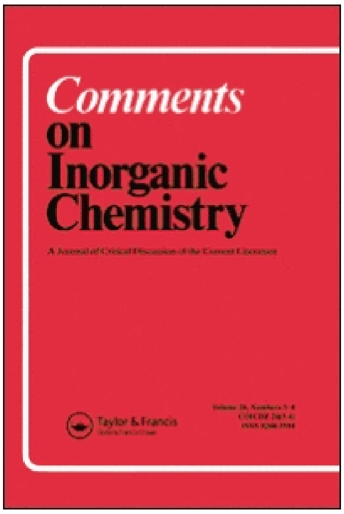

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STRONGLY DONATING SCORPIONATE LIGANDS

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STRONGLY DONATING SCORPIONATE LIGANDS

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The success of tris(pyrazolyl)borates has inspired the development of new scorpionate ligands that are based on other donor groups. These include borate ligands with thioimidazolyl, selenoimidazolyl, phosphine and N-heterocyclic carbene donors, ligands that provide a facial array of [S_3], [Se_3], [P_3], and [C_3] donors, respectively. These ligands are all more strongly donating than the tris(pyrazolyl)borates, with tris(carbene)borate ligands having the greatest donor strength. Despite the design similarities, strongly donating scorpionates differ in their topology and flexibility, donor properties and degradation pathways. The structural and electronic properties of these ligands are contrasted and related to their chemistry, particularly that of the transition metals. Bidentate congeners of all these ligands are also known and are briefly covered. The ability of strongly donating scorpionate ligands to stabilize metal ligand multiple bonds in late transition metal complexes is also briefly discussed.

ABBREVIATIONS

$PhBP^R$ – phenyltris(phosphinoborate)
$PhBC^R$ – phenyltris(imidazol-2-ylidine)borate
HBC^R – hydrotris(imidazol-2-ylidine)borate
HBS^R – hydrotris(thioimidazolyl)borate

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HBSe^{R} – hydrotris(selenoimidazolyl)borate
Tp – hydrotris(pyrazolyl)borate
Tp* – hydrotris(3,5-dimethylpyrazolyl)borate
DFT – Density Functional Theory
Ad – Adamantyl
dbabh – 2,3:5,6-dibenzo-7-azabicyclo[2.1.1]hepta-2,5-diene
NHC – *N*-heterocyclic carbene
Fc – Ferrocene

SCORPIONATE LIGANDS

As defined by Trofimenko, scorpionate ligands provide two groups (claws) to coordinate a metal ion, allowing the third group to arch over and "sting" the metal ion (Fig. 1). [1,2] The original scorpionate ligand, hydrotris(pyrazolyl)borate, was first introduced in 1966,[3] and has been the genesis of hundreds of variants.

Tris(pyrazolyl)borates have often been compared to cyclopentadienyl ligands since both ligand systems are anionic, $6e^{-}$ donor, face-capping ligands. There are also important differences between these two ligand classes. Electronically, tris(pyrazolyl)borates are hard σ-donor ligands, in contrast to the softer cyclopentadienyl ligands that have π-donor capabilities. Cyclopentadienyl and tris(pyrazolyl)borate ligands differ considerably in their topology, and suitably substituted tris(pyrazolyl)borates provide far greater steric protection of the metal

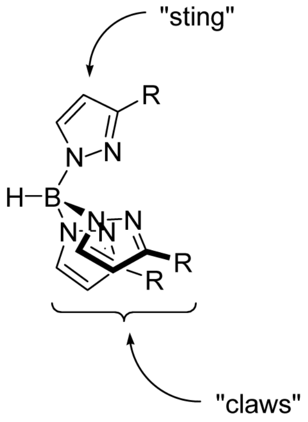


Figure 1. "Scorpionate" designation of tris(pyrazolyl)borate ligands.

center than cyclopentadienyls. This feature has allowed bulky "second generation" Tp ligands to stabilize coordinatively unsaturated transition metal complexes, which cannot be easily achieved with cyclopentadienyl ligands.

Tris(pyrazolyl)borates are a highly successful class of supporting ligands, and their complexes have found applications in fields such as catalysis, metal extraction and bioinorganic models. Their success stems largely from the flexibility they provide in tuning steric,[1] and to a lesser degree, electronic[4] properties. However, the donor strength range of Tp ligands is relatively limited, particularly with regards to stronger donating variants. The most strongly donating of the commonly used tris(pyrazolyl)borates are those with 3,5-dialkyl substituted pyrazolyl rings, e.g., Tp*.

STRONGLY DONATING SCORPIONATES

The success and versatility of tris(pyrazolyl)borates have inspired the development of new scorpionate ligands in which either the pyrazolyl donors or the bridgehead boron atom is replaced. Replacing the pyrazolyl groups by other donors is particularly attractive because this leads to a greater diversity in the electronic properties of scorpionate ligands while still retaining the negative charge of tris(pyrazolyl)borates. In the last 15 years, new scorpionates based on sulfur, selenium, phosphorus, and carbon donor groups have been introduced, providing ligands that are usually more strongly donating than the original tris(pyrazolyl)borates.

This review will cover the synthesis and properties of strongly donating scorpionate ligands and their metal complexes, as well as describe their decomposition pathways and highlight unusual properties and reactivity induced by these ligands. This review does not aim to provide a comprehensive overview of the chemistry of these ligands and their metal complexes, but rather a comparative evaluation of the properties of strongly donating scorpionates and their metal complexes. For the purposes of this review, strongly donating scorpionates meet the following criteria:

1. Face-capping ligands that are substantially more strongly donating than Tp*, the most strongly donating of the commonly used tris(pyrazolyl)borates. Less strongly donating scorpionates, such as tris(thioether)borates,[5] will not be covered.

2. Negatively charged ligands in which boron is the bridgehead atom. This excludes some neutral face-capping ligands that are strongly donating, e.g., tris(carbene)amines.[6]
3. Ligands in which the donor groups are the same, i.e., threefold symmetric ligands. Most of the known strongly donating scorpionates meet this requirement, although some mixed donor ligands are known and will be mentioned briefly.

Four types of scorpionates that fulfill these requirements are known: tris(thioimidazolyl)borates, tris(selenoimidazolyl)borates, tris(phosphino)borates, and tris(carbene)borates (Fig. 2), ligands that provide facial arrays of [S_3], [Se_3], [P_3], and [C_3] donors, respectively. All of these scorpionates also have properties that make them useful ligands: (1) straightforward preparation on a multigram scale; (2) the ability to modify steric (and in some cases, electronic) properties; and (3) the ability to coordinate to a variety of metals.

The strongly donating nature of these scorpionates is illustrated by the ν(NO) data of four-coordinate nickel nitrosyl $\{Ni(NO)\}^{10}$ complexes (Table 1, all nitrosyl ligands are linear by X-ray crystallography). It is clear that all these ligands increase the π-basicity of nickel when compared with the analogous tris(pyrazolyl)borate and cyclopentadienyl complexes. By this measure, the relative donor ability of the ligands is [C_3] > [P_3] > [S_3] > [Se_3]. A similar trend is observed for six-coordinate $Mn(CO)_3$ derivatives (Table 2). In general, other physical measures (e.g., IR, $E_{1/2}$, spin state preferences) are consistent with these observations and will be discussed at greater length below.

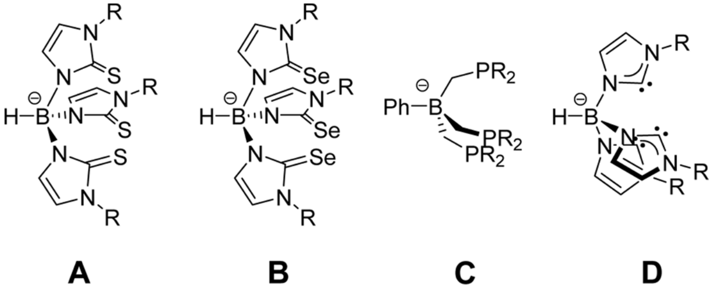


Figure 2. Strongly donating scorpionate ligands: **A**: tris(thioimidazolyl)borates; **B**: tris(selenoimidazolyl)borates; **C**: tris(phosphino)borates; **D**: tris(carbene)borates.

Table 1. IR spectroscopic data of $\{NiNO\}^{10}$ complexes supported by face-capping ligands

Ligand	$\nu(NO)$ (cm^{-1})	Reference
Cp	1830	130
Cp*	1787	131
Tp*	1786	53
Tp^{Ph2}	1803	132
$PhB(CH_2S^tBu)_3^-$	1785	133
$HBSe^{Me}$	1763, 1752[a]	53
HBS^{tBu}	1741	31
$PhBP^{Ph}$	1737	63
HBC^{tBu}	1703	94

[a] Two NO stretches observed.

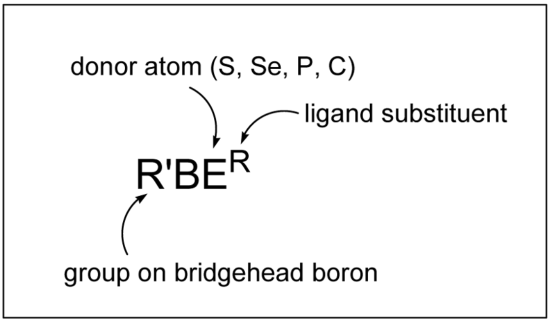
Aside from the different donor abilities, strongly donating scorpionate ligands differ in their flexibility and topology, modes of coordination, decomposition pathways, etc. These differences will be discussed below, particularly as they pertain to the structure and reactivity of their transition metal complexes. As befits the scorpionate moniker, all of these ligands have been observed to bind in tridentate and bidentate forms. One area where some strongly donating scorpionates have had a significant impact is in the stabilization of metal-ligand multiple bonds to late transition metals. These results will be briefly discussed.

A brief note on ligand abbreviations. Since the different classes of strongly donating scorpionate ligands have evolved separately, different abbreviation systems have also developed, e.g., Tm^R is commonly, although not ubiquitously, used for tris(thioimidazolyl)borates, while

Table 2. IR spectroscopic data of $Mn(CO)_3$ complexes supported by face-capping ligands

Ligand	A_1/cm^{-1}	E/cm^{-1}	Reference
Tp*	2032	1927	134
Cp*	2017	1929	134
$PhBP^{iPr}$[a]	1999	1906	64
$PhBS^{Me}$	1995	1894	30
$PhBC^{Me}$	1990	1889	95

[a] Complex was spectroscopically characterized but not isolated.



Scheme 1. Abbreviation scheme used in this review to describe strongly donating scorpionate ligands.

BP_3^R is typically used for tris(phosphino)borates. To assist in making comparisons between different ligand classes, an abbreviation scheme that is consistent for all the scorpionates discussed in this review has been adopted (Scheme 1). This scheme, which is based on that used for tris(phosphino)borates, has two major advantages: (1) it is consistent for all ligands under discussion; and (2) it shows all the ligand substituents (including at boron) in a single formula. While this scheme is not the accepted nomenclature for any of the ligand classes under discussion, it is has been adopted in the hope that it will improve the readability of this review. The Tp nomenclature for tris(pyrazolyl)borate ligands will be retained since it is well established and is generally used in a consistent manner.

RELATED REVIEWS

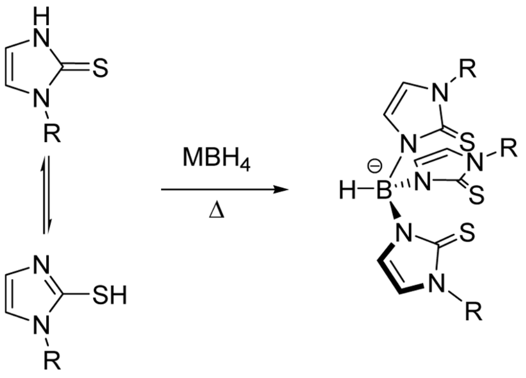
Some of the material under discussion has been covered in a number of recent reviews. Two books dealing with scorpionate ligands have been published. These books are focused on tris(pyrazolyl)borate ligands, but the more strongly donating variants are also covered.[1,2] There are two reviews dealing with tris(thioimidazolyl)borates. A review of their cadmium and mercury chemistry was published in 2006,[7] and a more general review of their chemistry has recently been submitted.[8] While there are no reviews that specifically deal with tris(phosphino)borates and tris(carbene)borates, the synthesis, structure and chemistry of iron tris(phosphino)borate imido and nitrido complexes was recently covered.[9]

TRIS(THIOIMIDAZOLYL)BORATES AND TRIS(SELENOIMIDAZOLYL)BORATES

Design and Synthesis

Tris(thioimidazolyl)borates were introduced in 1996[10] and the related tris(selenoimidazolyl)borate ligands in 2006.[11] These strongly donating ligands feature σ- and π-donors and have significantly greater flexibility than other scorpionate ligands (see below). Tris(thioimidazolyl)borates typically coordinate in a (usually desired) κ^3-*S,S,S* bicyclo[3.3.3] arrangement. The κ^3-*H,S,S* bicyclo[1.3.3] arrangement, which features three center, two electron B-H bond, is also commonly observed.

The key insight that led the development of these ligands was the recognition that methimazole is better represented as its thione tautomer, allowing for the synthesis of tripodal ligands by condensation with BH_4^- (Scheme 2).[10] The first tris(thioimidazolyl)borate ligand, HBS^{Me}, was prepared by a melt reaction between $NaBH_4$ and methimazole,[12] but the limitations of this route[13] have led to alternate synthetic methods. Substituted hydroborate ligands HBS^R (R = Et, Bz, ^{t}Bu, Ph, *p*-tol, Mes, 2,6-$^iPr_2C_6H_3$, etc.)[14-19] are prepared as their alkali metal salts by heating the *N*-substituted thioimidazole with MBH_4 (M = Li, Na, K) in a high boiling solvent such as toluene or xylene. More soluble ligands with methyl or phenyl groups at the bridgehead boron atom can be similarly prepared.[20,21] An alternate route to tris(thioimidazolyl)borates relies on the activation of $B(NMe_2)_3$ by imidazoles, leading to *N*-methylimidazole-tris(thioimidazolyl)borate ligands $ImBS^R$.[22]



Scheme 2. General scheme for synthesis of HBS^R ligands.

Tris(thioimidazolyl)borate ligands can usually be transferred to transition metals directly from the alkali metal salts, although prior conversion to thallium ligand transfer reagents is required in some cases.[23] Despite the expectation that "soft" tris(thioimidazolyl)borate ligands would be limited to complexes of "soft" metals (i.e., low valent, late transition metals), the ligands are quite versatile in their coordinating ability. For example, they are able to coordinate to high valent early transition metals, provided appropriate starting materials that attenuate the electrophilicity and Lewis acidity of the metal center are used.[24-28]

Electronic Properties

It may be somewhat surprising that tris(thioimidazolyl)borates are strongly donating ligands, given the poor donor abilities of the thione moiety. Their strong donor properties are ascribed to the thiolate tautomer, which is important in the interaction of this ligand with transition metals (Fig. 3). There is substantial evidence from IR spectroscopy that tris(thioimidazolyl)borates are strongly donating. Specifically, data for $Mn(CO)_3$,[29,30] $Ni(NO)$,[31] $Re(CO)_3$,[32] $W(CO)_2(\equiv CC_6H_4R)$ ($R = H$, Me),[33] $Mo(CO)_2(\eta^3\text{-}C_3H_5)$,[34] $W(CO)_3I$,[34] $M(CO)_2(NO)$ ($M = Mo$, W)[35] derivatives of tris(thioimidazolyl)borates show that these ligands are stronger electron donors than Cp and Tp ligands. The limited data from other physical methods is consistent with this conclusion. For example, cyclic voltammetry studies of six-coordinate $[HBS^{Me}]_2Co^+$ show that the tris(thioimidazolyl)borate complex is more difficult to reduce than its cyclopentadienyl and tris(pyrazolyl)borate congeners.[36]

The effect of ligand substituents on the donor properties of tris(thioimidazolyl)borates has been less extensively investigated. The most comprehensive dataset comes from $\nu(CO)$ measurements for a

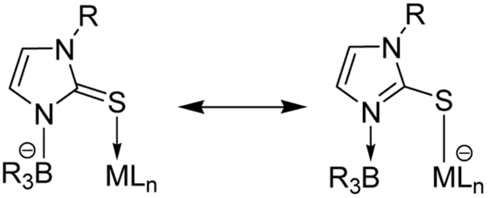


Figure 3. Resonance contributors to the binding of tris(thioimidazolyl)borate ligands to metals.

Table 3. IR spectroscopic data for substituted $[RBS^{R'}]Mn(CO)_3$ complexes

R	R′	ν(CO)/cm^{-1}	Medium	Reference
H	Me	2003, 1905	Toluene	29
H	Me	1994, 1984, 1896, 1884[a]	KBr	29, 30
H	Bz	1995, 1887	KBr	30
H	tbu	2003, 1923, 1895	KBr	30
H	*p*-tol	2003, 1909, 1892	KBr	30
Ph	Me	1995, 1884	KBr	30

[a] Additional stretches attributed to the presence of two independent molecules in the unit cell.

series of $[HBS^R]Mn(CO)_3$[29,30] and $[PhBS^R]Mn(CO)_3$[30] complexes (Table 3). Unfortunately, the complexity of the data makes it difficult to tease out the substituent effects on ligand donor strength. The ν(NO) data for two $[HBS^R]NiNO$ complexes show that an electron donating alkyl substituent makes the ligand slightly more strongly donating than an aryl substituent.[31] Changing the group on the bridgehead boron has little effect on the donor strength on the ligands, as shown by ν(CO) data for $[RBS^{Me}]Re(CO)_3$ complexes (Table 4).[20,32]

Although tris(thioimidazolyl)borates are strong electron donors, they are weak field ligands as a consequence of being both σ- and π-donors.[35] The relative position of the original tris(thioimidazolyl)borate ligand in the spectrochemical series is $Cl^- < HBS^{Me} < H_2O$, as determined from the electronic spectra of octahedral nickel(II) complexes.[37] The weak field nature of these ligands explains why octahedral $[HBS^{Me}]_2Fe$ complexes are high spin,[37] in contrast to ferrocene, which is diamagnetic, and Tp_2Fe, which exhibits spin crossover behavior.[38] The relative positions of these three ligands in the spectrochemical series is $Cp > Tp > HBS^{Me}$.

Table 4. IR spectroscopic data for $[RBS^{Me}]Re(CO)_3$ complexes

R	ν(CO)/cm^{-1}	Reference
H	1897, 1863	32
Me	1895, 1860	20
Ph	1895, 1865	20

Ligand Flexibility

The most significant difference between tris(thioimidazolyl)borates and other scorpionates is the extra atom between the boron and donor atoms in tris(thioimidazolyl)borate ligands. This means that tris(thioimidazolyl)borates form bicyclo[3.3.3] cages when coordinated to metal centers, in contrast to the bicyclo[2.2.2] cages of other scorpionate ligands. The greater flexibility of the resulting eight-membered chelate rings has both structural and chemical consequences. New reaction pathways that result from this flexibility are a recurring theme in tris(thioimidazolyl)-borate chemistry.

The bicyclo[3.3.3] cage formed by a tris(thioimidazolyl)borate ligand in the κ^3-*S*,*S*,*S* coordination imparts C_3 symmetry to the resulting metal complex, and thus the complex has two enantiomers (Fig. 4). Racemization of the enantiomers has been investigated in four- and six-coordinate complexes,[33,39] where it was found that the mechanism of racemization follows a dissociative pathway that involves decoordination of one of the ligand sulfur donors. The barrier towards racemization is smaller in four-coordinate d^{10} $[HBS^R]MX$ complexes (13–18 kcal/mol; R = Et, Bz) than in the low spin six-coordinate d^6 $[HBS^{Et}]Ru(p\text{-cymene})^+$ and $[HBS^{Et}]Mn(CO)_3$ complexes (>22 kcal/mol),[39] consistent with the relative barriers towards dissociation. This insight has been exploited in the design and synthesis of the six-coordinate C_3-symmetric Ru(II) complex $[ImBS^{CH(Me)Ph}{}_3]Ru(p\text{-cymene})^{2+}$ as a single diastereomer.[22] Similar

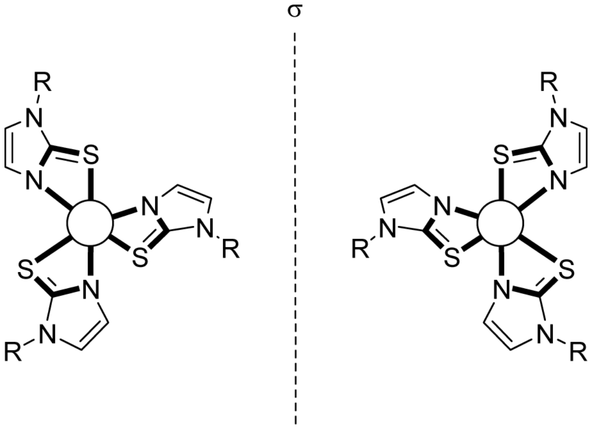


Figure 4. Enantiomers generated by the tris(thiomidazolyl)borate ligand conformation.

large barriers to racemization are observed in the seven-coordinate complex Cp[HBS^{Me}]ZrCl$_2$.[39] The ease of racemization in the six-coordinate [HBS^{Me}]W(CO)$_2$(CN^{i}Pr$_2$) and [HBS^{Me}]W(CO)$_2$(CC$\equiv$C^{t}Bu) complexes was found to depend on the nature of the *trans* alkylidyne ligand.[33]

The flexibility of tris(thioimidazolyl)borate ligands can result in unexpected coordination modes, even in relatively simple homoleptic complexes. For example, while [HBS^{Me}]$_2$Fe has the expected FeS$_6$ core,[37] an FeS$_4$H$_2$ core is observed in [HBS^{Ph}]$_2$Fe, in which both ligands bind to the metal through two sulfur atoms and B-H groups (Fig. 5).[40] Interestingly, oxidation of [HBS^{Ph}]$_2$Fe results in an iron(III) complex with an FeS$_6$ core. It has been suggested that this change may be due to increased electrostatic interactions in the higher oxidation state complex.[40] By contrast, [HBS^{Me}]$_2$Fe cannot be cleanly oxidized, and attempts to prepare [HBS^{Me}]$_2$Fe$^+$ from iron(III) salts were unsuccessful.[37] The reasons for the difference in accessibility of the iron(III) oxidation state are not clear.

Similar complexity is observed in homoleptic cobalt complexes. While the HBS^{Ph} ligand coordinates in the same manner as observed for iron, providing a six-coordinate cobalt(II) complex with CoS$_4$H$_2$ core,[40] only four coordinate [HBS^{Me}]CoX complexes could be prepared with the HBS^{Me} ligand.[36] As might be expected, similar four coordinate [HBS^{tBu}]CoX (X = Cl, Br, I) complexes can be prepared with the bulkier HBS^{tBu} ligand, but quite unexpectedly, with excess ligand the six coordinate complex [HBS^{tBu}]$_2$Co is formed. This complex has a CoS$_4$H$_2$ core.[23] The stability of these structures also depends on the nature of ancillary ligands. Thus, removing the halide from [HBS^{tBu}]CoX in the presence of a weakly coordinating anion Y results in formation of the

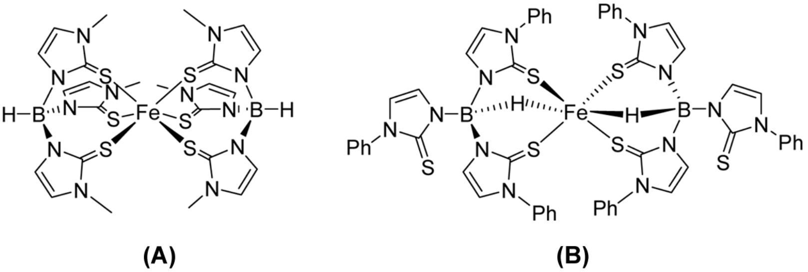
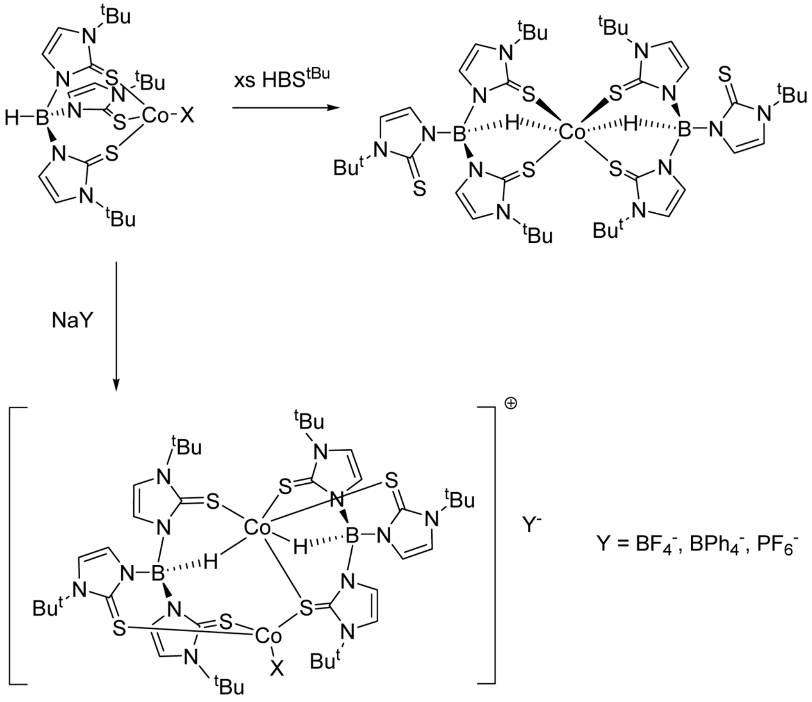


Figure 5. Differences in the binding of tris(thioimidazolyl)borate ligands in the homoleptic complexes [HBS^{Me}]$_2$Fe (A) and [HBS^{Ph}]$_2$Fe (B).



Scheme 3. Ligand rearrangements in cobalt(II) HBS^{tBu} ligands.

dimer $[Co_2[HBS^{tBu}]_2X]Y$ (Y = BF_4, BPh_4, PF_6). The solid state structure of the dimer shows that both tris(thioimidazolyl)borates bridge the cobalt ions; one ligand binds in a bidentate:tridentate fashion, the other is monodentate:tridentate (μ-κ^2-S:κ^3-S,S,H) (Scheme 3). It is not known if this structure is maintained in solution, since the ^1H NMR spectrum could only be tentatively assigned.[23] It is clear from these examples that tris(thioimidazolyl)borates have a high degree of conformational flexibility that can result in their metal complexes adopting unanticipated structures.

Ligand Reactivity

Among scorpionates, tris(thioimidazolyl)borate ligands are uniquely susceptible to the formation of metallaboratranes in which there is a M→B dative bond (Fig. 6). Metallaboratranes have been observed for Fe,[41] Ru,[42] Os,[43] Co,[23] Rh,[44–46] Ir,[46] Ni,[19] Pd[47] and Pt.[48] There is considerable circumstantial evidence that hydrometallation of a bridging

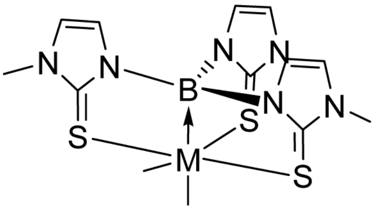


Figure 6. Metalloboratrane ligand formed from a tris(thioimidazolyl)borate.

M-H-B function is the key step in formation of the metallaboratrane.[49] Metallaboratrane formation is likely a consequence of the flexibility of tris(thioimidazolyl)borate ligands. Metallaboratrane formation is reversible in some instances,[50] and intriguingly, new tris(thioimidazolyl)-borate ligands can be produced through the formal 1,2-addition of reagents across the M-B bond.[41]

Tris(thioimidazolyl)borate ligands are often susceptible to decomposition under oxidizing conditions, typically by B-N bond cleavage. In contrast to stable TpCuX complexes (e.g., $Tp^{tBu}CuCl^{51}$), attempts to prepare hydrotris(thioimidazolyl)borate Cu(II) complexes have so far been unsuccessful, with ligand decomposition and copper reduction observed.[21] It has been proposed that interaction of the B-H bond with the metal center, which leads to the κ^3-*S,S,H* coordination mode with low oxidation state metals, results in ligand decomposition in the presence of an oxidizing metal. While replacing the B-H group may be expected to overcome these problems, no isolable Cu(II) complexes could be characterized when a ligand containing a B-Ph group was used, although there are promising hints of success.[21] Also in contrast to Tp ligands, oxidation of tris(thioimidazolyl)borate complexes often leads to decomposition, e.g., $[HBS^{Me}]_2Fe$ discussed above.[37] The synthesis of high oxidation state early metal complexes in particular usually requires starting materials in which the electrophilicity and Lewis acidity of the metal center is attenuated to avoid decomposition of the ligand.[24–28]

Related Ligands

Tris(selenoimidazolyl)borate ligands have been recently reported,[11] and are a logical extension to the tris(thioimidazolyl)borates. These ligands are prepared in a similar manner to the tris(thioimidazolyl)borates, using substituted imidazole-2-selones and BH_4^-.[11] These ligands are strongly

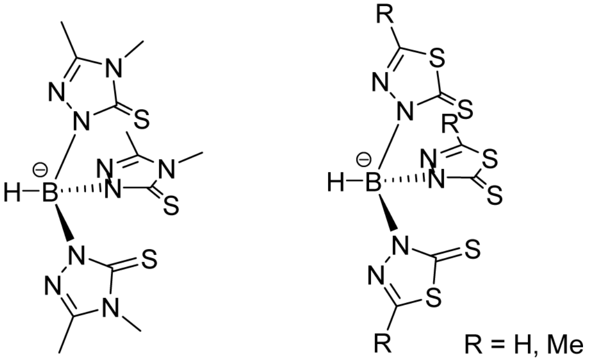


Figure 7. Ambidentate "Janus" ligands containing nitrogen and sulfur donors.

donating as determined by IR spectroscopy of $Re(CO)_3$[11,52] and $Ni(NO)$[53] (Table 1) derivatives. More electron donating substituents increase the electron donating ability of the $HBSe^R$ ligand.[52] Although it may be expected that these ligands will show similar properties to $RBS^{R'}$ ligands, initial observations on related bidentate versions show a greater tendency to bridge metals.[52]

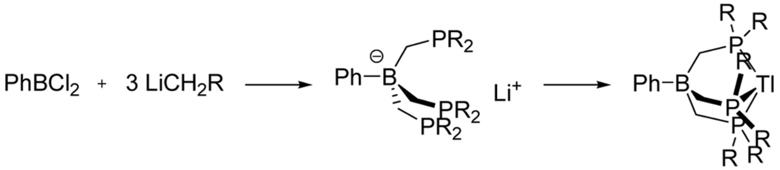
Scorpionate ligands that incorporate both nitrogen and sulfur donors, and which may be considered as hybrids of tris(pyrazolyl)borates and tris(thioimidazolyl)borates, have been developed (Fig. 7).[54,55] In general, these ambidentate "Janus" ligands bind to softer metals through sulfur and to harder metals through nitrogen. It has been found that the coordination preferences can be modulated by changes to the R groups,[56] potentially allowing the ligand donor strength to be tuned.

TRIS(PHOSPHINO)BORATES

Design and Synthesis

Tris(phosphino)borate ligands were first reported in 1999. These ligands provide an array of three phosphine donors, and are an anionic analogue of the neutral tris(phosphino)methane ligands.[57,58] Tris(phosphino)borate ligands are strongly donating, strong field ligands by virtue of the strong σ-donor and modest π-acceptor character of the phosphine donors.

Synthesis of tris(phosphino)phenylborates is achieved by the reaction of 3 equivalents of $LiCH_2PR_2$ with $PhBCl_2$, yielding $PhB(CH_2PR_2)_3^-$



Scheme 4. Synthesis of $PhBP^R$ ligands ($R = Ph$, ${}^iPr$, CH_2Cy).

($R = Ph$,[59] ${}^iPr$[60] and CH_2Cy[61]). These lithium reagents can be used for ligand transfer, although they are commonly converted to a thallium reagent for use in transmetallation (Scheme 4). N-Butyltris(phosphino)-borates ${}^nBuBP^R$ ($R = Ph$, ${}^iPr$) can be prepared by a similar method.[62] The coordination chemistry of tris(phosphino)borate ligands has so far been limited to complexes of the late transition metals.

Electronic Properties

Tris(phosphino)borates are significantly stronger donors than tris(pyrazolyl)borates as measured by IR spectroscopy. For example, ν_{CO} and ν_{NO} of $[PhBP^{iPr}]Ni(NO)$[63] and $[PhBP^{iPr}]Mn(CO)_3$[64] are at lower frequencies than for the analogous tris(pyrazolyl)borate complexes (Tables 1 and 2). Anionic tris(phosphino)borates also create a more electron rich metal center than related neutral tris(phosphino)methane ligands, as determined by IR spectroscopy. Thus, for both $[MeC(CH_2PEt_2)_3Ni(NO)][BF_4]$ ($\nu_{NO} = 1750\ cm^{-1}$),[65] and $[MeC(CH_2PPh_2)_3Mn(CO)_3]OTf$ ($\nu_{CO} = 2030$ and $1960\ cm^{-1}$),[66] the observed stretching frequencies are consistent with less π-backbonding than in the analogous $PhBP^{iPr}$ complexes (Tables 1 and 2). Similar results showing that tris(phosphino)borates are stronger donors than tris(phosphino)methanes have been obtained from IR spectroscopy of $Co(CO)_2$ and $RuCl(CO)_2$ derivatives (Table 5). These data also show that the alkyl substituted tris(phosphino)borate ligand $PhBP^{iPr}$ is a stronger donor than $PhBP^{Ph}$.[60]

A compelling illustration of the strongly donating properties of tris(phosphino)borate ligands is provided by the anionic complex $[PhBP^{Ph}]Ni(CO)^-$.[67] Structural, spectroscopic and computational investigations are consistent with the formation of a Ni-C≡O-Li isocarbonyl ligand, which suggests negative charge density at oxygen. This is the first example of an isocarbonyl ligand in a nickel complex.

Table 5. Selected IR data showing the strong donor ability of tris(phosphino)borate ligands

Complex	ν(CO)/cm^{-1}	Medium	Reference
$[PhBP^{iPr}]Co(CO)_2$	1990, 1904	Benzene	60
$[PhBP^{Ph}]Co(CO)_2$	2008, 1932	Benzene	103
$Cp^*Co(CO)_2$	2011, 1949	Cyclohexane	135
$Tp^{iPr,Me}Co(CO)_2$	2016, 1939	Toluene	136
$CpCo(CO)_2$	2028, 1967	$CHCl_3$	137
$Cp^*Ru(Cl)(CO)_2$	2028, 1974	THF	138
$[PhBP^{iPr}]Ru(Cl)(CO)_2$	2045, 1993	Benzene	60
$[PhBP^{Ph}]Ru(Cl)(CO)_2$	2068, 2021	CH_2Cl_2	60
$CpRu(Cl)(CO)_2$	2059, 2008	CH_2Cl_2	139
$TpRu(Cl)(CO)_2$	2074, 2012	CH_2Cl_2	140

Tris(phosphino)borates are strong field ligands, as illustrated by the spin state preferences of six coordinate iron(II) tetrahydroborate complexes. The tris(phosphino)borate complex $[PhBP^{Ph}]Fe(BH_4)$ is low spin (diamagnetic, $S = 0$), in contrast to the tris(pyrazolyl)borate complex $Tp^{Ph2}Fe(BH_4)$, which is high spin ($S = 2$).[68]

Tris(phosphino)borate ligands have uniquely allowed for the preparation of the low spin ($S = 1/2$) pseudotetrahedral Co(II) complexes, $[PhBP^{R}]CoX$.[69–72] Detailed investigations show that the stability of the low spin state depends on a combination of factors, including the nature of the X ligand, as well as the strong donor ability and the relative flexibility of the tris(phosphino)borate ligand.[72] With suitable X ligands, spin-crossover complexes can be prepared.[71,72] The low spin state is accompanied by distortion of the metal coordination sphere away from C_{3v} towards lower symmetry. Two major geometric distortions have been identified, and it is found that the off-axis distortion in which the Co-X vector is bent away from the B-Co vector always is always associated with the low spin state (Fig. 8). Interestingly, despite its greater donor strength, $PhBP^{iPr}$ is less likely to stabilize the low spin state, most likely because the greater bulk of this ligand prevents the geometric distortions required to access the low spin state.

The strongly donating nature of tris(phosphino)borate ligands has allowed for complexes with unusually high oxidation states to be prepared. Most notably, Fe(IV) complexes have been prepared, including the seven-coordinate trihydride $[PhBP^{iPr}]Fe(PR_3)(H)_3$[73] and the four-coordinate nitrido complex $[PhBP^{iPr}]Fe{\equiv}N$.[74]

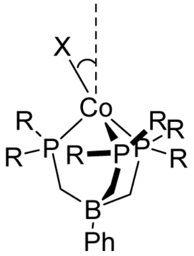


Figure 8. Off-axis distortion in low spin [PhBP^R]CoX complexes, R = Ph, ^{i}Pr.

Ligand Reactivity

In certain low valent complexes, the phosphine donor groups of tris(phosphino)borate ligands are susceptible to oxidation, leading to the formation of phosphine oxides. The extent of oxidation depends on the donor ability of the tris(phosphino)borate ligand. Thus, while [PhBP^{Ph}]CoI reacts with O_2 in a four-electron oxidation reaction to form κ^3-PhB(CH_2PPh_2)($CH_2P(O)Ph_2$)$_2$CoI (Fig. 9),[71] [PhBP^{iPr}]CoCl can be oxidized by either four and six electrons (depending on the reaction conditions), to provide κ^3-PhB($CH_2P^iPr_2$)($CH_2P(O)Ph_2$)$_2$CoCl and κ^3-PhB($CH_2P(O)^iPr_2$)$_3$CoCl, respectively.[60] Divalent iron and nickel complexes are similarly oxygen sensitive.[63]

Bidentate κ^2-*P,P* coordination of tris(phosphino)borate ligands has been observed in certain metal complexes. Electronic factors are most likely responsible for this coordination mode, which has been most commonly observed in d^8 metal complexes, such as square planar Rh(I)[75] and Pt(II).[76] Bidentate κ^2-*P,P* coordination of the tris(phosphino)borate ligand occurs in the anilido complexes κ^2-[PhBP^{iPr}]Ni(dbabh) (Fig. 10) and κ^2-[PhBP^{iPr}]Ni-N(H)Ar (Ar = C_6H_5, 2,6-$^iPr_2C_4H_3$), leading

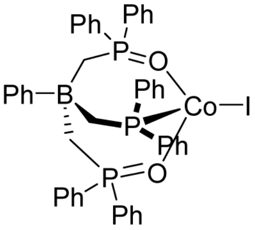


Figure 9. Cobalt(II) iodide complex of an oxidized tris(phosphino)borate ligand.

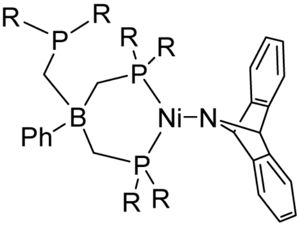


Figure 10. Decoordination of one phosphine arm in [PhBP^{R}]Ni(dbabh) complexes, R = Ph, ^{i}Pr.

to three coordinate nickel centers. The short Ni-N bond lengths and orientation of the anilido ligands suggest that π-interactions between the anilido ligands and nickel are important in preventing tridentate coordination of the PhBP^{iPr} ligand in these complexes.[63]

In some cases, the B-C bonds of tris(phosphino)borate ligands are susceptible to cleavage under reducing conditions. For example, reaction of [PhBP^{R}]NiCl with reducing agents results in formation of the complex [PhBP^{R}]Ni(κ^2-CH_2PR_2), R = Ph, ^{i}Pr (Fig. 11) as the major reaction product. The $CH_2PR_2^-$ ligand is most likely formed by tris(phosphino)borate degradation, although the mechanism of this reaction is not known.[63] Similar B-C bond cleavage occurs on hydrogenation of [PhBP^{iPr}]Fe-R (R = Me, CH_2Ph, CH_2CMe_3), yielding the spectroscopically characterized complex κ^2-[PhB($CH_2P^iPr_2$)$_2$]Fe(H)$_4$(P^iPr_2Me). This reaction proceeds through a series of transformations with one spectroscopically observable intermediate.[73] An interesting series of transformations involving the PhBP^{iPr} ligand is observed in certain rhodium(I) complexes (Scheme 5). Addition of Li[PhBP^{iPr}] to [RhCl(C_2H_4)$_2$]$_2$ results in cleavage of one B-C bond and formation of the square planar complex

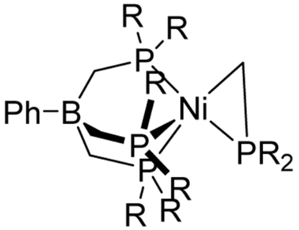
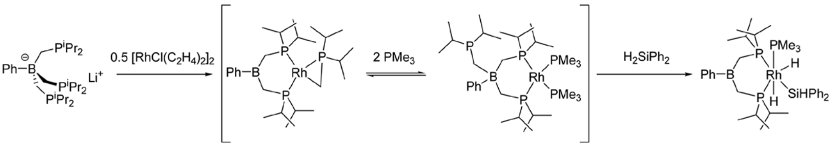


Figure 11. Structure of [PhBP^{R}]Ni(κ^2-CH2PR2), R = Ph, ^{i}Pr.



Scheme 5. Tris(phosphino)borate ligand rearrangements observed in Rh complexes.

κ^2-[PhB(CH$_2$P^{i}Pr$_2$)$_2$]Rh(κ^2-CH$_2$P^{i}Pr$_2$). Remarkably, addition of 2 equiv of PMe$_3$ to this complex results in B-C bond reformation along with decoordination of one phosphine arm to yield κ^2-[PhBP^{iPr}]Rh(PMe$_3$)$_2$. Addition of H$_2$SiPh$_2$ to κ^2-[PhBP^{iPr}]Rh(PMe$_3$)$_2$ also results in B-C bond cleavage to form κ^2-[PhB(CH$_2$P^{i}Pr$_2$)$_2$]Rh(PMe$_3$)(H)$_2$(SiHPh$_2$) in $<50\%$ yield.[75]

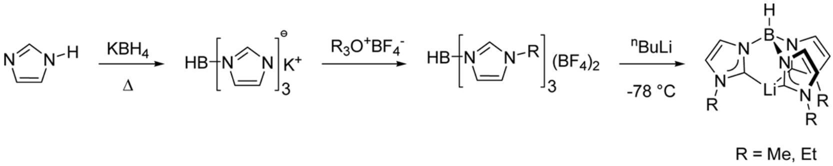
TRIS(CARBENE)BORATES

Design and Synthesis

Threefold symmetric tris(carbene)borate ligands provide a [C$_3$] donor array by virtue of the three imidazol-2-ylidine groups bound to boron. These ligands are among the few multidentate face-capping *N*-heterocyclic carbene donor ligands (others in this class include tris(carbene)-amines and tris(carbene)methylmethanes).[6] The neutral analogues of tris(carbene)borates, i.e., tris(carbene)methanes, are currently unknown.

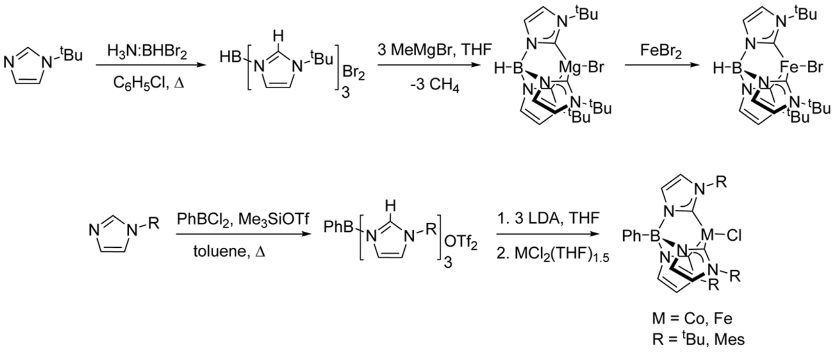
Tris(carbene)borates were first reported by Fehlhammer in 1996,[77] and were prepared by a route that is related to the synthesis of tris(pyrazolyl)borates (Scheme 6). Specifically, potassium hydrotris(1-imidazolyl)borate was prepared by the melt reaction of KBH$_4$ with imidazole. Threefold alkylation of this salt afforded the respective tris(imidazolium) borane dications, which were then deprotonated to yield tris(carbene)borate ligands.[78] Octahedral iron and cobalt complexes containing two tris(carbene)borates were obtained with these relatively unhindered methyl- and ethyl-substituted ligands.

A drawback of this synthetic route is that the alkylation step limits the range of ligand substituents, in particular bulkier alkyl and aryl substituents that would be expected to help stabilize low coordinate metal complexes. This limitation was overcome by a new synthetic route that uses preformed *N*-substituted imidazoles to introduce substituents into the tris(carbene)borate framework (Scheme 7A).[79] The key innovation



Scheme 6. Original synthesis of tris(carbene)borate ligands.

is preparation of the tris(imidazolium) borane dication by reaction of an appropriately substituted imidazole with $Me_3N{:}BHBr_2$. Use of $Me_2S{:}BHBr_2$ as the boron source allows the dications to prepared under milder conditions.[80] Threefold deprotonation of this salt affords bulkier hydrotris(carbene)borate ligands that allow for the isolation of four-coordinate complexes. Substituted phenyltris(carbene)borate ligands, whose complexes are generally more soluble in low polarity solvents, can be prepared by a similar synthetic route (Scheme 7B). In principle, these synthetic routes allow for a wide range of ligands to be prepared; to date tris(carbene)borates containing Me, Et, ^{t}Bu, and 2,4,6-$Me_3C_6H_2$ (mesityl) substituents have been reported. An interesting contrast with tris(pyrazolyl)borate ligands is that 1,2-boratropic shifts have never been observed in tris(carbene)borates. For example, mesityl-substituted tris(carbene)borates are found to be stable, in contrast to the tris(3-mesitylpyrazolyl)borate ligand, where isomerization to the bis(3-mesitylpyrazolyl)(5-mesitylpyrazolyl)borate ligand can occur.[81] Tris(carbene)borate ligands typically coordinate to metal complexes in a κ^3-*C*,*C*,*C* mode,



Scheme 7. Synthetic route providing access to bulky tris(carbene)borate ligands. Top: Hydrotris(carbene)borates. Bottom: Phenyltris(carbene)borates.

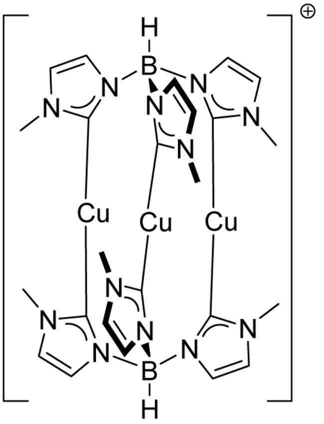


Figure 12. Trimer structure of $\{[HBC^{Me}]_2Cu\}_3[BF_4]$.

although the copper(I) complex $\{[HBC^{Me}]_2Cu\}_3[BF_4]$ is a trimer in which each copper ion is coordinated to both tris(carbene)borate ligands in an $\mu_3{:}\kappa^1{:}\kappa^1{:}\kappa^1$ mode (Fig. 12).[82] A similar coordination mode is believed to occur in the related silver and gold complexes.[80]

Electronic Properties

Imidazol-2-ylidine based *N* -heterocyclic carbenes are very strong σ-donors, as illustrated by the relatively high pK_a of the conjugate acid.[83,84] While the extent of π-interactions between NHC ligands and metal centers is still under debate, it is generally accepted that these ligands may have π-acceptor properties,[85,86] although in some instances π-donation has been proposed.[87,88] It is likely that the extent of π-bonding will depend on the nature of the metal complex.[89] The electrostatic component of bonding between NHC ligands and metals may also be significant.[90] Regardless of the precise nature of the metal NHC interaction, there is substantial evidence that monodentate NHCs are more strongly donating than the most strongly donating phosphines, e.g., P^tBu_3.[89]

With this in mind, it is perhaps not surprising that tris(carbene)borate ligands are the most strongly donating scorpionate ligands currently known. As described above, the position of ν(NO) in the IR spectrum of $[HBC^{Me}]Ni(NO)$ is at a longer wavelength than any related ligands. The position of ν(NO) in the IR spectra of other tris(carbene)borate nickel nitrosyl complexes shows the impact of ligand substituents on its

Table 6. IR spectroscopic data of $[RBC^{R'}]NiNO$ complexes

R	R′	$\nu(NO)/cm^{-1}$
H	^{t}Bu	1703
Ph	^{t}Bu	1701
Ph	Me	1697
Ph	Mes	1724

donating ability (Table 6): (1) there is a significant electronic difference between alkyl and aryl substituents, in contrast to monodentate *N*-heterocyclic carbene ligands;[89] and (2) the nature of the non-coordinating group on boron (i.e., H *vs*. Ph) has little effect on the electronic properties of the ligand.

Electrochemical measurements of octahedral homoleptic tris(carbene)borate complexes support these spectroscopic results. For example, both the $+2/+3$ and $+3/+4$ waves in the CV of $[PhBC^{Me}]_2Mn$ occur at potentials that are over 1 V lower than for analogous complexes of other face-capping ligands (Table 7). Thus the tris(carbene)borate ligand is significantly more stabilizing of higher oxidation states, presumably due to its very strong donor ability. Similar results are observed for $[HBC^{Me}]_2Fe$ (Table 8), where it was reported that the complex could also be electrochemically oxidized to Fe(IV). This high oxidation state was reported to be stable under inert conditions, although the complex was not isolated.[78] By comparison, oxidation of Cp_2Fe, Cp_2^* Fe and Tp_2Fe to Fe(IV) is much more difficult, and has only been accomplished in liquid SO_2 at −40°C.[91]

Table 7. Cyclic voltammetry data of six coordinate homoleptic manganese complexes supported by face-capping ligands. Potentials measured in $MeCN/NBu_4PF_6$ and referenced to Fc/Fc^+

Ligand	II/III	III/IV	Reference
PhB^{Me}	-2.09^a	−0.77	95
Tp^{*a}	−0.13	0.99	141
Cp^*	−0.94		142
Tp^b	0.06	1.31	141

[a] Quasireversible.

[b] In $C_2H_4Cl_2$, NBu_4PF_6 electrolyte.

Table 8. Cyclic voltammetry data of six coordinate homoleptic iron complexes supported by face-capping ligands. All potentials measured relative to Fc + /Fc

Ligand	II/III	III/IV	Reference
$HBC^{Me,a}$	− 1.23	0.87	78
Tp^{b}	− 0.17	1.73	91
Cp^{b}	0.00	1.87^{c}	91
$Cp^{*,b}$	− 0.48	1.39	91

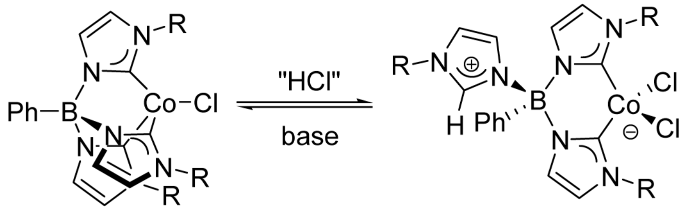
[a] Measured in MeCN, NBu_4PF_6 electrolyte.

[b] Measured in liquid SO_2, −40°C, NBu_4PF_6 electrolyte.

[c] Cp_2Fe^{2+} is reported to be unstable under these conditions.

Given their topological similarity to tris(pyrazolyl)borates, it is not surprising that suitably bulky tris(carbene)borate ligands are able to stabilize low coordinate metal complexes. Four-coordinate iron,[79,92] cobalt[93] and nickel[94] complexes have so far been prepared with *tert*-butyl and mesityl-substituted tris(carbene)borates. These ligands have not been as fully investigated as other strongly donating scorpionates, and the scope of their coordination chemistry has yet to be determined. However, it is striking that despite the very strong donor ability of tris(carbene)borates, all known four-coordinate tris(carbene)-borate Co(II) complexes are high spin, in contrast to the tris(phosphino)-borate complexes $[PhBP^{R}]CoX$ (see above). It is likely that the greater flexibility of $PhBP^{R}$ ligands play a significant role in stabilizing the low spin state.

The strong donor ability of tris(carbene)borate ligands has been found to induce unexpected chemistry. For example, the manganese tricarbonyl complex $[PhBC^{Me}]Mn(CO)_3$ is unexpectedly sensitive to oxygen, in stark contrast to the hundreds of air stable complexes containing the $Mn(CO)_3$ unit. In a remarkable transformation, $[PhBC^{Me}]Mn(CO)_3$ is oxidized by O_2 over the course of a few days to the homoleptic Mn(IV) complex $[PhBC^{Me}]_2Mn^{2+}$, a rare example of an air-stable Mn(IV) organometallic complex.[95] The nature of the counter ion initially formed is unknown, although carbonate has been excluded by IR spectroscopy. Following metathesis of the anion to tetrafluoroborate, the final product is obtained in almost 50% yield as based on manganese. The mechanism of this transformation is currently unknown.



Scheme 8. Reversible protonation of tris(carbene)borate ligand in PhBC^{R}CoCl (R = ^{t}Bu, Mes).

Ligand Reactivity

The high basicity of the tris(carbene)borate ligands can make them highly sensitive to sources of acid. In some cases, even trace acid is sufficient to protonate the ligand. The divalent cobalt complex [PhBC^{tBu}]CoCl is highly sensitive to trace sources of acid, and is reversibly protonated to form the zwitterion κ^2-PhB(^{t}BuIm)$_2$(^{t}BuImH)CoCl$_2$ (Scheme 8).[93] Both of these complexes have been isolated in the solid state. The related complex [PhBC^{Mes}]CoCl is even more acid sensitive, and all attempts to isolate this spectroscopically observable complex in the solid state have been unsuccessful. Only the zwitterion κ^2-PhB(MesIm)$_2$(MesImH)CoCl$_2$ has been isolated. Interestingly, addition of 1 equivalent of acid to the methyl complex [PhBC^{tBu}]CoMe results in a 1:1 mixture of [PhBC^{tBu}]CoCl and κ^2-PhB(^{t}BuIm)$_2$(^{t}BuImH)CoCl$_2$. The lower acid sensitivity of the methyl complex has been ascribed to two factors: (1) a change in the nature of the HOMO from Co-carbene antibonding in [PhBC^{tBu}]CoCl to Co-Me antibonding in [PhBC^{tBu}]CoMe; (2) greater steric protection of the metal center by the more bulky methyl group.

QUANTIFICATION OF SCORPIONATE FLEXIBILITY

As described in previous sections, the flexibility of the scorpionate ligand can influence the properties of the metal complex. Although all the strongly donating scorpionates discussed are facially coordinating, by virtue of the different linkages between boron and the metal center they vary in their flexibility. This flexibility affects the topology of the ligands as well as their steric properties.

The high degree of flexibility of tris(thioimidazolyl)borate ligands has previously been recognized and parameters to describe their flexibility have been proposed.[33] One such parameter is the angle θ, which

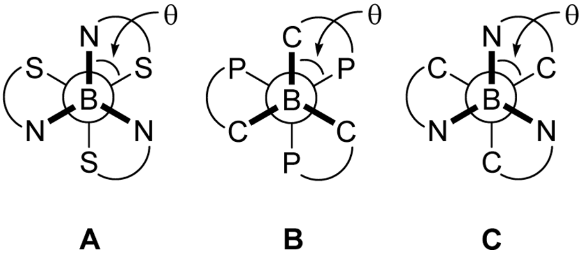


Figure 13. Definition of θ for **A**: tris(thioimidazolyl)borate; **B**: tris(phosphino)borate; and **C**: tris(carbene)borate ligands.

measures the N-B-M-S torsional angle for each thioimidazolyl arm (Fig. 13A), and describes the chiral twist of the tris(thioimidazolyl)-borate ligand (i.e., distortion from C_{3v}). The same parameter can be adopted to describe similar twisting in complexes of tris(phosphino)-borate and tris(carbene)borate ligands (Fig. 13 B and C). It should be noted that the sign of θ describes the absolute configuration of the ligand; only absolute values of this parameter are used in the discussion below.

Comparison of average absolute θ values obtained from crystallographic data clearly shows the differences in flexibility between the three ligands (Fig. 14). The ring strain inherent to the eight-membered chelate rings of the bicyclo[3.3.3] cage in tris(thioimidazolyl)borate complexes causes these ligands to have the greatest amount of twisting, and thus the largest average θ values. The methylene linker allows for some degree of twisting in PhBP ligands, as reflected by the intermediate θ values, while tris(carbene)borate ligands have the least amount of twisting due to the rigidity of the planar imidazol-2-ylidene rings. Substantial twisting of the tris(carbene)borate ligands ($\theta > 10°$) is only observed with bulky ancillary ligands.[96] Interestingly, the range of θ values (0 – 52°) observed for tris(phosphino)borate ligands is greater than the other two ligands, suggesting these ligands have some flexibility in accommodating the demands of the metal center and ancillary ligands.

While the metal center is always out of the plane defined by the three donor groups of the scorpionate, the extent to which this occurs is determined by the flexibility of the ligand. One measure of the out of plane displacement is ϕ, the average of the angles between the donor atoms of the scorpionate ligand and the fourth ligand, X, in four coordinate metal complexes (Fig. 15). Small ϕ values will be observed when the

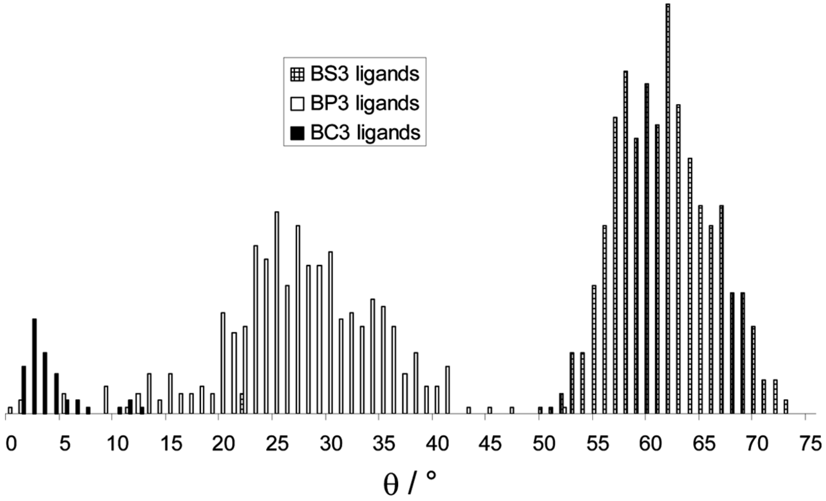


Figure 14. Histogram showing range of average absolute values of θ for strongly donating scorpionate ligands.

metal lies closer to the ligand plane ($\phi = 90\ ^\circ$ when the metal is in the plane). This parameter is independent of the nature of the metal center and donor atoms of the ligand.

The ϕ data show similar trends to the θ values. In general, tris(thioimidazolyl)borate ligands have the smallest ϕ angle, followed by tris(phosphino)borate and tris(carbene)borate ligands (Fig. 16). Thus, the metal is closest to the ligand plane in tris(thioimidazolyl)borates, reflecting the high degree of flexibility in these ligands. There is a greater degree of displacement in tris(phosphino)borate complexes, while the metal is displaced furthest from the plane in complexes supported by the rigid tris(carbene)borate ligands.

The steric properties of the scorpionate ligand will be affected by the substituents on the ligand, the size of the donor groups as well as the

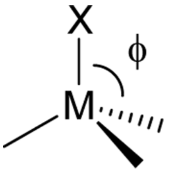


Figure 15. Definition of ϕ for four-coordinate scorpionate complexes.

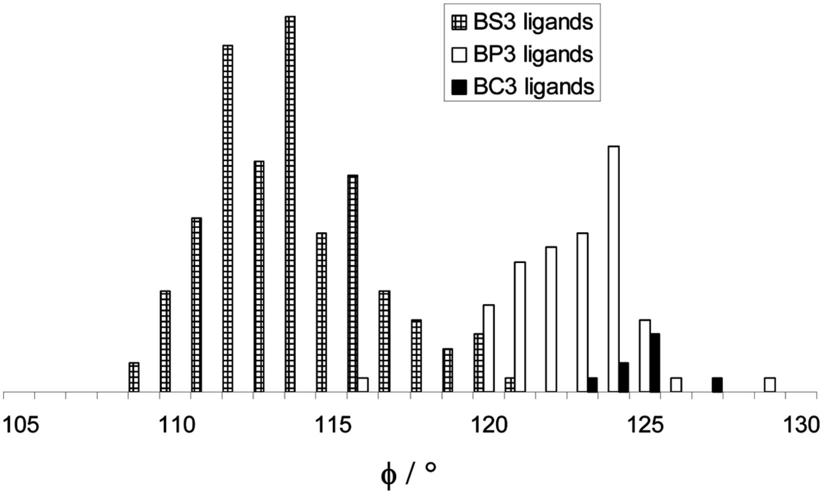


Figure 16. Histogram showing range of average ϕ values for strongly donating scorpionate ligands.

ligand flexibility. Space filling diagrams of [HBS^{tBu}]FeCl, [PhBP^{iPr}]FeCl and [PhBC^{tBu}]FeCl show that although the three ligands have similar substituents, their different topologies influence the size of the pocket created at the metal center (Fig. 17). The size of this pocket depends on the steric properties of the ligand, which can be quantified by the Tolman cone angle.[97]

Tolman cone angles for seven strongly donating scorpionate ligands have been calculated from crystallographic data (Table 9). To allow for direct comparison, the cone angles have been calculated from four

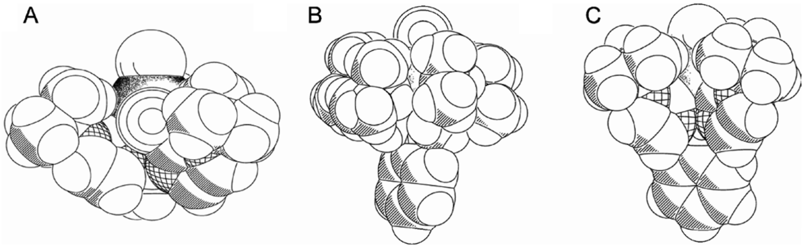


Figure 17. Space filling diagrams of iron(II) chloride complexes, showing the differences in topology between the scorpionate ligands. **A**: HBS^{tBu}; **B**: PhBP^{iPr}; **C**: PhBC^{tBu}.

Table 9. Tolman cone angles for scorpionate ligands, measured in high spin, four-coordinate iron(II) chloride complexes

Ligand class	Ligand	Cone angle (°)[a]
Tris(pyrazolyl)borates	Tp^{tBu}	290
Tris(thioimidazolyl)borates	HBS^{tBu}	258
	HBS^{Ph}	250
	$PhBS^{Ph}$	264
Tris(phosphino)borates	$PhBP^{iPr}$	281
	$PhBP^{CH2Cy}$	287
Tris(carbene)borates	$PhBC^{tBu}$	286
	$PhBC^{Mes}$	270

[a] Cone angles were calculated from crystallographic data using the program *Steric.*[143]

coordinate, high spin iron(II) chloride complexes, e.g., $[HBS^{tBu}]FeCl$. The cone angle of the bulky tris(pyrazolyl)borate, Tp^{tBu}, has also been calculated from the corresponding $Tp^{tBu}FeCl^{98}$ complex (this cone angle differs from the published value for Tp^{tBu}, which was calculated from the crystal structure of $Tp^{tBu}Tl$).[1] The cone angles reveal that tris(thioimidazolyl)borates are the least sterically encompassing. Tris(phosphino)-borate, tris(carbene)borate and tris(pyrazolyl)borate ligands with bulky alkyl substituents are the most demanding, with the relative order $PhBP^{iPr} < PhBC^{tBu} \approx PhBP^{CH2Cy} < Tp^{tBu}$. Aryl-substituted tris(carbene)borate and tris(phosphino)borate ligands are intermediate in size. For similar ligand substituents, the size of strongly donating scorpionate ligands follows the general order: $HBS^R < PhBP^R \leq PhBC^R$.

STABILIZATION OF METAL-LIGAND MULTIPLE BONDS

Strongly donating scorpionate ligands have proven to be very useful in stabilizing multiple bonds between late transition metals and ligands, in particular imidos (NR^{2-}) and nitridos (N^{3-}). Multiply bonded ligands in iron and cobalt complexes supported by tris(phosphino)borate and tris(carbene)borate ligands have been reported. Analogous complexes containing late metal-ligand multiple bonds supported tris(thioimidazolyl)borate ligands are as yet unknown.

The electronic reasons for stabilization of four-coordinate late metal ligand multiple bonds have been discussed in detail,[99–101] and will be briefly mentioned here. In C_{3v} symmetry, the metal d-orbitals are split

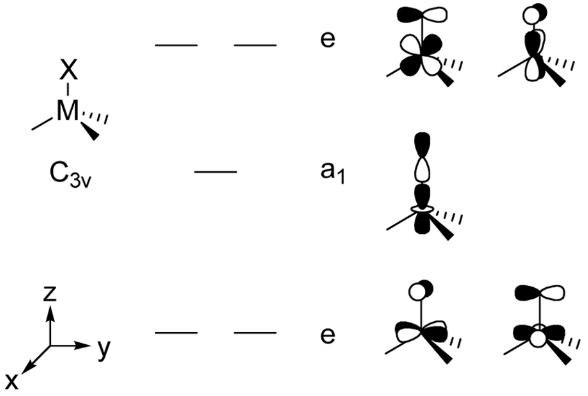
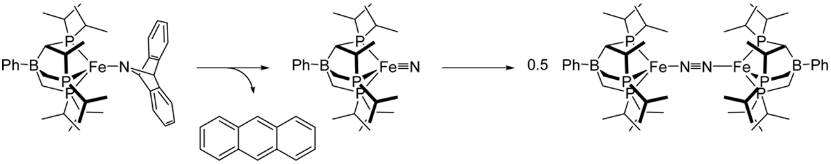


Figure 18. Generic MO diagram for metal complexes in C_{3v} symmetry.

into two e sets (d_{xy}, $d_{x^2-y^2}$ and d_{xz}, d_{yz}) and one a_1 set (d_{z^2}) (Fig. 18). A key feature of this orbital splitting is that the M≡L π^* orbitals (d_{xz}, d_{yz}) are highest in energy. This orbital arrangement allows more than two d electrons to be accommodated without destabilizing the M≡L bond. This is in contrast to octahedral geometry, where the addition of more than two d-electrons results in occupation of M = L antibonding orbitals. Additional stabilization of the a_1 orbital may occur through mixing of the metal nd_{z^2} orbital with empty (n + 1)s and $(n+1)p_z$ orbitals, which significantly reduces M-L σ^* interactions.[102]

The first examples of terminal imido complexes of cobalt(III),[103] iron(III)[104] and iron(II)[105] were supported by tris(phosphino)borate ligands. The trivalent complexes were formed by reaction of a monovalent synthon with an organic azide (RN_3) to produce the imido complex with loss of N_2. Despite the susceptibility of the tris(phosphino)borate ligand towards oxidation, it is striking that the locus of oxidation is the metal and not the ligand. This contrasts with the reaction of PhN_3 with cobalt(I) complexes of bis(phosphine)amido ligands, where one of the phosphine donors of the supporting ligand is ultimately oxidized.[106,107] The tris(phosphino)borate imido complexes are all sufficiently stable to be characterized by X-ray crystallography. Interestingly, an attempt to prepare an alkylidene complex from a cobalt(I) synthon and Ph_2CN_2 was not successful, leading instead to the diazenido complex $[PhBP^{Ph}]Co=N=N=CPh_2$ without loss of N_2.[103]

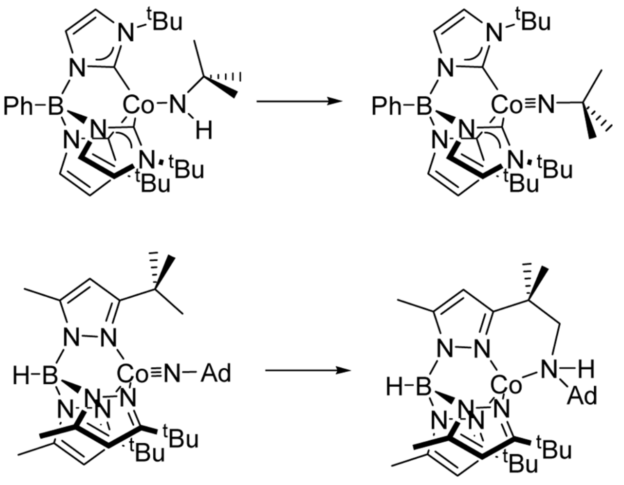


Scheme 9. Synthesis and decomposition of an iron(IV) nitrido complex supported by a tris(phosphino)borate ligand.

The first iron(IV) nitrido complex $[PhBP^{iPr}]Fe{\equiv}N$ was prepared by anthracene extrusion from $[PhBP^{iPr}]Fe(dbabh)$. The complex cannot be isolated in the solid state as it decomposes by reductive coupling to form the iron(I) dimer, $[PhBP^{iPr}]Fe\text{-}N{\equiv}N\text{-}Fe[PhBP^{iPr}]$ (Scheme 9).[74] The related complex $[PhBP^{CH_2Cy}]Fe{\equiv}N$ can also be prepared *in situ*, although it appears to decompose by different pathways.[108] A range of spectroscopic techniques have therefore been used to confirm the complexes' designation as four coordinate iron(IV) nitridos. Attempts to prepare $[PhBP^{Ph}]{\equiv}N$ have been unsuccessful.[105]

Tris(carbene)borates have also been found to be effective in stabilizing multiple bonds to late transition metals, specifically iron[92] and cobalt.[96]A diamagnetic cobalt(III) imido complex can be prepared from the corresponding cobalt(II) amido in a single step by reaction with the stable 2,4,6-tri-*tert*-butylphenoxy radical. The results of DFT calculations of the thermodynamic barriers towards stepwise and concerted mechanisms are most consistent with a concerted reaction involving the transfer of a hydrogen atom from the amido N-H to the phenoxy radical, i.e., proton-coupled electron transfer.[96] Intriguingly, this reaction proceeds in the *opposite* direction to that observed for the tris(pyrazolyl)-borate cobalt(III) imido complex $Tp^{tBu,Me}Co{\equiv}NAd$, which abstracts hydrogen atoms from C-H bonds of the tris(pyrazolyl)borate ligand (Scheme 10).[109,110] The difference in reactivity may be due to better stabilization of the higher oxidation state by the more strongly donating tris(carbene)borate ligand.

Similarly to tris(phosphino)borate complexes, tris(carbene)borate iron(III) imido complexes $[PhBC^{Mes}]Fe{\equiv}NR$ ($R = {}^{t}Bu$, Ad) can also be prepared by reaction of an iron(I) synthon with an organic azide.[92] An interesting contrast with tris(phosphino)borate iron imido complexes is that $[PhBC^{Mes}]Fe{\equiv}NAd$ is easily oxidized to a thermally stable iron(IV) complex, but cannot be reduced to iron(II).



Scheme 10. Dependence of the direction of hydrogen atom transfer in cobalt imido complexes on the nature of the supporting scorpionate ligand.

Bulky tris(carbene)borate ligands have also allowed iron(IV) nitrido complexes to be isolated.[102] It is notable that the only other iron(IV) nitrido complexes are also supported by tripodal NHC donor ligands; however, these complexes are positively charged since the tris(carbene)amine supporting ligand is neutral.[111] It is likely that the greater stability of these isolable nitrido complexes is in part due to the topology of the supporting tris(carbene) ligand, which prevents the reductive coupling reaction that is observed for $[PhBP^{iPr}]Fe{\equiv}N$. However, electronic factors cannot be completely excluded at this stage.

BIDENTATE LIGANDS

As with tris(pyrazolyl)borates, strongly donating borate ligands that contain only two donor groups have been reported, i.e., bis(phosphino)-borates, bis(thioimidazolyl)borates and bis(carbene)borates. These ligands are designed to bind to metals in a bidentate fashion, although tridentate binding involving B-H agostic bonds is also observed in some bis(thioimidazolyl)borate complexes.

Dihydrobis(thioimidazolyl)borate ligands H_2BS^R are prepared by heating stoichiometric amounts of the reagents at lower temperatures than used for the tripodal analogues. Despite the expectation that these ligands will bind to a metal center in a bidentate κ^2-S,S mode, the

κ^3-*S,S,H* coordination mode is a common structural motif. A similar coordination mode has been observed in some bis(pyrazolyl)borate complexes.[112] For example, the homoleptic nickel(II) complex $[H_2BS^{Me}]_2Ni$ is six coordinate with a distorted octahedral NiS_4H_2 core (Fig. 19).[113] Tridentate bis(thioimidazolyl)borate ligands are less strongly donating than tris(thioimidazolyl)borate ligands, as evidenced by the positions of ν(CO) in the IR spectra of $Re(CO)_3$[114] and $Mn(CO)_3$[30] derivatives, which are at higher frequencies than the corresponding tris(thioimidazolyl)borate complexes. In some cases,[115,116] but not all,[30] the B-H-M linkages can be disrupted to provide κ^2-*S,S* ligands.

Synthesis of bis(phosphino)borate ligands is achieved in a similar manner as tris(phosphino)borates.[117] A comprehensive investigation of platinum(II) carbonyl derivatives of substituted bis(phosphino)borate ligands has found that: (1) alkyl substituted phosphines have the greatest donor strength; (2) changes to the *p* -position of aryl substituted phosphines has a small effect on the ligand donor strength; and (3) changing the bridgehead boron groups has essentially no effect on the ligand donor strength. The anionic bis(phosphino)borates are found to be stronger donors than related neutral bis(phosphine) ligands.[117]

Depending on the desired ligand substituents, dihydrobis(carbene)-borate ligands can be prepared by suitable modification of either of the synthetic methods used for the hydrotris(carbene)borates.[118,119] The strong donor ability of bis(carbene)borate ligands is illustrated by the homoleptic nickel(II) complex $[H_2BC^{tBu}]_2Ni$, which is diamagnetic and square planar, in contrast to the related bis(pyrazolyl)borate

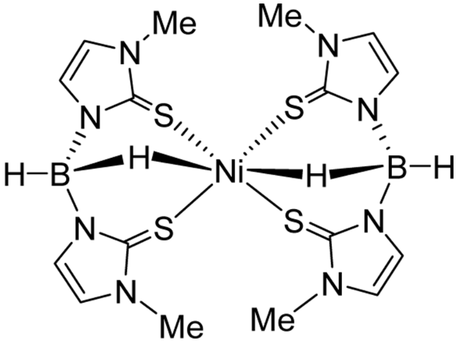


Figure 19. Six-coordinate structure of the homoleptic complex $[H_2BS^{Me}]_2Ni$ that has a NiS_4H_2 core.

complex $Tp_2^{tBu}Ni$, which is paramagnetic and six coordinate with an NiN_4H_2 core.[112]

SUMMARY AND OUTLOOK

In their relatively short existence, strongly donating scorpionate ligands have had a profound impact in coordination chemistry, with applications in catalysis,[73] bioinorganic modeling[9] and materials chemistry.[62,120] More importantly, these ligands have opened up new areas of research. For example, tris(thioimidazolyl)borates have allowed for synthesis of the first metalloboratrane complexes, while tris(phosphino)borate and tris(carbene)borate ligands have allowed for the isolation of the first terminal late metal imido and nitrido complexes. Subtle differences in the topology, flexibility, and donor properties of these ligands can lead to dramatically different properties in their metal complexes.

The design of strongly donating scorpionate ligands continues to evolve. Hybrid ligands that contain more than one type of donor have been introduced (e.g., bis(pyrazolyl)(phosphino)borates[121] and bis(phosphino)(pyrazolyl)borates[122]), and are expected to allow for finer tuning of electronic properties. Other design motifs that owe their inspiration to scorpionates include strongly donating tripodal ligands with carbon[123] and silicon[124] bridgehead atoms. It is likely that other boron-free ligand designs will be reported in future. New scorpionates with other strong donors are likely. For example, the bidentate bis(4-benzyl-1,2,4-triazol-5-ylidene-1-yl)dihydroborate ligand, which incorporates triazolylidene donors, has recently been reported (Fig. 20).[125] Extension of this ligand system to tridentate scorpionates should be straightforward. Provided synthetic challenges can be overcome, strongly donating scorpionates

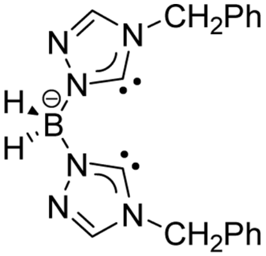


Figure 20. Bidentate bis(4-benzyl-1,2,4-triazol-5-ylidene-1-yl)borate ligand.

based on other donors can be envisioned, e.g., guanidines,[126] diaminocarbenes,[127] and other heterocyclic carbenes.[128,129]

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