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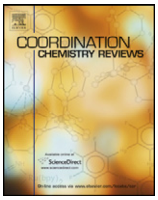

Review

# Coordination chemistry of poly(thioether)borate ligands

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**Contents**

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Dedicated to Daryle Busch in recognition of his broad ranging contributions to contemporary coordination chemistry.

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ABSTRACT

This review traces the development and application of the tris(thioether)borate ligands, tripodal ligands with highly polarizable thioether donors. Areas of emphasis include the basic coordination chemistry of the mid-to-late first row transition metals (Fe, Ni, Co, Cu), and the role of the thioether substituent in directing complex formation, the modeling of zinc thiolate protein active sites, high-spin organo-iron and organo-cobalt chemistry, the preparation of monovalent complexes of Fe, Co and Ni, and dioxygen and sulfur activation by monovalent nickel complexes.

## 1. Introduction

The development of polydentate ligands represents a central feature of modern synthetic chemistry with applications including coordination, supramolecular [1], organometallic and bioinorganic chemistry as well as catalyst development in areas as diverse as organic synthesis [2] and alternative energy production [3]. The ligand characteristics impact the resulting complex composition, structure and reactivity by controlling nuclearity, stereochemistry, spin states and the overall electronic structure of the metal ion. Further, while most attention has focused on attenuating the metal ion's primary coordination sphere, lessons from biology have inspired the development of rigid motifs that impinge on the second coordination sphere as well [4]. Among the most widely used polydentate ligands are tripodal frameworks that provide three donors in a facial arrangement. The archetype of this family is the cyclopentadienyl ligand (Cp) [5] and its relatives, e.g. pentamethylcyclopentadienyl ($Cp^*$), ligands that were the genesis of modern

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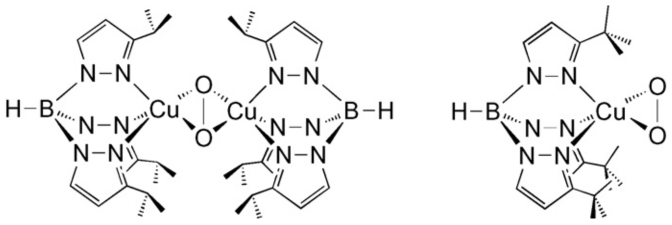
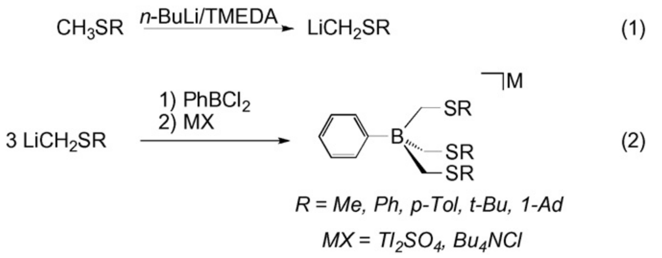


**Fig. 1.** Kitajima's $[Tp^R]Cu$ peroxo (left) and superoxo (right) complexes.



R = Me, Ph, p-Tol, t-Bu, 1-Ad

MX = $Tl_2SO_4$, $Bu_4NCl$

**Scheme 1.** Ligand synthesis.

organometallic chemistry. Cp is a pseudo-face capping ligand that binds as an anion providing six electrons. By a number of criteria the hydridotris(pyrazolyl)borates (Tp) [6] may be considered the second major member of the monoanionic tripodal ligand family. While isoelectronic with Cp ligands, the Tp donors afford significantly greater diversity due to the extensive range of pyrazole ring substituents that can be added [6]. One illustrative example is a comparison of the oxygen derivatives of $[Tp^{iPr2}]Cu$ and $[Tp^{tBu}]Cu$ (Fig. 1). Whereas, the former complex is dimeric with a $\mu$-$\eta^2$:$\eta^2$-peroxo bridge [7], the steric requirements of the 3-*tert*-butyl pyrazole substituents in the latter enforce a monomer, with side-on superoxide ligation [8].

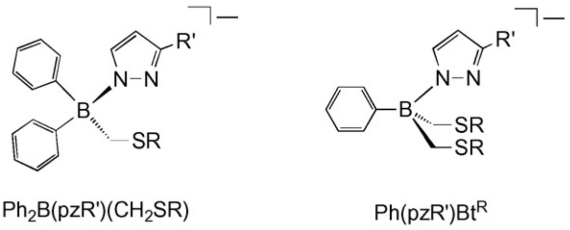
Inspired by the success of the Cp and Tp ligands in a diverse range of applications, a large number of $L_2X$ tripodal ligands have been introduced in the past fifteen years. Among these are ligands with strong field donors such as tris(phosphino)borates ($PhBP_3$) [9] and tris(carbene)borates [10] and hybrid ligands [11] containing two (or sometimes three) different heteroatom donors. Less common are tripodal ligands possessing sulfur heteroatom donors. Members of this latter class include the poly(thioether)borates (Tt) [12] and the poly(methimazolyl)borates (Tm). The latter donors were introduced by Reglinski and co-workers in 1996 [13]. The former ligands have been extensively developed in these laboratories. As highlighted in this review, since their inception in 1994 [12], the Tt ligands have been developed and used in a range of contexts with studies including evaluation of their fundamental coordination characteristics and selected applications in bioinorganic and organometallic chemistry and small molecule activation by monovalent complexes of nickel and iron.

## 2. Ligand design and synthesis

The poly(thioether)borate ligands were introduced by this laboratory fifteen years ago to fill a perceived void in the types of tripodal ligands available for a variety of coordination and bioinorganic chemistry pursuits [12]. Specifically, we sought a monoanionic tripodal ligand containing highly polarizable donor groups, e.g. thioether sulfurs, reasoning that the latter attribute would afford access to lower valent metal complexes, e.g. nickel(I). We were certainly inspired by the utility Trofimenko's Tp ligands in a broad range of synthetic applications. In particular, at the time our work commenced Trofimenko had already introduced his second-generation ligands [14], those with larger substituents on the pyrazole, that proved effective in supporting lower coordinate metal complexes of the form, $[Tp^R]MX$. We reasoned that substitution on the thioether sulfur of poly(thioether)borates could have similar steric and electronic impact on the ligand derivatives. Indeed, given the substituent of the poly(thioether)borate ligand is attached directly to the metal donor atom, their influence should in principle be more pronounced than those of the $[Tp^R]$ ligands. Analogy with 1,4,7-trithiacyclononane (ttcn), a neutral tris(thioether) ligand is also relevant [15]. The coordination chemistry of ttcn is dominated by coordinatively saturated complexes of the form $(ttcn)_2M$ due to the lack of steric bulk around the donor atoms. The further development of ttcn derivatives entails modifications of the carbon backbone of the ligand and synthetic approaches to such derivatives require potentially dangerous synthetic intermediates, i.e. mustard gas analogs. Alternatively, neutral analogs of the Tt in which the boron is replaced with silicon have been shown to be labile, dissociating in coordinating solvents [16], highlighting the importance of the anionic charge of the borate in stabilizing chelation to charged metal ions.

While the initial ligand introduced was tetrakis ((methylthio)methyl)borate (termed (RTt)), we quickly focused attention on tris(thioether)borates in which the fourth boron substituent is a phenyl group [17]. It should be noted that while the [Tp] (and [Bp]) ligands contain the B–H linkage, similar substitution in the poly(thioether)borates leads to derivatives, which are highly hydridic and consequently sensitive to moisture. This property is not surprising given the substitution pattern at boron of a hydride and three alkyl groups is analogous to the 'super hydride' reagent, $LiBEt_3H$. The phenyltris(thioether)borate ligands are prepared conveniently following the two-step protocol outlined in Scheme 1 [18]. The first step is deprotonation of a methyl sulfide by BuLi/TMEDA, followed by quenching of the resulting organolithium, $LiCH_2SR$, with 1/3 equivalent of $PhBCl_2$. The ligand salts are isolated as white air-stable solids, with the choice of counter ion dependent on the identity of the thioether. For example, we found it convenient to work with $NBu_4^+$ salts of [PhTt], whereas the $Tl^+$ salts of $[PhTt^{tBu}]$ and $[PhTt^{Ad}]$ are commonly employed. This strategy has been utilized to prepare bidentate ligands, $[Ph_2Bt^R]$ [19,20], although the coordination chemistry of these ligands is less extensively developed providing an avenue for future development. Replacement of $PhBCl_2$ with $Fc\text{-}BBr_2$ allows for the synthesis of tris(thioether)borates containing the redox active ferrocenyl moiety, [FcTt] [21].

Modifying the synthetic protocol allows for the preparation of hybrid ligands containing both thioether and pyrazole donor groups. Tridentate ligands containing two thioethers and one pyrazole and bidentate ligands with one thioether and one pyrazolyl donor have been synthesized (Fig. 2) [22]. The one thioether, two pyrazole hybrid ligand that completes the series, $[S_3]$, $[S_2N]$, $[SN_2]$, $[N_3]$ has recently been reported [23]. The mixed donor ligands were prepared in one pot by sequential addition of $LiCH_2SR$ followed by lithium pyrazolylate [24]. With R = Me, the ligands were isolated as their $Bu_4N^+$ salts, whereas when R = *t*-Bu, we found it convenient



$Ph_2B(pzR')(CH_2SR)$ $Ph(pzR')Bt^R$

R = Me, $^tBu$, R' = H, $^tBu$

**Fig. 2.** [SN] and $[S_2N]$ borate ligands.