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Soft Scorpionate Ligands Based on Imidazole-2-thione Donors

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This review describes the development of the anionic soft scorpionate ligand hydrotris(methimazolyl)borate (Tm^{Me}), its *N*-alkyl and *N*-aryl congeners and draws comparisons where appropriate with its close relatives, the dihydrobis(methimazolyl)borates (Bm^R). Key features of the interaction of these species with metal centres, including bonding modes, electron-donor properties, M···H–B interactions, ligand degradation and metallaboratrane formation are addressed and a summary of the coordination chemistry of these species with both main group and transition metals is given.

1. Introduction

The so-called *scorpionates* have become a hugely popular class of ligands in coordination chemistry. The first examples, the polypyrazolylborates $BH_n(pz)_{4-n}^-$ (pz = pyrazolyl; n = 0–2, Figure 1), were described by Trofimenko in 1966.[1] They are tripodal, anionic ligands which offer a N_3-donor set that caps one face of a coordination polyhedron, and on this basis an analogy has been drawn with the cyclopentadienyl family of ligands. This perceived analogy, coupled with their ease of synthesis and handling and their remarkable utility in the complexation of transition-metal ions rapidly established them as a widely used class of ligands. Furthermore, the ability to synthesise a very wide range of substituted pyrazole precursors facilitates the tuning of

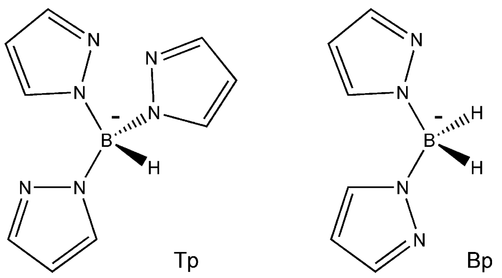

Figure 1. Bis- and tris(pyrazolyl)borates.

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John Reglinski received his first degree from University of Dundee in 1978 and his PhD (synthesis and reactivity of nitrosyl-based drugs) from the University of St. Andrews in 1981 (A. R. Butler and C. Glidewell). This was followed by postdoctoral work at the University of British Columbia Canada (1981–1983; W. R. Cullen, bioorganometallic chemistry of arsenic) and School of Inorganic Chemistry at the University of Bristol (1983–1984; M. Green, Mo-based organometallics). Having spent a year as a temporary lecturer at Kingston Polytechnic (now University) he returned to research in 1985 as a postdoctoral researcher at the University of Strathclyde (W. E. Smith, inorganic biochemistry of sulfur) from where he transferred to the teaching staff in 1988 being promoted to reader in 2005. His current research interests include soft tripodal ligands and their coordination chemistry, multimetallic complexes and inorganic biochemistry specifically the synthesis of biomimetic complexes and redox sensors.

their steric, and to a lesser extent, their electronic properties.[2,3]

One of the major areas in which the tris(pyrazolyl)-borates (Tp^R) have been used is in the modelling of metalloprotein active sites. Successful functional models of the family of molybdenum and tungsten pterin-based,[4] zinc[5]-containing and copper[6]-containing proteins have been developed using the pyrazolylborate ligands. Interestingly, these systems all have sulfur-rich coordination spheres at the active metal site. Thus, while the use of pyrazolylborates has proven useful in terms of modelling function, the structural parallels are incomplete and in particular, the bonding, and thus the electronic properties, will be somewhat different.

Therefore, we were exercised to attempt the preparation of sulfur donor analogues of the pyrazolylborate ligands in the belief that these would enable us to better model some of these sulfur-rich metalloenzyme sites. We were aware of the elegant work of Riordan on the tris(methylthioalkyl)-borate ligands,[7] but were keen to incorporate a heterocyclic sulfur donor, which would be more in keeping with the philosophy of the pyrazolylborate family of ligands, and would be closer analogues. Our initial pre-requisite for potential heterocycles was that they should have an acidic N–H group adjacent to a sulfur atom in a five-membered ring. However, few examples are reported in the literature and none were commercially available nor could be readily synthesised. Thus, an alternative strategy was required. The answer lay in the lab already in the shape of the heterocycle methimazole. While chemical suppliers name this 1-methyl-2-mercaptoimidazole, implying an S–H group, studies showed that in fact under normal conditions the predominant tautomer is the one in which the sulfur has thione character and the acidic proton resides not on sulfur, but on the nitrogen atom (Figure 2).[8] Thus, methimazole is an ideal precursor for the synthesis of new anionic scorpionate ligands based on a boron bridgehead.

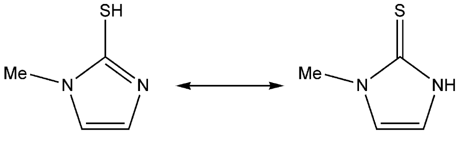
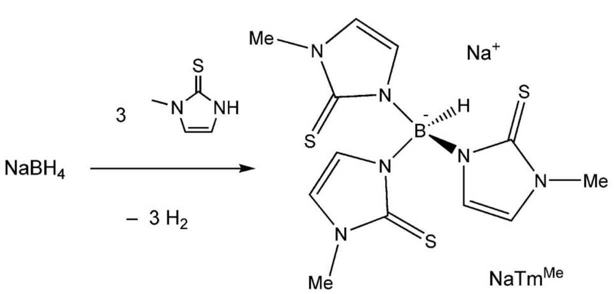


Figure 2. Methimazole tautomerisation.

2. Ligand Synthesis

In keeping with Trofimenko's synthesis of the pyrazolylborate ligands,[1] we attempted the reaction of methimazole (Scheme 1) with sodium borohydride in a solvent-free melt reaction.[9,10] As expected, hydrogen was evolved from the reaction as the methimazole melted resulting in formation of a solid with a high melting point. Soxhlet extraction of the resulting solid, firstly with hexane to remove unreacted methimazole, followed by chloroform, yielded anhydrous sodium hydrotris(methimazolyl)borate in good yield. Both lithium[11] and potassium[12] borohydride have also been used in the synthesis of these ligands.



Scheme 1. Synthesis of sodium hydrotris(methimazolyl)borate ($NaTm^{Me}$).

In the reaction of pyrazole with an alkali metal borohydride the product can be controlled by changing the temperature at which the reaction is conducted. Thus, at 110 °C the dihydrobis(pyrazolyl)borate (Bp) anion is obtained, at temperatures above 210 °C the tetrakis(pyrazolyl)borate is formed, while at intermediate temperatures (ca. 180 °C) the tris(pyrazolyl)borate results. The higher melting point of methimazole (ca. 147 °C) when compared to pyrazole (ca. 70 °C) renders formation of the dihydrobis(methimazolyl)-borate (Bm^{Me}) anion not viable by this method, because at the melting point the reaction generally proceeds directly to the trisubstituted Tm^{Me} species. In addition, decomposition (with the formation of highly coloured species) occurs at temperatures above ca. 180 °C. Consequently, the tetrakis-(methimazolyl)borate species remains as yet unknown.

Other groups have favoured a method for the synthesis of the Tm^{Me} anion which involves reflux of the reactants in toluene solution.[11] Adaptation of this methodology either using toluene below the reflux temperature or by performing the reaction in refluxing THF solution has allowed the successful synthesis of the Bm^{Me} anion.[13] Very recently, Santos has prepared a third member of the series, reacting methimazole with borohydride in THF at room temperature to form the trihydro(methimazolyl)borate.[14]

The Tm and Bm ligands, like the pyrazolylborates, have great potential for modification (Figure 3). The *N*-methyl group can be readily replaced by a wide range of alkyl (Et,[15] *t*Bu,[16,17] Bz[15,18] Cy[19]) or aryl (Ph,[11] *p*-tolyl,[18,20] *o*-tolyl,[19] mesityl,[16] cumenyl,[15] 2-biphenyl[19] 2,6-xylyl,[19] and 2,6-diisopropylphenyl[21]) groups. The synthesis of the 1-alkyl- or 1-aryl-imidazole-2-thiones is reasonably straightforward and most of the resulting Tm^R ligands are prepared by reaction with an alkali metal borohydride using the solution method described above. Substitution at C4 or C5 of the ring is also possible, although the only example of such substitution has been reported by Santos, who placed biologically active groups in the 5-position.[22]

The Tm ligands can be further altered by replacing the B–H moiety with other groups. Santos reported the first synthesis of such species,[23] replacing the borohydride with methyl and with phenyl groups by the method described in Scheme 2. We have since adapted this method to form $n\mathrm{Bu}Tm^{Me}$ and $p\text{-}FC_6H_4Tm^{Me}$.[24] Parkin has recently reported complexes which have B–Cl and B–OAc groups, derived by oxidative reaction of boratranes (vide infra).[25]

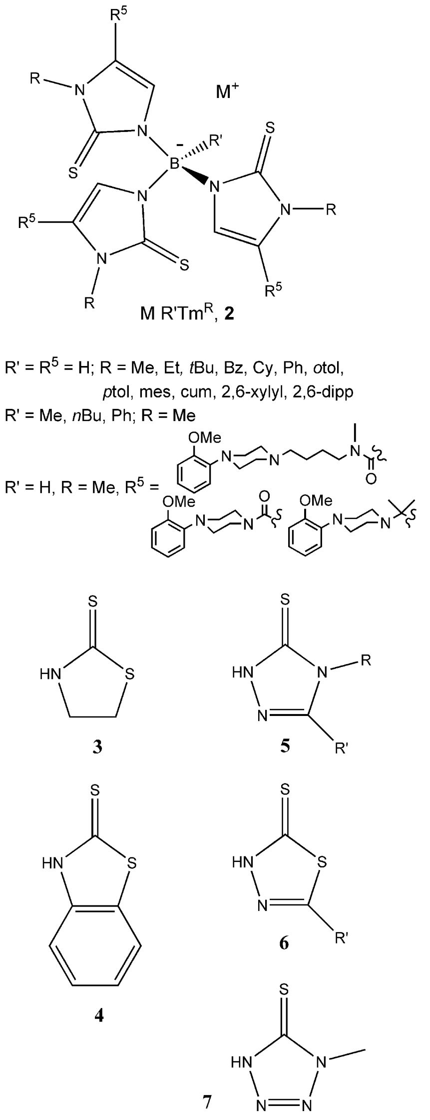
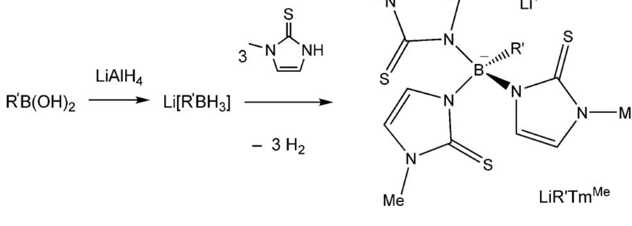


Figure 3. Substituted Tm ligands (top) and alternative heterocycles (bottom).



Scheme 2. Synthesis of LiR′Tm^{Me}.

The family of ligands has also been extended by using other heterocyclic thiones (Figure 3). Early on, we reported the synthesis of borates based on thiazolidine-2-thione (**3**) and benzothiazole-2-thione (**4**), again prepared in a melt reaction.[26] Subsequently a number of other related ligands have been prepared including those utilising 1,2,4-triazole-5-thiones (**5**),[27] 1,3,4-thiadiazole-2-thione (**6**)[28] (which have been dubbed "Janus ligands" due to their ability to coordinate either through an S_3- or an N_3-donor set) and 1-methyl-5-thiotetrazole (**7**).[29]

We were aware when we embarked upon the project that the S_3-donor Tm^R ligand and the N_3-donor Tp ligand were the opposite ends of a series of ligands, with intermediate S_2N and SN_2 donor ligands a possibility (Figure 4). Parkin prepared the S_2N donor ligand, pzBm^{Me} very soon after our first report of the Tm^{Me} ligand by reaction of LiBm^{Me} with pyrazole,[13a] and a series of S_2N ligands with a variety of substituents at nitrogen on the methimazole and the 3- and 5-positions on pyrazole were subsequently developed by Vahrenkamp.[30,31] The SN_2 donor ligand however proved much more resistant to synthetic efforts. A substituted version of this species, tim^{R}Bp (R = *i*Pr, *t*Bu) was eventually prepared by Vahrenkamp and co-workers utilising the reaction of Tp with *N*-substituted thioimidazoles, the driving force for the reaction being the sublimation of pyrazole from the reaction mixture. It is notable that the parent tim^{Me}Bp has still eluded synthesis.[32] Finally, Parkin has recently reported the synthesis of the selenium donor analogue of the Tm ligand.[33]

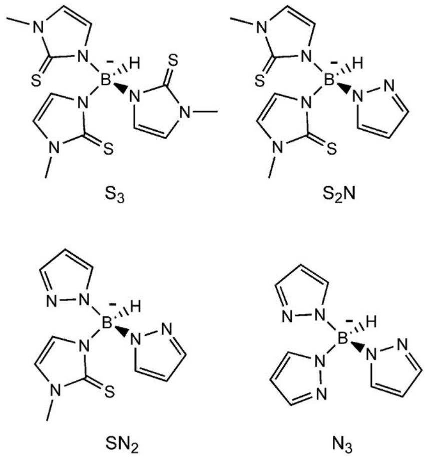


Figure 4. The series of scorpionate ligands with donor sets ranging from S_3 through to N_3.

This review will concentrate on the coordination chemistry of the potentially tridentate S_3-donor ligands of the R′Tm^R family. The Bm^R ligands and those based on other heterocycles will not be considered in detail, except where comparison is required. This review is not intended to be comprehensive in its coverage, but rather to explore the key features of the chemistry of this family of ligands.

A note on the nomenclature used for these systems is also warranted, as it has become somewhat confused. We originally used the abbreviation Tm for the hydrotris(methimazolyl)borate anion (m = methimazolyl). This is in the spirit of the Curtis nomenclature for the pyrazolylborates (Tp/Tp*, p = pyrazolyl)[34] and its subsequent extension by Trofimenko.[35] However, different groups have used alternative nomenclatures and thus there is considerable scope for confusion. For instance, the abbreviation Tt was first used by Riordan for his tris(methylthioalkyl)borates,[7] but has subsequently been used by Vahrenkamp for these ligands[16] and initially by Marchio et al. for his 1,3,4-triazole-2-thione based borate ligands,[27a] although this was later changed for Tr to avoid confusion.[27b–27e] There is undoubted logic for both of these assignments, but the duplication leads to potential confusion. We therefore believe that Tt should be reserved for the tris(methylthioalkyl)-borate ligands. Others have used a more explicit $HB(tim)_3$ type nomenclature (tim = thioimidazole), and this is perhaps more helpful in the mixed pyrazole/thioimidazole ligands. However, as interest in this area of chemistry shows no sign of diminishing it would be helpful to attempt to standardise the nomenclature and we suggest the following. We recognise that the Tm notation refers to a specific member of the series, but it is a unique identifier and has been adopted by a number of the major players in this area of chemistry. Furthermore, it can be adapted to accommodate substitution. Thus, Tm^R indicates *N*-substitution, $R'Tm^R$ indicates additional replacement of the B–H with B–R′, and $R'Tm^{R,4R,5R}$ indicates substitution at the 4 and/or 5-position of the imidazole ring. As with the Tp system, omission of the particular R implies an H-atom in that site. The bis(methimazolyl)borate family of ligands are denoted by the symbol Bm, which is modified similarly to denote substitution.

3. Coordination Chemistry

3.1 Preliminaries

On obtaining $NaTm^{Me}$ we were keen to establish its ability as a ligand towards a range of metal centres, to explore its analogy with Tp and Cp, and to understand its bonding to metal centres. Our initial reaction was with zinc bromide. A tetrahedral 1:1 adduct $[Zn(Tm^{Me})Br]$ was formed, and crystallography showed that Tm^{Me} indeed acted as a tripodal ligand.[9] It was also clearly apparent that in the $M(Tm^{Me})$ fragment the heterocyclic rings adopted a twisted, propeller-like conformation, leading to local C_3 symmetry. This contrasts with the C_{3v} symmetry observed in the corresponding M(Tp) fragments in which the pyrazole rings are co-planar with the H–B···M axis. This is clearly a result of the exocyclic sulfur donor, which leads to a larger eight-membered chelate ring size and thus considerably greater conformational flexibility. By contrast, Tp complexes form rigid six-membered chelate rings on complexation (Figure 5). The upshot of this twist is that complexes of Tm ligands have two enantiomeric forms, although in most cases a racemic mixture is observed. Furthermore, many Tm^R complexes are fluxional on the NMR timescale, which can be interpreted in terms of the interconversion of the two enantiomers. Bailey has studied this elegantly, using *N*-ethyl and *N*-benzyl Tm derivatives, in which the CH_2 protons adjacent to N are diastereotopic.[15] The measured inversion barriers suggest the racemisation process is dissociative, and DFT calculations show that the energy of a local C_{3v} transition state is prohibitively high for a non-dissociative interchange to be likely.

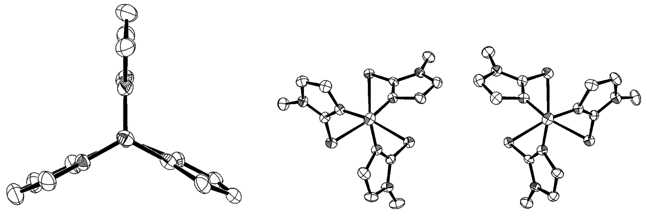


Figure 5. Conformations of the C_{3v} MTp fragment (left) and the two diastereomers of the C_3 MTm^R fragment (centre and right).

3.2 Donor Properties of Tm Ligands

Our early investigations of the coordination chemistry of the Tm^{Me} ligand were predicated on the contrast between the "hard" N_3 donor set of the Tp ligands and the "soft" S_3 donor set of the Tm^{Me} ligand. A rather beautiful example of this was found in the sequential reaction of $BiCl_3$ with Tm^{Me} and then Tp, which resulted not as hoped in a mixed Tm/Tp complex of bismuth, but rather in the formation of $[Bi(Tm^{Me})_2]^+[Na(Tp)_2]^-$ (Figure 6).[36] The partitioning of the soft Tm^{Me} ligands with the large soft bismuth ion and the Tp ligands with the small, hard sodium ion seemed to justify our approach. Initial ab initio calculations also supported this view.[10] The stabilisation on complexation was shown to be somewhat larger for the soft Cu^+ ion than the hard Na^+ ion, implying a stronger interaction between the soft-soft pairing. However, it soon became clear to us that this approach, while of some qualitative value, was not sufficient alone to explain the observed chemistry of the Tm ligands.

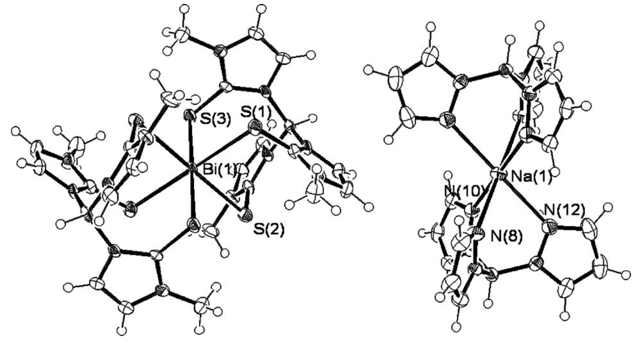


Figure 6. X-ray structure of $[Bi(Tm^{Me})_2][Na(Tp)_2]$, with the S_6-coordinated bismuth on the left and the N_6-coordinated sodium on the right.

One area of chemistry in which the Tp ligands had been extensively used was to mimic the Cp ligand in organometallic systems. We treated NaTm with $M(CO)_6$ (M = Mo, W) and quenched the reactions with iodine and allyl bromide. These reactions gave rise to the seven-coordinate $[M(Tm^{Me})(CO)_3I]$ and $M(Tm^{Me})(CO)_2(\eta^3\text{-allyl})$ complexes, respectively (Figure 7).[37]

Comparison of the C–O stretching frequencies in the IR spectrum for the structurally analogous Cp, Tp and Tm^{Me} complexes showed that the order was $Tp > Cp > Tm^{Me}$. That Tm^{Me} has the lowest stretching frequency implies this ligand has the greatest electron-donor ability of the three. This is readily explained in that the sulfur donor atoms have

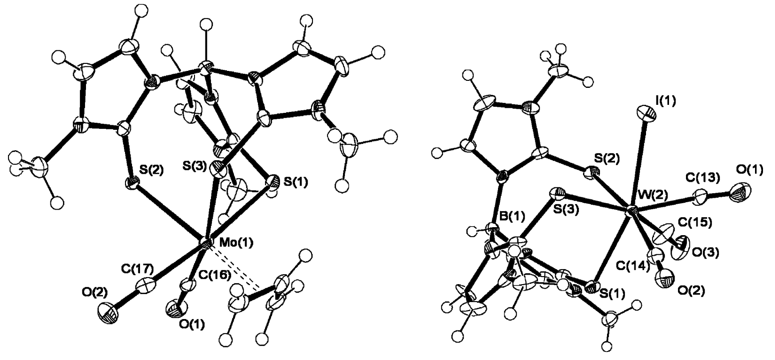


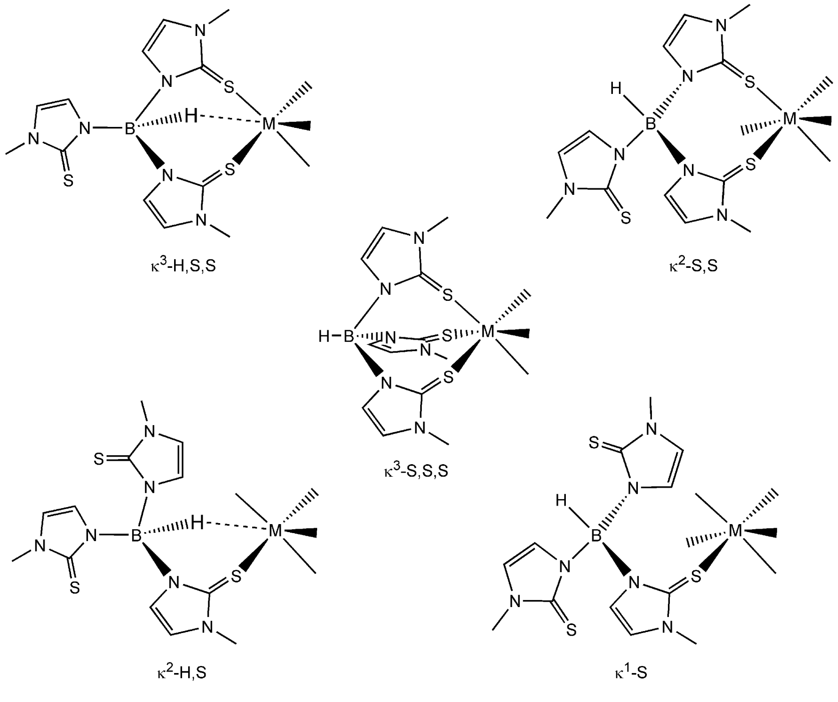
Figure 7. X-ray crystal structures of [Mo(Tm^{Me})(CO)$_2$(η^3-C$_3$H$_5$)] (left) and [W(Tm^{Me})(CO)$_3$I] (right).

lone pairs, which are able to add π-basic character to the metal–ligand interaction. These observations have been further supported by the work of Hill on other Mo and W carbonyl complexes,[38] Santos in her rhenium carbonyl complexes with Tm and Bm ligands[39,40] and Rabinovich on a series of Mn(Tm^R)(CO)$_3$ complexes.[41] We have also undertaken DFT studies of the [M(Tm^{Me})(CO)$_2$(NO)] complexes (M = Mo, W) and these confirm the π-type interactions of the sulfur donors with the metal centre.[42]

We also became interested in the ligand-field properties of the Tm^R ligands. Reaction of Tm^{Me} with iron(II) salts yielded the deep green-black complex [Fe(Tm^{Me})$_2$], which was shown to be the homoleptic "sandwich" complex in which the iron is in an S$_6$-coordination environment. The structural, spectroscopic (Mossbauer, electronic) and magnetic properties of the system were all consistent with a paramagnetic high-spin d^6 iron(II) ion.[43] Interestingly, the Cp analogue (ferrocene) is low spin (and thus diamagnetic), while the Tp analogue is an interesting spin-crossover system.[44] Thus the magnitude of the ligand-field splitting lies in the order Cp > Tp > Tm^{Me}. Further, in the homoleptic nickel(II) complex we were able to estimate Dq as 816 cm^{-1}, which places the Tm ligands between chloride (680 cm^{-1}) and water (850 cm^{-1}) in the spectrochemical series. Thus, we have a picture of the R′Tm^R ligands as weak field ligands but with strong electron donating abilities. Both of these properties arise from the strong π-donor interactions of the sulfur lone pairs with the metal centres.

3.3 Coordination Modes

It quickly became obvious that although the primary coordination mode of the Tm^R ligands is κ^3-S,S,S, the flexibility of the ligand and a combination of steric and electronic properties leads to observation of a number of alternative coordination modes. These are summarised in Figure 8. Inspection of the 217 unique structures in the Cambridge


κ^3-H,S,S

κ^2-S,S

κ^3-S,S,S

κ^2-H,S

κ^1-S

Figure 8. The non-bridging coordination modes of the Tm^R ligands.

Crystallographic Database[45] of complexes containing the R′Tm^{R} anions showed that 183 (ca 84%) contained this most common motif. This is not surprising given the strong affinity of sulfur donors for most metallic elements and the pre-organisation of the ligand to favour this motif.

The next most common (21 examples, 11.5%) is the κ^{3}-S,S,H motif, in which one of the sulfur donor atoms is non-coordinated and an interaction between the metal and the borohydride group of the ligand occurs. This interaction is discussed in detail below. It is notable that among the Bm^{R} family of ligands this is the most common structural type (28 out of 55 structures, 50.9%). The remaining mononuclear structural types, κ^{2}-S,S, κ^{2}-S,H, κ^{1}-S and κ^{0} (non-coordinated) account for just a handful of structures each. Finally, there are approximately 14 structures in which the Tm^{R} ligand bridges between two or more different metallic atoms. No single bridging structural type is dominant, indeed few are observed more than once. It can be seen, therefore, that the Tm^{R} ligands are extremely flexible, leading to a diversity of structural types, which are able to accommodate the electronic and steric needs of the metal centre.

3.4 The M···H–B Interaction

As described above, there are a significant number of examples of Tm^{R} and Bm^{R} complexes, which exhibit an interaction between the metal centre, and the B–H group, in what may be described as a κ^{3}-S,S,H bonding mode. Such interactions have been the subject of a great deal of conjecture and have been described variously as agostic bonds, inverse hydrogen bonds, 3-centre, 2-electron bonds and as electrostatic interactions.

The agostic description has been most widely espoused.[46] While its use is understandable, it is to some extent symptomatic of the poor appreciation of the true meaning of the term agostic, which is prevalent within the chemical community. Not only does the original description of the agostic bond[47] apply this term specifically to M···H–C interactions, but also there are relatively strict geometric constraints which describe such an interaction.[48] While a small subset do fall within the prescribed parameters, most of the observed M···H–B interactions in metal Tm^{Me} complexes do not meet these structural criteria. Indeed, more recent discussions by Desiraju and others[49] place even more stringent geometric limitations on the agostic bond [$d(\text{M}\cdots\text{H}) \approx d(\text{M}\cdots\text{C})$, M···H–C $< 100°$] which certainly preclude these M···H–B interactions from being considered in this way.

The inverse hydrogen-bond description[50] has limited merit. Certain M···H–C interactions have been characterised as hydrogen bonds, and the description as an inverse hydrogen bond recognises the hydridic nature of the borohydride and thus the fundamental polarity inversion between an M···H–B and an M···H–C interaction. However, a hydrogen bond is formally a 3-centre 4-electron bond, wherein these two models diverge. The M···H–B interactions here described are clearly 3-centre 2-electron bonds and are at least superficially similar to the M···H–B interactions in metal-borohydride complexes although the M···B distances are much longer in the Tm complexes. Thus, the shortest M···B distance in a Tm complex is 2.82 Å, whereas in [Cu(PPh$_{3}$)(BH$_{4}$)] the M···B distance is 2.18 Å, close to the sum of the Cu and B covalent radii.[51]

The descriptors which define agostic bonding are based on absolute ranges of M···H and M···C distances and M···H–C angles. We, however, have chosen to use the divergence of the observed M···H distances from the sum of the metal and hydrogen covalent radii as an indicator of the strength of any bonding interaction.[52] Using these criteria, the strength of the interaction varies considerably and inspection of the crystallographically obtained geometric parameters for these compounds reveals three distinct categories of interaction.[53] The first class is where a short metal to hydrogen distance occurs, such that the M···H distance is close (± 0.20 Å) to the sum of the metal and hydrogen covalent radii. Such interactions are seen in some transition metal complexes, such as [Co(Tm^{tBu})$_{2}$] where the Co···H distances are 0.05 and 0.09 Å greater than the sum of the Co and H covalent radii.[54] It is also observed in the complex [Ru(Tm^{Me})(PPh$_{3}$)(CO)H] (0.09 Å).[55] In the chemistry of the Bm^{R} family of ligands the short M···H–B interaction is prevalent and is seen in systems such as [Mn(Bm^{R})(CO)$_{3}$] (R = Me, 0.16 Å; R = *t*Bu, 0.03 Å)[41] and its rhenium analogues developed by Santos and co-workers[39,40] (Figure 9). A 3-centre 2-electron bond seems the most appropriate description of this bonding arrangement. Indeed, in some cases the chemical shift of the ^{1}H NMR resonance of the hydride is appreciably negative, consistent with a covalent interaction with the metal centre. A second category

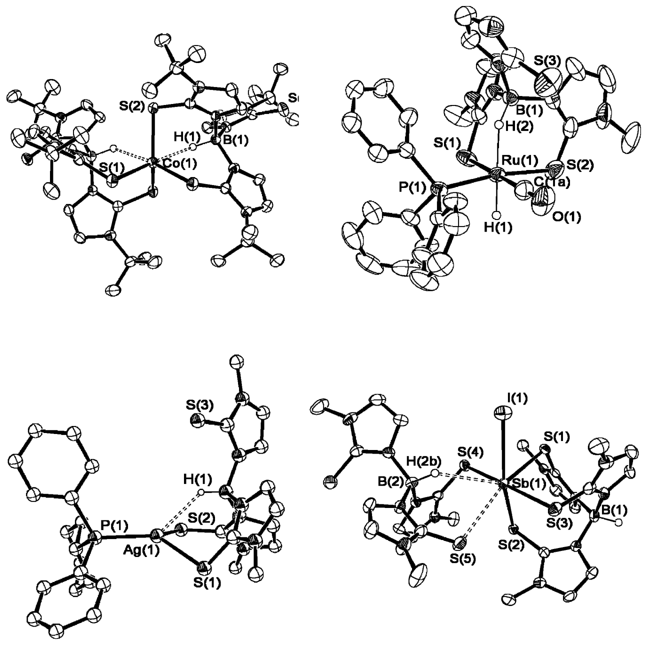


Figure 9. Crystal structures of some Tm^{R} complexes exhibiting M···H–B interactions. Top left: [Co(Tm^{tBu})$_{2}$]. Top right: [Ru(Tm^{Me})(PPh$_{3}$)(CO)H]. Bottom left: [Ag(Tm^{Me})(PCy$_{3}$)]. Bottom right: [Sb(Tm^{Me})$_{2}$I].

of interactions has longer M···H distances, where 0.25 Å $< d(\text{M}\cdots\text{H}) - \Sigma\, r_{\text{cov}} <$ 0.75 Å. These are most often seen when the metal has a d^{10} electron configuration and a primary coordination sphere which is trigonal planar (e.g. $[\text{Zn(Bm}^{\text{Me}})\text{Me}]$,[56] $[\text{Ag(Tm)(PCy}_3)]$,[57] Figure 9) in which case the secondary H···M interaction occurs in an axial position. A similar situation occurs in complexes with a distorted tetrahedral primary coordination sphere. Here the M···H interactions cause distortion which runs from a small compression of one S–M–S angle and expansion of another, as seen in $[\text{Cd(Tm}^{t\text{Bu}})_2]$,[58] through to formation of a pseudo-octahedral species as in $[\text{Fe(Tm}^{\text{Ph}})_2]$.[59] The final category occurs when the M···H distance is such that the value $d(\text{M}\cdots\text{H}) - \Sigma\, r_{\text{cov}} >$ 1 Å. These are very weak interactions, which are probably electrostatic in origin and mostly have M···H distances a little less than the sum of the van der Waals radii of the metal and the hydride ions. An example is in the complexes $[\text{Sb(Tm}^{\text{Me}})_2\text{X}]$ (X = Br, I).[60]

It is also of interest to consider what drives the adoption of a κ^3-S,S,H coordination mode over the expected κ^3-S,S,S mode. Initial observations of this phenomenon were with the "bulky" ligands Tm^{R} (R = Ph, *t*Bu) suggesting a steric origin. However, $[\text{Fe}^{\text{II}}(\text{Tm}^{\text{Ph}})_2]$ has an S_4H_2 coordination sphere, while the corresponding Fe^{III} complex (which has a nominally smaller metal cation, which should further favour this mode) in fact has a S_6-coordination sphere. Because the steric bulk of the substituents does not preclude formation of the sandwich complex, it seems therefore that the origin may well be electronic in nature. It seems that the M···H–B interactions are more prevalent with electron-rich metal centres either with d^n electron configurations where $n \geq 6$ or with a low formal oxidation state. Presumably, the high degree of orbital occupancy and high electron density at the metal ion, renders coordination of the π-donating S atom unfavourable. Instead, the less electronically demanding 3-centre-2e⁻ interaction with the hydride is preferred. The strength of the interaction in certain cases is underlined by the inability of either water or chloride ligands to disrupt the M···H–B interaction in the complexes $[\text{Re(Bm}^{\text{Me}})(\text{CO})_3]$, although stronger donors such as phosphanes and isonitriles do displace the B–H group from the coordination sphere.[40]

3.5 Ligand Reactivity

Oxidative Degradation: While the coordination chemistry of the Tm family of ligands is extensive, we very quickly became aware that in certain circumstances, particularly in oxidising conditions, they are subject to relatively facile degradation reactions. One of our initial aims in generating the Tm^{Me} ligand was to use it to model copper-containing metalloenzymes. However, to our disappointment, reaction of NaTm^{Me} with CuCl_2 results not in a copper(II) complex, but rather in the formation of the known compound $[\text{Cu}^{\text{I}}\text{Cl(mtH)}(\mu\text{-mtH})]_2$ in good yield (Figure 10).[24] This is apparently an oxidative degradation of the ligand with concomitant reduction of the metal. Subsequently several examples of such oxidative ligand cleavage have been observed in our group. For instance, reaction of Tm^{Me} with Fe^{3+} ions results not only in ligand cleavage, but in oxidative coupling of the resulting methimazolate ions to give the corresponding disulfide, which chelates to iron(II) through the imidazole nitrogen atoms. (Figure 10).[24] Furthermore, attempts to oxidise $[\text{M(Tm}^{\text{Me}})(\text{CO})_3]^-$ (M = Mo, W) to the corresponding neutral radical species using AgBF_4 resulted in formation of $[\text{Ag(mtH)}_2(\mu\text{-mt})]_2$ and $[\text{M(mtH)(CO)}_5]$.[24]

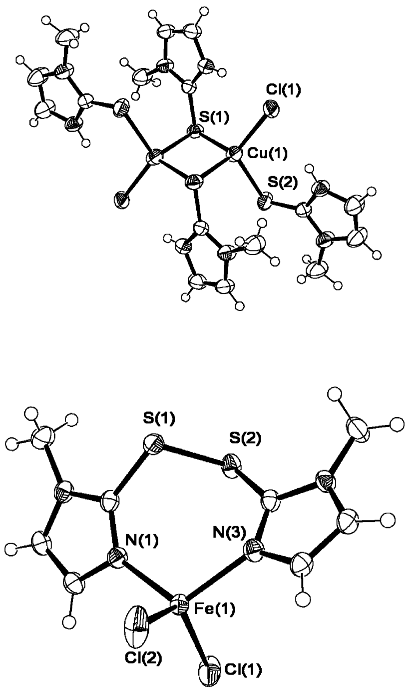
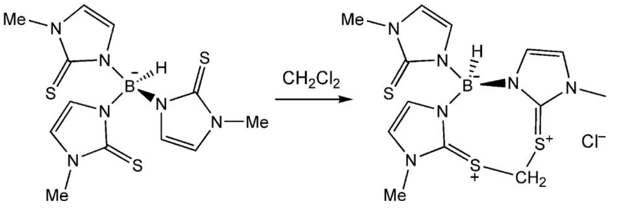
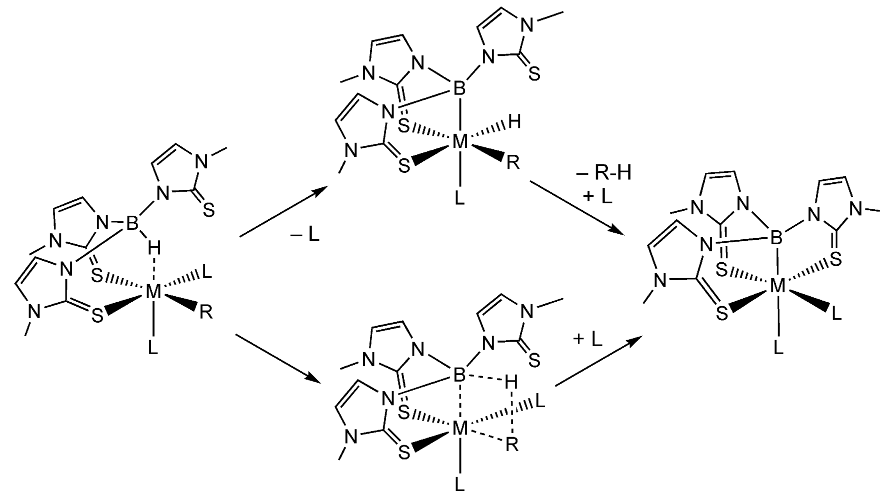


Figure 10. Structures of decomposition products $[\text{CuCl(mtH)}(\mu\text{-mtH})]_2$ (top) and $[\text{Fe(MeimS-SimMe)Cl}_2]$ (bottom).[24]

Non-Degradative Reactions: Not all reactions of the Tm^{Me} ligand lead to total ligand degradation. Hill has shown that dichloromethane reacts slowly with the free ligand, leading to formation of a heterocyclic salt (Scheme 3).[61] This is a cautionary result, since on the face of it dichloromethane would otherwise appear to be a good solvent for complexation reactions of the Tm ligand. We have also observed that reaction of $[\text{M(Tm}^{\text{Me}})(\text{CO})_3]^-$ (M = Mo, W) with NOBF_4 results not only in formation of the desired metal nitrosyl complexes, but also a neutral borane adduct, $\text{B(mt)}_3(\text{dmf})$.[42] The NO^+ ion is oxidising and presumably is responsible for removing the hydride from boron thus allowing the solvent adduct to form.



Scheme 3. Reaction of the Tm^{Me} anion with dichloromethane.



Scheme 4. Possible routes to metallaboratrane formation.

Metallaboratrane Formation: Perhaps the most spectacular reactivity of these ligands is observed in the formation of the metallaboratranes, in which the hydride is lost from boron and a formal bond between boron and the metal is formed (Scheme 4). These bonds can be considered examples of the long hypothesised metal to boron dative bonds.[62] The existence of such bonds has been questioned,[63] but these systems give the first unequivocal evidence for this interaction.[64] It is thought that the additional coordination of the methimazole arms with the formation of three five-membered chelate rings gives considerable stability to the structure. The mechanism of formation (Scheme 4) has not yet been elucidated unequivocally, but it seems likely that in the first instance a M···H–B interaction occurs which is followed by a metal mediated activation of the B–H bond which can be likened to an oxidative addition. If no hydrogen acceptor group (R) is present, the resulting metal hydride can on occasions be isolated,[55] but more normally this reacts rapidly, most typically by reductive elimination with an alkyl or aryl group leading to metallaboratrane formation. Alternatively, one could envisage a concerted process in which the borohydride activation leads to a cyclic transition state from which elimination of R–H occurs with concurrent M–B bond formation. In at least one case solvent has been clearly implicated in the process, with generation of CH_2Cl_2 from chloroform and the coordination of a chloride ligand being observed.[65]

There has been lively debate[66,67] regarding the most appropriate way to account for the valence electrons in these systems. Due to the rarity of occurrence, the consequence of "retro-dative" M→L bonding on d^n electron configuration is not well appreciated by coordination chemists. The confusion arises primarily in the assignment of formal oxidation states and d^n electron configurations. Typically, the d^n configuration is considered to be equal to the number of valence electrons in the neutral atom minus the oxidation number and in the majority of circumstances, an appropriate value for d^n is obtained by this method. In this particular case assignment of d^n is complicated by the ambiguity in determining oxidation number in the traditional way using electronegativity, as the Pauling electronegativities of the late transition elements (1.8–2.2) are very close to that of boron (2.0) and thus a consistency of assignment of electron pairs across a number of closely related systems is not easily achieved. A notation which assigns an overall electron configuration to the metallaboratrane sub-unit, similar

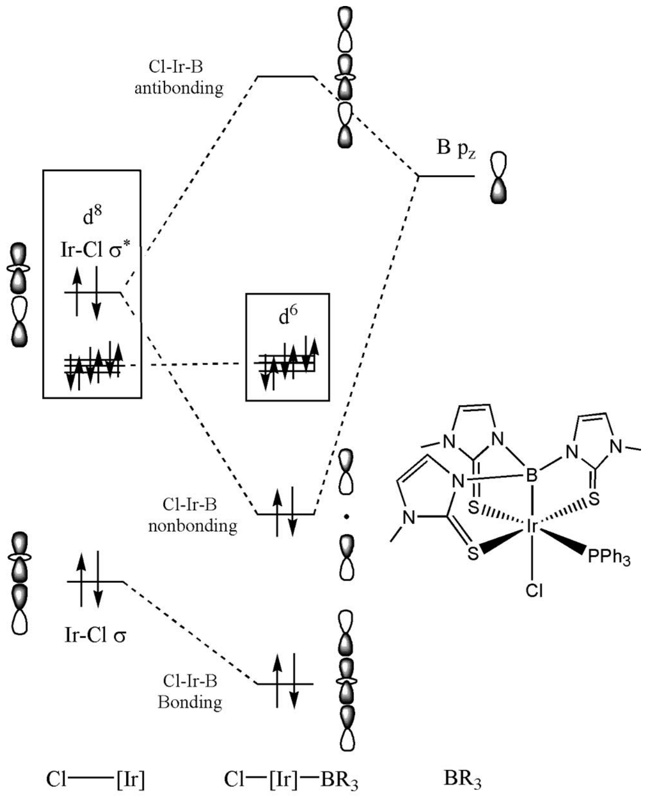


Figure 11. Partial MO correlation diagram depicting the axial Cl–Ir–B interaction in the iridaboratrane [Ir{B(mt)$_3$}(PPh$_3$)Cl].[68]

to that used in metal nitrosyl complexes, has been suggested, but this is not a truly analogous situation and sidesteps the issue. It is helpful to bear in mind that in terms of a MO bonding model the d^n configuration is best considered to be the number of electrons in essentially non-bonding molecular orbitals of d-character. These compounds represent a rare occasion where the d^n configuration is not in line with the accepted norms. Thus, Rh^I, Ir^I, Pd^{II} and Pt^{II} metallaboratranes all have d^6 electron configurations, not the expected d^8 configuration. This arises because the metal based electrons which form the dative bond to the ligand can be thought of as no longer occupying a non-bonded metal d-orbital, but rather a M–L bonding orbital (Figure 11). There is no net change in formal oxidation state of the metal in the generation of this interaction but a decrease of 2 in the d^n electron configuration. The subject of bonding in these compounds has been discussed in greater detail by Parkin.[68] Although the first metallaboratrane was observed in the reaction of $[Ru(\eta^1\text{-}CH{=}CH_2)(PPh_3)_2(CO)Cl]$ with $NaTm^{Me}$,[63] examples have now been synthesised for all of the elements from the Ni, Co and Fe triads and will be discussed further in the survey of transition metal chemistry below.

3.6 Main Group Chemistry

s-Block Chemistry: The Tm^R ligands are prepared as their alkali metal (Li, Na, K) salts, and we reported the structure of a hydrated Na salt in 1999.[10] The crystals were obtained from anhydrous $NaTm^{Me}$ in $CHCl_3$ solution. Moisture was not excluded and consequently water must have been sequestered from the atmosphere by the Na cations. The Tm^{Me} anion is not associated with the sodium cation, which is instead coordinated by water molecules forming disordered chains. More recently we have obtained two sodium Tm^{Me} structures in which the Tm^{Me} does coordinate to the sodium cation.[69] We obtained an anhydrous structure serendipitously from reaction of $NaTm^{Me}$ with an organometallic species in dry DMF (the organometallic has presumably acted as a water scavenger). The resulting structure (Figure 12, top) is a DMF-bridged dimer with a Tm^{Me} anion coordinated in a κ^3-S,S,H mode to each sodium ion. Attempts to obtain this species rationally by recrystallisation of anhydrous $NaTm^{Me}$ from dry DMF/diethyl ether mixtures have always resulted in a different structure (Figure 12, bottom). It has a chain of four Na^+ ions bridged by water and the two central sodium ions have a Tm^{Me} anion ligated in a κ^1-S mode and a terminal DMF ligand. The charge is balanced by two non-coordinated Tm^{Me} anions. This species may be considered an intermediate in the hydrolysis of the anhydrous structure above. Anhydrous KTm^{Me} has also been structurally characterised and remarkably the crystals were obtained from aqueous solution. The potassium ion is five-coordinate, with each Tm ligand having one terminal and two bridging sulfur donors. This results in an infinite 1-D chain structure.[12b] The formation of group 2 complexes of Tm^{Me} has recently been reported by Ziegler.[46c] Reaction of $NaTm^{Me}$ with $Ca(NO_3)_2$ in aqueous solution results in a solvent separated ion pair, $[Ca(OH_2)_6](Tm^{Me})_2$, but a similar reaction with $Ba(NO_3)_2$ gives a complex, $[Ba(Tm^{Me})_2(OH_2)_2]$ in which two Tm^{Me} ligands are coordinated to barium in a κ^3-S,S,H mode. The coordination sphere is completed with two water molecules resulting in an approximately square-prismatic geometry. It is surprising that Tm^{Me} is able to compete so effectively with water for a place in the barium coordination sphere.

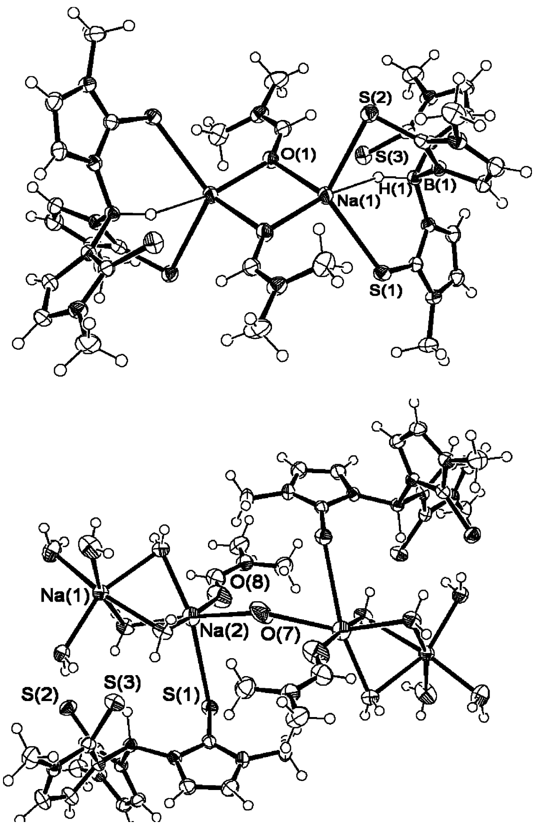


Figure 12. X-ray structure of $[Na(Tm^{Me})(\mu\text{-DMF})]_2$ (top) and $[Na_4(Tm^{Me})_2(OH_2)_{13}(DMF)_2]^{2+}$ (bottom).

p-Block Chemistry: Very early in our studies of the Tm^{Me} ligand we turned our attention to the chemistry of the lower p-block elements. The Tp chemistry of these elements is notoriously difficult, the complexes formed typically being somewhat thermally unstable and highly moisture sensitive.[70] We initially prepared a bismuth complex, $[Bi(Tm^{Me})_2]^+$, (vide supra)[36] and were surprised to find it to be stable and unaffected by moisture. Remarkably, the synthesis of this and many of the other species to be described below may be performed without need for exclusion of oxygen or water.

The most commonly obtained motif is the sandwich complex, $[E(Tm^{Me})_2]^{n+}$ (E = In^{III},[60] Tl^{III},[71,72] Sn^{IV},[73] As^{III},[73] Bi^{III};[36,60] see Figure 13). In these complexes the ligand is coordinated in a κ^3-S,S,S mode to give a regular S_6 coordination sphere, with E–S bond lengths all approximately equal. The intra-ligand S–E–S angles are typically slightly larger than 90°, while the inter-ligand S–E–S angles are slightly less than 90° resulting in a slight compression of the coordination octahedron. With the exception of the As^{III} complex (vide infra), the E–S distances are proportional to the ionic radii of the central ions.

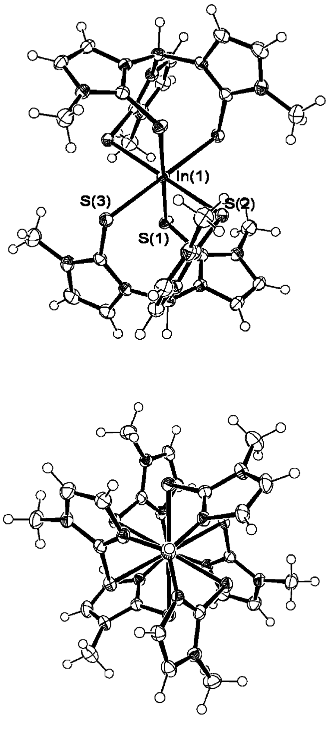


Figure 13. The commonly observed “sandwich” structure observed in p-block chemistry of the Tm^{Me} ligand (top) and as viewed down the B···M···B axis (bottom).

When stereochemically active (homo-directed) non-bonded electron pairs come into play then a variety of structures emerge. Among the elements studied thus far these should potentially be observed with In^{I}, Tl^{I}, Sn^{II}, Pb^{II}, As^{III}, Sb^{III}, Bi^{III} and Te^{II}. A complex with In^{I}, $[In(Tm^{tBu})]$, has recently been prepared.[74] It is pyramidal, and is able to donate retrodatively to $B(C_6F_5)_3$ and reacts with elemental sulfur to give $[In(Tm^{tBu})(\kappa^2\text{-}S_4)]$. By contrast, complexes with Tl^{I} show no directional lone pair, presumably due to the relativistic contraction of the 6s electrons. Instead Tl^{I} with both Tm and Bm forms ligand-bridged dimeric structures with a central Tl_2S_2 core,[13b,72,75] reminiscent of those seen with Cu^{I} and Ag^{I}. With Pb^{II} the structural effects of the lone pair are clearly seen. Parkin has prepared complexes $[Pb(Tm^{Ph})]ClO_4$ and $[Pb(Tm^{Ph})](Tm^{Ph})$[76] in which the metal has pyramidal geometry. In the former complex the Pb–S distance is 2.693 Å and perchlorate is remote from the metal centre, whereas in the latter the primary coordination has Pb–S distances of 2.848 Å while the second Tm^{Ph} ligand is more weakly associated with the metal centre with Pb–S distances of 3.171 Å. A short, and unusually, linear Pb···H–B interaction is also observed.

The group 15 elements exhibit particularly complex behaviour. The As^{III} complex, unexpectedly, has a regular S_6 coordination sphere, but the As–S distances are longer than would be predicted on the basis of the ionic radius. A plot of *d*(E–S) vs. ionic radius of E (E = In^{III}, Tl^{III}, Ge^{IV}, Sn^{IV}, As^{III}, Bi^{III}) based on the known $[E(Tm^{Me})_2]^{n+}$ (Figure 14) gives a straight line plot, with the exception of As^{III} which has bond length some 0.12 Å longer than would be expected on this basis. This is a rare, unambiguous example of the bond lengthening predicted when a holo-directed electron pair is present.[77]

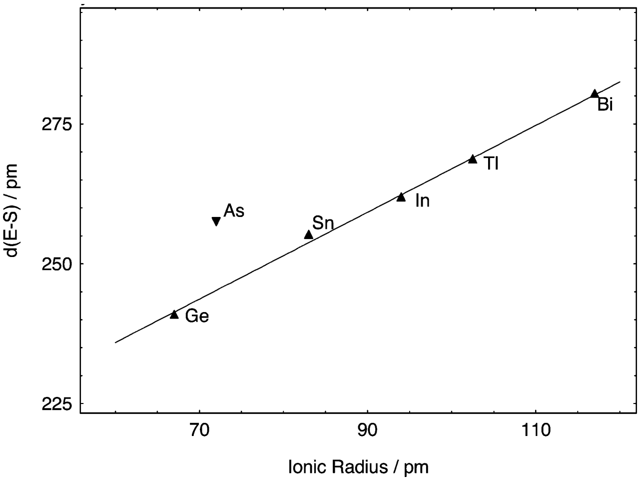


Figure 14. Plot of E–S bond length [pm] against ionic radius [pm] for the p-block complexes $[E(Tm^{Me})_2]^{n+}$ ($n = 3$, E = As, In, Tl, Bi; $n = 4$, E = Ge, Sn).

The chemistry of antimony with Tm^{Me} is complex.[60] With antimony halides two structures have been observed, both of which are isolated from the same reaction mixture, indicating that some ligand redistribution may occur. This is borne out by the NMR spectra of these species, which exhibit fluxionality at room temperature. The structures are a halide-bridged dimer, $[Sb(Tm^{Me})X(\mu\text{-}X)]_2$ (Figure 15) and a monomeric species, $[Sb(Tm^{Me})_2X]$ (X = Br, I; Figure 9). The latter has one Tm^{Me} ligand in a κ^3-S,S,S mode and one in a nominally κ^2-S,S mode, although one of the Sb–S distances is rather long (3.307 Å). In the presence of halide[36,78] and nitrate,[79] Bi^{III} also forms directly analogous species. In each of these complexes there is significant distortion of the coordination polyhedron, consistent with the presence of a homodirected electron pair. Curiously, bismuth is able to form a sandwich-type complex in the absence of halide. Thus, reaction of $Bi(NO_3)_3$ with excess $NaTm^{Me}$ gives the complex $[Bi(Tm^{Me})_2]NO_3$, which has a regular S_6 coordination sphere. By contrast, all attempts to form the sandwich complex with antimony have been fruitless. Reaction of $Sb(OAc)_3$ with excess $NaTm^{Me}$ gives rise to $[Sb(Tm^{Me})_2]Tm^{Me}$, in which the antimony ion is square pyramidally coordinated by a κ^3 and a κ^2 ligand and a Tm^{Me} counterion balances the charge. It is not readily apparent why both bismuth and arsenic can form the sandwich type of complex, while antimony does not. Finally, reaction of $[Te(tu)_4]Cl_2$ (tu = thiourea) results in the formation of $[Te(Tm^{Me})_2]$, which has square-planar geometry, as expected in the presence of two non-bonded pairs and both ligands are coordinated in the κ^2-S,S mode.[80] No complexes of indium(I) or tin(II) have yet been isolated, indeed, in our hands all reactions of tin(II) salts with NaTm^{Me} result in isolation of tin(IV) compounds even in rigorously anaerobic conditions.[73]

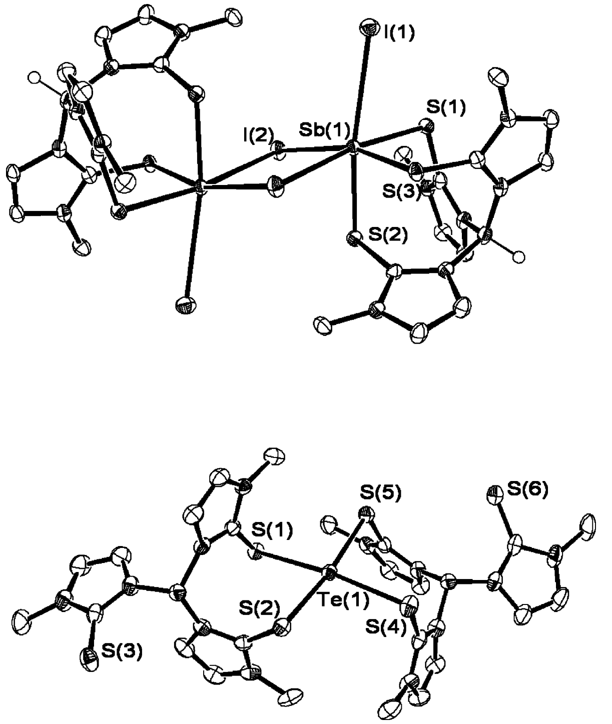


Figure 15. Complexes of the Tm^{Me} ligand with p-block elements having homodirected lone-pairs. Top: [Sb(Tm^{Me})Cl(μ-Cl)]$_2$ which shows distortion of the octahedral geometry; bottom: [Te(Tm^{Me})$_2$] which exhibits square-planar geometry.

Further structural motifs are obtained among the p-block organometallic derivatives of Tm^R. The reaction of R$_3$SnCl (R = Me, *n*Bu, Cy, Ph)[81] with NaTm^{Me} results in a complex with formula [Sn(Tm^{Me})R$_3$]. The tricyclohexyl[81] and triphenyl[82,83] tin complexes have been structurally characterised. Here the tin(IV) centre is tetracoordinate and the Tm ligand exhibits a κ^1-S coordination mode. ^{119}Sn NMR studies confirm that the four-coordinate geometry is maintained in solution. Reactions with R$_2$SnCl$_2$ (R = Me, Et, *n*Bu, Ph) and RSnCl$_3$ (R = Me, *n*Bu, Ph) result in complexes of empirical formula [Sn(Tm^{Me})R$_2$Cl] and [Sn(Tm^{Me})RCl$_2$] respectively.[81] On the basis of tin NMR coupling constants these are assigned as five-coordinate structures, although this assertion has not been fully confirmed. By way of contrast, the reaction of NaBm^{Me} with Me$_2$SnCl$_2$ results in a "salt", [Sn(Bm^{Me})(Me)$_2$]Cl.[84] The cation has a disphenoidal structure with methyl groups in the axial positions, while there is association into dimers via weak Sn–Cl–Sn interactions [*d*(Sn···Cl) = 3.00(2) Å]. Shimada et al. have reported the reaction of Me$_2$BiCl with NaTm$^{t\mathrm{Bu}}$, which yields [(BiMe$_2$)$_3$(Tm$^{t\mathrm{Bu}}$)$_2$][BiMe$_2$Cl$_2$]. This exhibits an unusual trinuclear structure in which a triangle of BiMe$_2$ units are sandwiched by two Tm$^{t\mathrm{Bu}}$ ligands (Figure 16).[78] Finally, reaction of pzBm^{Mes} with Me$_2$TlCl results in formation of four-coordinate [Tl(pzBm^{Mes})Me$_2$] in which the ligand binds in a κ^2-S,S, mode. Significant structural distortion is seen, with the C–Tl–C angle being 157.7°, despite the absence of non-bonded electron pairs.[72]

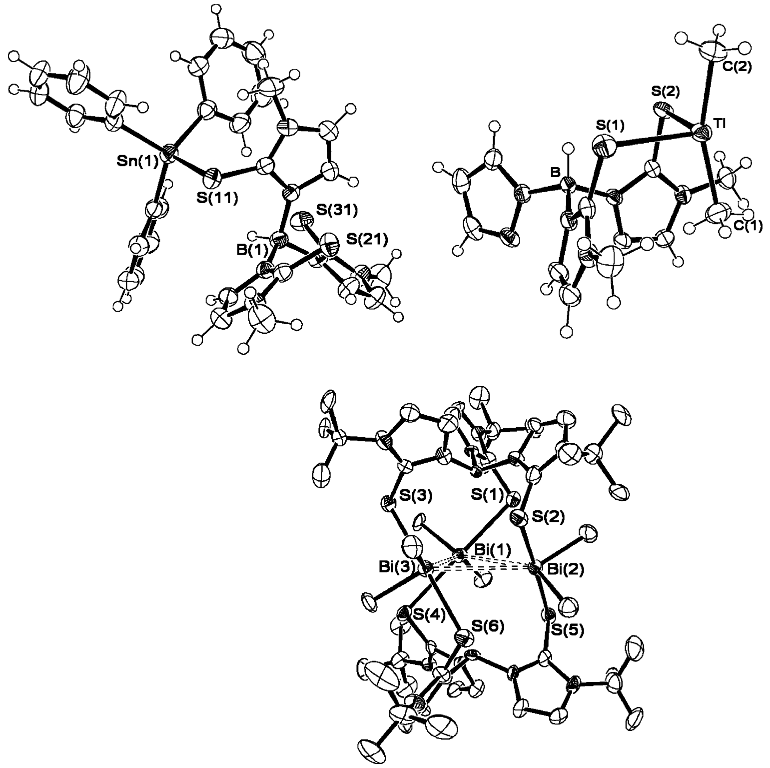


Figure 16. Structures of some organometallic p-block derivatives of methimazolyl borate ligands. Top left: Ph$_3$SnTm^{Me}. Top right: [Tl(pzBm^{Me})(CH$_3$)$_2$]. Bottom: [(BiMe$_2$)$_3$(Tm$^{t\mathrm{Bu}}$)$_2$]$^+$.

3.7 Transition-Metal Chemistry

Complexes of the Tm^{R} ligands with a large proportion of the d-block elements have been reported, and here the chemistry will be briefly surveyed by triad.

Group 3: No complexes with group-3 elements have been reported to date.

Group 4: Despite the apparent mismatch between the hard group-4 elements and the soft sulfur-donor atoms, a number of complexes have been reported.

Reaction of $[\mathrm{Ti}(\eta^8\text{-}\mathrm{C_8H_8})(\mathrm{THF})(\mu\text{-}\mathrm{Cl})]_2$ with NaTm^{Me} yields the Ti^{III} compound $[\mathrm{Ti}(\mathrm{Tm^{Me}})_2][\mathrm{Ti}(\mathrm{THF})_2\mathrm{Cl}_4]$, which is the first example of a S$_6$ coordination sphere in Ti^{III} chemistry.[85] While the geometry is clearly distorted from regular octahedral, this is in keeping with most $[\mathrm{M}(\mathrm{Tm^{Me}})_2]^{n+}$ sandwich complexes and cannot be ascribed to Jahn–Teller effects at the 3d^1 metal centre. To date no Ti^{IV} complex has been isolated with the Tm^{Me} ligand, but reaction of $[\mathrm{Ti}(=\mathrm{N}t\mathrm{Bu})(\mathrm{py})_3\mathrm{Cl}_2]$ with the Bm^{Me} ligand yields a complex $[\mathrm{Ti}(=\mathrm{N}^{t\mathrm{Bu}})(\mathrm{Bm^{Me}})_2]$,[86] which is six-coordinate with the four sulfur donors co-planar and a relatively short B–H···Ti interaction (2.09 Å) trans to the imido group. Thus, the complex has both κ^2-S,S and κ^3-S,S,H coordinated ligands.

The only zirconium Tm^{R} complex is Parkin's $[\mathrm{ZrCp}(\mathrm{Tm^{Me}})\mathrm{Cl}_2]$, synthesised by reaction of $[\mathrm{ZrCpCl}_3]$ with KTm^{Me}.[87] Comparison with the Cp and Tp analogues reveal that while these both have a mirror plane, the Tm^{Me} complex has C$_1$ symmetry at all times, as confirmed by resonances arising from three inequivalent methimazole rings in the ^{1}H NMR spectrum. $[\mathrm{ZrCp}(\mathrm{Tm^{Me}})\mathrm{Cl}_2]$ is able to polymerise ethylene in the presence of methylalumoxane (MAO), albeit with an activity of approximately one fifth of that of the $[\mathrm{ZrCp_2Cl_2}]$ analogue. Despite the lower activity, control of the symmetry by utilising single enantiomer ligands has potential in forming stereo-regular polymers from α-olefins. Reaction of $[\mathrm{Zr}(\eta^8\text{-}\mathrm{C_8H_8})(\mathrm{THF})\mathrm{Cl}_2]$ with NaBm^{Me} does result in formation of the three legged piano-stool complex $[\mathrm{Zr}(\eta^8\text{-}\mathrm{C_8H_8})(\mathrm{Bm^{Me}})\mathrm{Cl}]$ in which the Bm^{Me} ligand adopts a κ^2-S,S configuration.[88]

No complexes of Tm^{R} (or Bm^{R}) with hafnium have been reported to date.

Group 5: No Tm^{R} complexes with vanadium are known.

Direct reaction of M$_2$Cl$_{10}$ (M = Nb, Ta) with NaTm^{Me} (and NaBm^{Me}) results in the formation of intractable mixtures of products. Observation of methimazole among these products suggests that some oxidative cleavage may occur. Use of an organotin complex, Ph$_3$SnTm^{Me}, as a ligand transfer agent was similarly problematic with M$_2$Cl$_{10}$, but with $[\mathrm{MCpCl_4}]$ (M = Nb, Ta) orange compounds were obtained. These proved not to be simple Tm^{Me} complexes, but rather complexes of ClBm^{Me} (Figure 17), in which a single methimazole has been cleaved and replaced by a chloride abstracted either from the Ph$_3$SnCl precursor, or more likely, from an intermediate in the reaction of $[\mathrm{MCpCl_4}]$.[83]

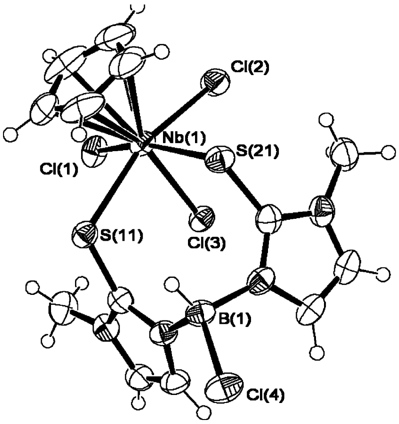


Figure 17. X-ray crystal structure of $[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{ClBm^{Me}})\mathrm{Cl_3}]$.

Reaction of NaTm^{Me} with the less Lewis acidic imido complexes, $[\mathrm{Nb}(=\mathrm{NR})\mathrm{Cl_3}(\mathrm{DME})]$ and $[\mathrm{Ta}(=\mathrm{NR})\mathrm{Cl_3}(\mathrm{THF})_2]$ results in the formation of the respective Tm^{Me} complexes $[\mathrm{M}(=\mathrm{NR})(\mathrm{Tm^{Me}})\mathrm{Cl_2}]$ (R = 2,6-diisopropylphenyl).[89] Similarly, reaction of $[\mathrm{Ta}(\eta^2\text{-}\mathrm{RC{\equiv}CR})\mathrm{Cl_3}(\mathrm{DME})]$ (R = Et, Ph) with NaTm^{Me} yields $[\mathrm{Ta}(\eta^2\text{-}\mathrm{RC{\equiv}CR})(\mathrm{Tm^{Me}})\mathrm{Cl_2}]$, the first Tm^{R} alkyne metal complexes.[90] Whereas in the Cp and Tp analogues the alkyne is symmetrically bound to the metal, in this Tm^{Me} complex the alkyne shows remarkable asymmetry in the M–C distance, perhaps hinting at the possibility of stereospecific reactivity at the alkyne. Finally, reaction of $[\mathrm{Ta^V}(\mathrm{Cp^*})\mathrm{Cl_4}]$ with Bm^{Me} results in a Ta^{IV} complex, $[\mathrm{Ta}(\mathrm{Cp^*})(\mathrm{Bm^{Me}})\mathrm{Cl_2}]$, which contains a close to linear (163°) Ta···H–B interaction (Figure 18).[91] It is presumed that the Bm^{Me} ligand acts as a reductant in this system as the best yields are obtained

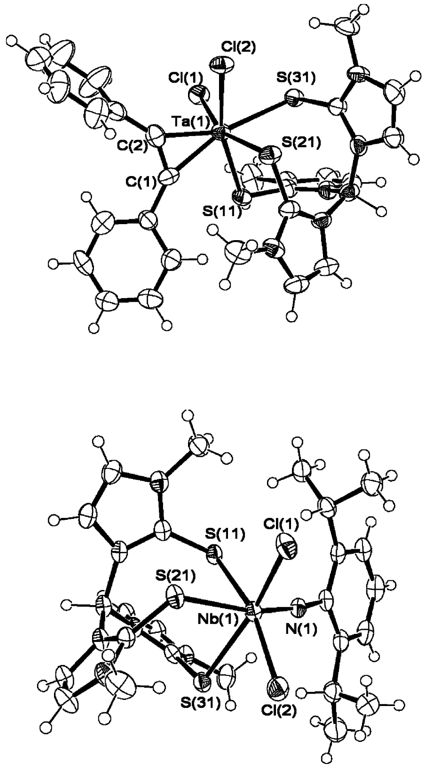


Figure 18. Structures of a niobium imido complex, $[\mathrm{Nb}(=\mathrm{NAr})(\mathrm{Tm^{Me}})\mathrm{Cl_2}]$ (bottom) and the tantalum alkyne complex, $[\mathrm{Ta}(\mathrm{Tm^{Me}})(\mathrm{PhC{\equiv}CPh})\mathrm{Cl_2}]$ (top).

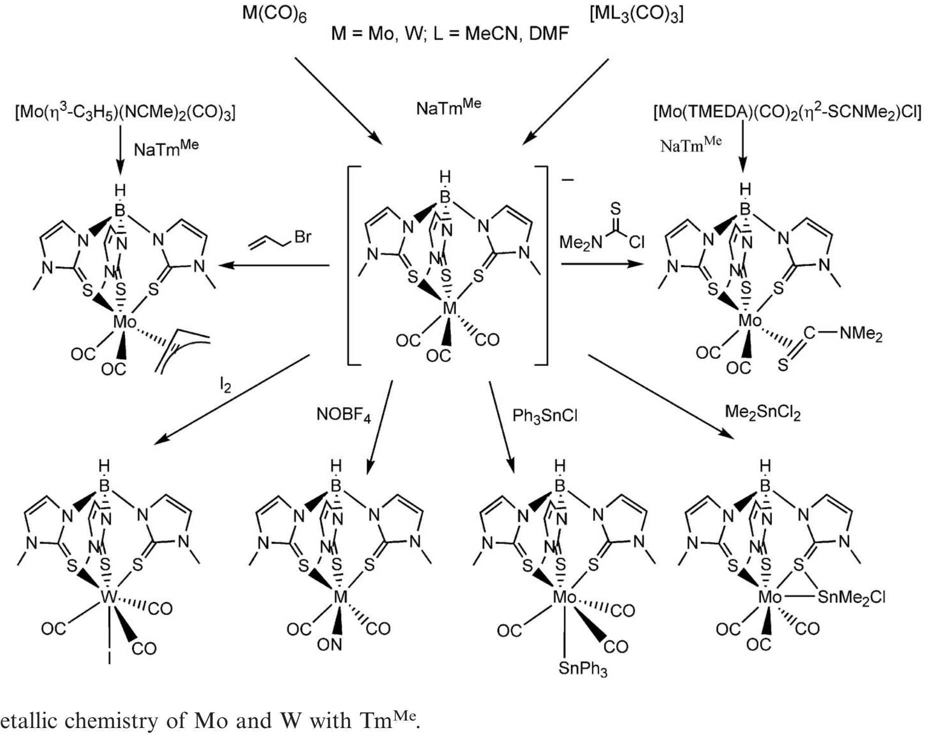
when an excess of ligand is used. These results further confirm that there is not an inherent incompatibility between the soft sulfur donors of these ligand systems and the hard, high-oxidation-state early-transition-metal centres provided appropriate precursors and synthetic routes can be found.

Group 6: No Tm^R complexes of chromium have yet been reported.

The organometallic chemistry of Tm^{Me} with molybdenum and tungsten carbonyls has been extensively studied and is summarised in Scheme 5. The first report was on the formation of $[Mo(Tm^{Me})(CO)_2(\eta^3\text{-}C_3H_5)]$, in which the ligation of the η3-allyl is substantially asymmetric and the internal C–C bond lengths are markedly inequivalent, presumably reflecting the asymmetry of the ligand coordination.[37] It was also noted that the NMR spectra were broadened, suggesting ligand exchange on the NMR timescale, a phenomenon which is almost universal in this area of chemistry. The seven-coordinate $[W(Tm^{Me})(CO)_3I]$ was also reported. The intermediates in these reactions are presumed to be the anions, $[M(Tm^{Me})(CO)_3]^-$ and these have also been reacted with either $NOBF_4$[42] or Diazald[92] to yield the nitrosyl species $[M(Tm^{Me})(CO)_2(NO)]$ and with *N*,*N'*-dimethylthiocarbamoyl chloride to yield η^2-thiocarbamoyl complexes,[93] $[Mo(\eta^2\text{-}SCNMe_2)(Tm^{Me})(CO)_2]$. Reaction of the anion with tin halides yields molybdenum stannyl complexes. Thus with Ph_3SnCl the presumably seven-coordinate terminal stannyl complex $[M(Tm^{Me})(SnPh_3)(CO)_3]$ (M = Mo, W) is formed, while with Me_2SnCl_2 one of the methimazole sulfur atoms bridges the Mo–Sn bond.[84] Recently, molybdenum and tungsten alkyne complexes, $[M(Tm^{Me})(MeC{\equiv}CMe)(CO)I]$ and for M = Mo, a second complex $[M(Tm^{Me})_2(PhC{\equiv}CPh)]$ have been obtained. The latter is revealed by crystallographic analysis to have one κ^3-S,S,S ligand, and unusually for transition-metal Tm^R complexes, one κ^1-S ligand.[94] A series of tungsten alkylidyne complexes supported by the Tm^{Me} ligand, $[W({\equiv}CR)(Tm^{Me})(CO)_2]$, has also been synthesised.[38]

A number of molybdenum complexes with higher oxidation state have also been synthesised as potential analogues of the pterin-ligated active sites of metalloenzymes such as sulfite oxidase. Two studies appeared concurrently. We described the synthesis and structure of $[Mo^{VI}(Tm^{Me})(O)_2Cl]$, the highest oxidation-state complex of Tm^R yet reported, and demonstrated the oxidation of sulfite by the complex using a novel ion chromatographic method.[95] Carrano has reported not only the Mo^{VI} species above, but also two Mo^V species, the monomeric $[Mo(Tm^{Me})(O)Cl_2]$ and the dimeric $[\{Mo(Tm^{Me})(O)Cl\}_2(\mu^2\text{-}O)]$ and also a Mo^{IV} complex supported by isocyanide ligands, $[Mo(Tm^{Me})(O)(CNtBu)_2]$. He has demonstrated catalytic oxygen atom transfer to phosphanes in DMSO solution.[96] These systems are both good functional models of the class of metalloenzymes, and improved structural models (when compared to the Tp analogues).[4]

Group 7: A range of complexes of form $[Mn(R'Tm^R)(CO)_3]$ have been prepared from $[Mn(NCMe)_3(CO)_3]PF_6$ by Bailey (Tm^{Me})[97] and $[Mn(CO)_5Br]$ by Rabinovich (Tm^{tBu}, Tm^{Bz}, Tm^{pTol}, $PhTm^{Me}$).[41] These have facially capping κ^3-S,S,S ligands, while the related Bm^R complexes have κ^3-S,S,H ligands, with rather short M···H–B distances, They illustrate once more, via the C–O stretching frequencies, that the magnitude of the electron donation from the Tm ligands is somewhat greater than in either the Tp or Cp analogues.



Scheme 5. Organometallic chemistry of Mo and W with Tm^{Me}.

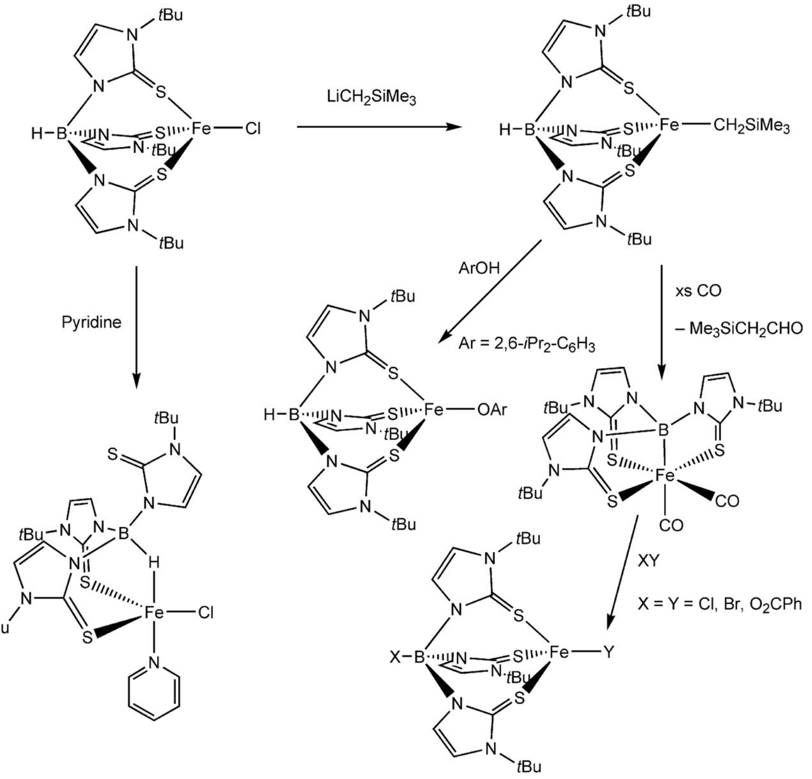
Tatsumi and co-workers have also prepared manganese(II) halide complexes with Tm^R ligands.[21b] With Tm^{Me} a dimeric complex, $[Mn(Tm^{Me})(\mu^2\text{-}Cl)]_2$, has been isolated and structurally characterised, revealing five-coordinate metal centres. With bulkier substituents (R = *t*Bu, Ph, 2,6-*i*Pr_2-C_6H_3) monomeric tetrahedral $[Mn(Tm^R)Cl]$ are obtained. Presumably the use of bulkier ligands precludes dimerisation. Conversion of the monomeric chloride complexes to the corresponding iodides is achieved by reaction with NaI, whereas attempts to synthesise these directly from MnI_2 gives an inseparable mixture of products.

Santos and co-workers have published a considerable body of work on Tc and Re carbonyl complexes of $R'Tm^R$ and the related $R'Bm^R$ ligands[22,23,39,40,98] (concentrating primarily on the latter) with particular emphasis on their potential use in radiopharmaceutical applications.[99] This area has been reviewed, both by Santos[100] and ourselves[101] and thus only a brief discussion will be offered here. ^{99m}Tc complexes with both Tm^R and $R'Bm^R$ ligands are formed rapidly (30 min) from $[^{99m}Tc(OH_2)_3(CO)_3]$ in close to quantitative yields for ligand concentrations as low as 10^{-5} M.[99] The Tm^R complexes, as expected, have facial κ^3-S,S,S coordination, while the $R'Bm^R$ complexes adopt the κ^3-S,S,H mode similar to the manganese analogues. In vitro testing shows these complexes to be stable over a 24-h period in various biologically relevant media. In vivo studies targeting the brain 5-HT_{1A} serotonin receptors indicate efficient uptake, but also rapid washout of these compounds. Thus, while they show promise in this application, and a patent has been filed,[102] some further development appears necessary. Corresponding rhenium compounds have been prepared by treatment of $LiR'Tm^{Me}$ (R′ = H, Me, Ph) with either $[Re(CO)_5Br]$ or $(NEt_4)_2[Re(CO)_3Br_3]$, even in aqueous, aerobic conditions. Their structures parallel those observed for the manganese analogues. Substitution reactions of the $[Re(R'Bm^{Me})(CO)_3]$ complexes lead to various outcomes. Addition of monodentate ligands results in formation of $[Re(R'Bm^{Me})L(CO)_3]$ (L = PPh_3, 4-DMAP, RN≡C, imidazole)[40,98b] with disruption of the M···H–B interaction. Addition of 1,2 diaminoethane results in the complex $[Re(R'Bm^{Me})(en)(CO)_3]$ in which the Bm ligand is κ^1-S coordinated and en is bidentate, while with the potentially bidentate ligand $Ph_2P(CH_2)_2PPh_2$ (dppe) a bridged compound $[\{Re(Bm^{Me})(CO)_3\}_2(\mu^2\text{-dppe})]$ is obtained.

Group 8: Reaction of iron(II) salts with $NaTm^{Me}$ results in the formation of the sandwich complex $[Fe(Tm^{Me})_2]$, regardless of stoichiometry and reaction conditions.[43] Spectroscopic and magnetic measurements show this to be a high spin complex and this is borne out by the rather long Fe–S bond lengths (ca 2.45 Å). Attempts to oxidise this species to $[Fe(Tm^{Me})_2]^+$ resulted in decomposition, while direct reaction of $NaTm^{Me}$ with iron(III) salts only yielded the same iron(II) complex in moderate yield. The effect of changing the *N*-methyl group for bulkier substituents has been investigated. Reaction of $LiTm^{Ph}$ with iron(II) salts also results in formation of a species with formula $[Fe(Tm^{Ph})_2]$, but in this case the ligands coordinate via a κ^3-S,S,H mode. Curiously, reaction with iron(III) perchlorate yields $[Fe(Tm^{Ph})_2]ClO_4$ which has the ligands in κ^3-S,S,S mode.[59] Reaction of Tm^R (R = Me, Ph) with an excess of $FeCl_2$ over an extended time period leads to formation of the 1:1 complexes $[Fe(Tm^R)Cl]$ {and possibly the dimeric $[Fe(Tm^{Me})(\mu^2\text{-}Cl)]_2$ in the case of the less bulky Tm^{Me} ligand}. Adoption of the yet bulkier ligand, Tm^{tBu}, results only in the isolation of the 1:1 complex $[Fe(Tm^{tBu})Cl]$.[21b] Parkin has used $[Fe(Tm^{tBu})Cl]$ as a precursor for the synthesis of ferraboratranes.[25] Reaction with $LiCH_2SiMe_3$ results in formation of the alkyl complex $[Fe(Tm^{tBu})(CH_2SiMe_3)]$ which reacts further with ArOH (Ar = 2,6-diisopropylphenyl) to yield the corresponding alkoxide. In the presence of excess CO the ferraboratrane $[Fe\{B(mt)_3\}(CO)_2]$ is formed with concomitant generation of the aldehyde Me_3SiCH_2CHO. The mechanism of formation presumably involves CO complexation and B–H activation at the metal centre followed by CO insertion and finally reductive elimination. It is thought that CO complexation causes the ligand to rearrange to a κ^3-S,S,H coordination mode, thus facilitating B–H activation, and this assertion is supported by the observation and isolation of $[Fe(\kappa^3\text{-S,S,H-}Tm^{tBu})(py)Cl]$ when pyridine is added to the starting material, $[Fe(Tm^{tBu})Cl]$ (Scheme 6). Finally, destruction of the M–B bond via formal 1,2-addition is seen in the reaction of the ferraboratrane with Cl_2, Br_2, dibenzoyl peroxide $[(PhC(O)O)_2]$ and $I_2/CHCl_3$ to yield $[Fe(XTm^{tBu})X]$.

The only "classical" coordination compound of ruthenium to have been reported to date is the octahedral $[Ru(Tm^{Me})(dmso)_2Cl]$, prepared from the $[Ru(dmso)_4Cl_2]$ precursor.[97] A number of organometallic Cp* and π-arene complexes of form $[Cp^*Ru(Tm^{Me})]$ and $[(\eta^6\text{-arene})Ru(Tm^{Me})]^+$ have been described. The π-arene complexes, synthesised from $[(\pi\text{-arene})RuCl_2]_2$ (arene = *p*-cymene, hexamethylbenzene) are air stable complexes with "mixed sandwich" structures.[97,103] The NMR spectra of the *p*-cymene complex with Tm^{Et} again confirms the inherent chirality of the system, since each of the arene C–H proton resonances and the ethyl CH_2 proton resonances are unique implying that they are diastereotopic.[15] Electrochemical studies show that the hexamethylbenzene complex is irreversibly oxidized to the corresponding Ru^{III} complex. By contrast, $[Cp^*Ru(Tm^{Me})]$ undergoes a reversible oxidation and the Ru^{III} complex has been directly synthesised, isolated and structurally characterised.[104] The Ru···H interaction in $[Cp^*Ru(Bm^{Me})]$ has been shown to be disrupted by addition of CO to form the complex $[Cp^*Ru(Bm^{Me})(CO)]$, which can be isolated. The CO is displaced on heating to reform the starting material.[105]

Hill reported the first example of a metallaboratrane (Figure 19), $[Ru\{B(mt)_3\}(PPh_3)(CO)]$ by reacting $[Ru(PPh_3)_2(CO)(R)Cl]$ (R = vinyl or aryl) with $NaTm^{Me}$.[64] In the absence of a suitable R group to drive B–H activation (by elimination of R–H), as in the reaction with $[Ru(PPh_3)_3(H)(CO)Cl]$, a κ^3-S,S,H coordinated complex, $[Ru(Tm^{Me})(PPh_3)(CO)(H)]$ results.[55] This is converted into the same ruthenaboratrane on addition of ethynyl benzene which is itself hydrogenated to yield styrene. The ruthenaboratrane



Scheme 6. Reactions of [Fe(Tm^{tBu})Cl]: substitution, metathesis, ferraboratrane formation and subsequent reactivity.

readily undergoes phosphane displacement. With CO the process is reversible, yielding [Ru{B(mt)$_3$}(CO)$_2$] while with a variety of isonitriles irreversible formation of [Ru{B(mt)$_3$}(CO)(NCR)] occurs (Scheme 7). Analogous thiocarbonyl complexes have also been prepared.[106]

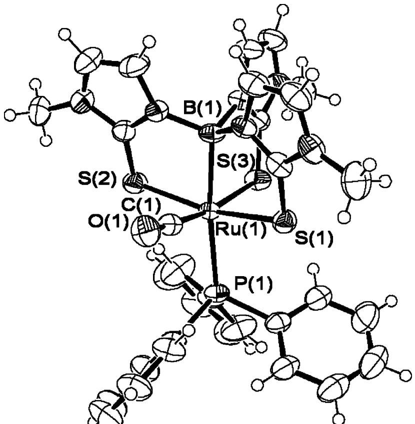
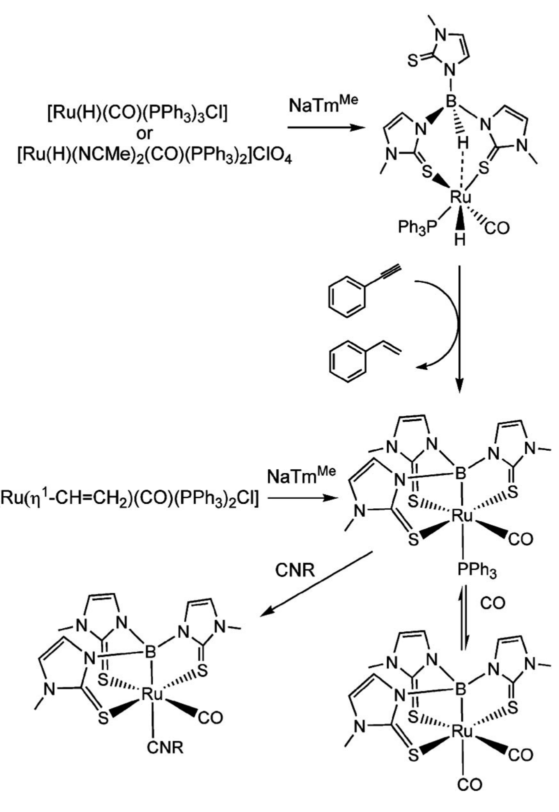


Figure 19. X-ray crystal structure confirming the first metallaboratrane complex, [Ru{B(mt)$_3$}(PPh$_3$)(CO)].

The only osmium chemistry as yet described with the Tm^R ligands is the reaction with [Os(η^1-C$_6$H$_5$)(PPh$_3$)$_2$(CO)Cl] which results in the formation of an osmaboratrane, [Os{B(mt)$_3$}(PPh$_3$)(CO)],[107] which is the direct structural analogue of the first ruthenaboratrane described above.



Scheme 7. Synthesis and reactivity of ruthenaboratranes.

Group 9: A number of studies have appeared on the chemistry of the $\mathrm{Tm^R}$ ligands with cobalt. Simple 1:1 complexes, $[\mathrm{Co(Tm^R)X}]$ (R = Me, *t*Bu; X = Cl, Br, I) have been isolated and have pseudo-tetrahedral geometry.[17,21b,108] These species are highly labile and undergo extensive rearrangement in solution as evidenced by mass spectrometry. The most readily isolated species is the product of oxidation, the octahedral cobalt(III) complex $[\mathrm{Co(Tm^{Me})_2}]^+$,[108] while Rabinovich[17] has also isolated a dinuclear cobalt(II) complex, $[\mathrm{Co_2(Tm^{\mathit{t}Bu})_2X}]X'$ (X = Cl, X′ = $\mathrm{BPh_4}$; X = Br, X′ = $\mathrm{BPh_4}$, $\mathrm{BF_4}$ and $\mathrm{PF_6}$) by reaction of $[\mathrm{Co(Tm^{\mathit{t}Bu})X}]$ with $\mathrm{NH_4X'}$ in methanol. Similar reactions in acetonitrile, in the presence of $\mathrm{PPh_3}$ results in formation of $[\mathrm{Co(Tm^{\mathit{t}Bu})(PPh_3)}]X'$ (X′ = $\mathrm{BPh_4}$, $\mathrm{PF_6}$). Attempts to crystallise the $\mathrm{BPh_4}$ salt of this complex also resulted in the isolation in low yield of crystals of the trigonal bipyramidal cobaltaboratrane $[\mathrm{Co\{B(mt)_3\}(PPh_3)}]$. Attempts to prepare the cobalt(II) complex $[\mathrm{Co(Tm^{Me})_2}]$ have been unsuccessful,[108] but with the bulkier ligands $\mathrm{Tm^R}$ (R = *t*Bu,[17] Ph[59]) complexes with this empirical formula have been obtained. However, these both have the ligands complexed in a κ^3-S,S,H coordination mode rather than the expected κ^3-S,S,S mode. A "mixed sandwich" complex $[\mathrm{Co(Cp^{Me})(Tm^{Me})}]\mathrm{I}$ has been prepared by reaction of $[\mathrm{Co(Cp^{Me})(CO)I_2}]$ with $\mathrm{NaTm^{Me}}$. The corresponding Cp complex is formed, but is much less stable and has not been fully characterised. The electrochemistry of a series of compounds shows that $[\mathrm{Co(Tm^{Me})_2}]^+$ is more difficult to reduce (by about 200 mV) than any of its Cp, Tp or mixed analogues, perhaps explaining in part why the $\mathrm{Co^{II}}$ complex has proven resistant to synthetic efforts.[108]

Rhodium and iridium chemistry with the $\mathrm{Tm^R}$ ligands is relatively restricted. Indeed, no simple $\mathrm{Tm^R}$ complexes have been reported, although a number of rhodaboratrane species are known. Reaction of $[\mathrm{Rh(PPh_3)_2(Ph)Cl_2}]$ with $\mathrm{NaTm^{Me}}$ in EtOH/DCM (1:10) at room temperature results in a good yield of $[\mathrm{Rh\{B(mt)_3\}(PPh_3)Cl}]$ (Figure 20).[109,65] Attempts to prepare $\mathrm{Tm^{Me}}$ complexes from Wilkinson's catalyst also result in small quantities of the same rhodaboratranes, despite the lack of a hydrogen acceptor co-ligand. It is believed that the putative intermediate rhodaboratrane hydride, $[\mathrm{Rh\{B(mt)_3\}(PPh_3)(H)}]$, may undergo halogen exchange with the solvent ($\mathrm{CHCl_3}$) as observed in a number of organometallic systems.[65] The hydride species has been identified in the reaction of $[\mathrm{Rh(COD)(PPh_3)Cl}]$ with $\mathrm{NaTm^{Me}}$. However, it is somewhat unstable and has not been obtained completely free from contaminants.[65]

The metallaboratrane $[\mathrm{Rh\{B(mt)_3\}(PPh_3)Cl}]$ is labile at the chloride *trans* to boron and undergoes ligand substitution at room temperature with i{onitriles and trimethylphosphane to form $[\mathrm{Rh\{B(mt)_3\}(PPh_3)(L)}]^+$. It is notable that the triphenylphosphane is now *trans* to the M–B bond in these complexes. If more forcing conditions are used $[\mathrm{Rh\{B(mt)_3\}(PMe_3)_2}]^+$ (Figure 20) can be obtained, but with isonitriles the triphenylphosphane is not displaced. With diethyldithiocarbamate ($\mathrm{Et_2dtc}$) the chelating species

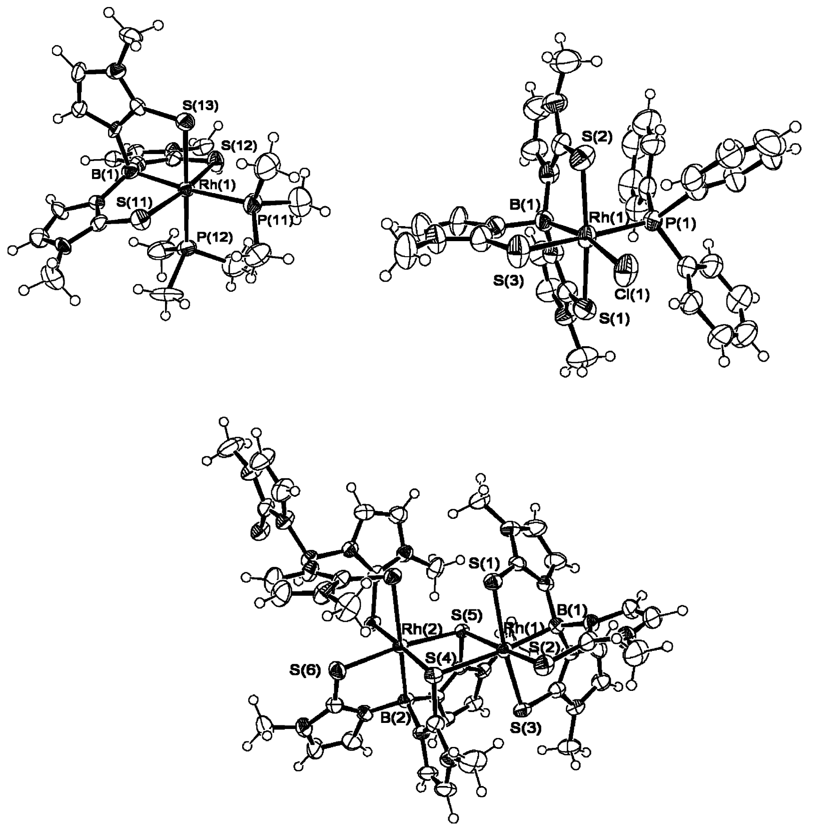
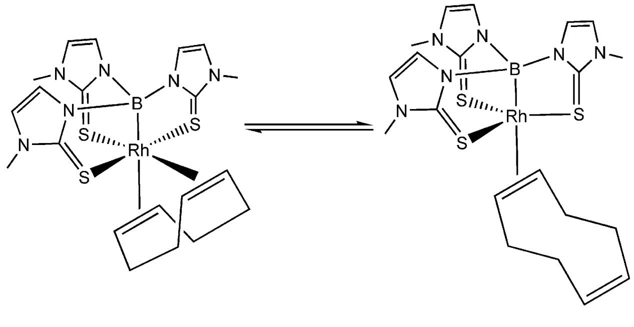


Figure 20. Structures of rhodaboratrane complexes. Top left, $[\mathrm{Rh\{B(mt)_3\}(PPh_3)Cl}]$; top right, $[\mathrm{Rh\{B(mt)_3\}(PMe_3)_2}]^+$; bottom, $[\mathrm{Rh_2\{B(mt)_3\}_2(Tm^{Me})}]^+$.

[Rh{B(mt)$_3$}(Et$_2$dtc)] is formed. It is thought that the steric demands of the rigid rhodaboratrane drive the observed stereochemistry of these products and contributes to the inability to form [Rh{B(mt)$_3$(CNR)$_2$}]$^+$.[65]

Reaction of [Rh(COD)Cl]$_2$ with NaTm^{Me} gives the phosphane-free rhodaboratrane, [Rh{B(mt)$_3$}(COD)], which is highly fluxional at room temperature (Scheme 8). Since at room temperature all the methimazole rings are equivalent in the NMR spectrum, the process is thought to involve dissociation of alkene to yield a trigonal-bipyramidal species. Addition of further NaTm^{Me} to this species results in the formation of a bimetallic rhodaboratrane (Figure 20) which is also observed as a decomposition product from [Rh{B(mt)$_3$}(PPh$_3$)Cl].[110]



Scheme 8. A proposed exchange process in the fluxional, phosphane-free rhodaboratrane [Rh{B(mt)$_3$}(COD)].

Both Hill[111] and Parkin[68] have reacted Vaska's complex, [Ir(PPh$_3$)(CO)Cl], with Tm^R (R = Me, *t*Bu, Ph) yielding the iridaboratrane [Ir{B(mt)$_3$}(PPh$_3$)(CO)H] in which the boratrane has κ^3-B,S,S coordination, with a pendant thioimidazole arm. The analogous Bm^{Me} complex has also been prepared. However, in the absence of a CO ligand (reacting [Ir(COD)(PPh$_3$)Cl] with NaTm^R) the metallaboratrane complex [Ir{B(mt)$_3$(PPh$_3$)Cl}] is obtained in which κ^4-B,S,S,S coordination is observed analogous to the Rh system described above. These species have been the subject of extensive DFT calculations to yield an insight into the metallaboratrane bonding (vide supra).

Group 10: Reaction of NaTm^{Me} with nickel(II) salts results in the rapid formation of a somewhat insoluble yellow powder which was confirmed to be [Ni(Tm^{Me})$_2$]. Attempts to prepare [Ni(Tm^{Me})Br] by reaction with TlTm^{Me} led to the same complex and an olive green solution, from which was crystallised the apparently nickel(III) complex [Ni(Tm^{Me})$_2$]Br. However, insufficient material could be obtained for full characterisation.[43] With more bulky Tm^R ligands (R = Ph, 2,6-*i*Pr$_2$-C$_6$H$_3$-) and an excess of NiCl$_2$ the 1:1 monomeric complexes [Ni(Tm^R)Cl] were formed, while with Tm^{Me} the dimeric form [Ni(Tm^{Me})(μ-Cl)]$_2$ was observed. Metathesis with NaI yielded the corresponding iodides in good yields. With Tm^{tBu}, however, a nickelaboratrane [Ni{B(mt)$_3$}Cl] was the only observed product.[21b] Parkin has reported metathesis reactions with this species, replacing Cl with acetate, azide and thiocyanate, and has demonstrated activation of the Ni–B bond with I$_2$, XeF$_2$ and CHY$_3$ (Y = Cl, Br) to give various complexes of the form [Ni(XTm^R)Y].[112] Reaction of NaBm^{Me} with nickel halides produces [Ni(Bm^{Me})$_2$], in which the ligands are κ^3-S,S,H coordinated with rather short Ni···H distances to give a pseudooctahedral geometry.[113] Rabinovich has reacted Ni(dppe)Cl$_2$ with TlTm^R (R = Me, *t*Bu, *p*Tol) to yield the diamagnetic square pyramidal complexes [Ni(Tm^R)(dppe)]Cl, in which the ligand exhibits κ^3-S,S,H coordination, with the hydride in an approximately axial position.[114] The nitrosyl complex [Ni(PPh$_3$)$_2$(NO)Br] combines with NaTm^R (R = *t*Bu, *p*Tol) to form a tetrahedral complex [Ni(Tm^R)(NO)] in which the metal nitrosyl linkage is close to linear (Ni–N–O = 173.9).[115] By contrast, with Bm^R (R = Me, *t*Bu)[115] and its selenium donor analogue[116] a complex [Ni(Bm^{Me})(PPh$_3$)(NO)] is obtained in which the ligand is κ^3-S,S,H coordinated. The coordination geometry is trigonal pyramidal with a weak (but significant) axial Ni···H interaction and a metal nitrosyl linkage which is appreciably bent (Ni–N–O = 149.64° (S-donor) and 149.1° (Se-donor), Figure 21).

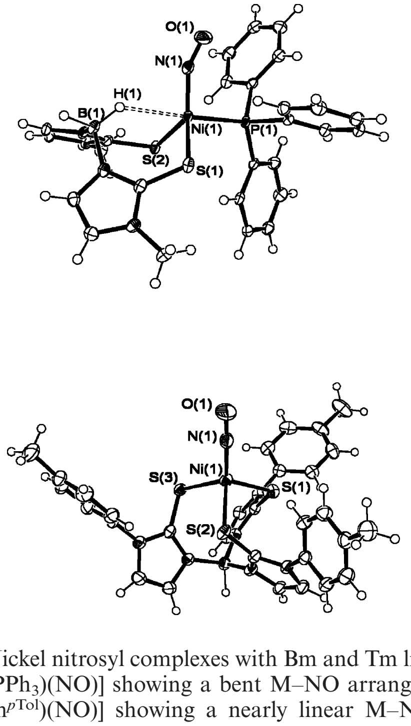
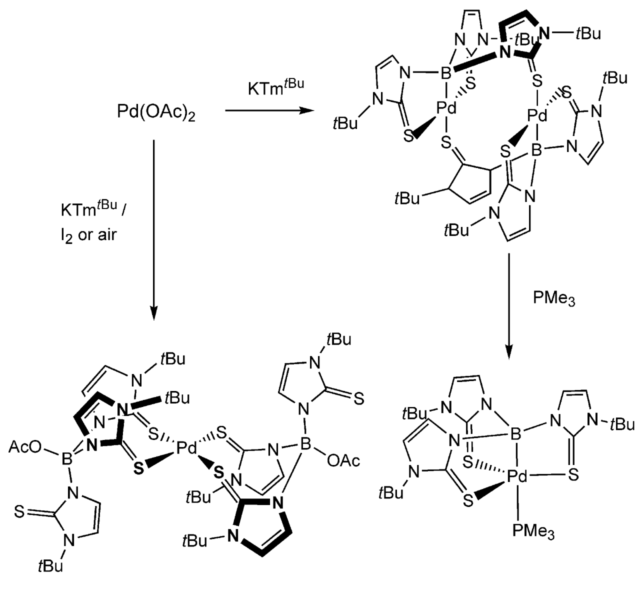


Figure 21. Nickel nitrosyl complexes with Bm and Tm ligands. Top: [Ni(Bm^{Me})(PPh$_3$)(NO)] showing a bent M–NO arrangement. Bottom: [Ni(Tm^{pTol})(NO)] showing a nearly linear M–NO arrangement.

Palladium and platinum chemistry with the Tm^R ligands, like that of the other noble metals is fairly restricted and dominated by metallaboratrane formation. Reaction of Pd(OAc)$_2$ with KTm^{tBu} in inert atmospheres results in formation of a bridged dipalladaboratrane in which the ligand adopts a κ^3(B,S,S),κ^1(S) mode. The species is fluxional and the bridge may be cleaved by addition of PMe$_3$ with formation of the mononuclear trigonal bipyramidal complex [Pd{B(tim*t*Bu)$_3$}(PMe$_3$)] (tim*t*Bu = 1-*tert*-butylimidazole-2-thione). Interestingly, if the Pd(OAc)$_2$ reaction is carried out in air or in the presence of I$_2$ the square-planar complex

[Pd(AcOTm$^{t\mathrm{Bu}}$)$_2$] is obtained, in which the hydride on boron is replaced by an acetate group (Scheme 9).[117]



Scheme 9. Palladium chemistry with the Tm$^{t\mathrm{Bu}}$ ligand.

The only platinum Tm complex to date was obtained by reaction of NaTm$^{\mathrm{Me}}$ with PtMe$_3$I to give the surprisingly robust octahedral platinum(IV) complex [Pt(Tm$^{\mathrm{Me}}$)Me$_3$]. The corresponding reaction with NaBm$^{\mathrm{Me}}$ yields the expected [Pt(Bm$^{\mathrm{Me}}$)Me$_3$] in which the ligand has a κ^3-S,S,H coordination mode, and if allowed to stand in the presence of excess PtMe$_3$I forms a sulfur-bridged dimer (Figure 22).[118] Reaction of [Pt(PPh$_3$)$_2$Cl$_2$] with NaTm$^{\mathrm{Me}}$ results in formation of a yellow intermediate (presumably square planar [Pt(Tm$^{\mathrm{Me}}$)(PPh$_3$)Cl]) which reacts further to yield the boratrane [Pt{B(mt)}(PPh$_3$)] which has remarkable ^{195}Pt NMR spectra showing well resolved coupling to ^{11}B, confirming its formulation as a boratrane.[119] This species undergoes oxidative addition reactions at the metal centre with X$_2$ (X = Cl, Br, I) and MeI to yield the corresponding six-coordinate Pt$^{\mathrm{II}}$ boratrane complexes [Pt{B(mt)$_3$}X$_2$] and [Pt{B(mt)$_3$}(Me)I], respectively. Furthermore, reaction with ethanolic HCl results in formation of [Pt{B(mt)$_3$}(PPh$_3$)H]$^+$.[120]

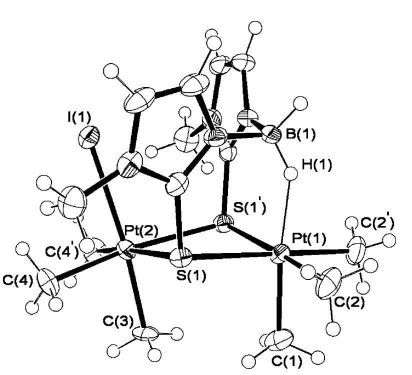


Figure 22. The dinuclear platinum complex, [Me$_3$Pt{μ-Bm$^{\mathrm{Me}}$}PtMe$_3$I].

Group 11: Reaction of CuCl or AgNO$_3$ with NaTm$^{\mathrm{R}}$ results in the formation of a species with empirical formula [M(Tm$^{\mathrm{R}}$)]$_n$.[9,12a,46b,121,122] The silver complex has been shown to be a dimer, with bridging Tm$^{\mathrm{R}}$ ligands, while structurally different copper-containing dimers, [Cu(Tm$^{\mathrm{Mes}}$)]$_2$[33] and [Cu(PhTm$^{\mathrm{Me}}$)]$_2$[123] have also been obtained. The insolubility of [Cu(Tm$^{\mathrm{Me}}$)]$_n$ begs the question whether this too is dimeric or whether it forms a higher oligomer. An extensive series of complexes of form [M$^{\mathrm{I}}$(R′Tm$^{\mathrm{R}}$)(PR″$_3$)] [M = Cu, R′Tm$^{\mathrm{R}}$ = Tm$^{\mathrm{Me}}$, PR″$_3$ = PPh$_3$, PMePh$_3$, PEtPh$_2$, PCy$_3$, P(*m*Tol)$_3$, P(*o*Tol)$_3$;[46b] M = Cu, R′Tm$^{\mathrm{R}}$ = Tm$^{\mathrm{Et}}$, PR″$_3$ = PPh$_3$;[15] M = Cu, R′Tm$^{\mathrm{R}}$ = PhTm$^{\mathrm{Me}}$, PR″$_3$ = PPh$_3$;[123] M = Cu, R′Tm$^{\mathrm{R}}$ = Tm$^{t\mathrm{Bu}}$, PR″$_3$ = PPh$_3$;[122] M = Ag, R′Tm$^{\mathrm{R}}$ = Tm$^{\mathrm{Me}}$, PR″$_3$ = PPh$_3$, PBz$_3$, PCy$_3$, PEtPh$_2$, P(*p*Tol)$_3$, PMes$_3$, P*i*Bu$_3$;[12a,57,124] M = Ag, R′Tm$^{\mathrm{R}}$ = PhTm$^{\mathrm{Me}}$, PR″$_3$ = PPh$_3$, PEt$_3$;[123] M = Ag, R′Tm$^{\mathrm{R}}$ = Tm$^{\mathrm{Et}}$, PR″$_3$ = PPh$_3$;[15] M = Au, R′Tm$^{\mathrm{R}}$ = Tm$^{t\mathrm{Bu}}$, PR″$_3$ = PPh$_3$;[122] M = Au, R′Tm$^{\mathrm{R}}$ = PhTm$^{\mathrm{Me}}$, PR″$_3$ = PPh$_3$, PEt$_3$[123]] have been prepared. The copper complexes are all tetrahedral with S$_3$P donor sets. The silver complexes exhibit both the analogous tetrahedral geometry and trigonal planar geometry with a S$_2$P donor set and a weaker axial Ag···H interaction depending on the combination of phosphane and R′Tm$^{\mathrm{R}}$ ligands. The latter arrangement is also observed in [M(PhBm$^{\mathrm{Me}}$)(PPh$_3$)] (M = Cu, Ag).[123] There is insufficient data at present to unequivocally establish the factors which cause one geometry to be preferred over the other. The gold complexes are all close to linear with SP donor sets and κ^1-S coordinated R′Tm$^{\mathrm{R}}$ ligands, although axial interactions are observed. These are reasonably strong in [Au(Tm$^{t\mathrm{Bu}}$)(PPh$_3$)] and its Bm$^{\mathrm{Me}}$ analogues [*d*(Au–S) = ca 2.8 Å][125] resulting in S–Au–P angles of ca 160°, while in [Au(PhTm$^{\mathrm{Me}}$)(PEt$_3$)] the *d*(Au···S) = 3.63 Å resulting in a more linear S–Au–P angle of 172°.[123] With silver, complexes exhibiting alternative stoichiometries have been reported. For example, with monodentate phosphanes [Ag(Tm$^{\mathrm{Me}}$)(PMePh$_2$)$_2$] and [Ag$_2$(Tm$^{\mathrm{Me}}$)$_2${P(*m*Tol)$_3$}] have been identified, and with bidentate phosphanes [Ag(Tm$^{\mathrm{Me}}$)(P–P)] [P–P = 1,2-bis(diphenylphosphanyl)ethane and 1,2-bis(diphenylphospanyl)ferrocene] is also observed, although no structural data has been reported as yet.[57] Reaction of [Au(tht)Cl] (tht = tetrahydrothiophene) with NaTm$^{t\mathrm{Bu}}$ yields [Au(Tm$^{t\mathrm{Bu}}$)]$_2$. In contrast to the copper and silver dimers, each gold atom has linear coordination geometry and the ligands exhibit a κ^1,κ^1 bridging mode.[122] Finally, the same reagents in a 3:2 stoichiometry give rise to [Au$_3$(Tm$^{t\mathrm{Bu}}$)$_2$]$^+$, in which a triangle of gold atoms [*d*(Au···Au) = 3.39–3.86 Å] is sandwiched by two Tm$^{t\mathrm{Bu}}$ ligands each in a bridging tris monodentate coordination mode.[126] This structural motif is also observed in the [(BiMe$_2$)$_3$(Tm$^{t\mathrm{Bu}}$)$_2$]$^+$ cation (vide supra).

Group 12: The chemistry of zinc has been extensively studied in the context of the modelling of zinc-containing enzymes. This has been reviewed by Parkin[5c–5e] and Vahrenkamp[127] and thus only a brief summary of the Zn chemistry with Tm$^{\mathrm{R}}$ ligands will be given. The vast majority of the reported chemistry is of the mononuclear pseudo-tetrahedral complexes of types [Zn(Tm$^{\mathrm{R}}$)L]$^+$ (L =

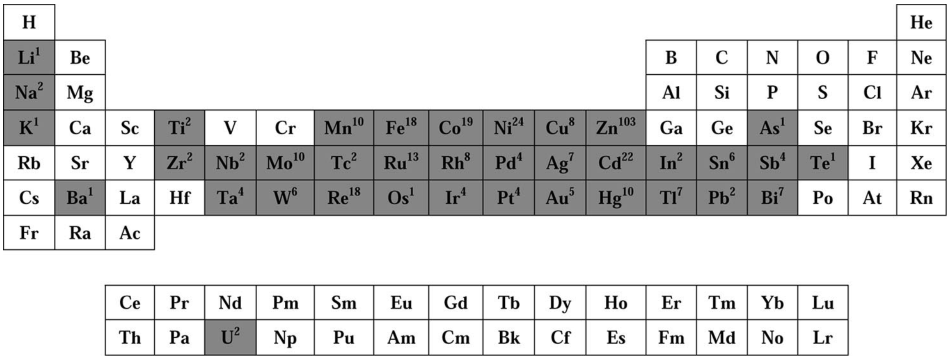
ROH,[11,16a,128] H_2O,[21a] NCMe,[129] *N*-alkyl or aryl imidazole-2-thione[20,130]), [Zn(Tm^{R})X] (X = halide,[16a,131,132] SR,[129,133] SeR/TeR,[56] SH/SeH[56]) and [Zn(Tm^{R})$_2$].[16a] A number of higher aggregates are also known, including hydroxy-bridged dimers,[19] [{Zn(Tm^{R})}$_2$(μ-OH)], an asymmetric Tm-bridged trimer with 2-pyridylbenzyl alcohol co-ligands,[134] and a cyclic Tm-bridged tetramer.[135] Furthermore, a variety of reactions pertaining to the function of zinc-containing metalloenzymes have been investigated. These include the dehydrogenation of *i*PrOH and hydrogenation of pentafluorobenzaldehyde,[16a] methylation of [Zn(Tm^{R})(SR′)] to give MeSR′ using methyl iodide[31,133,136] or trimethyl phosphate,[137] the protonation of [Zn(Tm^{R})(SR′)] to give R′SH,[129] and the kinetics of thiolate exchange reactions.[138,139]

With cadmium and mercury the predominant structural type to date is [M(Tm^{R})X] (X = halide,[17,131,132] CH_3,[58] SAr,[58,140] and SeAr[58]). The halide complexes have a more distorted coordination sphere than their zinc analogues, tending to trigonal pyramidal geometry. With the Bm^{R} ligands, complexes having the formula [Cd(Bm^{R})$_2$], which have an S_4 primary coordination sphere, and two Cd···H–B interactions are observed.[141,142] In the presence of thiolate co-ligands a thiolate-bridged dimer, [Cd(Bm^{Me})(μ-SAr)]$_2$, has also been obtained.[143] Finally, linear alkyl mercury complexes [Hg(Tm$^{t\mathrm{Bu}}$)R] (R = CH_3, CH_2CN) have been obtained and react with PhSH to give RH.[144]

The f-Block Elements: As yet, no complexes with the lanthanide series have been reported. While no Tm^{R} complexes with the actinides are known, Santos has reported RBm^{Me} complexes of uranium(III), [U(RBm^{Me})$_2$(THF)$_3$] (R = H, Ph), obtained by reaction of NaRBm^{Me} with [U(THF)$_4$I$_3$] in the presence of TlBPh$_4$.[145] The Bm ligands coordinate in a κ^3-S,S,H mode, resulting in a nine-coordinate face-capped trigonal prismatic structure. The ability to isolate these species indicates that there are real, yet untapped possibilities in this area of the periodic table.

4. Conclusions

From the first report of the methimazole based soft scorpionates in 1996 there has been a remarkable uptake in usage of these species as ligands for both main group and transition metals. The scope of the chemistry has greatly exceeded our expectations, both in terms of the breadth of coverage of the periodic table, and in terms of the variety observed. As a measure of the scope of the chemistry, the periodic table in Figure 23 highlights the elements for which crystal structures of Tm^{R} or Bm^{R} complexes have been reported, the superscripted numbers indicating the number of structures for the given element. A total of 351 unique structures with Tm or Bm ligands and their derivatives are present in the Cambridge Crystallographic Database.[44] Of these, 340 have sulfur coordinated to a metal ion. It can be seen that a very high proportion of these complexes (103 structures, ca 30%) are with zinc, indicative of the intense efforts of Parkin and Vahrenkamp in utilising these ligands as models of zinc-containing metalloenzymes. The remaining structures cover almost every area of the periodic table. Only a handful of d-block transition elements have no reported chemistry with these ligands. By contrast, in the f-block no lanthanide complexes have been reported, and only a handful of uranium Bm^{R} complexes are known, suggesting this is an area ripe for development. In the s- and p-blocks, while surprisingly good coverage has been attained, it is clear that there is a great deal of scope for development of the chemistry, especially with organometallic species. As discussed previously, the Tm ligands, because of their greater flexibility, are able to adopt a greater variety of bonding modes, and as such show far greater diversity of chemistry than the pyrazolylborate ligands. This has led in particular to the remarkable discovery of the metallaboratranes, long sought after examples of M→B "retrodative" bonding. Although the chemistry is still to some degree in its infancy, it is also gratifying to see applications beginning to develop. The extensive work on metalloenzyme models has been discussed previously, but in addition applications of the Tm ligands in surface coordination chemistry,[146] mass spectrometry,[147] as sensors for zinc and thiocyanate in biological and environmental samples[148] and in cadmium ion selective membrane sensors[149] underlines the potential yet to be tapped. A recent review of strongly donating scorpionate ligands (including Tm and related ligands) has recently been published.[150]



H																	He
Li^{1}	Be											B	C	N	O	F	Ne
Na^{2}	Mg											Al	Si	P	S	Cl	Ar
K^{1}	Ca	Sc	Ti^{2}	V	Cr	Mn^{10}	Fe^{18}	Co^{19}	Ni^{24}	Cu^{8}	Zn^{103}	Ga	Ge	As^{1}	Se	Br	Kr
Rb	Sr	Y	Zr^{2}	Nb^{2}	Mo^{10}	Tc^{2}	Ru^{13}	Rh^{8}	Pd^{4}	Ag^{7}	Cd^{22}	In^{2}	Sn^{6}	Sb^{4}	Te^{1}	I	Xe
Cs	Ba^{1}	La	Hf	Ta^{4}	W^{6}	Re^{18}	Os^{1}	Ir^{4}	Pt^{4}	Au^{5}	Hg^{10}	Tl^{7}	Pb^{2}	Bi^{7}	Po	At	Rn
Fr	Ra	Ac															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U^{2}	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 23. A representation of the scope of R′Tm^{R} chemistry by the number of crystal structures reported in the CCDC.[45] Shaded squares represent elements for which a R′Tm^{R} or R′Bm^{R} complex (including metallaboratranes) has been crystallographically characterised and the superscripts indicate the number of structures reported.

Supporting Information (see footnote on the first page of this article): Table of data describing the key structural parameters of complexes with M···H–B interactions.

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We wish to acknowledge the contributions of all students, both undergraduate and post-graduate, who have contributed to our efforts to understand and further develop the chemistry of these ligand systems. In particular we would like to thank Dr Mark Garner, who prepared the first sample of $NaTm^{Me}$ in 1993 and thus paved the way for many others.

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[53] Table S1 in the Supporting Information summarises these key structural parameters for all $\mathrm{Tm^R}$ complexes which exhibit a M···H–B interaction.

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