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Tris(pyridyl)borates: an emergent class of versatile and robust polydentate ligands for catalysis and materials applications

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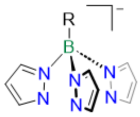
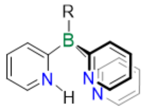
Tridentate ligands that incorporate pyridyl rather than pyrazolyl groups are emerging as an attractive class of “scorpionate”-type ligands with enhanced electron donation, increased stability, and divergent geometry at the metal centre relative to tris(pyrazolyl)borates originally introduced by Trofimenko. Following our initial reports, the tris(pyridyl)borate (Tpyb) ligand architecture has been adopted by several research groups in pursuit of functional metal complexes that offer new opportunities in catalysis and materials science. While earlier work had been focused on symmetric octahedral complexes, ML_2, which are advantageous as highly robust building blocks in materials sciences, recently introduced new ligand designs provide access to heteroleptic metal complexes with vacant sites that lend themselves to applications in catalysis. Signficant progress has also been made in the post-complexation functionalization of these ligands via electrophilic and nucleophilic substitution reactions at the boron centres, opening up new routes for integration of Tpyb complexes with diverse functional materials while also raising interesting mechanistic questions.

Introduction

Since the introduction of tris(pyrazolyl)borates (Tp) in 1966,[1] “scorpionates” have become one of the most-studied classes of ligands in organometallic chemistry.[2-8] Scorpionates consist of three (usually heterocyclic) ligating functional groups attached to a bridgehead atom, resulting in tridentate ligands that typically adopt a facial coordination geometry. Altering the ligating groups allows for the coordinating atom to be varied, along with the sterics and electronics of the Lewis basic functionality, while changing the bridgehead atom can adjust the charge, bite angle, and electronic structure of the ligand. The bond between the bridgehead and the heterocycle is also of great importance to the stability and reactivity of the respective metal complexes, with labile bonds potentially leading to undesired reactivity and ligand/complex decomposition. Specifically, the lability of the B-N bond in tris(pyrazolyl)borate ligands can hamper the stability of their complexes and thus in some cases limit their utility in catalysis and other applications.[9, 10]


Trofimenko et. al., 1966


Jäkle et. al., 2012

	Tp	Tpyb
Bond Dissociation Energy (kJ/mol)		
	B-N 378	B-C 448
Thermochemical Electronegativity Difference		
	B-N 0.52	B-C 0.11
Ligand Steric Effects		
	B-N shorter	B-C longer
	B-N-N larger	B-C-N smaller
pK_a of Constituting Donor		
	Pyrazole 9.1	Pyridine 12.5

Figure 1. Comparison of tris(pyrazolyl)borate (Tp) and tris(pyridyl)borate (Tpyb) ligands. Data from references 16 (bond dissociation energies), 11 (thermochemical electronegativities) and 17 (pK_a values).

In 2012, our group introduced tris(pyridyl)borate (Tpyb) ligands which replace the B-N bonds with stronger and less polar[11] B-C bonds (Figure 1).[12] The replacement of the five-membered pyrazole (Pz) with six-membered pyridine (Py) rings also alters the binding geometry and bite angle of the ligand. This is evident, for example, when comparing the B-N (Tp, average 1.55 Å) and B-C (Tpyb, average 1.64 Å) bond lengths and the B-N-N (Tp, average 119.1) and B-C-N (Tpyb, average 116.9) bond angles for the octahedral Fe(II) complexes[12-15] of Ph-substituted Tp and Tpyb ligands. Furthermore, as a better σ-donor than pyrazole, pyridine is expected to more strongly donate to the metal centre (pK_a (pyridine) = 12.5, pK_a (pyrazole) = 9.1 for conjugate acid in CH_3CN).[17] This trend was recently verified computationally for the 6-trifluoromethylated Tpyb derivative, $[PhB(6\text{-}(CF_3)Py)_3]^-$, for which a much higher proton affinity is predicted (1121.0 kJ mol^{-1}) in comparison to the Tp analog $[PhB(3\text{-}(CF_3)Pz)_3]^-$ (1069.2 kJ mol^{-1}).[18]

In an earlier review we have summarized the initial discovery of Typb ligands and the formation of homoleptic complexes.[6] This Frontier article describes our work on Tpyb ligands and metal complexes, as well as recent efforts by other groups exploring the properties and applications of this family of ligands and their complexes. Our work to date has focused primarily on the formation of homoleptic octahedral metal complexes, their further elaboration via post-functionalization,[19, 20] supramolecular assembly,[21] as well as incorporation into polymeric materials[22, 23]. Recently,

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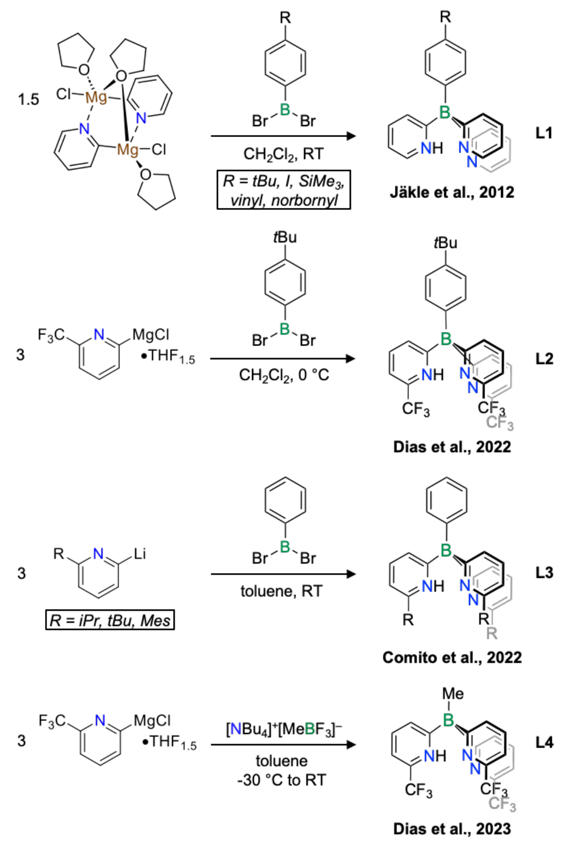
heteroleptic complexes have been developed in parallel by the Comito, Dias, and Hikichi groups. The Dias group has reported pyridyl ring-substituted, sterically demanding Tpyb versions and explored their coordination chemistry with coinage metals.[18, 24, 25] The Comito group has explored the catalytic activity of heteroleptic Vanadium complexes in ethylene polymerization[26, 27] and of Group 2 and Group 12 complexes in the polymerization of lactones and carbonates.[28] The Hikichi group has explored Typb complexes in catalytic oxidations of alkanes, employing sterically hindered ligands to generate catalytically relevant Ni(II) bromide complexes.[29]

Ligand synthesis approaches

Molecular Tris(pyridyl)borate Ligands.

While several closely related ligands, such as bis(pyridyl)borates[30, 31] tris(2-pyridonyl)borates,[32] and tris(pyridyl)aluminates[33, 34] were known at the time of our first report, the strong Lewis acidity of tricoordinate boron precursors and resultant dative bonding with pyridines, as well as reactivity toward ether solvents, had hindered the development of tris(pyridyl)borate ligands. Isolation of the 2-pyridyl Grignard reagent, followed by reaction with aryldibromoboranes in dichloromethane as a non-coordinating solvent, furnished the tris(pyridyl)borate ligands in their zwitterionic mono-protonated form in good yields (**L1**, Scheme 1).[12] The metal complexes are then conveniently accessed by deprotonation of the ligand in the presence of metal salts or direct reaction with organometallic reagents (*vide infra*).



Scheme 1. Synthetic routes to molecular tris(pyridyl)borate ligands

A wide variety of aryldibromoboranes are known and easily accessible, allowing the ligand to be endowed with a range of different functionalities, including iodo, silyl, and polymerizable vinyl and norbornyl groups.[19, 22, 23] Functionalized Tpyb ligands can also be generated by modifying the pyridine precursors. Thus far, alkyl,[28, 29] aryl,[28] and electron-withdrawing fluoroalkyl[18] groups have been incorporated at the pyridyl 6-position (**L2**–**L4**, Scheme 1). Substituents at this position sterically crowd the metal centre, allowing the ligands to be used to generate heteroleptic complexes as described below. Additional opportunities to confer desirable properties on the metal complexes are envisioned by introduction of functional groups at other positions on the pyridine rings. For instance, judicious placement of hydrophobic or hydrophilic groups may allow for tuning of the solubility characteristics, whereas electron-withdrawing and electron-donating groups could be used to further modulate the electronic properties of the ligands.

Recently, the Dias group has demonstrated the synthesis of Tpyb ligands **L4** from bench-stable trifluoroborate salts, further simplifying the handling of the starting materials and thereby facilitating access to and expanding the scope of this ligand class.[25]

Polymer-Supported Tris(pyridyl)borate Ligands.

While polymer modification reactions had been explored to attach tris(pyrazolyl)borates and other borane functional groups to polymers,[35, 36] our efforts toward polymer-supported Tpyb ligands have focused on the preparation of pre-functionalized ligands that incorporate a polymerizable group (Figure 2). An advantage is that high functional group fidelity can be achieved. However, this approach does require that the polymerizable functional group well tolerates the borylation of the substrate with BBr_3 to generate the aryldibromoborane, as well as the reaction with pyridyl Grignard reagents to assemble the ligand.

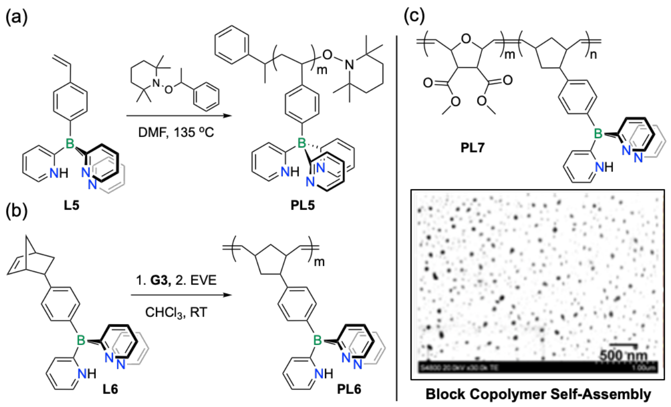


Figure 2. Synthetic routes to polymer-supported tris(pyridyl)borate ligands; G3 = Grubbs 3rd Generation catalyst, EVE = ethyl vinyl ether

We first investigated polymerizable Tpyb ligands derived from styryldibromoborane, which were then subjected to nitroxide-mediated controlled radical polymerization (NMP).[22] Borylation of styryltrimethylsilane with BBr_3 and *in-situ* reaction of the crude product with the pyridyl Grignard reagent furnished the styryl-functionalized ligand **L5** in 20% yield. NMP mediated by 2,2,6,6-tetramethyl-1-(1-phenylethoxy)-piperidine at 135 °C gave a homopolymer of the ligand (**PL5**, M_n = 27,400, *Đ* = 1.21), and an amphiphilic block copolymer was generated by sequential copolymerization with styrene. To enable polymerization under milder conditions, (4-norbornylphenyl)trimethylsilane was prepared from styryltrimethylsilane using a microwave-promoted Diels-Alder reaction with cyclopentadiene and then converted to the norbornyl-functionalized Tpyb ligand **L6**.[23] Ring-opening metathesis polymerization (ROMP)[37, 38] at room temperature in chloroform using Grubbs 3rd generation catalyst furnished well-defined polyligand **PL6** with low dispersity (M_n = 28,200, *Đ* = 1.33). Block copolymers such as **PL7** were also readily accessed through sequential addition of the ligand monomer and other cyclic monomers. In addition to exploring the coordination behaviour of these polyligands, the copolymers exhibited pH responsive properties when combined with suitable comonomers: copolymers derived from dimethyl norbornene-*exo,exo*-2,3-dicarboxylate as comonomer were protonated at the pyridine nitrogens under acidic conditions and deprotonated at the carboxylic acids under basic conditions, resulting in pH switchable micelles. We have recently reported a more convenient route to norbornene-functionalized boranes through reductive Heck coupling with norbornadiene,[39] which could offer even more facile access to these types of multifunctional stimuli-responsive self-assemblies. Self-assembled block copolymer micelles play important roles in areas ranging from use as drug delivery vehicles[40-42] to the development of nano-structured materials,[43-46] and stimuli-responsive properties[47-49] are of particular significance in these applications.

Homoleptic complexes with two Typb ligands

In our first reports, the Tpyb ligand in its zwitterionic monoprotonated form was combined with metal salts in the presence of base to form homoleptic octahedral “sandwich”-type complexes (Figure 3a).[12] The magnesium complex was also observed as a by-product during ligand synthesis. The metal centres in such complexes are coordinatively saturated. While complexes with Mg(II) or d^{10} metal ions such Zn(II), Cu(I) are expected to be labile, those with d^6 metal ions and especially from the heavier d-block elements are expected to form robust low-spin complexes. Particularly strong complexes are formed with Fe(II)[12] and even more so Ru(II), hence those were further explored with respect to their supramolecular assembly behaviour,[21] in post-functionalization reactions,[20] and in the crosslinking of polymers through metal-ligand coordination.[22, 23]

When the *t*-butylphenyl-Tpyb ligand was converted to the Mg(II), Fe(II) and Mn(II) complexes, single crystal structures revealed unusual extrinsically microporous structures with large solvent-filled channels, held together only by C–H···π interactions and dispersion forces arising from the presence of the *t*-butyl groups (Figure 3b).[21] These permanently porous organic solids were shown to be exceptionally robust to removal of the solvent under high vacuum and at high temperatures. The structural integrity of the Mg complex after solvent removal was exploited for uptake of gases such as CO_2 and CH_4. Similar porous structures were later also observed for trimethylsilyl-functionalized Tpyb ligands.[19]

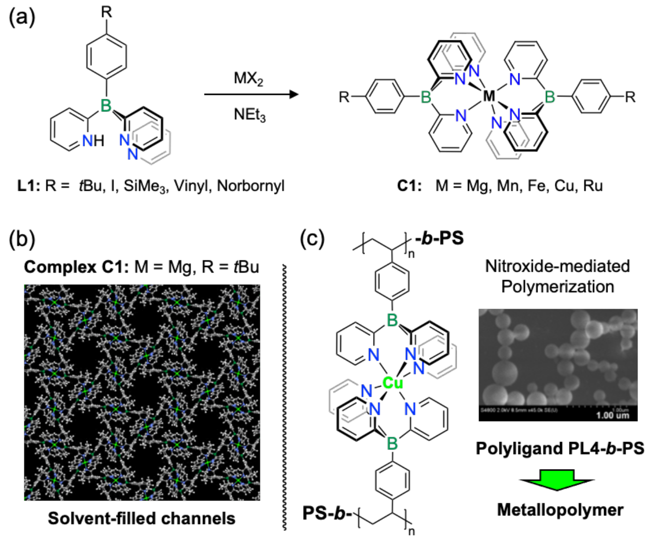
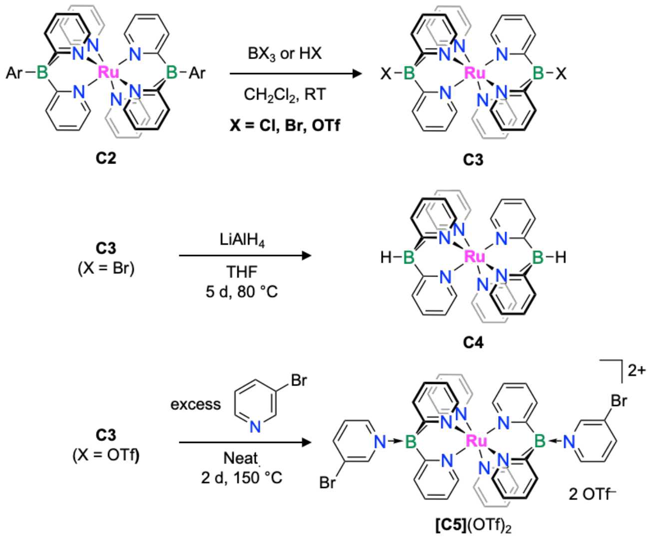


Figure 3. (a) Synthesis of homoleptic Tpyb complexes; (b) their assembly into extrinsically microporous materials; (c) formation of dynamically crosslinked polymeric materials via metal-ligand coordination.

Metal complexation also lends itself to (reversible) crosslinking of polymers.[23,22] For instance, micelles derived from ligand-functionalized block copolymers were linked together by treatment with Cu(II) salts in the presence of a base as depicted in Figure 3c.[22] As the Cu(II) complexation is a reversible process, the copper ions can be displaced by other metal ions, such as Fe(II) that form stronger complexes with the Tpyb ligands. While these initial studies demonstrate the great potential of Tpyb ligand-functionalized polymers as scaffolds for metallopolymers, the diverse potential applications in self-assembly,[50] dynamic bonding, polymer-supported catalysis, emissive materials among others are yet to be fully exploited.[51]

Recently, we have explored post-functionalization reactions at the borane bridgehead positions of iron and ruthenium Tpyb complexes as a new approach to further diversify the Tpyb ligand platform while also allowing us to incorporate them into different functional materials.[19, 20] Using iodo- and trimethylsilyl (TMS)-substituted precursors enabled the incorporation of these functional groups at the *para*-position of the phenyl substituents. The iodine-functionalized complex was conveniently derivatized with alkynyl groups by Sonogashira-Hagihara coupling. Borylation of the TMS-functionalized complex using BBr_3 led to unexpected reactivity: electrophilic displacement was observed not only of the silyl groups but also the entire aryl groups, along with bromination of the bridgehead boron. We subsequently developed a deliberate and more selective approach to achieve the bridgehead functionalization by reacting $Ru(Tpyb)_2$ complexes **C2** containing electron-rich *t*-butylphenyl substituents with boron halides as electrophiles, as well as with strong Brønsted acids

(Scheme 2).[20] Furthermore, we showed that the halide and triflate-substituted complexes **C3** thus obtained undergo nucleophilic displacement with lithium aluminium hydride or 3-bromopyridine to give complexes **C4** and **C5** respectively (Scheme 2). The effect of the substituents on the electronics of the complexes was investigated by DFT calculations, cyclic voltammetry and UV-Vis spectroscopy, showing increasing oxidation potential and a hypsochromic shift of the longest-wavelength UV absorption with increased electron-deficiency of the substituents. This demonstrates that substitution at the bridgehead can directly affect the electron density of both the ligand and at the Ru centre.



Scheme 2. Electrophilic and nucleophilic substitutions at $Ru(Tpyb)_2$ complexes with Ar = 4-(trimethylsilyl)phenyl or 4-*t*-butylphenyl.

The post-functionalization reactions also raise some intriguing mechanistic questions. One such question is whether a pyramidalized tricoordinate boron intermediate may play a role in bridgehead substitution reactions. Highly electron-deficient geometrically-constrained Lewis acids with similar triptycene-like geometries have been isolated and structurally characterized by the Berionni[52-54] and Wagner[55] groups. This suggests that a pyramidalized boron intermediate might be accessible through an S_N1-type reaction pathway, but in the case of Tpyb complexes pyridyl dissociation from Ru with ensuing planarization at boron could occur as well. Future isolation of a species **C3** where X represents a very weakly coordinating anion may not only shed light on the mechanisms but could also result in an intriguing new class of strong Lewis acids.

Heteroleptic complexes with one Tpyb ligand

Recently, various heteroleptic Tpyb complexes have been reported, enabling reactivity at the metal centre and, potentially, catalytic applications. These complexes have been obtained both by investigating the complexation to metals outside the previously studied divalent ions, and through new, sterically optimized Tpyb ligands (Figure 4).

The first such heteroleptic complexes were reported by Qian and Comito in 2021, building on previous studies with heteroleptic vanadium tris(pyrazolyl)borate complexes[56-58] which have been reported as long-lived soluble ethylene polymerization catalysts.[26] The parent phenyl-functionalized Tpyb ligand was reacted with vanadium(V) oxo- and phenylimido-complexes to furnish piano-stool complexes **C6**. Isopropoxide ligands were utilized for their steric bulk.

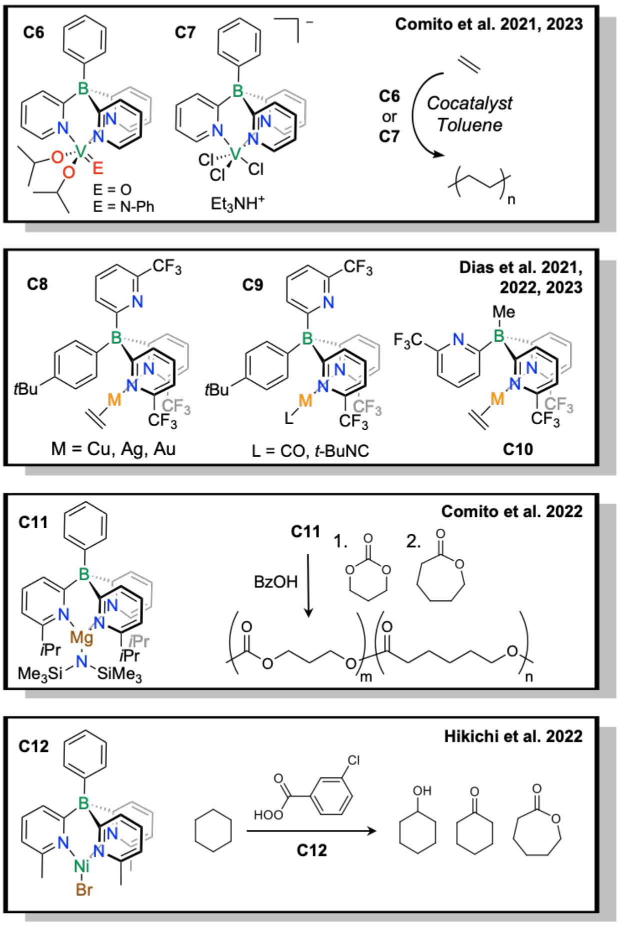


Figure 4. Selected heteroleptic Tpyb complexes and their applications

When combined with a modified methyl-aluminoxane cocatalyst (MMAO-12), the phenylimido-functionalized complex was found to be a particularly long-lived ethylene polymerization catalyst. The lifetime of 1 hour at 105 °C is longer than that of any previously reported homogeneous vanadium catalyst at that temperature, and turnover numbers of up to 1.4 x 10^5 at 75 °C were achieved. The longevity of the catalyst was attributed to the robust nature of the Tpyb complexes, which have strong B-C bonds as opposed to the more labile B-N bonds found in Tp ligands. However, the molecular weight of the polymers remained relatively low as determined by size exclusion chromatography (SEC) analysis ($M_n \approx 60$ kDa). More recently, Comito and coworkers prepared a vanadium(III) complex **C7** by combining the Tpyb ligand with VCl_3 in the presence of triethylamine.[27] This complex exhibited catalytic activity for ethylene polymerization at temperatures up to 135 °C using ethylaluminum sesquichloride as cocatalyst. High molecular weight polymers ($M_n \approx 350$ kDa) with moderate dispersities (*Đ* < 2) were obtained.

Electron-donating or electron-withdrawing substituents can also be utilized to modify the electronics of the metal centre, as shown in the work of Dias and coworkers.[18, 24] In 2022, they reported sterically hindered 6-trifluoromethyl-substituted Tpyb ligand as an analogue of their previously-reported fluoroalkyl-substituted Tp ligands.[59-61] The ligand was generated by the Grignard route and reacted with coinage metal precursors (copper, silver and gold) under ethylene atmosphere. Unlike previously reported Tp complexes, the resultant ethylene complexes (**C8**) feature a κ^2-coordinated Tpyb ligand, with only two of the pyridine groups bound to the metal centre which adopts a trigonal planar geometry. Significant lengthening of the ethylene C=C bond in the gold complex compared to free ethylene indicates the presence of strong Au-ethylene σ/π interactions. Similar geometries were also observed in the respective coinage metal complexes with isocyanide and carbonyl ligands (**C9**).[24] Most recently, the Dias group has generated trifluoromethylpyridine-functionalized ligands from methyltrifluoroborate and dimethylboron bromide, yielding trispyridyl- and bispyridylborates.[25] When incorporated into coinage metal ethylene complexes (**C10**), they again adopted a κ^2-coordination geometry. FTIR studies of the silver and copper isocyanide and carbonyl complexes allow the electronics of the complexes to be investigated and compared with previously reported analogues. The copper-isocyanide complex **C9** exhibited a CN stretching frequency of 2168 cm^{-1}, significantly increased compared to free *t*BuNC (2138 cm^{-1}) and comparable to previously-reported bis- and tris-pyrazolylborate complexes (2161 – 2196 cm^{-1}).[24] The frequencies for the silver derivatives of **C9** are higher, in line with the reduced backbonding ability of the larger Ag(I). In contrast, the carbonyl stretches decreased upon coordination consistent with M→CO π backdonation. Relative to free CO (2143 cm^{-1}), the $\bar{\upsilon}$(CO) value for the Cu(Tpyb)CO complex of 2110 cm^{-1} was significantly smaller but similar to that of 2112 cm^{-1} for the Tp analogue. It is important to note that these values do not offer direct insights into the σ-donor/π-acceptor strength of the Tpyb vs Tp ligand classes because of the different coordination modes (κ^2 for Tpyb and κ^3 for Tp complexes).

In parallel, the Comito group generated sterically hindered Tpyb ligands from 6-alkylated and 6-arylated pyridines *via* a lithiation route, resulting in site-isolated complexes of the earth-abundant main-group metals calcium, magnesium, and zinc.[28] In combination with benzyl alcohol as a cocatalyst, the site-isolated magnesium complex incorporating isopropyl substituents on the pyridyl groups (**C11**) was found to catalyse the polymerization of l-lactide, ε-caprolactone, and trimethylene carbonate with moderate dispersities (Đ = 1.47-1.61), and a block copolymer was obtained by adding ε-caprolactone to a propagating poly(trimethylene carbonate) chain. The complex was also found to be an effective catalyst for melt-phase polymerization of lactide, achieving 97% conversion of the monomer over 18 hours to give a polymer with a dispersity of *Đ* = 1.51.

Concurrently, the Hikichi group developed the methyl-substituted Tpyb ligand, generated from 6-methyl pyridyl magnesium chloride.[29] This ligand was used to prepare a nickel(II) bromide complex (**C12**), which showed high activity in the catalytic oxidation of cyclohexane in the presence of *meta*-chloroperbenzoic acid as the oxidant. The steric shielding of the metal centre is more effective for the methylated Tpyb complex than for the methylated tris(pyrazolyl)borate or tris(oxazolinyl)-borate analogues due to the geometry of the 6-membered pyridine ring. This, along with the more electron-donating nature of the pyridyl moieties, resulted in a relatively longer Ni-Br bond, and thus higher catalytic activity. Only the Tpyb but not the Tp system exhibited a pseudo-reversible Ni(II)/Ni(I) redox wave, indicative of a complex that is robust even when the Ni centre is reduced.

Conclusions and Outlook

The convenient synthesis routes that are available nowadays to generate Tpyb ligands and their complexes enable a host of different applications in materials sciences and catalysis. Of particular significance is that trifluoroborate precursors pioneered by Dias[25] should allow researchers to install a broader range of functional groups onto the ligands by avoiding the need to go through a highly reactive aryldibromoborane intermediate. Combined with the increased scope of pyridyl derivatives that are now being explored, we expect a wide variety of Tpyb ligands to emerge over the coming years. Beyond these synthetic advances, we anticipate opportunities for further progress in both catalysis and the development of advanced materials with unusual optical, electronic, redox, or magnetic properties.

Most of the Tpyb complexes studied thus far feature metals in low to moderate oxidation states, whereas complexes with earth-abundant transition metals in high oxidation states remain to be fully explored. High oxidation state metals have a number of interesting applications as oxidizing agents and catalysts,[62] as well as exhibiting intriguing electronic properties such as charge separation and superconductivity.[63] Abundant first-row transition metals in high oxidation states can react in ways resembling precious metal catalysts and are believed to be important intermediates in enzymatic pathways.[64] Strongly σ-donating ligands can stabilize high metal oxidation states, and tris(pyrazolyl)borates, tris(pyridyl)methanes, tris(pyridyl)-aluminates, and related ligand architectures have been successfully utilized in this regard.[65-71] Comito's work on vanadium(V) complexes[26] highlights that the strong electron-donation and robustness of Tpyb ligands can lead to stable high oxidation state metal complexes, and we expect further development of high oxidation state complexes to enable new catalytic and materials applications.

We also anticipate that Typb metal complexes will play an increasingly prominent role in the development of new materials with unusual optical, redox, and magnetic properties. In previous studies, iron complexes of tris(pyrazolyl)borates have been utilized in the development of single molecule magnets and lanthanide complexes have been explored for use in organic light emitting diodes (OLEDs), whereas iron complexes of tris(methylimidazol-1-ylidene)borate have made waves for their unusual luminescent metal-to-ligand charge-transfer excited state character.[72-74] The tunability of the tris(pyridyl)borate ligand platform bodes well for exploration in these application fields.

Finally, the incorporation of functional Tpyb metal complexes into polymeric materials to generate metallopolymers remains to be fully explored. Metallopolymers enjoy wide applications, for example as semiconducting and redox-responsive materials, as components of optoelectronic devices, battery membranes, antibacterial materials, and as polymer-supported catalysts.[75-80] Significant advances have been made with respect to the development of polyolefin-supported Tpyb ligands, their metal complexation and self-assembly properties.[22, 23] However, they have yet to be incorporated into the backbone of polymeric materials, and in this respect the development of polytopic ligands is a particularly promising direction. Nucleophilic displacement reactions on reactive Tpyb complexes such as **C3**[20] could also serve as an interesting approach to install these redox-active functional groups onto polymers, dendrimers, and other nanostructured materials containing Lewis basic functional groups. Again, the strongly sigma-donating character of Tpyb ligands, combined with the demonstrated robustness, redox and catalytic activity of the respective metal complexes, suggest great potential for such metallopolymer materials.

Conflicts of interest

The authors declare that there are no conflicts of interest.

Acknowledgements

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