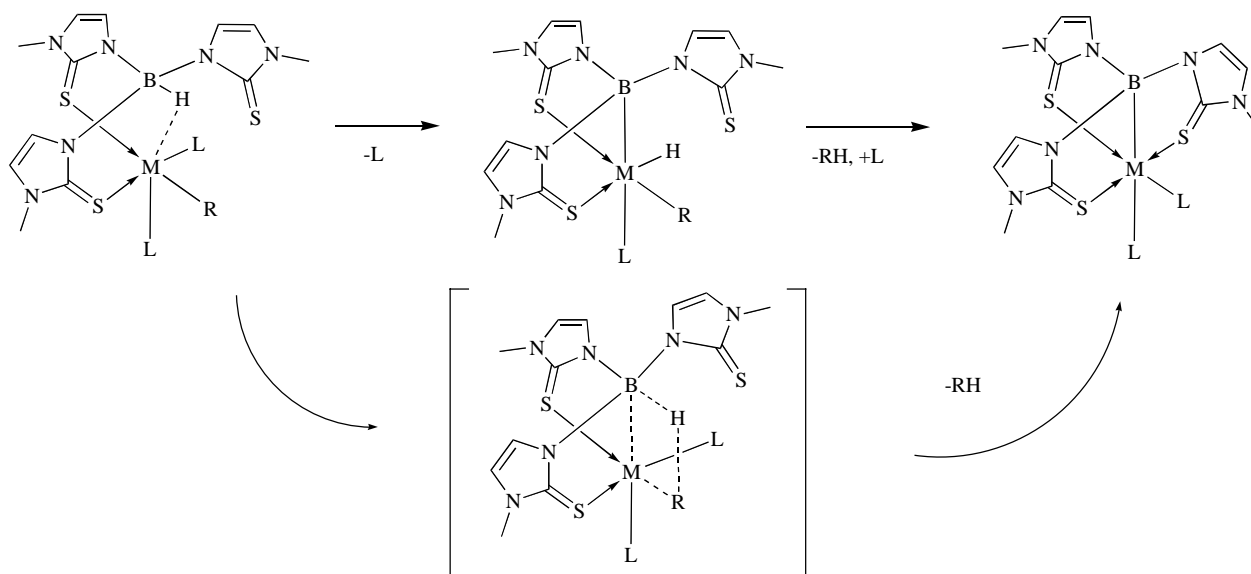


Fig. (23). Synthesis of metallaboratranes.

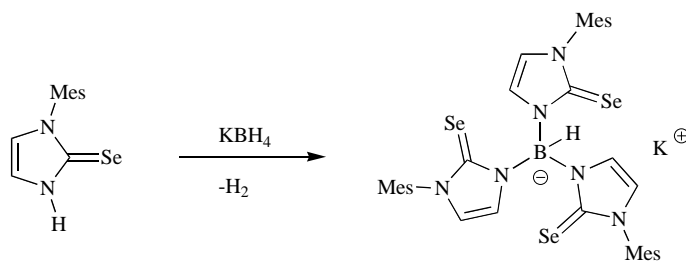


Fig. (24). Synthesis of $K[HB(Seim^{Mes})_3]$.

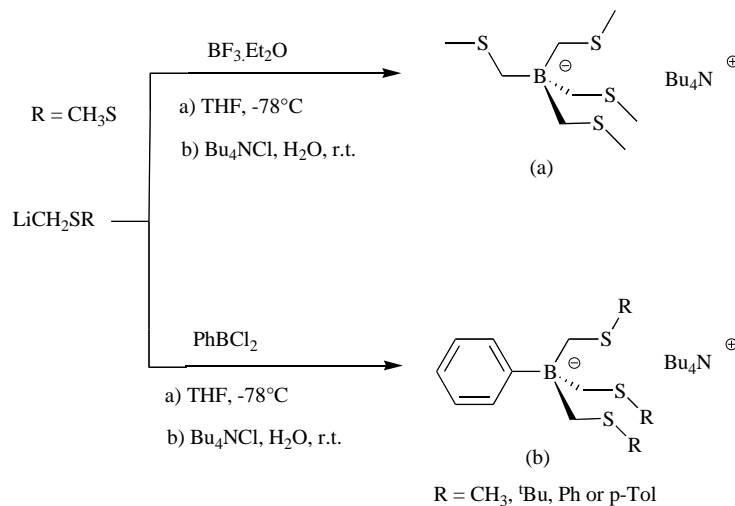


Fig. (25). Synthesis of $Bu_4N[B(CH_2SCH_3)_4]$ (a) and $Bu_4N[PhB(CH_2SR)_3]$ ($R = CH_3, tBu, Ph, p-Tol$) (b).

imidazole-2-selenone [160], as illustrated in Fig. (24) [159]. $K[HB(Seim^{Mes})_3]$ is a convenient reagent for a variety of derivatives of both the main group metals and transition metals and complexes of type $[HB(Seim^{Mes})_3]MI$ ($M = Co, Zn, Cd, Hg$) [159], $\{[HB(Seim^{Mes})_3]_2M\}[MCl_4]$ ($M = Ga, In$) [159], $\{[HB(Seim^{Mes})_3]Cu\}_2$ [159], $[HB(Seim^{Mes})_3]Re(CO)_3$ [159] and $[HB(Seim^{Mes})_3]NiNO$ [161] have been obtained.

Using a similar method, the bis- and tris-(3-methyl-2-selenoxoimidazol-1-yl)borate ligands, $K[H_2B(Seim^{Me})_2]$ and $Na[HB(Seim^{Me})_3]$, have been constructed by reaction of 1-methylimidazole-2-selenone [160, 162] with KBH_4 and $NaBH_4$,

respectively [163]. These ligands have been used to synthesize other derivatives of the type $\{[H_2B(Seim^{Me})_2]ZnX\}_2$ ($X = Cl, I$), $[H_2B(Seim^{Me})_2]_2Zn$, $[HB(Seim^{Me})_3]Re(CO)_3$ [163] and $[H_2B(Seim^{Me})_2]Ni(PPh_3)(NO)$ [164].

4.4. Poly(thioalkyl)borates

Riordan and co-workers prepared the monoanionic $Bu_4N[B(CH_2SCH_3)_4]$ species (Table 8) [132] from the *in situ* reaction of an excess of $LiCH_2SCH_3$ with BF_3Et_2O in THF at $-78^\circ C$ (Fig. 25a). The anion is precipitated from aqueous solutions as its

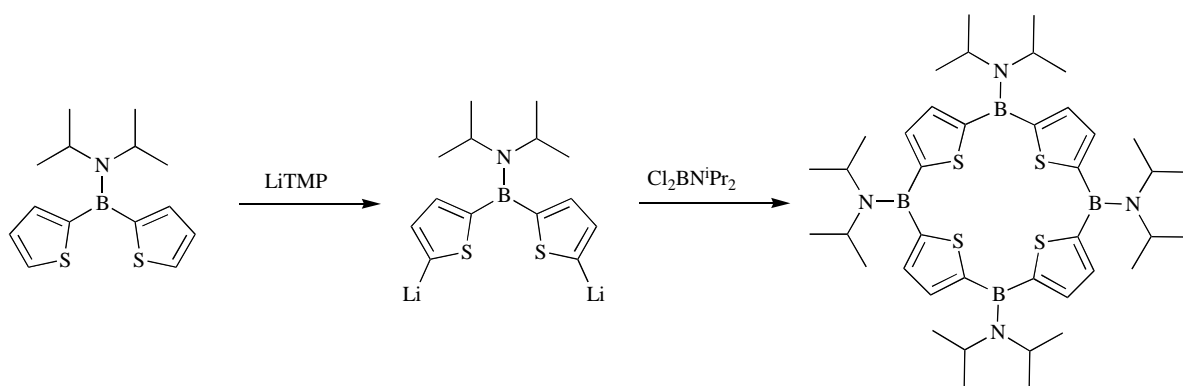


Fig. (26). Synthesis of macrocycle boron-bridged $[(N^iPr_2)B(thi)]_4$.

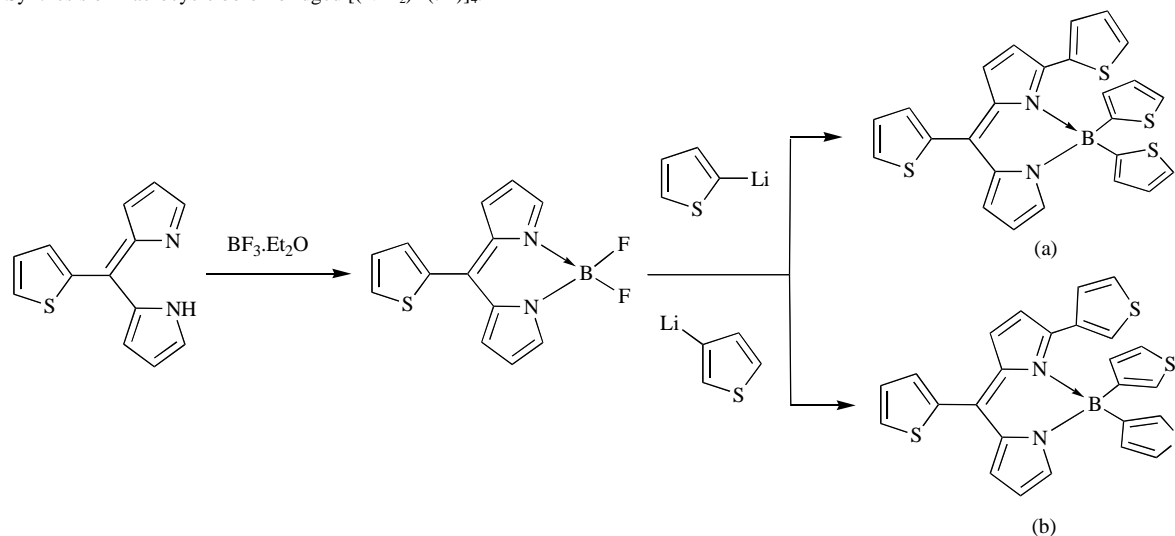


Fig. (27). Synthesis of tetra-thienyl-substituted boron-dipyrrin-type systems: BODIPY-2T (a) and BODIPY-3T (b).

Bu_4N^+ salt and is potentially a C_3 -symmetric face-capping ligand. Poly(thioalkyl)borate ligands represent sulphur analogs of the versatile poly(pyrazolyl)borates. The thioether ligand provides a softer coordination sphere for metal ions and, consequently, a different metal environment.

Their donor aptitudes are established via the synthesis of a range of metal complexes [165]. The analogous phenyltris(methylthio)alkylborates $Bu_4N[PhB(CH_2SCH_3)_4]$ [165], $Bu_4N[PhB(CH_2S^tBu)_3]$ [151], $Bu_4N[PhB(CH_2SPh)_3]$ [166], $Bu_4N[PhB(CH_2S(p-Tol)_3)]$ [135] and $Tl[PhB(CH_2SAd)_3]$ (Ad = adamantyl) [152] have also been prepared. CH_3SR (R = CH_3 , tBu , Ph, p-Tol or Ad) was readily and quantitatively deprotonated by nBuLi in the presence of TMEDA (TMEDA = tetraethylmethylenediamine); the resulting carbanion, $LiCH_2SR$, reacts with $PhBCl_2$ to yield the $Li[PhB(CH_2SR)_3]$ ligands. The Bu_4N^+ or thallium(I) salts were precipitated from aqueous solutions upon addition of $[Bu_4N]Cl$ (Fig. 25b) [165] or Tl_2SO_4 [152], respectively. The same reaction work-up was used to synthesize the species $Bu_4N[FcB(CH_2SCH_3)_3]$ (Fc = ferrocenyl) starting from the appropriate carbanion $LiCH_2SCH_3$ and using the $FcBBr_2$ species [133].

The corresponding bidentate borate species, $[Ph_2B(CH_2SR)_2]$, were prepared conveniently following protocols developed for the tridentate ligands [135]. In particular, the requisite sulfide, CH_3SR (R = CH_3 , tBu), was readily and quantitatively deprotonated by nBuLi in the presence of TMEDA. The resulting carbanion, $LiCH_2SR$, was added slowly to Ph_2BBr yielding the desired product. Aqueous work-up with either $[Bu_4N]Br$ or $CsCl$ as the cation source yielded the ligands, $[Bu_4N][Ph_2B(CH_2SCH_3)_2]$ and $Cs[Ph_2B(CH_2S^tBu)_2]$ [167]. The species $[Bu_4N][Et_2B(CH_2SCH_3)_2]$

was prepared according to the previously reported procedure replacing Ph_2BBr with $Et_2B(OTs)$ [135].

Poly(thioalkyl)borates have found widespread applications and examples of metal complexes are known for a number of transition elements such as Fe(II) [133, 165, 168, 169], Co(II) [133, 165, 168, 170-172], Ni(I) [152, 171, 173-176], Ni(II) [133, 151, 152, 165, 167, 168, 177-179], Zn(II) [168, 180], Cu(I) [134, 135, 166, 179, 181], Cu(II) [133, 181] and Mo(CO)₃ [132].

The sulfur-rich anion, tetrakis(2-thienyl)borate (Table 8), $K[B(thi)_4]$, which is the thiophene analogue of the polythioether ligand tetrakis((methylthio)methyl)borate, was reported by Pacey and Moore [182] and by Sargent *et al.* along with a molecular orbital analysis of its coordination to a metal center [183].

Boron-bridged tetrahydroporphyrinogen was reported by Siebert and coworkers [184] starting from the N,N-diisopropyl-1,1-di-2-thienylboranamine [185] followed by dimetalation and treatment with the stoichiometric quantity of $Cl_2BN^iPr_2$ to give the macrocycle boron-bridged $[(N^iPr_2)B(thi)]_4$ [184] (Fig. 26). No polymer formation was observed. To avoid any attack at boron, the sterically hindered strong base lithium 2,2,6,6-tetramethylpiperidide (LiTMP) was used.

Interestingly, porphyrins with boron atoms in side chains have been used for BNCT (boron neutron capture therapy) studies [186].

“Scorpionate”-like tetra-thienyl-substituted boron-dipyrrin-type systems (BODIPY-type) [187] complexes, 3-(R')-4,4-di(R')-8-R-4-bora-3a,4a-diaza-s-indacene (Table 8), have been prepared by Choi *et al.* [188] (Fig. 27).

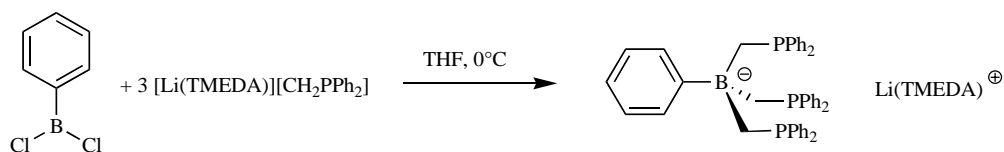


Fig. (28). Synthesis of Li(TMEDA)[PhB(CH₂PPh₂)₃].

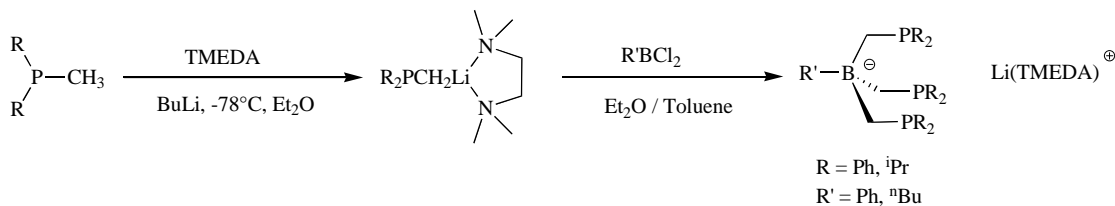


Fig. (29). Synthesis of Li(TMEDA)[R'B(CH₂PR₂)₃] (R = Ph or ⁱPr; R' = Ph or ⁿBu).

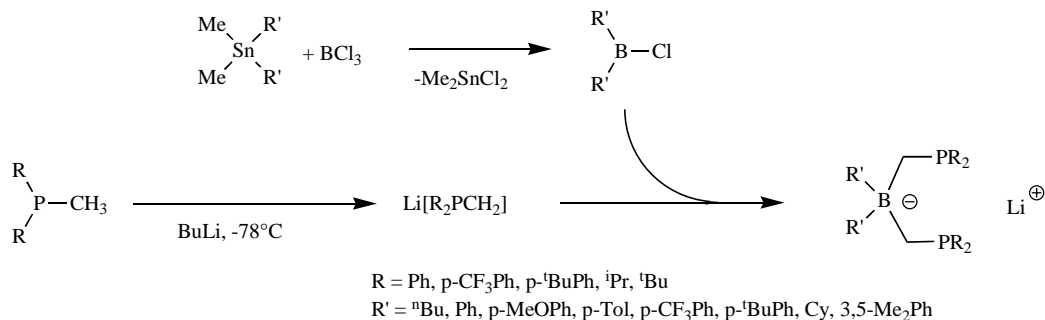


Fig. (30). General synthesis of bis(phosphino)borates.

The synthesis of the species illustrated in Fig. (27) involved four convenient steps from commercially available and inexpensive starting materials: preparation of 5-substituted dipyrromethanes [189, 190]; oxidation of dipyrromethanes to dipyrins or dipyrromethenes [191]; preparation of BF₂-dipyrin [192]; finally, treatment of BF₂-dipyrin with thienyllithium was performed obtaining bis-substituted boron analogues (Fig. 27) [188].

A variety of *meso*-thienyl dipyrin species is also accessible, as shown by Churchill and coworkers [193], to yield an array of robust products.

4.5. Poly(phosphinomethyl)borates

As amply demonstrated in pyrazoylborates chemistry [1] and in the synthesis of [PhB(CH₂SR)₃] by Riordan and coworkers [151], the borate bridgehead provides both the desired negative charge and a scaffold to support three ligating arms with a hybridization that sustains a *fac* conformation about a metal center. Within the context, the tris(diphenylphosphinomethyl)phenylborate, [PhB(CH₂PPh₂)₃], first reported by Nocera and coworkers [129], features a negative charge proximate to a highly polarizable six-electron phosphine donor set, exhibiting a propensity to associate to soft metals. In particular the Li(TMEDA)[PhB(CH₂PPh₂)₃] (Table 9) was synthesized by addition of diphenylphosphinomethide to dichlorophenylborane yielding a borate salt, which subsequently undergoes substitution of its chlorides by two additional equivalents of diphenylphosphinomethide to provide the tris(diphenylphosphinomethyl)phenylborate ligand [129] (Fig. 28).

Following this methodology Betley and Peters [131] described the preparation of the tris(diisopropylphosphino)phenylborate, Li(TMEDA)[PhB(CH₂PⁱPr)₃] and examined aspects of its electronic and structural properties in comparison to those of the parent [PhB(CH₂PPh₂)₃] ligand. The thallium(I) complex, Tl[PhB(CH₂PⁱPr)₃], was also synthesized and characterized in the solid-state by X-ray diffraction analysis [131].

Tris(phosphino)borate silver(I) complexes, in which substituent on the boron atom is varied from phenyl to alkyl groups, were synthesized by Marks *et al.* [194] in a three step procedure (Fig. 29) modified from that of Peters *et al.* [131, 195-198] using commercially available reagents.

Although isoelectronic with Cp and tris(pyrazolyl)borate (Tp) ligands, tris(phosphinomethyl)borates differ significantly from these as they coordinate via three soft phosphine σ-donor groups. Accordingly, the tris(phosphinomethyl)phenylborates have enabled the isolation of transition-metal complexes that have no counterpart in Cp- or Tp-ligated systems, such as Ir(III)-silylene [130, 199, 200], Fe(II)-silyl complexes [201], Fe(II) and terminal Co(III) [202] and Fe(III)-imido complexes [203].

Thomas and Peters [204] provided detailed methods for the preparation of a series of bis(phosphino)borate ligands comprising diverse electronic and steric properties. The general method chosen for preparing bis(phosphino)borate ligands relies on the delivery of a phosphinoalkyl carbanion to a borane electrophile (Fig. 30). The advantage of this strategy is its convergent approach: a host of borane electrophiles and appropriate carbanions are synthetically accessible. Also, the synthesis of borate-based ligands by nucleophilic addition to borane precursors has precedence in the literature [135, 151, 165, 173]. Each of the bis(phosphino)borates shown in Table 9 was prepared adhering to the following methodologies: (i) synthesis of di(organyl)chloroborane electrophiles of the formula R₂BCl; (ii) generation of phosphine carbanions of the general formula [R₂PCH₂]⁻; (iii) synthesis of lithium salts Li[R₂B(CH₂PPh₂)₂] or Li[Ph₂B(CH₂PR₂)₂]; (iv) generation of synthetically useful ammonium and thallium salts of bis(phosphino)borates.

Thomas and Peters [205] also described the synthesis of the bis(phosphino)borate species (ASN)[Ph₂B(CH₂PPh₂)₂](ASN = 5-azonia-spiro[4.4]nonane) (Table 9) and examined its ability to promote C-H bond activation chemistry at a platinum(II) center.

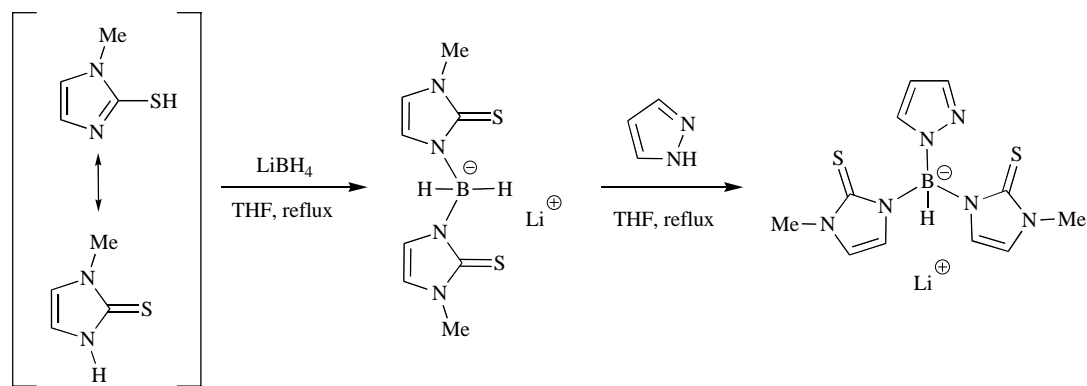


Fig. (31). Synthesis of $\text{Li}[\text{HB}(\text{pz})(\text{tim}^{\text{Me}})_2]$.

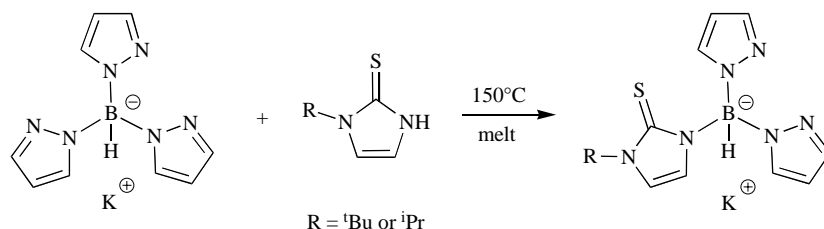


Fig. (32). Synthesis of bis(pyrazolyl)(thioimidazolyl)borates.

The bis(phosphino)borate ligands are unique in that they preserve the essential properties of a neutral bis(phosphine) chelate while also being anionic in nature. Their chemical properties derive in part from the borate charge fastened into the alkyl chain of the ligand backbone.

5. HYBRID SCORPIONATE LIGANDS

Among the scorpionates, the tris(pyrazolyl)borates are by far the most prominent ones. As a companion to these N_3 -donors [4], the tris(thioimidazolyl)borates, which were introduced by Reglinski *et al.* [98] as S_3 -donors, are gaining ground due to their similarly favorable properties [97]. Therefore, it became attractive to make use of the corresponding scorpionates with nitrogen, sulfur and phosphorus donor sets, such as (N_2S) [206], (NS_2) [114, 168, 207-210], (N_2P) [211, 212] and (NP_2) [213], derived from mixed poly(pyrazolyl)(thioimidazolyl)borates, poly(pyrazolyl)(phosphanyl)borates and the ambidentate poly(azolyl)borates based on thioxotriazoles and mercaptothiadiazoles. These derivatives are most interesting, because they allow a smooth modulation of the coordination environment between the extremes (N_3) of tris(pyrazolyl)borates, (S_3) of tris(thioimidazolyl)borates or tris(thioalkyl)borates and (P_3) of tris(phosphino)borates. Complete homogeneous series of closely related ligands facilitate an evaluation of the influence of gradual changes in the donor set of tripods on the chemical properties of the coordinated metal ion [167, 181, 214-217].

5.1. Mixed poly(pyrazolyl)(thioimidazolyl)borates

The bis(thioimidazolyl)(pyrazolyl)borate (Table 10), $[\text{HB}(\text{pz}^x)(\text{tim}^x)_2]^-$, can be prepared essentially by the same procedure used for the species $[\text{HB}(\text{pz}^x)_3]^-$ and $[\text{HB}(\text{tim}^x)_3]^-$, which consists of the high-temperature reaction between KBH_4 and a stoichiometric amount of the pyrazole and/or thioimidazole [114]. The ligand $\text{Li}[\text{HB}(\text{pz})(\text{tim}^{\text{Me}})_2]$ (Fig. 31) has been prepared by Parkin *et al.* [114] and applied successfully for modeling aspects of the bioinorganic chemistry of zinc enzymes [100, 114, 209].

Complexes of the type $\text{M}[\text{HB}(\text{pz})(\text{tim}^{\text{Me}})_2]_2$, ($\text{M} = \text{Zn}, \text{Co}$ or Cd), despite their similar composition, adopt different structures: 1)

the zinc complex shows a tetrahedral $\text{Zn}[\text{S}_4]$ core in which only the sulfur donors are coordinated to metal; 2) the cobalt complex presents a trigonal-bipyramidal $\text{Co}[\text{S}_3\text{NH}]$ structure, in which one of the pyrazolyl groups and one of the BH coordinate to metal; 3) the cadmium complex exhibits a six-coordinate $\text{Cd}[\text{S}_4\text{H}_2]$ structure in which both BH interact with the metal. In addition Parkin and co-workers demonstrated that the mixed bis(thioimidazolyl)(pyrazolyl)borates open the way to tetrahedral ($\kappa^3\text{N}, \text{S}, \text{S}'$) Zn-X complexes [100, 218].

Nine tripodal ligands of the type $[\text{HB}(\text{pz}^x)(\text{tim}^x)_2]^-$ with varying 3-R-thioimidazolyl moieties were prepared as their potassium salts and their zinc complexes identified by a total of twelve structure determinations by Vahrenkamp *et al.* [210]. They fill half of the gap between the analogous $\kappa^3\text{N}, \text{N}', \text{N}''$ (i.e. pyrazolylborate) and $\kappa^3\text{S}, \text{S}', \text{S}''$ (i.e. mercaptoimidazolylborate) ligands. Provided that the as-yet-unknown tripodal $\kappa^3\text{N}, \text{N}', \text{S}$ ligands of this type are also accessible, the door would be open for a complete set of comparative investigations of metal complexes with homologous tripodal $\kappa^3\text{N}, \text{N}', \text{N}''$, $\kappa^3\text{N}, \text{N}', \text{S}$, $\kappa^3\text{N}, \text{S}, \text{S}'$ and $\kappa^3\text{S}, \text{S}', \text{S}''$ ligands.

On the basis of Vahrenkamp *et al.* works [206], the synthetic procedure used for bis(thioimidazolyl)(pyrazolyl)borates doesn't work for system type bis(pyrazolyl)(thioimidazolyl)borates, $[\text{HB}(\text{pz}^x)_2(\text{tim}^x)]^-$, and it is possible to obtain $[\text{HB}(\text{pz})_2(\text{tim}^{\text{tBu}})]^-$ and $[\text{HB}(\text{pz})_2(\text{tim}^{\text{iPr}})]^-$ (Table 10) ligands by reaction between unsubstituted $[\text{HB}(\text{pz})_3]^-$ and the corresponding thioimidazole in their own melt at 150°C [206] (Fig. 32).

It corresponds to a substitution of the pyrazolyl groups by the thioimidazolyl groups, the driving force for the reaction being the sublimation of pyrazole out of the reaction mixture. However, the reaction produces mixtures of type $[\text{HB}(\text{pz})_3]$, $[\text{HB}(\text{pz})(\text{tim}^{\text{R}})_2]$, and $[\text{HB}(\text{pz})_2(\text{tim}^{\text{R}})]^-$. Their separation, which is accompanied by serious losses, reduces the isolated yields to 10-20%.

The mixed pyrazole/thioimidazoles donor ligands, along with $[\text{HB}(\text{tim}^{\text{Me}})_3]^-$, have great potential for tuning the electron density at the metal centre and hence the redox properties, a factor which is of great importance when exploiting the coordination chemistry of organometallic compounds in catalysis and material science.

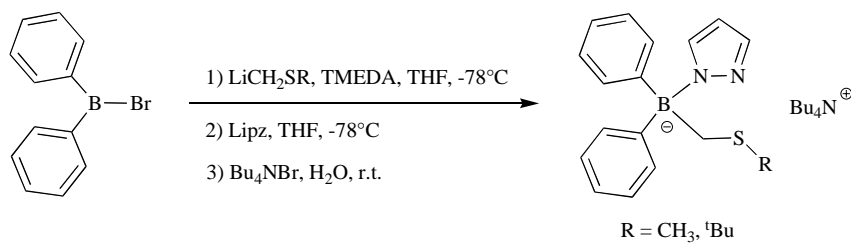


Fig. (33). Synthesis of hybrid N- and S-donor borate ligands: $\text{Bu}_4\text{N}[\text{Ph}_2\text{B}(\text{pz})(\text{CH}_2\text{SR})]$ (R = CH₃ or ^tBu).

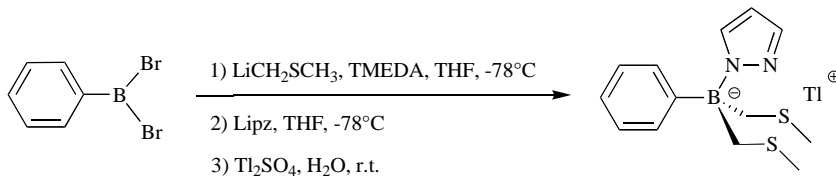


Fig. (34). Synthesis of $\text{Tl}[\text{PhB}(\text{pz})(\text{CH}_2\text{SCH}_3)_2]$.

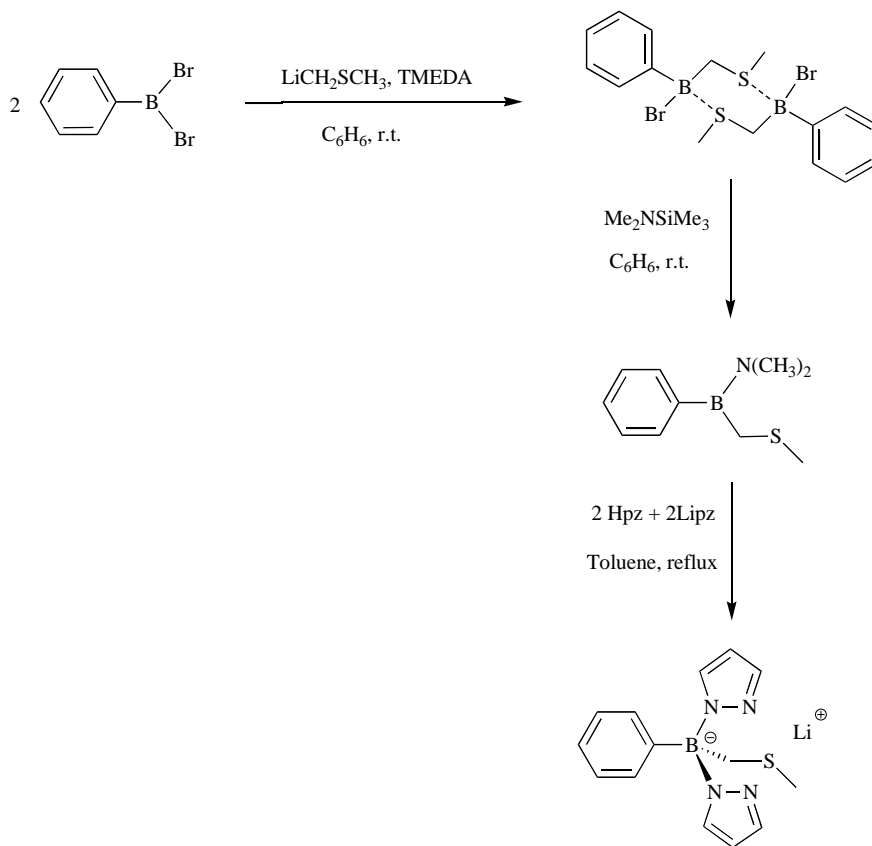


Fig. (35). Synthesis of $\text{Li}[\text{PhB}(\text{pz})_2(\text{CH}_2\text{SCH}_3)]$.

5.2. Mixed poly(pyrazolyl)(thioalkyl)borates

Hybrid N- and S-donor borate ligands (Table 11), $\text{Bu}_4\text{N}[\text{Ph}_2\text{B}(\text{pz})(\text{CH}_2\text{SR})]$, containing one thioether and one pyrazolyl donor, were prepared by Riordan *et al.* [167] using the stepwise, in situ procedure described in Fig. (33).

In particular, addition of equimolar LiCH_2SR (R = CH₃, ^tBu) to Ph_2BBr at -78°C in THF effected the incorporation of one thioether substituent to the borane. The presumed product, $\text{Li}[\text{Ph}_2\text{B}(\text{Br})(\text{CH}_2\text{SR})]$, was not isolated. To the THF solution was introduced 1 equiv of Lipz. The desired species was precipitated by addition of aqueous $[\text{Bu}_4\text{N}]\text{Br}$ [167]. Similar preparative approaches have led to the isolation of the analogous $\text{Tl}[\text{PhB}(\text{pz})(\text{CH}_2\text{SCH}_3)_2]$ borato ligand [168] (Fig. 34).

The lithium (and potassium) scorpionates $\text{M}[\text{PhB}(\text{pz})_2(\text{CH}_2\text{SCH}_3)]$ are accessible through a three-step sequence starting from PhBBr_2 [181] (Fig. 35).

For the synthesis of the heteroditopic scorpionates $\text{M}_2[(\text{pz})_3\text{BC}_6\text{H}_4\text{B}(\text{pz})_2(\text{CH}_2\text{SCH}_3)]$ (M = Li or K), the p-silylated borylbenzene [219, 220] was chosen by Wagner and co-workers [181] as starting material (Fig. 36a). Introduction of the thio-ether substituent by using donor-free LiCH_2SMe gave the silylated species (Fig. 36b) that exists as dimer in solution and in the solid state; this is of critical importance for the entire synthesis concept, because B-S adduct formation protects the thioether groups from BBr_3 attack in the subsequent reaction step, thereby allowing the clean conversion via silicon/boron exchange. Treatment with 6 equiv of

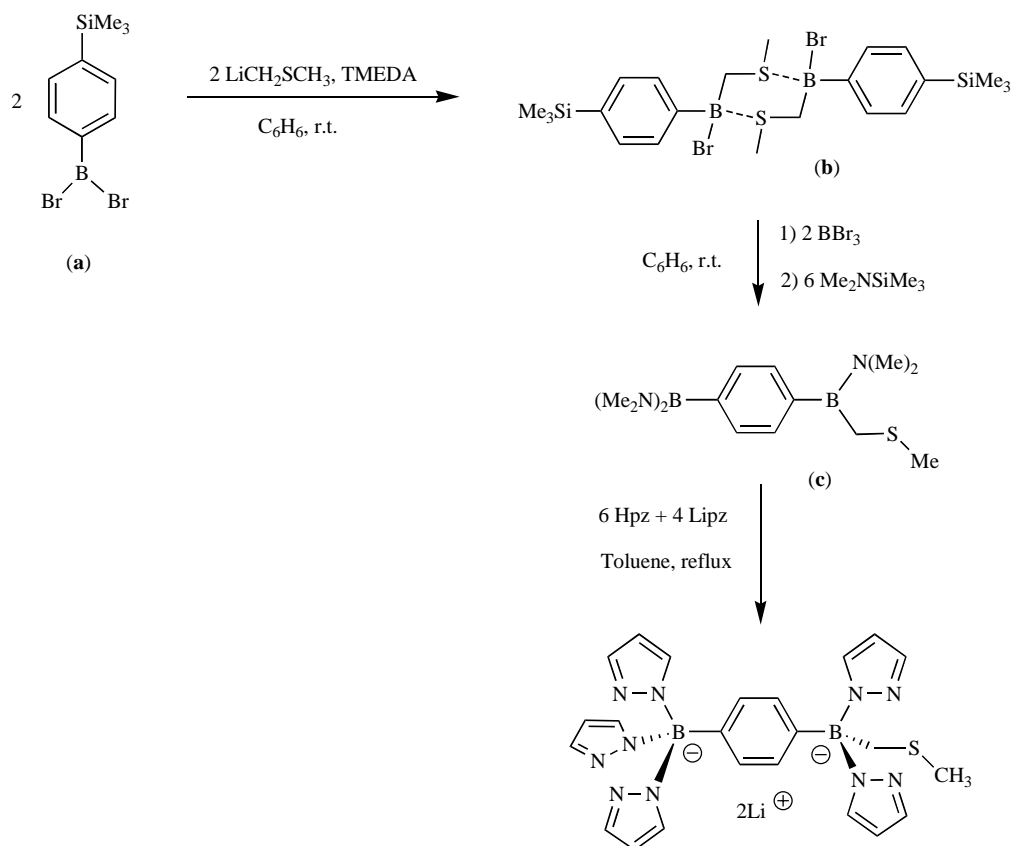


Fig. (36). Synthesis of the heteroditopic scorpionate ligand $\text{Li}_2[(\text{pz})_3\text{BC}_6\text{H}_4\text{B}(\text{pz})_2(\text{CH}_2\text{SCH}_3)]$.

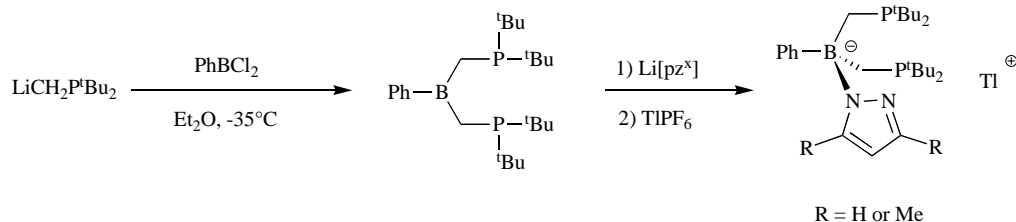


Fig. (37). Synthesis of $[\text{PhB}(\text{CH}_2\text{P}^t\text{Bu}_2)_2(\text{pz}^x)]\text{Li}$ ($\text{Hpz}^x = \text{pyrazole}$ or 3,5-dimethylpyrazole).

$\text{Me}_2\text{NSiMe}_3$ led to the replacement of all bromide substituents by dimethylamino groups and consequently to the break-up of the 1,4-dithionia-2,5-diboratacyclohexane ring. The resulting monomer (Fig. 36c) was transformed into the heteroditopic scorpionates $\text{M}_2[(\text{pz})_3\text{BC}_6\text{H}_4\text{B}(\text{pz})_2(\text{CH}_2\text{SCH}_3)]$ ($\text{M} = \text{Li}$ or K) by reaction with Hpz/Mpz (6:4; $\text{M} = \text{Li}$, K) in toluene at reflux temperature [181].

5.3. Mixed poly(pyrazolyl)(phosphino)borates

The hybrid bis(pyrazolyl)(phosphino)borate ligands (Table 11) are achieved by initial preparation of the bis(phosphino)borane precursor $\text{Li}[\text{PhB}(\text{CH}_2\text{P}^t\text{Bu}_2)_2]$ via metathesis between PhBCl_2 and 2 equiv. of $\text{LiCH}_2\text{P}^t\text{Bu}_2$ (Fig. 37). Reaction of Lipz with $\text{Li}[\text{PhB}(\text{CH}_2\text{P}^t\text{Bu}_2)_2]$ followed immediately by salt metathesis with TlPF_6 , leads to the clean formation of $[\text{PhB}(\text{CH}_2\text{P}^t\text{Bu}_2)_2(\text{pz}^x)]\text{Li}$ ($\text{Hpz}^x = \text{pyrazole}$ or 3,5-dimethylpyrazole) [213].

The use of the bulky $\text{LiCH}_2\text{P}^t\text{Bu}_2$ carbanion is critically important in the preparation of this type of hybrid borate ligands because: (i) effective di- rather than tri-substitution at boron can be achieved, which could not be realized using less hindered carbanions, such as $\text{LiCH}_2\text{P}^i\text{Pr}_2$ and $\text{LiCH}_2\text{PPh}_2$; (ii) the borane product, $\text{PhB}(\text{CH}_2\text{P}^t\text{Bu}_2)_2$, does not appear to dimerize to an appreciable

degree in solution. This fact allows the efficient introduction of a third donor arm [213].

A related bis(pyrazolyl)(phosphino)borate ligand was recently reported by Oro *et al.* [211]. In particular, the reaction of $\text{CH}_2=\text{CH}-\text{CH}_2\text{B}(\text{O}^i\text{Pr})_2$ with 1 equivalent of $[\text{Li}(\text{TMEDA})][\text{CH}_2\text{PPh}_2]$ and 2 equivalents of pyrazole in refluxing toluene gave the lithium salt of the anionic ligand $\text{Li}(\text{TMEDA})[[\text{CH}_2=\text{CHCH}_2\text{B}(\text{CH}_2\text{PPh}_2)(\text{pz})_2]$ (Fig. 38).

This synthetic strategy leads to an allyl bis(pyrazolyl)borate ligand bifunctionalized with a phosphine group that, in addition, can be attached to the periphery of carbosilane dendrimers through the allyl linker to give polyanionic starbursts and, ultimately, neutral metallodendrimers [211].

5.4. Ambidentate poly(azolyl)borates Based on Thioxotriazoles and Mercaptothiadiazoles

Treatment of the heterocycle 3,4-dimethyl-1,2,4-triazole-5-thione with sodium tetrahydroborate at 210°C (Fig. 39) provided the $[\text{N}_3/\text{S}_3]$ ambidentate tripod ligand tris(thioxotriazolyl)borate (Table 12) as its sodium complex salt $\text{Na}[\text{HB}(\text{ttz}^{3\text{Me},4\text{Me}})_3]$ [221].

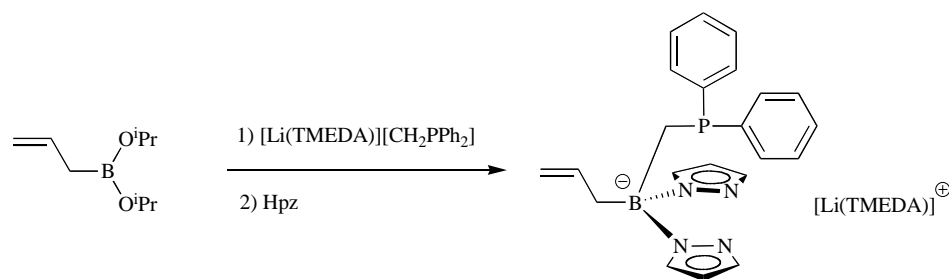


Fig. (38). Synthesis of $[\text{Li}(\text{TMEDA})][\text{CH}_2=\text{CHCH}_2\text{B}(\text{CH}_2\text{PPh}_2)(\text{pz})_2]$.

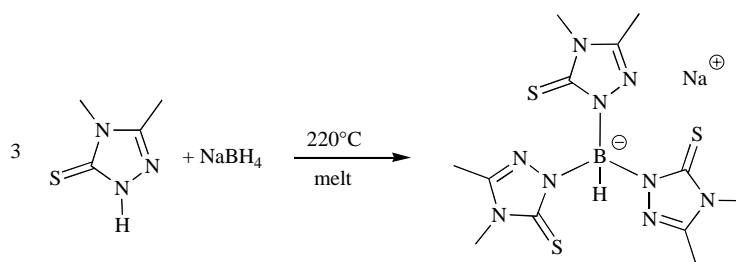


Fig. (39). Synthesis of $[\text{Na}[\text{HB}(\text{ttz}^{3\text{Me},4\text{Me}})_3]]$.

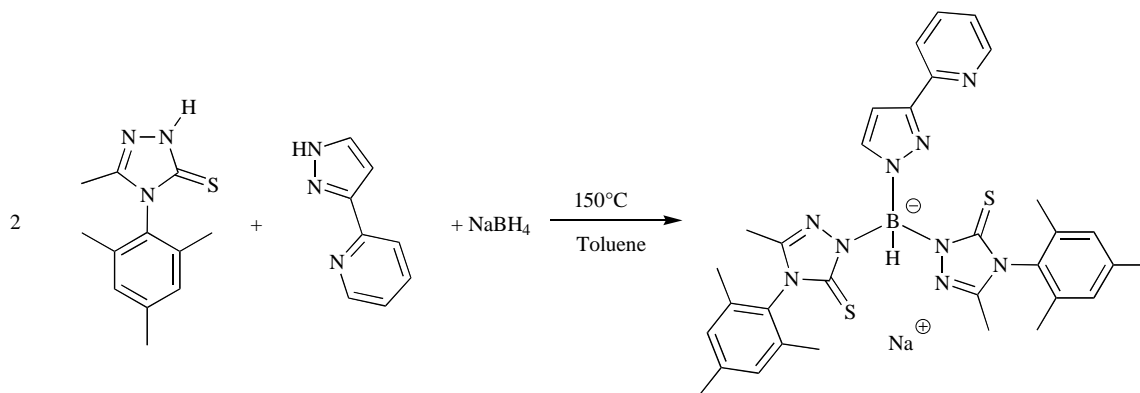


Fig. (40). Synthesis of $[\text{Na}[\text{HB}(\text{ttz}^{3\text{Me},4\text{Me}})_2(\text{pz}^{\text{o-Py}})]]$.

Complexes of this ligand with sodium, bismuth(III), tin(IV), and manganese(I) have been synthesized and characterized by X-ray crystallography. The structures of these complexes illustrate the ambidentate character of the ligand with the softer metals bismuth and tin exhibiting sulfur coordination, while sodium and manganese(I) bond via the ligand nitrogen donors. In the $[\text{S}_3]$ coordination mode the ligand creates eight-membered chelate rings with the metal with the consequence that the metal ligand unit adopts a propeller-type conformation with C_3 -symmetry. However, in the $[\text{N}_3]$ mode six-membered chelate rings are formed analogous to the familiar tris(pyrazolyl)borate (Tp^x) ligands.

The bifunctionalized homoscorpionate ligands (Table 12), tris[4-methyl-3-(pyridin-2-yl)-5-thioxo-1,2,4-triazolyl]borate, $[\text{Li}[\text{HB}(\text{ttz}^{3(\text{o-Py}),4\text{Me}})_3]]$ [222] and tris[4-mesityl-3-methyl-5-thioxo-1,2,4-triazolyl]borate, $[\text{Li}[\text{HB}(\text{ttz}^{3\text{Me},4\text{Mes}})_3]]$, [223] and the heteroscorpionate ligand bis[4-mesityl-3-methyl-5-thioxo-1,2,4-triazolyl][3-(pyridin-2-yl)-pyrazolyl]borate $[\text{K}[\text{HB}(\text{ttz}^{3\text{Me},4\text{Mes}})_2(\text{pz}^{\text{o-Py}})]]$ [223] were synthesized and crystallographically characterized. The synthesis of the tripodal ligands $[\text{Li}[\text{HB}(\text{ttz}^{3(\text{o-Py}),4\text{Me}})_3]]$ and $[\text{Li}[\text{HB}(\text{ttz}^{3\text{Me},4\text{Mes}})_3]]$ were performed at high temperature in toluene by reacting triazoles and LiBH_4 in 3/1 ratio. The method extensively employed to produce tris(pyrazolyl)borates [37, 224], tris(thioimidazolyl)borates [99] and tris(thioxotriazolyl)borate [221], which involves the reaction between borohydrides and heterocycles in the melt, could not be followed here due to the high

and prohibitive melting temperatures of triazoles ($>200^\circ\text{C}$). Different strategies were attempted to synthesize the heteroleptic ligand $[\text{M}[\text{HB}(\text{ttz}^{3\text{Me},4\text{Mes}})_2(\text{pz}^{\text{o-Py}})]]$. In particular, the successful synthesis was obtained by a one-pot reaction [210] between NaBH_4 , 3-(2-pyridyl)pyrazole, and 4-mesityl-3-methyl-5-thioxo-1,2,4-triazole in 1/1/2 ratio (toluene, 150°C) [223] (Fig. 40).

Dinuclear Cu(I) complexes $\{[\text{Cu}[\text{HB}(\text{ttz}^{3\text{Me},4\text{Mes}})_3]]_2\}$, $\{[\text{Cu}[\text{HB}(\text{ttz}^{3(\text{o-Py}),4\text{Me}})_3]]_2\}$ and $\{[\text{Cu}[\text{HB}(\text{ttz}^{3\text{Me},4\text{Mes}})_2(\text{pz}^{\text{o-Py}})]]_2\}$ have been obtained with these bifunctionalized scorpionate ligands [223].

The hybrid ligands tris[2-thioxo-1,3,4-thiadiazol-3-yl]borate (Table 12), $[\text{HB}(\text{mtdz})_3]$, (mtdz = 2-thioxo-1,3,4-thiadiazol-3-yl) [225] and tris[5-methyl-2-thioxo-1,3,4-thiadiazol-3-yl]borate, $[\text{HB}(\text{mtdz}^{5\text{Me}})_3]$ [226] ($\text{mtdz}^{5\text{Me}}$ = 5-methyl-2-thioxo-1,3,4-thiadiazol-3-yl), containing *N*-heterocyclic rings with both hard nitrogen donors and soft sulfur donors, have been prepared by Gardinier *et al.* [225]. These ligands are close relatives of Marchiò and coworkers' poly(thioxotriazolyl)borates [221, 223] and are able to promote the controlled organization of metallochains according to Pearson's hard-soft acid-base theory [227, 228]. Gardinier and coworkers refer to these species and their derivatives as *Janus scorpionates* [225, 226, 229], after the Roman mythological god of gates and doors that is commonly depicted as a two-faced figure [225] (Fig. 41).

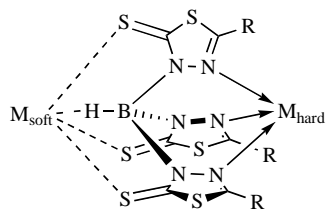


Fig. (41). Potential coordination behavior of Janus scorpionates.

These anionic ligands differ in the presence of methyl groups situated proximal to the nitrogen atoms of the constituent heterocy-

cles that would be available for metal binding. The Janus scorpionates exhibit remarkable diversity in their binding behavior toward main group metals [229]. It was expected that steric interactions involving the methyl groups might change the binding preferences of the ligand to metal cations by decreasing the tendency for MN_6 coordination in sandwich complexes or coordination polymers, possibly promoting lower coordination numbers or making metal-sulfur bonding more favorable.

TABLES 1-11

Structure of ligands and references to their synthesis.

Table 1. Poly(imidazol-1-yl)borates

N.	Abbreviation and References	Structure
1	$K[H_2B(im)_2](DMAC)$ [42]	
2	$Tl[HB(im)_3]$ [41]	
3	R = H: $Li[B(im)_4]$ [40]	
4	R = Me: $Tl[B(im^{4Me})_4]$ [47]	
5	$B(Him)(im)_3$ [48]	
6	$[H_2B(Him^{2Br})_2]Cl$ [52]	
7	R = H, R' = H: $K[H_2B(bzim)_2]$ [49]	
8	R = H, R' = bzim: $K[HB(bzim)_3]$ [230]	
9	R = bzim, R' = bzim: $K[B(bzim)_4]$ [230]	
10	R = H, R' = R'' = H: $[H_2B(im)]_4$ [50]	
11	R = H, R' = Me, R'' = H: $[H_2B(im^{4Me,5Me})]_4$ [50]	
12	R = Me, R' = R'' = H: $[Me_2B(im)]_4$ [50]	
13	R = H, R' = H, R'' = Br: $[H_2B(im^{2Br})]_4$ [52]	

Table 1. contd...

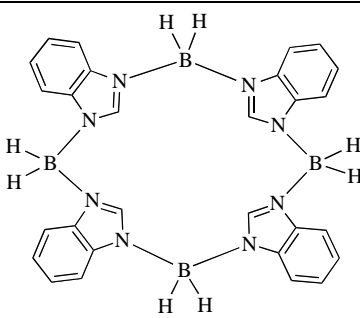
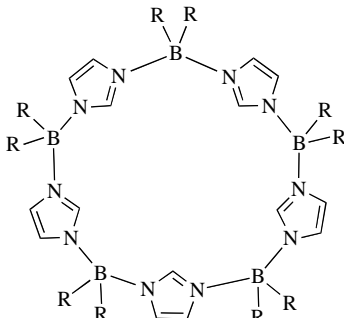
N.	Abbreviation and References	Structure
14	$[\text{H}_2\text{B}(\text{bzim})_4]$ [52]	
15 16	R = H: $[\text{H}_2\text{B}(\text{im})_5]$ [50] R = Me: $[\text{Me}_2\text{B}(\text{im})_5]$ [50]	

Table 2. Poly(imidazol-2-yl)borates

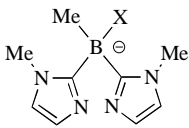
N.	Abbreviation and References	Structure
17	X = O ⁱ Pr: $\text{Li}[\text{Me}(\text{O}^i\text{Pr})\text{B}(\text{imc}^{\text{Me}})_2]$ [53]	
18	X = Cl: $\text{Li}[\text{Me}(\text{Cl})\text{B}(\text{imc}^{\text{Me}})_2]$ [53]	
19	X = Ph: $\text{Li}[\text{Me}(\text{Ph})\text{B}(\text{imc}^{\text{Me}})_2]$ [53]	
20	X = Pz: $\text{Li}[\text{Me}(\text{pz})\text{B}(\text{imc}^{\text{Me}})_2]$ [53]	

Table 3. Poly(oxazol-2-yl)borates

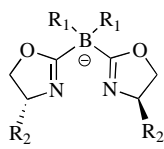
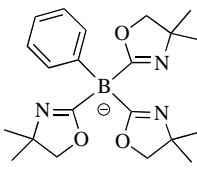
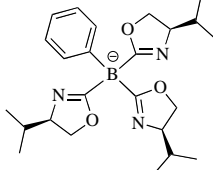
N.	Abbreviation and References	Structure
21	$\text{R}^1 = \text{Ph}, \text{R}^2 = {}^i\text{Pr}$: $\text{Li}[\text{Ph}_2\text{B}(\text{ozc}^{\text{4iPr}})_2]$ [57]	
22	$\text{R}^1 = \text{Ph}, \text{R}^2 = {}^i\text{Bu}$: $\text{Li}[\text{Ph}_2\text{B}(\text{ozc}^{\text{4iBu}})_2]$ [57]	
23	$\text{R}^1 = \text{Cy}, \text{R}^2 = {}^i\text{Pr}$: $\text{Li}[\text{Cy}_2\text{B}(\text{ozc}^{\text{4iPr}})_2]$ [146]	
24	$\text{R}^1 = \text{Et}, \text{R}^2 = {}^i\text{Bu}$: $\text{Li}[\text{Et}_2\text{B}(\text{ozc}^{\text{4iBu}})_2]$ [57]	
25	$\text{R}^1 = \text{Cy}, \text{R}^2 = {}^i\text{Bu}$: $\text{Li}[\text{Cy}_2\text{B}(\text{ozc}^{\text{4iBu}})_2]$ [57]	
26	$\text{R}^1 = \text{Et}, \text{R}^2 = \text{Benzyl}$: $\text{Li}[\text{Et}_2\text{B}(\text{ozc}^{\text{4Bz}})_2]$ [57]	
27	$\text{R}^1 = 3,5\text{-CF}_3\text{-C}_6\text{H}_3, \text{R}^2 = {}^i\text{Bu}$: $\text{Li}[(3,5\text{-CF}_3\text{-C}_6\text{H}_3)_2\text{B}(\text{ozc}^{\text{4iBu}})_2]$ [57]	
28	$\text{R}^1 = 3,5\text{-CF}_3\text{-C}_6\text{H}_3, \text{R}^2 = \text{Benzyl}$: $\text{Li}[(3,5\text{-CF}_3\text{-C}_6\text{H}_3)_2\text{B}(\text{ozc}^{\text{4Bz}})_2]$ [57]	
29	$\text{Li}[\text{PhB}(\text{ozc}^{\text{4Me}_2})_3]$ [55]	
30	$\text{Li}[\text{PhB}(\text{ozc}^{\text{4iPr}})_3]$ [58]	

Table 4. Poly(1,2,4-triazol-1-yl)borates

N.	Abbreviation and References	Structure
31	R = R' = H: K[H ₂ B(tz) ₂] [64]	
32	R = NO ₂ , R' = H: K[H ₂ B(tz ^{3NO2}) ₂] [73]	
33	R = R' = Me: K[H ₂ B(tz ^{3Me,5Me}) ₂] [68]	
34	R = R' = H: K[HB(tz) ₃] [62, 63]	
35	R = R' = Me: K[HB(tz ^{3Me,5Me}) ₃] [69]	
36	R = 'Bu; R' = Me: K[HB(tz ^{3iBu,5Me}) ₃] [70]	
37	R = Ph; R' = Me: K[HB(tz ^{3Ph,5Me}) ₃] [72]	
38	R = NO ₂ , R' = H: Na[HB(tz ^{3NO2}) ₃] [231]	
39	R = R' = CF ₃ : Na[HB(tz ^{3CF3,5CF3}) ₃] [76]	

Table 5. Poly(azol-1-yl)borates (Azole = 1,2,3-benzotriazole, tetrazole, 7-azaindole)

N.	Abbreviation and References	Structure
40	K[H ₂ B(btz) ₂] [85]	
41	K[HB(btz) ₃] [85]	
42	K[H ₂ B(tet) ₂] [93]	
43	K[HB(7-azn) ₃] [96]	

Table 6. Poly(thioimidazolyl)borates

N.	Abbreviation and References	Structure
44	R = Me: Na[H ₃ B(tim ^{Me}) ₂] [113]	
45	R = Bupip: Na[H ₃ B(tim ^{Bupip}) ₂] [113]	
46	R = Me: Li[H ₂ B(tim ^{Me}) ₂] [114]	
47	R = Mesityl: Li[H ₂ B(tim ^{Mes}) ₂] [114, 115]	
48	R = Benzyl: Na[H ₂ B(tim ^{Bz}) ₂] [116]	
49	R = ^t Bu: Na[H ₂ B(tim ^{tBu}) ₂] [116]	
50	R = p-Tolyl: Na[H ₂ B(tim ^{p-Tol}) ₂] [116]	
51	R = pip: Na[H ₂ B(tim ^{Me,4pip}) ₂] [117]	
52	R = CH ₂ -pip: Na[H ₂ B(tim ^{Me,4(CH2)2pip}) ₂] [117]	
53	R = Me: Na[HB(tim ^{Me}) ₃] [98, 99]	
54	R = Me: K[HB(tim ^{Me}) ₃] [101]	
55	R = Et: Na[HB(tim ^{Et}) ₃] [108]	
56	R = Benzyl: Na[HB(tim ^{Bz}) ₃] [108, 111]	
57	R = ^t Bu: K[HB(tim ^{tBu}) ₃] [109]	
58	R = ^t Bu: Tl[HB(tim ^{tBu}) ₃] [140]	
59	R = Cy: K[HB(tim ^{Cy}) ₃] [110]	
60	R = Ph: Li[HB(tim ^{Ph}) ₃] [100]	
61	R = o-Tolyl: K[HB(tim ^{o-Tol}) ₃] [110]	
62	R = p-Tolyl: Li[HB(tim ^{p-Tol}) ₃] [232]	
63	R = p-Tolyl: Na[HB(tim ^{p-Tol}) ₃] [111]	
64	R = 2,6- ⁱ Pr ₂ C ₆ H ₃ : Li[HB(tim ^{2,6-iPr2C6H3}) ₃] [112]	
65	R = 2-Biphenyl: K[HB(tim ^{2-Bipb}) ₃] [110]	
66	R = 2,6-Xylyl: K[HB(tim ^{2,6-Xyl}) ₃] [110]	
67	R = Mesityl: K[HB(tim ^{Mes}) ₃] [109]	
68	R = Cumenyl: K[HB(tim ^{Cum}) ₃] [109]	
69	R = Me: Li[(CH ₃)HB(tim ^{Me}) ₂] [119]	
70	R = Ph: Li[(Ph)HB(tim ^{Me}) ₂] [121]	
71	R = Benzyl: Na[(Bz)HB(tim ^{Me}) ₂] [122]	
72	R = Me: Li[(Me)B(tim ^{Me}) ₃] [124]	
73	R = Ph: Li[(MeOH) ₄ (Ph)B(tim ^{Me}) ₃] [124, 125]	
74	[H ₂ C(tim ^{Me}) ₂ BH ₂]Cl [127]	
75	[H ₂ C(tim ^{Me}) ₂ BH(tim ^{Me})]Cl [127]	

Table 6. contd...

N.	Abbreviation and References	Structure
76	$[\text{H}_2\text{C}(\text{tim}^{\text{Me}})_2\text{BBN}]\text{Cl}$ [127]	
77	$(\text{Me}_2\text{NCHO})\text{B}(\text{tim}^{\text{Me}})_3$ [128]	
78	$\text{Na}[(\text{Ph})\text{HB}(\text{tim}^{\text{Me}})(\text{tim}^{\text{Me},4\text{pip}})]$ [117]	
79	$\text{Na}[(\text{Ph})\text{HB}(\text{tim}^{\text{Me}})(\text{tim}^{\text{Me},4(\text{CH}_2\text{-pip})})]$ [117]	

Table 7. Se-donor Ligands

N.	Abbreviation and References	Structure
80	R = Mesityl: $\text{K}[\text{HB}(\text{Seim}^{\text{Me}})_3]$ [160]	
81	R = Me: $\text{Na}[\text{HB}(\text{Seim}^{\text{Me}})_3]$ [163]	
82	$\text{K}[\text{H}_2\text{B}(\text{Seim}^{\text{Me}})_2]$ [163]	

Table 8. Poly(thioalkyl)borates

N.	Abbreviation and References	Structure
83	R = CH_3SCH_2 : $\text{Bu}_4\text{N}[\text{B}(\text{CH}_2\text{SCH}_3)_4]$ [132]	
84	R = Ferrocenyl: $\text{Bu}_4\text{N}[\text{FcB}(\text{CH}_2\text{SCH}_3)_3]$ [133]	

Table 8. contd...

N.	Abbreviation and References	Structure
85	R = Ph: $\text{Bu}_4\text{N}[\text{PhB}(\text{CH}_2\text{SPh})_3]$ [165]	
86	R = Me: $\text{Bu}_4\text{N}[\text{PhB}(\text{CH}_2\text{SCH}_3)_3]$ [165]	
87	R = ^t Bu: $\text{Bu}_4\text{N}[\text{PhB}(\text{CH}_2\text{S}^t\text{Bu})_3]$ [151]	
88	R = p-Tolyl: $\text{Bu}_4\text{N}[\text{PhB}(\text{CH}_2\text{S}^p\text{Tol})_3]$ [135]	
89	R = Adamantly: $\text{Ti}[\text{PhB}(\text{CH}_2\text{SAd})_3]$ [152]	
90	R = Me: $\text{Bu}_4\text{N}[\text{Ph}_2\text{B}(\text{CH}_2\text{SCH}_3)_2]$ [167]	
91	R = ^t Bu: $\text{Cs}[\text{Ph}_2\text{B}(\text{CH}_2\text{S}^t\text{Bu})_2]$ [167]	
92	$\text{Bu}_4\text{N}[\text{Et}_2\text{B}(\text{CH}_2\text{SCH}_3)_2]$ [135]	
93	$\text{K}[\text{B}(\text{thi})_4]$ [182, 183]	
94	$[(\text{N}^i\text{Pr}_2)\text{B}(\text{thi})_4]$ [184]	
95	BODIPY-2T [188]	
96	BODIPY-3T [188]	

Table 9. Poly(phosphinomethyl)borates

N.	Abbreviation and References	Structure
97	R = Ph: $\text{Li}(\text{TMEDA})[\text{PhB}(\text{CH}_2\text{PPh}_2)_3]$ [129]	
98	R = ⁱ Pr: $\text{Li}(\text{TMEDA})[\text{PhB}(\text{CH}_2\text{P}^i\text{Pr}_2)_3]$ [131]	
99	R = ^t Pr: $\text{Ti}[\text{PhB}(\text{CH}_2\text{P}^t\text{Pr}_2)_3]$ [131]	
100	R = Ph: $\text{Li}(\text{TMEDA})[(^t\text{Bu})\text{B}(\text{CH}_2\text{PPh}_2)_3]$ [194]	
101	R = ⁱ Pr: $\text{Li}(\text{TMEDA})[(^t\text{Bu})\text{B}(\text{CH}_2\text{P}^i\text{Pr}_2)_3]$ [194]	

Table 9. contd...

N.	Abbreviation and References	Structure
102 103	(ASN)[Ph ₂ B(CH ₂ PPh ₂) ₂] [205] Li[Ph ₂ B(CH ₂ PPh ₂) ₂] [204]	
104 105 106 107	R = p-CF ₃ Ph: Li[Ph ₂ B(CH ₂ P(p-CF ₃ Ph) ₂) ₂] [204] R = p ⁻ BuPh: Li[Ph ₂ B(CH ₂ P(p ⁻ BuPh) ₂) ₂] [204] R = ⁱ Pr: Li[Ph ₂ B(CH ₂ P ⁱ Pr ₂) ₂] [204] R = ^t Bu: Li[Ph ₂ B(CH ₂ P ^t Bu ₂) ₂] [204]	
108 109 110 111 112	R = Cy: Li[Cy ₂ B(CH ₂ PPh ₂) ₂] [204] R = p-Tolyl: Li[(p-Tol) ₂ B(CH ₂ PPh ₂) ₂] [204] R = p-MeOPh: Li[(p-MeOPh) ₂ B(CH ₂ PPh ₂) ₂] [204] R = p-CF ₃ Ph: Li[(p-CF ₃ Ph) ₂ B(CH ₂ PPh ₂) ₂] [204] R = p ⁻ BuPh: Li[(p ⁻ BuPh) ₂ B(CH ₂ PPh ₂) ₂] [204]	
113	Li[(p-MeOPh) ₂ B(CH ₂ P(p ⁻ BuPh) ₂) ₂] [204]	
114	Li[(3,5-Me ₂ Ph) ₂ B(CH ₂ P ^t Bu ₂) ₂] [204]	

Table 10. Mixed poly(pyrazolyl)(thioimidazolyl)borates

N.	Abbreviation and References	Structure
115	Li[HB(pz)(tim ^{Me}) ₂] [114]	
116 117 118 119 120 121 122 123 124	R = 2,6-dimethylphenyl: K[HB(pz ^{Ph,Me})(tim ^{2,6-Me2Ph}) ₂] [233] R = Me: K[HB(pz ^{Ph,Me})(tim ^{Me}) ₂] [210] R = Ph: K[HB(pz ^{Ph,Me})(tim ^{Ph}) ₂] [210] R = o-Tolyl: K[HB(pz ^{Ph,Me})(tim ^{o-Tol}) ₂] [210] R = p-Tolyl: K[HB(pz ^{Ph,Me})(tim ^{p-Tol}) ₂] [210] R = 2,4-(CH ₃) ₂ C ₆ H ₃ : K[HB(pz ^{Ph,Me})(tim ^{2,4-(CH3)2C6H3}) ₂] [210] R = 4-(ⁱ Pr)C ₆ H ₄ : K[HB(pz ^{Ph,Me})(tim ^{4-(iPr)C6H4}) ₂] [210] R = 4-(OMe)C ₆ H ₄ : K[HB(pz ^{Ph,Me})(tim ^{4-(OMe)C6H4}) ₂] [210] R = 2-(OMe)C ₆ H ₄ : K[HB(pz ^{Ph,Me})(tim ^{2-(OMe)C6H4}) ₂] [210]	

Table 10. contd...

N.	Abbreviation and References	Structure
125	$K[HB(pz^{iBu,Me})(tim^{iBu})_2]$ [210]	
126	R = ⁱ Pr: $K[HB(pz)_2(tim^{iPr})]$ [206]	
127	R = ^t Bu: $K[HB(pz)_2(tim^{tBu})]$ [206]	

Table 11. Mixed poly(pyrazolyl)(thioalkyl)- and poly(pyrazolyl)(phosphino)-borates

N.	Abbreviation and References	Structure
128	R = Me: $Bu_4N[Ph_2B(pz)(CH_2SCH_3)]$ [167]	
129	R = ^t Bu: $Bu_4N[Ph_2B(pz)(CH_2S^tBu)]$ [167]	
130	$Bu_4N[PhB(pz)(CH_2SCH_3)_2]$ [168]	
131	$Li[PhB(pz)_2(CH_2SCH_3)]$ [181]	
132	$K[PhB(pz)_2(CH_2SCH_3)]$ [181]	
133	$Li_2[(pz)_3BC_6H_4B(pz)_2(CH_2SCH_3)]$ [181]	
134	R = H: $Tl[PhB(CH_2P^tBu_2)(pz)]$ [213]	
135	R = Me: $Tl[PhB(CH_2P^tBu_2)(pz^{Me_2})]$ [213]	
136	$Li(TMEDA)[CH_2=CHCH_2B(CH_2PPh_2)(pz)_2]$ [211]	

Table 12. Ambidentate poly(azolyl)borates

N.	Abbreviation and References	Structure
137 138	R = Me: Na[HB(ttz ^{3Me,4Me}) ₃] [221] R = Mesithyl: Li[HB(ttz ^{3Me,4Mes}) ₃] [223]	
139	Li[HB(ttz ^{3(o-Py),4Me}) ₃] [222, 223]	
140	K[HB(ttz ^{3Me,4Mes}) ₂ (pz ^{o-Py})] [223]	
141 142 143 144 145 146	R = H: Na[HB(mtdz) ₃] [225] R = H: K[HB(mtdz) ₃] [225] R = H: Bu ₄ N[HB(mtdz) ₃] [225] R = Me: Na[HB(mtdz ^{5Me}) ₃] [226] R = Me: K[HB(mtdz ^{5Me}) ₃] [226] R = Me: Bu ₄ N[HB(mtdz ^{5Me}) ₃] [226]	

ACKNOWLEDGMENTS

This work was financially supported by Ministero dell'Istruzione dell'Università e della Ricerca (PRIN 20078EWK9B). We are grateful to CIRCMSB (Consorzio Interuniversitario di Ricerca in Chimica dei Metalli nei Sistemi Biologici).

ABBREVIATIONS

3-carboxy-PROXYL	=	3-carboxy-2,2,5,5-tetramethylpyrrolidinyloxy
4-carboxy-TEMPO	=	4-carboxy-2,2,6,6-tetramethylpiperidinyloxy
7-azn	=	7-azaindol-1-yl
Ad	=	Adamantyl
ASN	=	5-azonia-spiro[4.4]nonane
BBN	=	9-borabicyclononyl

Biph	=	Biphenyl
BNCT	=	Boron neutron capture therapy
BODIPY	=	Boron-dipyrrin
Bz	=	Benzyl
bzim	=	Benzoimidazol-1-yl
bztz	=	1,2,3-benzotriazol-1-yl
Cum	=	Cumenyl
Fc	=	Ferrocenyl
Htim ^{Bupip}	=	1-(4-(4-(2-methoxyphenyl)piperazin-1-yl)butyl)-1H-imidazole-2(3H)-thione
Htim ^{Me,4(CH₂-pip)}	=	5-((4-(2-methoxyphenyl)piperazin-1-yl)methyl)-1-methyl-1H-imidazole-2(3H)-thione

Hüm ^{Me,4pip}	=	(4-(2-methoxyphenyl)piperazin-1-yl)(3-methyl-2-thioxo-2,3-dihydro-1H-imidazol-4-yl)methanone
im	=	Imidazol-1-yl
imc	=	Imidazol-2-yl
Mes	=	Mesityl
methimazole	=	1-methyl-1H-imidazole-2(3H)-thione)
Mtd	=	Mercaptothiadiazolyl
mtdz	=	2-thioxo-1,3,4-thiadiazol-3-yl
ozc	=	Oxazol-2-yl
pip	=	Piperazin-1-yl
pz	=	Pyrazol-1-yl
Seim	=	Selenoimidazol-1-yl
tet	=	Tetrazol-1-yl
thi	=	2-thienyl
tim	=	Thioimidazol-1-yl
TMEDA	=	Tetraethylmethylenediamine
TMP	=	2,2,6,6-tetramethylpiperidine
Tt	=	Thioxotriazolyl
ttz	=	5-thioxo-1,2,4-triazol-1-yl
tz	=	1,2,4-triazol-1-yl
Xyl	=	Xylyl

REFERENCES

- Trofimenko, S. *Scorpionates: The Coordination Chemistry of Poly(pyrazolyl)borate Ligands*. Imperial College Press: London, **1999**.
- Edelmann, F.T. Versatile scorpionate-new developments in the coordination chemistry of pyrazolylborate ligands. *Angew. Chem. Int. Ed. Engl.*, **2001**, *40*, 1656-1660.
- Ferrence, G.M.; Takats, J. [(Tp^{Bu,Me})Yb(u-H)]₂: a fecund precursor to a host of divalent, hydrotris(pyrazolyl)borate supported f-element complexes. *J. Organomet. Chem.*, **2002**, *647*, 84-93.
- Pettinari, C.; Santini, C. Polypyrazolylborate and scorpionate ligands. In *Compr. Coord. Chem. II*, McCleverty, J.A.; Meyer, T.J., Eds. Fundamentals: Ligands, Complexes, Synthesis, Purification, and Structure. Elsevier Pergamon, **2004**; Vol. 1, pp. 159-210.
- Keane, J.M.; Harman, W.D. A New Generation of π -Basic Dearomatization Agents. *Organometallics*, **2005**, *24*, 1786-1798.
- Sessler, J.L.; Melfi, P.J.; Pantos, G.D. Uranium complexes of multidentate N-donor ligands. *Coord. Chem. Rev.*, **2006**, *250*, 816-843.
- Dias, H.V.R.; Fianchini, M. Fluorinated Tris(Pyrazolyl)Borates and Silver(I) complexes of group 14 ligands. *Comments Inorg. Chem.*, **2007**, *28*, 73-92.
- Frohnäpfel, D.S.; Templeton, J.L. Transition metal η^2 -vinyl complexes. *Coord. Chem. Rev.*, **2000**, *206-207*, 199-235.
- Sadimenko, A.P. Organometallic complexes of pyrazolylborates and related ligands. *Adv. Heterocycl. Chem.*, **2001**, *81*, 167-252.
- Carmona, E.; Paneque, M.; Poveda, M.L. Generation and reactivity of sterically hindered iridium carbenes. Competitive α - vs. β -hydrogen elimination in iridium(III) alkyls. *Dalton Trans.*, **2003**, 4022-4029.
- Akita, M. Coordinatively unsaturated organometallic system based on Tp ligand: tetrahedral Tp^RM-R' and Tp^RM-M'Ln species. *J. Organomet. Chem.*, **2004**, *689*, 4540-4551.
- Slugovc, C.; Schmid, R.; Kirchner, K. Hydridotris(pyrazolyl)borate ruthenium complexes-properties and applications. *Coord. Chem. Rev.*, **1999**, *185-186*, 109-126.
- Slugovc, C.; Padilla-Martinez, I.; Sirol, S.; Carmona, E. Rhodium- and iridium-trispyrazolylborate complexes C-H activation and coordination chemistry. *Coord. Chem. Rev.*, **2001**, *213*, 129-157.
- Diaz-Requejo, M.M.; Perez, P.J. Copper, silver and gold-based catalysts for carbene addition or insertion reactions. *J. Organomet. Chem.*, **2005**, *690*, 5441-5450.
- Dias, H.V.R.; Lovely, C.J. Carbonyl and Olefin adducts of coinage metals supported by Poly(pyrazolyl)borate and Poly(pyrazolyl)alkane ligands and silver mediated atom transfer reactions. *Chem. Rev.*, **2008**, *108*, 3223-3238.
- Hikichi, S.; Akita, M.; Moro-oka, Y. New aspects of the cobalt-dioxygen complex chemistry opened by hydrotris(pyrazolyl)borate ligands (Tp^R): unique properties of Tp^RCo-dioxygen complexes. *Coord. Chem. Rev.*, **2000**, *198*, 61-87.
- Parkin, G. Probing of proteins by metal ions and their low-molecular-weight complexes. In *Metal Ions in Biological Systems*, Sigel, A.; Sigel, H., Eds. Marcel Dekker, Inc.: New York, **2001**; Vol. 38, pp. 411-460.
- Akita, M.; Hikichi, S. Inorganic chemistry based on Tp ligands - From Dioxygen complexes to organometallic systems. *Bull. Chem. Soc. Jpn.*, **2002**, *75*, 1657-1679.
- Wasser, I.M.; de Vries, S.; Moenne-Loccoz, P.; Schroder, I.; Karlin, K.D. Nitric Oxide in biological denitrification: Fe/Cu metalloenzyme and metal complex NOx redox chemistry. *Chem. Rev.*, **2002**, *102*, 1201-1234.
- Mirica, L.M.; Ottenwaelder, X.; Stack, T.D.P. Structure and spectroscopy of copper-dioxygen complexes. *Chem. Rev.*, **2004**, *104*, 1013-1046.
- Tolman, W.B. Using synthetic chemistry to understand copper protein active sites: a personal perspective. *J. Biol. Inorg. Chem.*, **2006**, *11*, 261-271.
- Caldwell, L.M. Alkylidyne Complexes Ligated by Poly(pyrazolyl)borates. In *Adv. Organomet. Chem.*, West, R.; Hill, A.F.; Fink, M.J., Eds. Elsevier Inc. USA: **2008**; Vol. 56, pp. 1-94.
- Lail, M.; Pittard, K.A.; Gunnoe, T.B. Chemistry surrounding group 7 complexes that possess poly(pyrazolyl)borate ligands. In *Adv. Organomet. Chem.*, West, R.; Hill, A.F.; Fink, M.J., Eds. Elsevier Inc. USA: **2008**; Vol. 56, pp. 95-153.
- Becker, E.; Pavlik, S.; Kirchner, K., The Organometallic Chemistry of Group 8 Tris(pyrazolyl)borate Complexes. In *Adv. Organomet. Chem.*, West, R.; Hill, A.F.; Fink, M.J., Eds. Elsevier Inc. USA: **2008**; Vol. 56, pp. 155-197.
- Crossley, I.R. The organometallic chemistry of group 9 Poly(pyrazolyl)borate complexes. In *Adv. Organomet. Chem.*, West, R.; Hill, A.F.; Fink, M.J., Eds. Elsevier Inc.: **2008**; Vol. 56, pp. 199-321.
- Vahrenkamp, H. Transitions, transition states, transition state analogs: zinc pyrazolylborate chemistry related to zinc enzymes. *Acc. Chem. Res.*, **1999**, *32*, 589-596.
- Parkin, G. The bioinorganic chemistry of zinc: synthetic analogues of zinc enzymes that feature tripodal ligands. *Chem. Commun.*, **2000**, 1971-1985.
- Parkin, G. Synthetic analogues relevant to the structure and function of zinc enzymes. *Chem. Rev.*, **2004**, *104*, 699-767.
- Santini, C.; Pellei, M. Applications of scorpionate ligands in enzyme modeling and biological studies. *Curr. Bioact. Compd.*, **2009**, In press.
- Gennari, M.; Marchiò, L. Cu-complexes with scorpionate ligands as models for the binding sites of copper proteins. *Curr. Bioact. Compd.*, **2009**, *5*, 243-263.
- Reglinski, J.; Spicer, M.D. The bioinorganic chemistry of methimazole based soft scorpionates. *Curr. Bioact. Compd.*, **2009**, *5*, 264-276.
- Fischer, N.V.; Türkoglu, G.; Burzlaff, N. Scorpionate complexes suitable for enzyme inhibitor studies. *Curr. Bioact. Compd.*, **2009**, *5*, 271-295.
- Tyagi, P.; Singh, U.P. Manganese pyrazolylborate complexes as model for Mn-containing metalloproteins. *Curr. Bioact. Compd.*, **2009**, *5*, 296-320.
- Pellei, M.; Papini, G.; Gioia Lobbia, G.; Santini, C. Chemistry and relevant biomimetic applications of group 6 metals systems supported by scorpionates. *Curr. Bioact. Compd.*, **2009**, *5*, 321-352.
- Curtis, M.D.; Shiu, K.B.; Butler, W.M. Sterically induced η^2 -acyl formation: syntheses and structures of TpMo(CO)₂(η^2 -COR) (R = Me, Ph) and TpMo(CO)₃Br (Tp = hydridotrispyrazolylborate). *Organometallics*, **1983**, *2*, 1475-1477.
- Curtis, M.D.; Shiu, K.B.; Butler, W.M. Synthetic, structural, and theoretical studies of η^2 -acyl complexes of molybdenum. *J. Am. Chem. Soc.*, **1986**, *108*, 1550-1561.
- Trofimenko, S. Recent advances in poly(pyrazolyl)borate (scorpionate) chemistry. *Chem. Rev.*, **1993**, *93*, 943-980.
- Zaidi, S.A.A.; Khan, T.A.; Siddiqi, Z.A. The synthesis and ligand properties of the dihydrobis(imidazolyl)borate anion. *Synth. React. Inorg. Met.-Org. Chem.*, **1984**, *14*, 717-729.
- Zaidi, S.A.A.; Khan, T.A.; Zaidi, S.R.A.; Siddiqi, Z.A. Transition metal complexes of hydrotris(imidazolyl)borate anion. *Polyhedron*, **1985**, *4*, 1163-1166.
- Knop, O.; Bakshi, P.K. Crystal chemistry of tetradial species. Part 7. Lithium tetrakis(1-imidazolyl)borate solvate, Li^{IV}[Li^{IV}(H₂O)(MeOH)] [B(C₂H₃N₂)₄]₂MeOH, a 3-dimensional polymer; with observations on the geometry of imidazole rings. *Can. J. Chem.*, **1995**, *73*, 151-160.
- Janiak, C.; Temizdemir, S.; Rohr, C. The structure of hydrotris(imidazolyl)boratothallium(I). The first structurally authenticated tris(imidazolyl)borate metal complex. *Z. Anorg. Allg. Chem.*, **2000**, *626*, 1265-1267.
- Effendy; Gioia Lobbia, G.; Pellei, M.; Pettinari, C.; Santini, C.; Skelton, B.W.; White, A.H. Bridged poly(1-imidazolyl)borate silver(I) complexes containing tertiary mono(phosphine) ligands. The first structurally authenticated bis(imidazolyl)borate metal complex. *J. Chem. Soc., Dalton Trans.*, **2001**, 528-534.
- Hamilton, B.H.; Kelly, K.A.; Wagler, T.A.; Espe, M.P.; Ziegler, C.J. Construction of a functional layered solid using the Tetrakis(imidazolyl)borate coordinating anion. *Inorg. Chem.*, **2002**, *41*, 4984-4986.
- Hamilton, B.H.; Kelly, K.A.; Wagler, T.A.; Espe, M.P.; Ziegler, C.J. Lead Tetrakis(imidazolyl)borate solids: anion exchange, solvent intercalation, and self assembly of an organic anion. *Inorg. Chem.*, **2004**, *43*, 50-56.
- Hamilton, B.H.; Cardon, T.B.; Lorigan, G.A.; Ziegler, C.J. The assembly of organic radical anions between metal-borate scaffolds. *Dalton Trans.*, **2005**,

- 2941-2944.
- [46] Cetin, A.; Ortiz-Colon, S.; Espe, M.P.; Ziegler, C.J. Investigating the topological polymerization of aniline derivatives in Pb(II) borate scaffolds. *Dalton Trans.*, **2008**, 64-70.
- [47] Hamilton, B.H.; Ziegler, C.J. Lead and thallium Tetrakis(imidazolyl)borates: modifying structure by varying metal and anion. *Inorg. Chem.*, **2004**, *43*, 4272-4277.
- [48] Hamilton, B.H.; Kelly, K.A.; Malasi, W.; Ziegler, C.J. Tetrakis(imidazolyl)borate-based coordination polymers: group II network Solids, $M[B(Im)_4]_2(H_2O)_2$ (M = Mg, Ca, Sr). *Inorg. Chem.*, **2003**, *42*, 3067-3073.
- [49] Khan, T.A.; Khan, M.A.; Haq, M.M. Polymeric metal dihydrido-bis(benzimidazolyl)borates. Synthesis and spectral properties of some lanthanide chelates of dihydridobis(benzimidazolyl)borate. *Synth. React. Inorg. Met.-Org. Chem.*, **1996**, *26*, 1467-1476.
- [50] Weiss, A.; Pritzkow, H.; Siebert, W. Macrocyclic imidazolylboranes. *Angew. Chem., Int. Ed.*, **2000**, *39*, 547-549.
- [51] Kirk, K.L. Facile synthesis of 2-substituted imidazoles. *J. Org. Chem.*, **1978**, *43*, 4381-4383.
- [52] Weiss, A.; Barba, V.; Pritzkow, H.; Siebert, W. Synthesis, structures and reactivity of macrocyclic imidazolylboranes. *J. Organomet. Chem.*, **2003**, *680*, 294-300.
- [53] Fujita, K.; Hikichi, S.; Akita, M.; Moro-oka, Y. Synthesis and structural characterization of a new class of organoborate ligands containing imidazolyl functional groups $[MeB(ImN-Me)_2(X)]$. *J. Chem. Soc., Dalton Trans.*, **2000**, 1255-1260.
- [54] Bianchini, C.; Meli, A.; Laschi, F.; Vizza, F.; Zanello, P. Novel reactions of the $[BPh_4]^-$ salt of the bifunctional complex $[(triphos)Rh(S_2CO)]^+$ (triphos = $MeC(CH_2PPh_2)_3$): one-electron reduction, cleavage of B-H and B-C bonds, and metathesis of CS_2 -like heteroallene molecules. *Inorg. Chem.*, **1989**, *28*, 227-233.
- [55] Dunne, J.F.; Su, J.; Ellern, A.; Sadov, A.D. A new scorpionate ligand: Tris(4,4-dimethyl-2-oxazolonyl)borate and its Zirconium(IV) complexes. *Organometallics*, **2008**, *27*, 2399-2401.
- [56] Meyers, A.I.; Novachek, K.A. Pd-mediated cross-coupling of aryl, alkenyl, and alkynyl stannanes with chiral 2-bromooxazolines. *Tetrahedron Lett.*, **1996**, *37*, 1747-1748.
- [57] Mazet, C.; Kohler, V.; Pfaltz, A. Chiral boron-bridged bisoxazolines: Readily available anionic ligands for asymmetric catalysis. *Angew. Chem., Int. Ed.*, **2005**, *44*, 4888-4891.
- [58] Baird, B.; Pawlikowski, A.V.; Su, J.; Wiench, J.W.; Pruski, M.; Sadov, A.D. Easily prepared chiral scorpionates: Tris(2-oxazolonyl)boratoiridium(I) compounds and their interactions with MeOTf. *Inorg. Chem.*, **2008**, *47*, 10208-10210.
- [59] Pfaltz, A. Chiral semicorrins and related nitrogen heterocycles as ligands in asymmetric catalysis. *Acc. Chem. Res.*, **1993**, *26*, 339-345.
- [60] McManus, H.A.; Guiry, P.J. Recent developments in the application of oxazoline-containing ligands in asymmetric catalysis. *Chem. Rev.*, **2004**, *104*, 4151-4202.
- [61] Desimoni, G.; Faita, G.; Jorgensen, K.A. C_2 -Symmetric chiral bis(oxazoline) ligands in asymmetric catalysis. *Chem. Rev.*, **2006**, *106*, 3561-3651.
- [62] Trofimenko, S. Boron-pyrazole chemistry. II. Poly(1-pyrazolyl)-borates. *J. Am. Chem. Soc.*, **1967**, *89*, 3170-3177.
- [63] Gioia Lobbia, G.; Bonati, F.; Cecchi, P. A preparation of potassium tris(1,2,4-triazol-1-yl)hydroborate and of some metal derivatives. *Synth. React. Inorg. Met.-Org. Chem.*, **1991**, *21*, 1141-1151.
- [64] Janiak, C.; Scharmann, T.G.; Hemling, H.; Lentz, D.; Pickardt, J. Transition-metal complexes with the novel poly(1,2,4-triazolyl)borate ligands $[H_nB(C_2H_2N_3)_{4-n}]$ (n = 1 and 2): synthesis and characterization of metal complexes of dihydrobis(1,2,4-triazolyl)borate as one- or two-dimensional coordination polymers with six-membered ring water substructures and the structure of two-dimensional liquid and solid water as organized in the intercalate $[Ni\{HB(C_2H_2N_3)_2\}_2]_2 \cdot 6H_2O$ (x-ray studies at 293 and 160 K). *Chem. Ber.*, **1995**, *128*, 235-244.
- [65] Janiak, C.; Scharmann, T.G.; Albrecht, P.; Marlow, F.; Macdonald, R. [Hydrotris(1,2,4-triazolyl)borato]silver(I): Structure and optical properties of a coordination polymer constructed from a modified Poly(pyrazolyl)borate ligand. *J. Am. Chem. Soc.*, **1996**, *118*, 6307-6308.
- [66] Janiak, C.; Scharmann, T.G.; Guenther, W.; Hinrichs, W.; Lentz, D. Copper coordination polymers with infinite chloride ion channels and different directions of the Jahn-Teller distortion built from tris(1,2,4-triazolyl)borate as a modified tris(pyrazolyl)borate ligand. *Chem. Ber.*, **1996**, *129*, 991-995.
- [67] Youm, K.-T.; Kim, M.G.; Ko, J.; Jun, M.-J. A noninterpenetrating three-dimensional 4669 iron(II) coordination polymer built with a trigonal-antiprismatic iron(III) metallo-ligand. *Angew. Chem., Int. Ed.*, **2006**, *45*, 4003-4007.
- [68] Shen, W.-Z.; Kang, F.; Sun, Y.-J.; Cheng, P.; Yan, S.-P.; Liao, D.-Z.; Jiang, Z.-H. The synthesis and crystal structure of $[M\{H_2B(tz^*)_2\}_2(H_2O)]$ (M = Cu, Zn and $tz^* = 3,5$ -dimethyl-1,2,4-triazole). *Inorg. Chem. Commun.*, **2003**, *6*, 408-411.
- [69] Xiao, Z.; Gable, R.W.; Wedd, A.G.; Young, C.G. The cis-dioxomolybdenum(V) radical anion, $[\{HB(Me_2C_2N_3)_3\}MoO_2(SPh)]^-$. *J. Chem. Soc., Chem. Commun.*, **1994**, 1295-1296.
- [70] Jernigan, F.E., III; Sieracki, N.A.; Taylor, M.T.; Jenkins, A.S.; Engel, S.E.; Rowe, B.W.; Jove, F.A.; Yap, G.P.A.; Papish, E.T.; Ferrence, G.M. Sterically bulky Tris(triazolyl)borate ligands as water-soluble analogues of Tris(pyrazolyl)borate. *Inorg. Chem.*, **2007**, *46*, 360-362.
- [71] Papish, E.T.; Donahue, T.M.; Wells, K.R.; Yap, G.P.A. How are tris(triazolyl)borate ligands electronically different from tris(pyrazolyl)borate ligands? A study of $(Ttz^{Bu,Me})_3CuCO$ [$Ttz^{Bu,Me} = tris(3$ -t-butyl-5-methyl-1,2,4-triazolyl)borate]. *Dalton Trans.*, **2008**, 2923-2925.
- [72] Gardner, S.R.; Papish, E.T.; Monillas, W.H.; Yap, G.P.A. Tris(triazolyl)borate ligands of intermediate steric bulk for the synthesis of biomimetic structures with hydrogen bonding and solubility in hydrophilic solvents. *J. Inorg. Biochem.*, **2008**, *102*, 2179-2183.
- [73] Pellei, M.; Benetollo, F.; Gioia Lobbia, G.; Alidori, S.; Santini, C. The first nitro-substituted heteroscorpionate ligand. *Inorg. Chem.*, **2005**, *44*, 846-848.
- [74] Santini, C.; Pellei, M.; Alidori, S.; Gioia Lobbia, G.; Benetollo, F. Silver(I)-organophosphane complexes of the dihydrobis(3-nitro-1,2,4-triazolyl)borate ligand. X-ray crystal structure of $\{[H_2B(tz^{NO_2})_2]Ag[IP(m-toly)_3]_2\}$ with the scorpionate ligand co-ordinated in a unidentate k^1-N fashion. *Inorg. Chim. Acta*, **2007**, *360*, 2121-2127.
- [75] Marzano, C.; Pellei, M.; Alidori, S.; Brossa, A.; Gioia Lobbia, G.; Tisato, F.; Santini, C. New copper(I) phosphane complexes of dihydrobis(3-nitro-1,2,4-triazolyl)borate ligand showing cytotoxic activity. *J. Inorg. Biochem.*, **2006**, *100*, 299-304.
- [76] Kou, X.; Wu, J.; Cundari Thomas, R.; Dias, H.V.R. Sandwiched sodium and half-sandwiched copper carbonyl complexes featuring polyfluorinated tris(triazolyl)borate $[HB(3,5-(CF_3)_2Tz)_3]$. *Dalton Trans.*, **2009**, 915-917.
- [77] Abdul-Ghani, M.M.; Tipping, A.E. Unsaturated nitrogen compounds containing fluorine. Part 17. The reactions of 3,5-bis(trifluoromethyl)-1H-1,2,4-triazole with alkynes, alkenes and diazomethane, and of sodium 3,5-bis(trifluoromethyl)-1,2,4-triazolide with halogen compounds. *J. Fluor. Chem.*, **1995**, *72*, 135-145.
- [78] Lupineti, A.J.; Strauss, S.H.; Frenking, G. Nonclassical metal carbonyls. *Prog. Inorg. Chem.*, **2001**, *49*, 1-112.
- [79] Casarin, M.; Pandolfo, L.; Vittadini, A. Carbonyl copper(I) complexes with hydrotris(1,2,4-triazolyl)borate, hydrotris(pyrazolyl)borate, and tris(pyrazolyl)methane ligands: a DFT study. *Phys. Chem. Chem. Phys.*, **2009**, *11*, 94-96.
- [80] Singh, R.P.; Verma, R.D.; Meshri, D.T.; Shreeve, J.n.M. Energetic nitrogen-rich salts and ionic liquids. *Angew. Chem., Int. Ed.*, **2006**, *45*, 3584-3601.
- [81] Ye, C.; Xiao, J.-C.; Twamley, B.; Shreeve, J.n.M. Energetic salts of azetrotetrazolate, iminobis(5-tetrazolate) and 5,5'-bis(tetrazolate). *Chem. Commun.*, **2005**, 2750-2752.
- [82] Xue, H.; Gao, Y.; Twamley, B.; Shreeve, J.n.M. New Energetic Salts Based on Nitrogen-Containing Heterocycles. *Chem. Mater.*, **2005**, *17*, 191-198.
- [83] Gao, H.; Wang, R.; Twamley, B.; Hiskey, M.A.; Shreeve, J.n.M. 3-Amino-6-nitroamino-tetrazine (ANAT)-based energetic salts. *Chem. Commun.*, **2006**, 4007-4009.
- [84] Zeng, Z.; Twamley, B.; Shreeve, J.N.M. Structure and properties of substituted imidazolium, triazolium, and tetrazolium Poly(1,2,4-triazolyl)borate salts. *Organometallics*, **2007**, *26*, 1782-1787.
- [85] Lalor, F.J.; Miller, S.; Garvey, N. Unexpected regiochemistry in the reaction of benzotriazole with KBH_4 : synthesis of a new class of poly(azolyl)borate ligands. *J. Organomet. Chem.*, **1988**, *356*, C57-C60.
- [86] Shiu, K.B.; Shen, F.M.; Wang, S.L.; Wei, S.C. Organotransition metal complexes of multidentate ligands. IX. Synthesis and structure of hydrodrotis(benzotriazol-1-yl)borate derivatives of the Group VI metal carbonyls. *J. Organomet. Chem.*, **1989**, *372*, 251-261.
- [87] Cecchi, P.; Gioia Lobbia, G.; Leonesi, D.; Pettinari, C.; Sepe, C.; Vinciguerra, V. First-row transition- and Groups 12 and 14 metal bis[hydrotis(3a,7a-benzo-1,2,3-1H-triazol-1-yl)borate] derivatives. *Gazz. Chim. Ital.*, **1993**, *123*, 569-572.
- [88] Anderson, S.; Harman, A.; Hill, A.F. Poly(azolyl)chelate chemistry. V. Synthesis of bis(benzotriazolyl)borato complexes of rhodium(I). *J. Organomet. Chem.*, **1995**, *498*, 251-255.
- [89] Cartwright, J.; Harman, A.; Hill, A.F. Bis(benzotriazol-1-yl)borato complexes of ruthenium and rhodium. *J. Organomet. Chem.*, **1990**, *396*, C31-C34.
- [90] Burns, I.D.; Hill, A.F.; White, A.J.P.; Williams, D.J.; Wilton-Ely, J.D.E.T. Polyazolyl Chelate Chemistry. 6. Bidentate Coordination of $HB(pz)_2$ ($pz = Pyrazol-1-yl$) to Ruthenium and Osmium: Crystal Structure of $[RuH(CO)(PPh_3)_2\{k^2-HB(pz)_2\}]$. *Organometallics*, **1998**, *17*, 1552-1557.
- [91] Gioia Lobbia, G.; Pellei, M.; Pettinari, C.; Santini, C.; Skelton, B.W.; White, A.H. Silver(I) poly(1,2,4-triazolyl)borate complexes containing monodentate phosphane ligands. *Inorg. Chim. Acta*, **2005**, *358*, 1162-1170.
- [92] Gioia Lobbia, G.; Pellei, M.; Pettinari, C.; Santini, C.; Skelton, B.W.; White, A.H. Silver(I) poly(1,2,3-benzotriazolyl)borate complexes containing mono- and bidentate phosphine coligands. *Inorg. Chim. Acta*, **2005**, *358*, 3633-3641.
- [93] Janiak, C.; Esser, L. The bishydrotis(tetrazol-1-yl)borate anion, $[H_2B(CHN_4)_2]^-$ - Synthesis and structure of the 1st tetrazolylborate. *Z. Naturforsch. (B)*, **1993**, *48*, 394-396.
- [94] Janiak, C.; Scharmann, T.G.; Brzezinka, K.-W.; Reich, P. Transition-metal complexes with the novel scorpionate ligand dihydrotis(tetrazolyl)borate: synthesis and characterization of infinite two-dimensional metal-ligand frameworks and one-dimensional water substructures. *Chem. Ber.*, **1995**, *128*, 323-328.
- [95] Janiak, C.; Scharmann, T.G. Supramolecular C---H...O, C---H...N and C---

- H...Cl interactions in metal compounds with multi-topic poly(pyrazolyl)borate ligands. *Polyhedron*, **2003**, *22*, 1123-1133.
- [96] Song, D.; Jia, W.L.; Wu, G.; Wang, S. Cu(I) and Zn(II) complexes of 7-azaindole-containing scorpionates: Structures, luminescence and fluxionality. *Dalton Trans.*, **2005**, 433-438.
- [97] Spicer, M.D.; Reglinski, J. Soft scorpionate ligands based on imidazole-2-thione donors. *Eur. J. Inorg. Chem.*, **2009**, 1553-1574.
- [98] Garner, M.; Reglinski, J.; Cassidy, I.; Spicer, M.D.; Kennedy, A.R. Hydrotris(methimazolyl)borate, a soft analog of hydrotris(pyrazolyl)borate. Preparation and crystal structure of a novel zinc complex. *Chem. Commun.*, **1996**, 1975-1976.
- [99] Reglinski, J.; Garner, M.; Cassidy, I.D.; Slavin, P.A.; Spicer, M.D.; Armstrong, D.R. Sodium hydrotris(methimazolyl)borate, a novel soft, tridentate ligand: preparation, structure and comparisons with sodium hydrotris(pyrazolyl)borate. *J. Chem. Soc., Dalton Trans.*, **1999**, 2119-2126.
- [100] Kimblin, C.; Bridgewater, B.M.; Churchill, D.G.; Parkin, G. Mononuclear tris(2-mercapto-1-arylimidazolyl)hydroborato complexes of zinc, $[Tm^A]ZnX$: structural evidence that a sulfur rich coordination environment promotes the formation of a tetrahedral alcohol complex in a synthetic analogue of LADH. *Chem. Commun.*, **1999**, 2301-2302.
- [101] Santini, C.; Gioia Lobbia, G.; Pettinari, C.; Pellei, M.; Valle, G.; Calogero, S. Syntheses and spectroscopic and structural characterization of Silver(I) complexes containing tertiary phosphines and hydrotris(pyrazol-1-yl)-, Hydrotris(4-bromopyrazol-1-yl)-, Hydrotris(3,5-dimethylpyrazol-1-yl)-, and Hydrotris(3-methyl-2-thioxo-1-imidazolyl)borates. *Inorg. Chem.*, **1998**, *37*, 890-900.
- [102] Soares, L.F.; Silva, R.M.; Doriguetto, A.C.; Ellena, J.; Mascarenhas, Y.P.; Castellano, E.E. Syntheses, characterization and X-ray structure of potassium hydrotris(2-mercaptothiazolyl)borate, KMT, and potassium hydrotris(methimazole)borate, KTM. *J. Br. Chem. Soc.*, **2004**, *15*, 695-700.
- [103] Soares, L.F.; Silva, R.M.; Smece, J.; Darensbourg, M. Compounds of general interest. Hydrotris(methimazolyl)borate. *Inorg. Synth.*, **2002**, *33*, 199-202.
- [104] Garner, M.; Armstrong, D.R.; Reglinski, J.; Smith, W.E.; Wilson, R.; McKillop, J.H. The structure of methimazole and its consequences for current therapeutic models of Graves' disease. *Bioorg. Med. Chem. Lett.*, **1994**, *4*, 1357-1360.
- [105] Balestrero, R.S.; Forkey, D.M.; Russell, J.G. Nitrogen-15 NMR: iminothiothioamide tautomerism of 2-mercaptobenzazoles and 1-methyl-2-mercaptoimidazole. *Magn. Reson. Chem.*, **1986**, *24*, 651-655.
- [106] Kister, J.; Assef, G.; Mille, G.; Metzger, J. Synthesis and study of the SR .dblharw. NR rearrangement of 1,3-diazoles: 1-alkyl-2-alkylthio (allylthio, arylthio, cycloalkylthio) imidazoles. Part I. Synthesis and physicochemical studies. *Can. J. Chem.*, **1979**, *57*, 813-821.
- [107] Kister, J.; Assef, G.; Mille, G.; Metzger, J. Synthesis and study of the SR .dblharw. NR rearrangement of 1,3-diazoles: 1-alkyl-2-alkylthio (allylthio, arylthio, cycloalkylthio) imidazoles. Part II. Rearrangement and stray reactions. *Can. J. Chem.*, **1979**, *57*, 822-830.
- [108] Bailey, P.J.; Dawson, A.; McCormack, C.; Moggach, S.A.; Oswald, I.D.H.; Parsons, S.; Rankin, D.W.H.; Turner, A. Barriers to racemization in *cis*-symmetric complexes containing the Hydrotris(2-mercapto-1-ethylimidazolyl)borate (TmEt) ligand. *Inorg. Chem.*, **2005**, *44*, 8884-8898.
- [109] Tesmer, M.; Shu, M.; Vahrenkamp, H. Sulfur-rich zinc chemistry: new tris(thioimidazolyl)hydroborate ligands and their zinc complex chemistry related to the structure and function of alcohol dehydrogenase. *Inorg. Chem.*, **2001**, *40*, 4022-4029.
- [110] Ibrahim, M.M.; Shu, M.; Vahrenkamp, H. New tris(thioimidazolyl)borate ligands and some zinc complexes thereof. *Eur. J. Inorg. Chem.*, **2005**, 1388-1397.
- [111] Bakbak, S.; Bhatia, V.K.; Incarvito, C.D.; Rheingold, A.L.; Rabinovich, D. Synthesis and characterization of two new bulky tris(mercaptoimidazolyl)borate ligands and their zinc and cadmium complexes. *Polyhedron*, **2001**, *20*, 3343-3348.
- [112] Senda, S.; Ohki, Y.; Hirayama, T.; Toda, D.; Chen, J.L.; Matsumoto, T.; Kawaguchi, H.; Tatsumi, K. Mono{hydrotris(mercaptoimidazolyl)borato} complexes of Manganese(II), Iron(II), Cobalt(II), and Nickel(II) halides. *Inorg. Chem.*, **2006**, *45*, 9914-9925.
- [113] Maria, L.; Paulo, A.; Santos, I.C.; Santos, I.; Kurz, P.; Spingler, B.; Alberto, R. Very small and soft scorpionates: water stable Technetium Tricarbonyl complexes combining a Bis-agostic (k^3 -H, H, S) binding motif with pendant and integrated bioactive molecules. *J. Am. Chem. Soc.*, **2006**, *128*, 14590-14598.
- [114] Kimblin, C.; Hascall, T.; Parkin, G. Modeling the catalytic site of liver alcohol dehydrogenase: Synthesis and structural characterization of a [Bis(thioimidazolyl)(pyrazolyl)hydroborato]zinc complex, $[HB(tim^M)ppz]ZnI$. *Inorg. Chem.*, **1997**, *36*, 5680-5681.
- [115] Kimblin, C.; Bridgewater, B.M.; Hascall, T.; Parkin, G. The synthesis and structural characterization of bis(mercaptoimidazolyl)hydroborato complexes of lithium, thallium and zinc. *J. Chem. Soc., Dalton Trans.*, **2000**, 891-897.
- [116] Alvarez, H.M.; Tran, T.B.; Richter, M.A.; Alyounes, D.M.; Rabinovich, D.; Tanski, J.M.; Krawiec, M. Homoleptic group 12 metal Bis(mercaptoimidazolyl)borate complexes $M(Bm^R)_2$ ($M = Zn, Cd, Hg$). *Inorg. Chem.*, **2003**, *42*, 2149-2156.
- [117] Garcia, R.; King, Y.-H.; Paulo, A.; Domingos, A.; Santos, I. Rhenium(I) tricarbonyl complexes with mercaptoimidazolylborate ligands bearing piperazine fragments. *J. Chem. Soc., Dalton Trans.*, **2002**, 4236-4241.
- [118] Brown, H.C.; Choi, Y.M.; Narasimhan, S. Selective reductions. 29. A simple technique to achieve an enhanced rate of reduction of representative organic compounds by borane-dimethyl sulfide. *J. Org. Chem.*, **1982**, *47*, 3153-3163.
- [119] Garcia, R.; Paulo, A.; Domingos, A.; Santos, I. Rhenium(I) organometallic complexes with novel bis(mercaptoimidazolyl)borates and with hydrotris(mercaptoimidazolyl)borate: chemical and structural studies. *J. Organomet. Chem.*, **2001**, *632*, 41-48.
- [120] Singaram, B.; Cole, T.E.; Brown, H.C. Addition compounds of alkali-metal hydrides. 25. Rapid reaction of boronic esters and acids with lithium aluminum hydride. A novel and quantitative synthesis of lithium monoorganyl-borohydrides. *Organometallics*, **1984**, *3*, 774-777.
- [121] Maria, L.; Domingos, A.; Santos, I. Unique Uranium(III) cations anchored by polydentate sulfur-based ligands: Synthesis and structure of $[U\{H(R)B(tim^M)_2\}_2(THF)_3][BPh_4]$ ($R = H, Ph$). *Inorg. Chem.*, **2001**, *40*, 6863-6864.
- [122] Rudolf, G.C.; Hamilton, A.; Orpen, A.G.; Owen, G.R. A sting' on Grubbs' catalyst: an insight into hydride migration between boron and a transition metal. *Chem. Commun.*, **2009**, 553-555.
- [123] Figueroa, J.S.; Melnick, J.G.; Parkin, G. Reactivity of the Metal \rightarrow BX₃ Dative s-Bond: 1,2-Addition Reactions of the Fe \rightarrow BX₃ Moiety of the Fer-raboratrane Complex $[k^4-B(mim^B)_3]Fe(CO)_2$. *Inorg. Chem.*, **2006**, *45*, 7056-7058.
- [124] Garcia, R.; Paulo, A.; Domingos, A.; Santos, I. Rhenium(I) tris(carbonyl) complexes with soft scorpionates. *Dalton Trans.*, **2003**, 2757-2760.
- [125] Dodds, C.A.; Garner, M.; Reglinski, J.; Spicer, M.D. Coinage Metal complexes of a Boron-substituted soft scorpionate ligand. *Inorg. Chem.*, **2006**, *45*, 2733-2741.
- [126] Parkin, G. Applications of tripodal [S3] and [Se3] L₂X donor ligands to zinc, cadmium and mercury chemistry: Organometallic and bioinorganic perspectives. *New J. Chem.*, **2007**, *31*, 1996-2014.
- [127] Crossley, I.R.; Hill, A.F.; Humphrey, E.R.; Smith, M.K.; Tshabang, N.; Willis, A.C. Caveats for poly(methimazolyl)borate chemistry: the novel inorganic heterocycles $[H_2C(mt)_2BR_2]Cl$ ($mt = methimazolyl$; $BR_2 = BH_2, BH(mt), 9-BBN$). *Chem. Commun.*, **2004**, 1878-1879.
- [128] Schwalbe, M.; Andrikopoulos, P.C.; Armstrong, D.R.; Reglinski, J.; Spicer, M.D. Structural and theoretical insights into metal-scorpionate ligand complexes. *Eur. J. Inorg. Chem.*, **2007**, 1351-1360.
- [129] Barney, A.A.; Heyduk, A.F.; Nocera, D.G. Synthesis of an anionic tridentate phosphinoborate and its reaction chemistry with Sn(II). *Chem. Commun.*, **1999**, 2379-2380.
- [130] Peters, J.C.; Feldman, J.D.; Tilley, T.D. Silylene extrusion from a silane: direct conversion of Me_2SiH_2 to an iridium silylene dihydride. *J. Am. Chem. Soc.*, **1999**, *121*, 9871-9872.
- [131] Betley, T.A.; Peters, J.C. The strong-field tripodal phosphine donor, $[PhB(CH_2PPr_2)_3]^+$, provides access to electronically and coordinatively unsaturated transition metal complexes. *Inorg. Chem.*, **2003**, *42*, 5074-5084.
- [132] Ge, P.; Haggerty, B.S.; Rheingold, A.L.; Riordan, C.G. Poly(methylthiomethyl)borates: A New Class of Sulfur-Rich Ligands for Metal Ions. *J. Am. Chem. Soc.*, **1994**, *116*, 8406-8407.
- [133] Schebler, P.J.; Riordan, C.G.; Liable-Sands, L.; Rheingold, A.L. Ferrocenyl-derived face-capping ligands: syntheses and molecular structures of $[(FcT)Cu]_4$ and $[FcT]_2M$ ($M = Fe, Co, Ni$; $FcT = ferrocenyl-tris(methylthio)methylborate$). *Inorg. Chim. Acta*, **1998**, *270*, 543-549.
- [134] Ohrenberg, C.; Saleem, M.M.; Riordan, C.G.; Yap, G.P.A.; Verma, A.K.; Rheingold, A.L. Molecular structure and reactivity of a copper(I) tetramer. *Chem. Commun.*, **1996**, 1081-1082.
- [135] Ohrenberg, C.; Liable-Sands, L.M.; Rheingold, A.L.; Riordan, C.G. Structural diversity in a family of Copper(I) thioether complexes. *Inorg. Chem.*, **2001**, *40*, 4276-4283.
- [136] Hill, A.F.; Owen, G.R.; White, A.J.P.; Williams, D.J. The sting of the scorpion: a metallaboratrane. *Angew. Chem. Int. Ed. Engl.*, **1999**, *38*, 2759-2761.
- [137] Crossley, I.R.; Foreman, M.R.S.J.; Hill, A.F.; White, A.J.P.; Williams, D.J. The first rhodaboratrane: $[RhCl(PPh_3)_3(B(mt)_3)](Rh\rightarrow B)$ ($mt = methimazolyl$). *Chem. Commun.*, **2005**, 221-223.
- [138] Braunschweig, H. Transition metal complexes of boron. *Angew. Chem., Int. Ed.*, **1998**, *37*, 1786-1801.
- [139] Foreman, M.R.S.J.; Hill, A.F.; White, A.J.P.; Williams, D.J. Polyazolyl chelate chemistry. 13. an osmaboratrane. *Organometallics*, **2004**, *23*, 913-916.
- [140] Mihalcic, D.J.; White, J.L.; Tanski, J.M.; Zakharov, L.N.; Yap, G.P.A.; Incarvito, C.D.; Rheingold, A.L.; Rabinovich, D. Cobalt tris(mercaptoimidazolyl)borate complexes: synthetic studies and the structure of the first cobaltaboratrane. *Dalton Trans.*, **2004**, 1626-1634.
- [141] Crossley, I.R.; Hill, A.F.; Willis, A.C. Metallaboratranes: Tris(methimazolyl)borane complexes of Rhodium(I). *Organometallics*, **2006**, *25*, 289-299.
- [142] Landry, V.K.; Melnick, J.G.; Buccella, D.; Pang, K.; Ulichny, J.C.; Parkin, G. Synthesis and structural characterization of $[k^3-B.S.S-B(mim^R)_3]Ir(CO)(PPh_3)H$ ($R = But, Ph$) and $[k^4-B(mim^B)_3]M(PPh_3)Cl$ ($M = Rh, Ir$): Analysis of the bonding in metal Borane compounds. *Inorg. Chem.*, **2006**, *45*, 2588-2597.
- [143] Crossley, I.R.; Hill, A.F.; Willis, A.C. Formation of Metallaboratranes: The Missing Link. The First Iridaboratranes, $[IrH(CO)(PPh_3)\{k^3-B.S.S'-B(mt)_2R\}][Ir\rightarrow B]$ ($mt = Methimazolyl$, $R = mt, H$). *Organometallics*, **2005**,

- 24, 1062-1064.
- [144] Pang, K.; Tanski, J.M.; Parkin, G. Reactivity of the Ni→B dative s-bond in the nickel boratrane compounds $[k^4\text{-B}(\text{mim}^{\text{bu}})_3]\text{NiX}$ (X = Cl, OAc, NCS, N3): synthesis of a series of B-functionalized tris(2-mercapto-1-tert-butylimidazolyl)borato complexes, *[YTm^{bu}]₃NiZ*. *Chem. Commun.*, **2008**, 1008-1010.
- [145] Pang, K.; Quan, S.M.; Parkin, G. Palladium complexes with Pd→B dative bonds: Analysis of the bonding in the palladaboratrane compound $[k^4\text{-B}(\text{mim}^{\text{bu}})_3]\text{Pd}(\text{PMe}_3)$. *Chem. Commun.*, **2006**, 5015-5017.
- [146] Crossley, I.R.; Hill, A.F.; Willis, A.C. Retention of Pt→B bonding in oxidative addition reactions of the platinaboratrane $[\text{Pt}(\text{PPh}_3)_2\{\text{B}(\text{mt})_3\}](\text{Pt}→\text{B})^{10}$ (mt = methimazolyl). *Organometallics*, **2008**, *27*, 312-315.
- [147] Crossley, I.R.; Hill, A.F. Unlocking the metallaboratrane cage: reversible B-H activation in platinaboratrane. *Dalton Trans.*, **2008**, 201-203.
- [148] Crossley, I.R.; Hill, A.F. Di- and Zerovalent Platinaboratrane: The first Pentacoordinate d^{10} Platinum(0) complex. *Organometallics*, **2004**, *23*, 5656-5658.
- [149] Foreman, M.R.S.J.; Hill, A.F.; Owen, G.R.; White, A.J.P.; Williams, D.J. Polyazolyl chelate chemistry. 12. An unusual mode of coordination for the Hydrotris(methimazolyl)borato ligand. *Organometallics*, **2003**, *22*, 4446-4450.
- [150] Parshall, G.W. Borane complexes of transition metals. *J. Am. Chem. Soc.*, **1964**, *86*, 361-364.
- [151] Schebler, P.J.; Riordan, C.G.; Guzei, I.A.; Rheingold, A.L. Phenyltris(tert-butylthio)methylborate: A second generation S_3 ligand that enforces Tetrahedral coordination. *Inorg. Chem.*, **1998**, *37*, 4754-4755.
- [152] Fujita, K.; Rheingold, A.L.; Riordan, C.G. Thioether-ligated nickel(I) complexes for the activation of dioxygen. *Dalton Trans.*, **2003**, 2004-2008.
- [153] Levason, W.; Reid, G. Acyclic thio-, seleno-, and telluroether ligands. *Compr. Coord. Chem. II*, **2004**, *1*, 391-398.
- [154] Levason, W.; Reid, G. Macrocyclic thio-, seleno-, and telluroether ligands. *Compr. Coord. Chem. II*, **2004**, *1*, 399-410.
- [155] Barton, A.J.; Genge, A.R.J.; Hill, N.J.; Levason, W.; Orchard, S.D.; Patel, B.; Reid, G.; Ward, A.J. Recent developments in thio-, seleno-, and telluroether ligand chemistry. *Heteroatom. Chem.*, **2002**, *13*, 550-560.
- [156] Levason, W.; Orchard, S.D.; Reid, G. Recent developments in the chemistry of selenoethers and telluroethers. *Coord. Chem. Rev.*, **2002**, *225*, 159-199.
- [157] Gulliver, D.J.; Hope, E.G.; Levason, W.; Murray, S.G.; Potter, D.M.; Marshall, G.L. Synthesis, properties, and multinuclear (proton, carbon-13, selenium-77) nuclear magnetic resonance studies of selenoethers containing two or more selenium atoms. *J. Chem. Soc., Perkin Trans. 2*, **1984**, 429-434.
- [158] Morlok, M.M.; Janak, K.E.; Zhu, G.; Quarless, D.A.; Parkin, G. Intramolecular N-H...S hydrogen bonding in the zinc thiolate complex $[\text{Tm}^{\text{ph}}]\text{ZnSCH}_2\text{C}(\text{O})\text{NHPh}$: A mechanistic investigation of thiolate alkylation as probed by kinetics studies and by kinetic isotope effects. *J. Am. Chem. Soc.*, **2005**, *127*, 14039-14050.
- [159] Minoura, M.; Landry, V.K.; Melnick, J.G.; Pang, K.; Marchiò, L.; Parkin, G. Synthesis and structural characterization of tris(2-seleno-1-mesitylimidazolyl)hydroborato complexes: A new type of strongly electron donating tripodal selenium ligand. *Chem. Commun.*, **2006**, 3990-3992.
- [160] Guziec, L.J.; Guziec, F.S., Jr. A Directed metalation route to the selenium analog of methimazole. *J. Org. Chem.*, **1994**, *59*, 4691-4692.
- [161] Landry, V.K.; Pang, K.; Quan, S.M.; Parkin, G. Tetrahedral nickel nitrosyl complexes with tripodal [N3] and [Se3] donor ancillary ligands: structural and computational evidence that a linear nitrosyl is a trivalent ligand. *Dalton Trans.*, **2007**, 820-824.
- [162] Landry, V.K.; Minoura, M.; Pang, K.; Buccella, D.; Kelly, B.V.; Parkin, G. Synthesis and structural characterization of 1-mesityl-1,3-dihydro-imidazole-2-selone and bis(1-mesitylimidazol-2-yl)diselenide: Experimental evidence that the selone is more stable than the selenol tautomer. *J. Am. Chem. Soc.*, **2006**, *128*, 12490-12497.
- [163] Landry, V.K.; Buccella, D.; Pang, K.; Parkin, G. Bis- and tris(2-seleno-1-methylimidazolyl)hydroborato complexes, $\{[\text{Bse}^{\text{Me}}]\text{ZnX}\}_2$ (X = Cl, I), $[\text{Bse}^{\text{Me}}]_2\text{Zn}$ and $[\text{Tse}^{\text{Me}}]\text{Re}(\text{CO})_3$: Structural evidence that the $[\text{Bse}^{\text{Me}}]$ ligand is not merely a "heavier" version of the sulfur counterpart, $[\text{Bm}^{\text{Me}}]$. *Dalton Trans.*, **2007**, 866-870.
- [164] Landry, V.K.; Parkin, G. Synthesis and structural characterization of $[\text{Bse}^{\text{Me}}]\text{Ni}(\text{PPh}_3)(\text{NO})$, a nickel complex with a bent nitrosyl ligand. *Polyhedron*, **2007**, *26*, 4751-4757.
- [165] Ohrenberg, C.; Ge, P.; Schebler, P.; Riordan, C.G.; Yap, G.P.A.; Rheingold, A.L. Synthesis, molecular structure, and physical properties of $[\text{tetrakis}(\text{methylthio})\text{methyl}]\text{borate}\}_2\text{M}$ (M = Fe, Co, Ni). *Inorg. Chem.*, **1996**, *35*, 749-754.
- [166] Ohrenberg, C.; Riordan, C.G.; Liabile-Sands, L.; Rheingold, A.L. Synthesis, solid-state structure and reactivity of $[\text{PhTt}^{\text{ph}}]\text{Cu}$. *Coord. Chem. Rev.*, **1998**, *174*, 301-311.
- [167] Ge, P.; Rheingold, A.L.; Riordan, C.G. Nickel complexes of bidentate [S2] and [SN] Borato Ligands. *Inorg. Chem.*, **2002**, *41*, 1383-1390.
- [168] Chiou, S.-J.; Ge, P.; Riordan, C.G.; Liabile-Sands, L.M.; Rheingold, A.L. Pyrazolyl(methylthio)methylborates: hybrid ligands providing nitrogen and sulfur donors. *Chem. Commun.*, **1999**, 159-160.
- [169] Mock, M.T.; Popescu, C.V.; Yap, G.P.A.; Dougherty, W.G.; Riordan, C.G. Monovalent iron in a sulfur-rich environment. *Inorg. Chem.*, **2008**, *47*, 1889-1891.
- [170] DuPont, J.A.; Yap, G.P.A.; Riordan, C.G. Influence of ligand electronic effects on the structure of monovalent cobalt complexes. *Inorg. Chem.*, **2008**, *47*, 10700-10707.
- [171] Schebler, P.J.; Mandimutsira, B.S.; Riordan, C.G.; Liabile-Sands, L.M.; Incarvito, C.D.; Rheingold, A.L. Organometallic Cobalt(II) and Nickel(II) complexes supported by thioether ligation: unexpected nickel alkylation by the borato ligand phenyltris(tert-butylthio)methylborate. *J. Am. Chem. Soc.*, **2001**, *123*, 331-332.
- [172] DuPont, J.A.; Coxey, M.B.; Schebler, P.J.; Incarvito, C.D.; Dougherty, W.B.; Yap, G.P.A.; Rheingold, A.L.; Riordan, C.G. High-spin organocobalt(II) complexes in a thioether coordination environment. *Organometallics*, **2007**, *26*, 971-979.
- [173] Ge, P.; Riordan, C.G.; Yap, G.P.A.; Rheingold, A.L. A homoleptic thioether coordination sphere that supports Nickel(I). *Inorg. Chem.*, **1996**, *35*, 5408-5409.
- [174] Mandimutsira, B.S.; Yamarik, J.L.; Brunold, T.C.; Gu, W.; Cramer, S.P.; Riordan, C.G. Dioxygen activation by a nickel thioether complex: characterization of a $\text{Ni}^{\text{III}}(\mu\text{-O})_2$ core. *J. Am. Chem. Soc.*, **2001**, *123*, 9194-9195.
- [175] Schenker, R.; Mandimutsira, B.S.; Riordan, C.G.; Brunold, T.C. Spectroscopic and computational studies on $[(\text{PhTt}^{\text{bu}})\text{Ni}_2(\mu\text{-O})_2]$: Nature of the Bis- $\mu\text{-oxo}$ (Ni^{3+}) "Diamond" core. *J. Am. Chem. Soc.*, **2002**, *124*, 13842-13855.
- [176] Fujita, K.; Schenker, R.; Gu, W.; Brunold, T.C.; Cramer, S.P.; Riordan, C.G. A monomeric nickel-dioxygen adduct derived from a Nickel(I) complex and O_2 . *Inorg. Chem.*, **2004**, *43*, 3324-3326.
- [177] Cho, J.; Yap, G.P.A.; Riordan, C.G. Structural, spectroscopic, and electrochemical properties of a series of high-spin thiolatonickel(II) complexes. *Inorg. Chem.*, **2007**, *46*, 11308-11315.
- [178] Cho, J.; Van Heuvelen, K.M.; Yap, G.P.A.; Brunold, T.C.; Riordan, C.G. New synthetic routes to a disulfidodicknickel(II) complex: characterization and reactivity of a $\text{Ni}_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-S}_2)$ core. *Inorg. Chem.*, **2008**, *47*, 3931-3933.
- [179] Krishnan, R.; Voo, J.K.; Riordan, C.G.; Zahkarov, L.; Rheingold, A.L. Thiolate-bridged nickel-copper complexes: a binuclear model for the catalytic site of acetyl coenzyme c synthase? *J. Am. Chem. Soc.*, **2003**, *125*, 4422-4423.
- [180] Picot, D.; Ohanessian, G.; Frison, G. The alkylation mechanism of zinc-bound thiolates depends upon the zinc ligands. *Inorg. Chem.*, **2008**, *47*, 8167-8178.
- [181] Ruth, K.; Tuellmann, S.; Vitze, H.; Bolte, M.; Lerner, H.-W.; Holthausen, M.C.; Wagner, M. Copper complexes of mono- and ditopic [(methylthio)methyl]borates: missing links and linked systems en route to copper enzyme models. *Chem. Eur. J.*, **2008**, *14*, 6754-6770.
- [182] Pacey, G.E.; Moore, C.E. Studies in the tetraarylboration. Part 8. The synthesis and reagent properties of tetraethenylborates. *Anal. Chim. Acta*, **1979**, *105*, 353-359.
- [183] Sargent, A.L.; Titus, E.P.; Riordan, C.G.; Rheingold, A.L.; Ge, P. Poly(2-thienyl)borates: An investigation into the coordination of thiophene and its derivatives. *Inorg. Chem.*, **1996**, *35*, 7095-7101.
- [184] Carre, F.H.; Corriu, R.J.P.; Deforh, T.; Douglas, W.E.; Siebert, W.S.; Weinmann, W. A boron-bridged tetrathiaporphyrinogen. *Angew. Chem., Int. Ed.*, **1998**, *37*, 652-654.
- [185] Wrackmeyer, B.; Noeth, H. Nuclear magnetic resonance studies on boron compounds, X. Boron-11, nitrogen-14 and proton NMR studies on boryl-substituted thiophene, furan, and N-methylpyrrole and related systems: interaction of sp^2 -boron atoms with pi-systems. *Chem. Ber.*, **1976**, *109*, 1075-1088.
- [186] Soloway, A.H.; Tjarks, W.; Barnum, B.A.; Rong, F.-G.; Barth, R.F.; Codogni, I.M.; Wilson, J.G. The chemistry of neutron capture therapy. *Chem. Rev.*, **1998**, *98*, 1515-1562.
- [187] Qi, X.; Jun, E.J.; Xu, L.; Kim, S.-J.; Hong, J.S.J.; Yoon, Y.J.; Yoon, J. New BODIPY derivatives as OFF-ON fluorescent chemosensor and fluorescent chemodosimeter for Cu^{2+} : Cooperative selectivity enhancement toward Cu^{2+} . *J. Org. Chem.*, **2006**, *71*, 2881-2884.
- [188] Choi, S.H.; Pang, K.; Kim, K.; Churchill, D.G. Cu^{2+} colorimetric sensing and fluorescence enhancement and Hg^{2+} fluorescence diminution in "Scorpionate"-like Tetrathienyl-Substituted Boron-Dipyrrins. *Inorg. Chem.*, **2007**, *46*, 10564-10577.
- [189] Lee, C.-H.; Lindsey, J.S. One-flask synthesis of meso-substituted dipyrromethanes and their application in the synthesis of trans-substituted porphyrin building blocks. *Tetrahedron*, **1994**, *50*, 11427-11440.
- [190] Littler, B.J.; Miller, M.A.; Hung, C.-H.; Wagner, R.W.; O'Shea, D.F.; Boyle, P.D.; Lindsey, J.S. Refined synthesis of 5-Substituted dipyrromethanes. *J. Org. Chem.*, **1999**, *64*, 1391-1396.
- [191] Bruckner, C.; Karunaratne, V.; Rettig, S.J.; Dolphin, D. Synthesis of meso-phenyl-4,6-dipyrrins, preparation of their Cu(II), Ni(II), and Zn(II) chelates, and structural characterization of bis(meso-phenyl-4,6-dipyrrinato)Ni(II). *Can. J. Chem.*, **1996**, *74*, 2182-2193.
- [192] Treibs, A.; Kreuzer, F.H. Difluoroboryl complexes of di- and tripyrrylmethenes. *Justus Liebigs Ann. Chem.*, **1968**, *718*, 208-223.
- [193] Choi, S.H.; Kim, K.; Jeon, J.; Meka, B.; Buccella, D.; Pang, K.; Khatua, S.; Lee, J.; Churchill, D.G. Optical effects of S-Oxidation and Mn^+ binding in meso-Thienyl dipyrin systems and of stepwise bromination of 4,4-Difluoro-8-(2,5-dibromo-3-thienyl)-4-bora-3a,4a-diazas-indacene. *Inorg. Chem.*, **2008**, *47*, 11071-11083.
- [194] McCain, M.N.; Schneider, S.; Salata, M.R.; Marks, T.J.

- Tris(phosphino)borato silver(I) complexes as Precursors for metallic silver aerosol-assisted chemical vapor deposition. *Inorg. Chem.*, **2008**, *47*, 2534-2542.
- [195] Lu, C.C.; Peters, J.C. Pseudotetrahedral manganese complexes supported by the anionic tris(phosphino)borate ligand [PhBPPr₃]. *Inorg. Chem.*, **2006**, *45*, 8597-8607.
- [196] MacBeth, C.E.; Thomas, J.C.; Betley, T.A.; Peters, J.C. The coordination chemistry of "[BP₃]NiX" Platforms: targeting low-valent nickel sources as promising candidates to L₂Ni=E and L₃Ni=E linkages. *Inorg. Chem.*, **2004**, *43*, 4645-4662.
- [197] Daida, E.J.; Peters, J.C. Considering Fe^{IV} redox processes as mechanistically relevant to the catalytic hydrogenation of Olefins by [PhBPPr₃]Fe-H_x species. *Inorg. Chem.*, **2004**, *43*, 7474-7485.
- [198] Jenkins, D.M.; Di Bilio, A.J.; Allen, M.J.; Betley, T.A.; Peters, J.C. Elucidation of a low spin Cobalt(II) system in a distorted Tetrahedral geometry. *J. Am. Chem. Soc.*, **2002**, *124*, 15336-15350.
- [199] Feldman, J.D.; Peters, J.C.; Tilley, T.D. Activations of silanes with [PhB(CH₂PPh₂)₃]Ir(H)(η³-C₈H₁₃). formation of iridium silylene complexes via the extrusion of silylenes from secondary silanes R₂SiH₂. *Organometallics*, **2002**, *21*, 4065-4075.
- [200] Feldman, J.D.; Peters, J.C.; Tilley, T.D. Structural and chemical properties of Zwitterionic Iridium Complexes featuring the Tripodal phosphine ligand [PhB(CH₂PPh₂)₃]. *Organometallics*, **2002**, *21*, 4050-4064.
- [201] Turculet, L.; Feldman, J.D.; Tilley, T.D. Coordinatively and electronically unsaturated Zwitterionic Iron Silyl Complexes featuring the Tripodal Phosphine ligand [PhB(CH₂PPr₂)₃]. *Organometallics*, **2003**, *22*, 4627-4629.
- [202] Jenkins, D.M.; Betley, T.A.; Peters, J.C. Oxidative group transfer to Co(I) affords a terminal Co(III) Imido complex. *J. Am. Chem. Soc.*, **2002**, *124*, 11238-11239.
- [203] Brown, S.D.; Betley, T.A.; Peters, J.C. A Low-Spin d⁵ Iron Imide: nitrene capture by low-coordinate iron(I) provides the 4-Coordinate Fe(III) complex [PhB(CH₂PPh₂)₃]Fe=N-p-tolyl. *J. Am. Chem. Soc.*, **2003**, *125*, 322-323.
- [204] Thomas, J.C.; Peters, J.C. Bis(phosphino)borates: A new family of monoanionic chelating phosphine ligands. *Inorg. Chem.*, **2003**, *42*, 5055-5073.
- [205] Thomas, J.C.; Peters, J.C. Benzene C-H Activation at a charge neutral Zwitterionic Platinum(II) Complex. *J. Am. Chem. Soc.*, **2001**, *123*, 5100-5101.
- [206] Benkmil, B.; Ji, M.; Vahrenkamp, H. Bis(pyrazolyl)(thioimidazolyl)borate Ligands: The Missing Member in the N₃...S₃ scorpionate series. *Inorg. Chem.*, **2004**, *43*, 8212-8214.
- [207] Chiou, S.-J.; Innocent, J.; Riordan, C.G.; Lam, K.-C.; Liable-Sands, L.; Rheingold, A.L. Synthetic models for the Zinc sites in the methionine synthases. *Inorg. Chem.*, **2000**, *39*, 4347-4353.
- [208] Kimblin, C.; Bridgewater, B.M.; Hascall, T.; Parkin, G. The synthesis and structural characterization of bis(mercaptoimidazolyl)(pyrazolyl)hydroborato and tris(mercaptoimidazolyl)hydroborato complexes of thallium(I) and thallium(III). *J. Chem. Soc., Dalton Trans.*, **2000**, 1267-1274.
- [209] Kimblin, C.; Bridgewater, B.M.; Churchill, D.G.; Hascall, T.; Parkin, G. Bis(mercaptoimidazolyl)(pyrazolyl)hydroborato complexes of Zinc, Cadmium, and Cobalt: Structural evidence for the enhanced tendency of Zinc in biological systems to adopt Tetrahedral M[S₄] coordination. *Inorg. Chem.*, **2000**, *39*, 4240-4243.
- [210] Shu, M.; Walz, R.; Wu, B.; Seebacher, J.; Vahrenkamp, H. New bis(mercaptoimidazolyl)(pyrazolyl)borate ligands and their zinc complex chemistry. *Eur. J. Inorg. Chem.*, **2003**, 2502-2511.
- [211] Casado, M.A.; Hack, V.; Camerano, J.A.; Ciriano, M.A.; Tejel, C.; Oro, L.A. Unprecedented hybrid scorpionate/phosphine ligand able to be anchored to carbosilane dendrimers. *Inorg. Chem.*, **2005**, *44*, 9122-9124.
- [212] Camerano, J.A.; Casado, M.A.; Ciriano, M.A.; Tejel, C.; Oro, L.A. Coordination features of a hybrid scorpionate/phosphane ligand exemplified with iridium. *Chem. Eur. J.*, **2008**, *14*, 1897-1905.
- [213] Thomas, C.M.; Mankad, N.P.; Peters, J.C. Characterization of the terminal iron(IV) Imides {[PhBP'Bu₂(pz')]₂Fe^{IV}=NAd}⁺. *J. Am. Chem. Soc.*, **2006**, *128*, 4956-4957.
- [214] Brand, U.; Rombach, M.; Seebacher, J.; Vahrenkamp, H. Functional modeling of Cobalamine-Independent methionine synthase with pyrazolylborate-Zinc-Thiolate complexes. *Inorg. Chem.*, **2001**, *40*, 6151-6157.
- [215] Ji, M.; Benkmil, B.; Vahrenkamp, H. Zinc-thiolate complexes of the bis(pyrazolyl)(thioimidazolyl)hydroborate tripods for the modeling of thiolate alkylating enzymes. *Inorg. Chem.*, **2005**, *44*, 3518-3523.
- [216] Ibrahim, M.M.; He, G.; Seebacher, J.; Benkmil, B.; Vahrenkamp, H. Biomimetic thiolate alkylation with zinc pyrazolylbis(thioimidazolyl)borate complexes. *Eur. J. Inorg. Chem.*, **2005**, 4070-4077.
- [217] Ibrahim, M.M.; Seebacher, J.; Steinfeld, G.; Vahrenkamp, H. Tris(thioimidazolyl)borate-zinc-thiolate complexes for the modeling of biological thiolate alkylations. *Inorg. Chem.*, **2005**, *44*, 8531-8538.
- [218] Kimblin, C.; Parkin, G. Comparison of zinc and cadmium coordination environments in synthetic analogs of carbonic anhydrase: synthesis and structure of {[Pim^{Phi,Bu}]Cd(OH₂)(OCIO₃)}(ClO₄). *Inorg. Chem.*, **1996**, *35*, 6912-6913.
- [219] Kaufmann, D. Borylation of arylsilanes. II. Synthesis and reactions of silylated dihalophenylboranes. *Chem. Ber.*, **1987**, *120*, 901-905.
- [220] Haberecht, M.C.; Heilmann, J.B.; Haghiri, A.; Bolte, M.; Bats, J.W.; Lerner, H.-W.; Holthausen, M.C.; Wagner, M. Multiply borylated arenes: x-ray crystal structure analyses and quantum chemical calculations. *Z. Anorg. Allg. Chem.*, **2004**, *630*, 904-913.
- [221] Bailey, P.J.; Lanfranchi, M.; Marchiò, L.; Parsons, S. Hydridotris(thioxotriazolyl)borate (Tt), an ambidentate (N₃/S₃) tripodal ligand. X-ray crystal structures of Sodium, Bismuth(III), Tin(IV), and Manganese(I) complexes. *Inorg. Chem.*, **2001**, *40*, 5030-5035.
- [222] Gennari, M.; Giannetto, M.; Lanfranchi, M.; Marchiò, L.; Pellinghelli, M.A.; Tegoni, M. Synthesis, structure and electrochemical properties of a nickel complex with the hydrotris(thioxotriazolyl-3-(2-pyridyl))borate podand ligand. *Polyhedron*, **2004**, *23*, 1829-1835.
- [223] Cammi, R.; Gennari, M.; Giannetto, M.; Lanfranchi, M.; Marchiò, L.; Mori, G.; Paiola, C.; Pellinghelli, M.A. Synthesis, structure, and electrochemical properties of copper(I) complexes with S/N homoscorpionate and heteroscorpionate ligands. *Inorg. Chem.*, **2005**, *44*, 4333-4345.
- [224] Trofimenko, S. Poly(1-pyrazolyl)borates, their transition-metal complexes, and pyrazaboles. *Inorg. Synth.*, **1970**, *12*, 99-109.
- [225] Silva, R.M.; Gwengo, C.; Lindeman, S.V.; Smith, M.D.; Gardinier, J.R. Janus Scorpionates: supramolecular tectons for the directed assembly of hard-soft alkali metalopolymer chains. *Inorg. Chem.*, **2006**, *45*, 10998-11007.
- [226] Silva, R.M.; Gwengo, C.; Lindeman, S.V.; Smith, M.D.; Long, G.J.; Grandjean, F.; Gardinier, J.R. A second-generation Janus scorpionate ligand: Controlling coordination modes in Iron(II) complexes by steric modulation. *Inorg. Chem.*, **2008**, *47*, 7233-7242.
- [227] Pearson, R.G. Hard and soft acids and bases. *J. Am. Chem. Soc.*, **1963**, *85*, 3533-3539.
- [228] Krautscheid, H.; Emig, N.; Klaassen, N.; Seringer, P. Thiocyanato complexes of the coinage metals: synthesis and crystal structures of the polymeric pyridine complexes [Ag₂Cu₂(SCN)_x + y(pyz)_z]. *J. Chem. Soc., Dalton Trans.*, **1998**, 3071-3078.
- [229] Gardinier, J.R.; Silva, R.M.; Gwengo, C.; Lindeman, S.V. A 'metallic tape' stabilized by an unprecedented (μ₂-k², k², k¹, k¹-) scorpionate binding mode. *Chem. Commun.*, **2007**, 1524-1526.
- [230] Khan, T.A.; Khan, M.A.; Khan, Z.; Haq, M.M. Metal poly(benzimidazol-1-yl)borates. Synthesis and spectral characterization of some lanthanide chelates of hydridotris- and tetrakis(benzimidazol-1-yl)borate anions. *Synth. React. Inorg. Met.-Org. Chem.*, **2003**, *33*, 297-308.
- [231] Santini, C.; Dias, H.V.R.; Gioia Lobbia, G.; Papini, G.; Pellei, M. *Unpublished work*.
- [232] Docrat, A.; Morlok, M.M.; Bridgewater, B.M.; Churchill, D.G.; Parkin, G. N-H...O hydrogen bonding interactions in tetrahedral [ZnS₄] complexes of relevance to zinc enzymes: the synthesis, structures and reactivity of tris(2-mercapto-1-arylimidazolyl)hydroborato zinc(2-mercapto-1-arylimidazole) complexes, {[Tm^{Ar}]Zn(mim^{Ar})}[ClO₄] (Ar = Ph, p-Tol). *Polyhedron*, **2004**, *23*, 481-488.
- [233] He, G.S.; Vahrenkamp, H. A dinuclear zinc complex with a bridging dithioacetal ligand. *Z. Anorg. Allg. Chem.*, **2007**, *633*, 51-53.