

## Observations on the steric impact of N- and S- donor scorpionate ligands

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Dedication In memory of Jerry and 50 years of scorpionate chemistry

**Keywords:** cone angles, scorpionates, steric influence

### Abstract

A comparison is made between the steric influences of a range of zinc hydrotris(pyrazolyl)borates and zinc hydrotris(thio-imidazolyl)borates ( $[\text{Zn}(\text{Tp}^{\text{R}})\text{Cl}]$ ,  $[\text{Zn}(\text{Tm}^{\text{R}})\text{Cl}]$ ,: R = Me, <sup>i</sup>Pr, Ph <sup>t</sup>Bu)) using inverse cone angle analysis. The study combines the crystallographic analysis of  $[\text{Zn}(\text{Tm}^{\text{iPr}})\text{Cl}]$  and  $[\text{Zn}(\text{Tm}^{\text{Ph}})\text{Cl}]$  with the data previously deposited with the Cambridge Crystallographic Data Centre. The study suggests that despite efforts to manipulate the reactive pocket around the metal centre in  $\text{M}(\text{Tm}^{\text{R}})$  complexes, the incorporation of sterically confining substituents onto the framework has a minimal effect at the metal centre unless the group attached is very large.

## Introduction

The family of ligands commonly known as the soft scorpionates continues to increase in number. Originally based on thio-imidazole, the system has expanded to include other heterocyclic secondary amine-thiones and more recently selones and ketones.<sup>[1-13]</sup> The S- donor family of ligands arose from the simple replacement of pyrazole by thioimidazole in the synthetic protocol first reported by Trofimenko and consequently throughout the development of their chemistry direct comparisons have been made to the parent Tp ligand system.<sup>[2, 3, 14-16]</sup> Since the early development of the pyrazolylborates it was apparent that minor modifications to the skeletal structure of the pyrazole at C3 could have a marked effect on the structure of the metal complex produced (figure 1).<sup>[14,15]</sup> As the importance of steric effects became accepted, an attempt to grade their impact on the chemistry of  $Tp^R$  was briefly attempted by measuring the effects of the various substituents on the cone and wedge angles (figure 1).<sup>[15]</sup>

When soft S-donor scorpionates were introduced researchers naturally applied the information obtained on Tp to the chemistry of  $Tm^R$ .<sup>[3, 16]</sup> However, there are some fundamental differences between the two systems (figure 1).  $Tp^R$  forms complexes with six membered chelate rings whereas  $Tm^R$ , as a result of the donor atoms lying exo to the rings, forms 8 membered chelate rings. In Tp complexes, the pyrazol rings do not articulate significantly around the B-N bond. In contrast the presence of eight member rings allows the methimazoles to rotate around the B-N bond in such a way that the heterocycle is rarely found parallel to the nominal H-B-M axis. The formation of eight membered rings allows the substituents on  $Tm^R$  to be directed away from the metal pocket and thus the space available to reactants is much larger.<sup>[17]</sup> It is notable that with  $Tm^R$  ligands and so-called bulky substituents (i.e. R= <sup>t</sup>Bu) metals such as gallium and indium still form sandwich complexes.<sup>[18-19]</sup> It is also notable that the reaction of  $Tm^{Ph}$  ligand with  $Fe^{2+}$  and  $Fe^{3+}$  produces a counter intuitive result. The former, larger cation forms an octahedral complex in  $\kappa^3$ -H,S,S mode whereas the latter, smaller cation forms a  $\kappa^3$ -S,S,S bound complex.<sup>[20]</sup> Thus the direct application of data collected using  $Tp^R$  ligands to the chemistry of  $Tm^R$  chemistry is thought to lack rigour.

The ability to control and predict the steric effects of the various ligands is extremely important. Consequently, the aim of this investigation is to explore and grade the steric effects of  $Tm^R$  complexes and make due comparison with their  $Tp^R$  analogues. This study will be achieved by studying the coordination chemistry of zinc. Zinc, as the chloride, has been

chosen as it is representative of  $\text{Tp}^{\text{R}}$  and  $\text{Tm}^{\text{R}}$  in a sterically confined tetrahedral environment. A short series of substituents ( $\text{Tp}^{\text{R}}$ :  $\text{Tm}^{\text{R}}$ ; R = Me, Ph, iPr, tBu) was selected for analysis.<sup>[21-27]</sup>

## Results and Discussion

Many of the complexes required for this study have been reported previously and their relevant structural data in cif format have been accessed using the Cambridge Crystallographic Data Centre (CCDC, table 1).<sup>[21]</sup> However, to complete the analysis it was necessary to prepare, crystallize and structurally characterize the two missing species *viz*  $[\text{Zn}(\text{Tm}^{\text{Ph}})\text{Cl}]$  and  $[\text{Zn}(\text{Tm}^{\text{iPr}})\text{Cl}]$  (scheme 1).<sup>[28, 29]</sup>§ As expected these two complexes adopted the expected  $\kappa^3\text{-S,S,S}$  motif which is isostructural with the previously reported species.

The steric impact of the substituents (R, figure 1) were analysed using the cone angle approach of Tolman.<sup>[30-31]</sup> However, the availability of key modelling packages such as GaussView in conjunction with the CCDC allows us to better model compounds than previous studies.<sup>[32]</sup>§ GaussView allows the manipulation of the crystallographic data and we have employed it to modulate a torsion angle such that we could manoeuvre the substituents (figure 1, scheme 1) into their most and least sterically confining form. Thus far the cone angles have been defined by the van der Waals radius of the hydrogen atoms on the substituents. However, using Gaussview it was noted that in the case of R = Ph, in certain conformations it was the *para*-carbon atoms which best defined the inverse cone angle. For the plethora of information deposited at the CCDC in conjunction with Vista it is also possible to identify a structurally preferred torsion angle for the substituents and thus a “most favoured” form ( $\alpha_{\text{mf}}$ ).<sup>§</sup> Initially we re-analysed  $[\text{Tl}(\text{Tp}^*)]$  using our methods (table 1) to check that we had good agreement with the data reported previously by Trofimenko (121°).<sup>[15, 33]</sup>

The data (table 1) shows that the most favoured inverse cone angles ( $\alpha_{\text{mf}}$ ) for the substituted pyrazolylborates are quite confining ( $<95^\circ$ ) and in agreement with the experimental observation that it is difficult to generate sandwich compounds (i.e.  $[\text{M}(\text{Tp}^{\text{R}})_2]$ ). The use of GaussView in the analysis also allows us to calculate minimum ( $\alpha_{\text{min}}$ ) and maximum ( $\alpha_{\text{max}}$ ) values which reflect the ability of the substituents to rotate within the scorpionate motif.

However, it is probably the maximum values which best reflect the accommodating nature of the ligands as this allows for an increase in the inverse cone angle ( $\alpha_{\max} < 108^\circ$ ). Despite this adjustment, it will still be difficult to form sandwich complexes ( $[\text{Zn}(\text{Tp}^{\text{R}})_2]$ ; R = Ph, <sup>t</sup>Bu) even if one allows the interdigitation of the substituents (table 1). The introduction of the concept of ligand adjustment during reaction shows that despite the presence of larger substituents (R = Ph, <sup>t</sup>Bu) the space to the fore of the metal centre does not change markedly (figure 2). The analysis of the corresponding  $\text{Tm}^{\text{R}}$  compounds (table 1, figure 2) immediately identifies a significant difference between  $\text{Tm}^{\text{R}}$  and  $\text{Tp}^{\text{R}}$ . A consequence of the eight membered rings and the positioning of the substituents (R) there is a large increase in the inverse cone angle ( $\alpha_{\text{mf}}$ ). Although a marked drop in the inverse cone angle is observed as the bulk of the substituent increases (table 1, figure 2), the angles for the S-donor species are still all significantly larger ( $>109^\circ$ ) than their N-donor counterparts and  $\text{Tp}^*$  itself. Using GaussView to maximise the inverse cone angles of the  $\text{Tm}^{\text{R}}$  species gives rise to values which confirm that the substituents (R) will have only a minimal effect on the metal binding pocket. Consistent with the chemistry of  $\text{Tp}^{\text{R}}$  this data clearly explains why sandwich compounds remain prominent in  $\text{Tm}^{\text{R}}$  chemistry despite the presence of so-called bulky N-substituents.<sup>[18, 19]</sup> It is also notable that in our analysis, which takes into account the van der Waals radius of the *para* carbon (R = Ph) that the phenyl substituted ligands of both Tp and Tm impart a steric influence comparable to  $\text{Tm}^{\text{tBu}}$  and  $\text{Tp}^{\text{tBu}}$ .

Parkin et al. have recently reported the adamantyl (Ad) substituted thioimidazoles (e.g.  $[\text{Zn}(\text{Tm}^{\text{ad}})\text{I}]$ ) in an attempt to further increase the steric influence of  $\text{Tm}^{\text{R}}$ .<sup>[34]</sup> In a desire to incorporate this species into our analysis we have extended our study to also include  $[\text{Zn}(\text{Tm}^{\text{Ph}})\text{I}]$ .<sup>[35]</sup> The change in halide (Cl, I table 1) only introduces a small (1-2%) increase in the inverse cone angle. As such it can be postulated that metrics for  $[\text{Zn}(\text{Tm}^{\text{ad}})\text{Cl}]$  would be comparable to those of  $[\text{Zn}(\text{Tm}^{\text{ad}})\text{I}]$ . Our analysis shows that in  $[\text{Zn}(\text{Tm}^{\text{ad}})\text{I}]$  the ligand has an inverse cone angle ( $\alpha_{\text{mf}}$  and  $\alpha_{\max}$ ) of  $109^\circ$ , which is comparable to that of  $\text{Tp}^*$  (table 1). The analysis of  $[\text{Zn}(\text{Tm}^{\text{ad}})\text{I}]$  thus shows that only with ligands of comparable bulk to the adamantyl substituent is it possible to influence the protected pocket of the metal.

## Conclusions

The calculations show that the two classes of scorpionates ( $\text{Tp}^{\text{R}}$ ,  $\text{Tm}^{\text{R}}$ ) have markedly different abilities to influence the steric properties of metal complexes due to the positioning of the substituent on the rings (figure 1). Unsurprisingly, the proximity of the substituent to the metal in  $\text{Tp}$  has a significant effect. However, for  $\text{Tm}^{\text{R}}$ , the donor atom lies exo to the heterocyclic ring and, as a result, the influence of the substituent groups are heavily diminished (table 1, figure 2).

We have conducted our analysis using a metal centre (zinc) which has a modest ionic radius ( $\text{Zn}^{2+}$  74 pm) when placed in a tetrahedral geometry. From the outset, the choice of metal and geometry was designed to highlight the steric effects in the ligands ( $\text{Tp}^{\text{R}}$ ,  $\text{Tm}^{\text{R}}$ ). It is obvious that moving to larger cations and higher coordination numbers will dilute the steric influence of the substituents on  $\text{Tm}^{\text{R}}$  further. Thus, many of the soft scorpionate ligands discussed in the literature as being bulky will have only a modest effect at best. Indeed much of the difference in the chemistry of substituted  $\text{Tm}^{\text{R}}$  ligands will probable result from the electron withdrawing and donating effects of the substituent on the heterocyclic ring.<sup>[36]</sup>

## Experimental Section

$[\text{Zn}(\text{Tm}^{\text{Ph}})\text{Cl}]$  and  $[\text{Zn}(\text{Tm}^{\text{iPr}})\text{Cl}]$  were prepared as reported in the literature.<sup>[28, 29]</sup> Crystals suitable for X-ray diffraction analysis were grown by vapour diffusion (DMF/diethyl-ether). Further details on the synthesis and structural characterisation of  $[\text{Zn}(\text{Tm}^{\text{Ph}})\text{Cl}]$  and  $[\text{Zn}(\text{Tm}^{\text{iPr}})\text{Cl}]$  can be found in the supporting information.

The inverse cone angles were calculated by first importing the cif file into GaussView.<sup>[32]</sup> This allowed the extraction of the key distances and angles required to perform the calculation. The various substituents ( $\text{Tm}^{\text{R}}$ ,  $\text{Tp}^{\text{R}}$ : R = Me,  $^{\text{i}}\text{Pr}$ , Ph and  $^{\text{t}}\text{Bu}$ ) were rotated in GaussView to achieve conformations which gave rise to the maximum and minimum inverse cone angles for each complex. A more detailed description of the calculations performed can be found in the supporting information.

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Captions for figures, schemes and tables

**Figure 1.** A Pictorial representation of cone angle and wedge angle in  $\text{Tp}^{\text{R}}$ . Left: the cone angle =  $(360-\alpha)$ . Middle: the wedge angle ( $\beta$ ). Cone angles in scorpionates are calculated by measuring the angle ( $\alpha$ ) formed from the outermost hydrogen in the substituent with the metal. Wedge angles ( $\beta$ ) are calculated by measuring the angle formed by the heterocyclic rings (in this case pyrazole) with the metal.<sup>[15]</sup> Right: A pictorial representation of a thioimidazolylborate showing, in outline, the impact of the formation of eight membered rings.<sup>[1-3]</sup> The important parameter in the chemistry of the scorpionates is the inverse cone angle,  $\alpha$ , which defines the pocket/space at the metal centre. For the purpose of this study it is  $\alpha$  which will be quoted.

**Figure 2.** A schematic representation of the inverse cone angles ( $\alpha$ ) for  $\text{Tp}^{\text{R}}$  and  $\text{Tm}^{\text{R}}$  ( $\text{R} = \text{Me}, ^i\text{Pr}, ^t\text{Bu Ph}$ ).  $\blacklozenge$  represents the inverse cone angle derived from the ligand conformation observed in the crystal structure and the dotted lines represent the range of inverse cone angle accessible by rotation of the pendant groups. In all cases the  $\text{Tm}^{\text{R}}$  inverse cone angles exceed that of  $\text{Tp}^{\text{R}}$  and as such sandwich complexes ( $\text{M}(\text{Tm}^{\text{R}})_2$ ) will prevail.  $\text{Zn}(\text{Tp}^*)_2$  has been used in the analysis above in the absence of  $\text{Zn}(\text{Tp}^{\text{Me}})_2$ .

**Scheme 1.** Synthesis of  $[\text{Zn}(\text{Tm}^{\text{R}})\text{Cl}]$ ,  $\text{R} = \text{Ph}, ^i\text{Pr}$ .

**Table 1.** The inverse cone angles ( $\alpha$ ) which define the available space in the reaction pocket of  $\text{Zn}(\text{Tp}^{\text{R}})\text{Cl}$  and  $\text{Zn}(\text{Tm}^{\text{R}})\text{Cl}$  complexes.  $\alpha_{\text{mf}}$  - most favoured;  $\alpha_{\text{min}}, \alpha_{\text{max}}$ ; the minimum and maximum values identified using Gaussview. The value for  $\text{TlTp}^*$  calculated using the method developed in this study agrees well with that previously reported ( $121^\circ$ ) by Trofimenko.<sup>[15, 33]</sup> The structures identified for use in the ccd were chosen on the basis of their r-factors

Figure 1

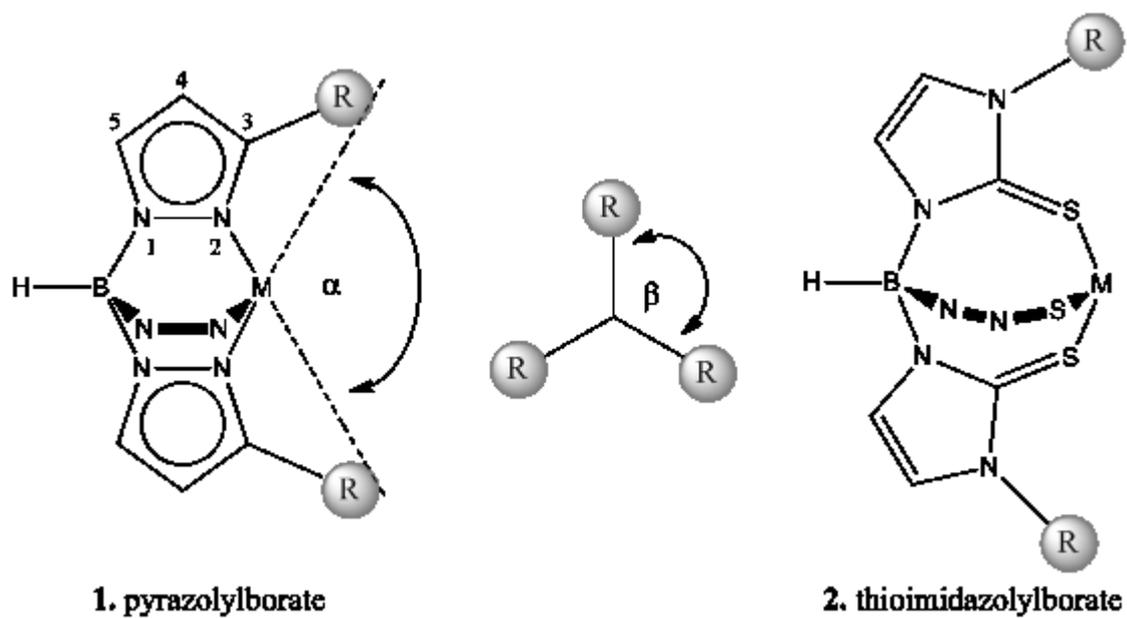
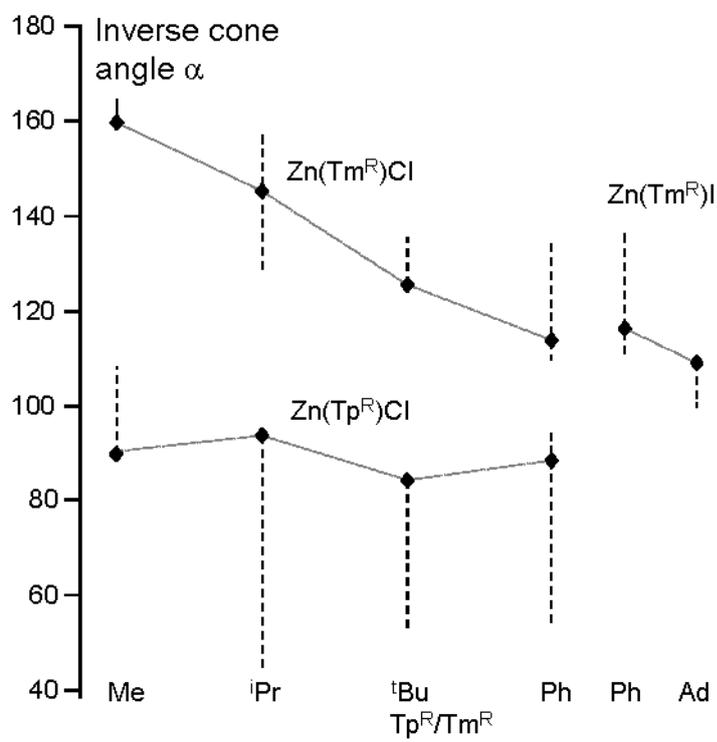


Figure 2



## Scheme 1



**Table 1**

	CCDC Ref code	R-factor	$\alpha_{\text{mf}}$	$\alpha_{\text{min}}$	$\alpha_{\text{max}}$
TlTp*	DILSEW <sup>[33]</sup>	4.79	135°	122°	138°
Zn(Tp*)Cl	HOQBUK <sup>[22]</sup>	3.85	90°	90°	108°
Zn(Tp <sup>iPr</sup> )Cl	LEVVAK <sup>[23]</sup>	6.2	93°	45°	94°
Zn(Tp <sup>Ph</sup> )Cl	YAZXEC <sup>[24]</sup>	3.0	88°	54°	94°
Zn(Tp <sup>tBu</sup> )Cl	VOJWEW <sup>[25]</sup>	3.75	84°	53°	88°
Zn(Tm <sup>Me</sup> )Cl	AGEZAN <sup>[26]</sup>	2.67	160°	160°	165°
Zn(Tm <sup>iPr</sup> )Cl	This work§	4.35	145°	129°	157°
Zn(Tm <sup>ph</sup> )Cl	This work§	3.63	114°	110°	135°
Zn(Tm <sup>tBu</sup> )Cl	NEBNOX <sup>[27]</sup>	3.68	125°	125°	138°
Zn(Tm <sup>ph</sup> )I	LEYROW <sup>[34]</sup>	4.17	116	110	136
Zn(Tm <sup>ad</sup> )I	BAZSEC <sup>[35]</sup>	3.81	109	100	109

TOC details

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