Terminal hydrochalcogenido and bridging selenido derivatives of magnesium supported by tris(3-*p*-tolylpyrazolyl)hydroborate ligation: the syntheses and structures of [Tp$^{p\text{-Tol}}$]MgEH (E = S, Se) and {[Tp$^{p\text{-Tol}}$]Mg}$_2$Se

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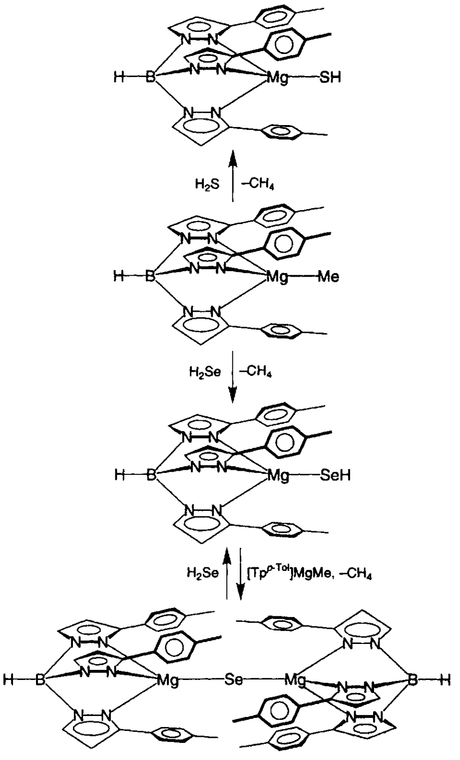
The first structurally characterized monomeric hydrosulfido and hydroselenido complexes of magnesium, [Tp$^{p\text{-Tol}}$]MgEH (E = S, Se), are synthesized by the reaction of [Tp$^{p\text{-Tol}}$]MgMe with H_2S and H_2Se, respectively; the hydroselenido complex reacts with [Tp$^{p\text{-Tol}}$]MgMe to give the dinuclear bridging selenido complex {[Tp$^{p\text{-Tol}}$]Mg}$_2$Se.

In contrast to the many examples of complexes with Mg–O bonds,[1] complexes with bonds between magnesium and the heavier chalcogens (S, Se, Te) are surprisingly rare.[2,3] Consequently, a detailed comparison of the reactivity of magnesium–chalcogen bonds as a function of the chalcogen is yet to be described. For this reason, we have sought to synthesize a series of well defined magnesium chalcogenolate complexes that may be amenable to reactivity studies. In this paper, we report the use of tris(3-*p*-tolylpyrazolyl)hydroborato ligation[4] to prepare the first structurally characterized terminal hydrosulfido and hydroselenido complexes of magnesium, [Tp$^{p\text{-Tol}}$]MgEH (E = S, Se). In addition, we also describe the conversion of the terminal hydroselenido complex [Tp$^{p\text{-Tol}}$]MgSeH to its linear bridging selenido derivative {[Tp$^{p\text{-Tol}}$]Mg}$_2$Se.

The terminal hydrosulfido and hydroselenido derivatives [Tp$^{p\text{-Tol}}$]MgSH and [Tp$^{p\text{-Tol}}$]MgSeH are conveniently obtained *via* cleavage of the Mg–C bond of the alkyl derivative [Tp$^{p\text{-Tol}}$]MgMe[5] with H_2S and H_2Se, respectively (Scheme 1).[6] While excellent evidence for the identification of [Tp$^{p\text{-Tol}}$]MgSH and [Tp$^{p\text{-Tol}}$]MgSeH was obtained by NMR spectroscopy,[7] definitive characterization as monomeric terminal hydrochalcogenido complexes was provided by X-ray diffraction (Fig. 1).† [Tp$^{p\text{-Tol}}$]MgSH and [Tp$^{p\text{-Tol}}$]MgSeH are the first structurally characterized terminal hydrosulfido and hydroselenido complexes of magnesium, so that the lengths of the Mg–SH [2.348(2) Å] and Mg–SeH [2.465(2) Å] bonds are of particular interest. Few other complexes with unbridged Mg–E (E = S, Se) bonds have been structurally characterized, but those structures that have been determined exhibit bond lengths that are comparable to those in [Tp$^{p\text{-Tol}}$]MgSH and [Tp$^{p\text{-Tol}}$]MgSeH: *e.g.* the thiolate complexes $[(\mathrm{CuMes})_4(\mu\text{-SAr})_2\mathrm{MgSAr})_2]$ [Ar = $C_6H_4(CHMeNMe_2)$, 2.375(4) Å],[3b] $[\mathrm{Mg(SC_6H_2Ph_3)_2}]_2$ [2.349(5) Å],[3a] and $\mathrm{Mg[S(C_6H_2Bu^t{}_3)]_2(Et_2O)_2}$ [2.382(2), 2.392(2) Å],[3a] and the selenolate complexes $\mathrm{Mg[Se(C_6H_2Bu^t{}_3)]_2(THF)_2}$ [2.536(3), 2.539(3) Å][3a] and $[\eta^2\text{-}\mathrm{Bu^tSi(CH_2PMe_2)_3}]\mathrm{Mg[SeSi(SiMe_3)_3]_2}$ [2.483(8), 2.500(8)].[3c]

The monomeric nature of the hydrosulfido and hydroselenido derivatives [Tp$^{p\text{-Tol}}$]MgSH and [Tp$^{p\text{-Tol}}$]MgSeH provides a striking contrast with the structure of the related hydroxide derivative {[Tp$^{\mathrm{Ar,Me}}$]Mg(μ-OH)}$_2$ (Ar = $C_6H_4Bu^t$-*p*)[8] which exists as a hydroxide-bridged dimer in the solid state. Moreover, since the [Tp$^{\mathrm{Ar,Me}}$] ligand is more sterically demanding than the [Tp$^{p\text{-Tol}}$] ligand, the distinction between the structures is even more interesting. The increased tendency for the –OH rather than –SH or –SeH ligands to bridge is presumably a reflection of the high oxophilicity of magnesium.

The mononuclear hydroselenido complex [Tp$^{p\text{-Tol}}$]MgSeH is readily converted to a dinuclear selenido bridged complex {[Tp$^{p\text{-Tol}}$]Mg}$_2$Se upon reaction with 1 equiv. of [Tp$^{p\text{-Tol}}$]MgMe (Scheme 1). However, the selenido bridge in {[Tp$^{p\text{-Tol}}$]Mg}$_2$Se is not inert and is readily cleaved upon reaction with H_2Se to regenerate [Tp$^{p\text{-Tol}}$]MgSeH (Scheme 1).



Scheme 1

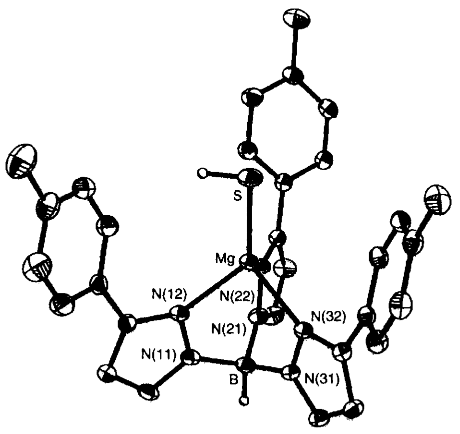


Fig. 1 ORTEP drawing of [Tp$^{p\text{-Tol}}$]MgSH

The molecular structure of $\{[\mathrm{Tp}^{p\text{-Tol}}]\mathrm{Mg}\}_2\mathrm{Se}$ has also been determined by X-ray diffraction (Fig. 2).† Of most significance is the linear arrangement of the Mg–Se–Mg moiety [180.0°], which is in contrast to the bent geometry [139°] that is observed for the related zinc sulfido complex $\{[\mathrm{Tp}^{\mathrm{Ar',Me}}]\mathrm{Zn}\}_2\mathrm{S}$ (Ar′ = $\mathrm{C_6H_4Pr^i}$-*p*).[9] Although complexes with single selenido bridges are not common, structurally characterized examples fall into two classes that may be distinguished according to their M–Se–M bond angle, *i.e.* complexes with linear (*ca.* 180°) M–Se–M interactions, and those with bent M–Se–M interactions ($\leqslant$120°).‡ For example, $[(\mathrm{C_5Me_5})_2\mathrm{Sc}]_2\mathrm{Se}$ [173.7(1)°],[10] $[(\mathrm{C_5Me_5})_2\mathrm{Yb}]_2\mathrm{Se}$ [171.09(6)°],[11] $[(\mathrm{C_5Me_5})_2\mathrm{Sm}]_2\mathrm{Se}$ [169.7(1)°],[12] $[(\mathrm{dppe})(\mathrm{CO})_3\mathrm{V}]_2\mathrm{Se}$ [180.0°],[13] $[(\mathrm{C_5Me_5})(\mathrm{CO})_2\mathrm{Cr}]_2\mathrm{Se}$ [178.25(3)°],[14] and $\{[\mathrm{Tp}](\mathrm{CO})_2\mathrm{Mo}\}_2\mathrm{Se}$ [180.0°[15] and 178.3(1)°][16] have M–Se–M bond angles close to 180°, while $[(\mathrm{Me_3P})_2(\mathrm{CO})_3\mathrm{Re}]_2\mathrm{Se}$ [116.1(1)°],[17] $[\mathrm{Ph_3Sn}]_2\mathrm{Se}$ [103.4(1)° and 105.2(1)°],[18] and $[(\mathrm{Ph_3P})\mathrm{Au}]_2\mathrm{Se}$ [79.1(1)°][19] have M–Se–M bond angles $\leqslant$120°. Linear M–Se–M interactions are typically rationalized in terms of π donation from Se to an electron-deficient metal centre;[20] for example, '16' = electron $[(\mathrm{dppe})(\mathrm{CO})_3\mathrm{V}]_2\mathrm{Se}$[13] is linear, while the closely related complex $[(\mathrm{Me_3P})_2(\mathrm{CO})_3\mathrm{Re}]_2\mathrm{Se}$ is bent [116.1(1)°],[17] since it does not require π donation from Se to achieve an 18-electron configuration. The observation of a linear Mg–Se–Mg interaction in $\{[\mathrm{Tp}^{p\text{-Tol}}]\mathrm{Mg}\}_2\mathrm{Se}$ is, therefore, consistent with the existence of π interactions between Mg and Se; indeed, the Mg–Se bond lengths in $\{[\mathrm{Tp}^{p\text{-Tol}}]\mathrm{Mg}\}_2\mathrm{Se}$ [2.404(3), 2.408(3) Å] are slightly shorter than that in $[\mathrm{Tp}^{p\text{-Tol}}]\mathrm{MgSeH}$ and, in fact, are the shortest of all Mg–Se bond lengths listed in the Cambridge Structural Database. However, it must be recognized that the linearity of the Mg–Se–Mg moiety in $\{[\mathrm{Tp}^{p\text{-Tol}}]\mathrm{Mg}\}_2\mathrm{Se}$ may rather be a consequence of the steric interactions between the bulky $[\mathrm{Tp}^{p\text{-Tol}}]$ ligands attached to each magnesium centre.[21]

In summary, the tris(3-*p*-tolylpyrazolyl)hydroborato ligand has been used to prepare the first structurally characterized terminal hydrosulfido and hydroselenido derivatives of magnesium, $[\mathrm{Tp}^{p\text{-Tol}}]\mathrm{MgSH}$ and $[\mathrm{Tp}^{p\text{-Tol}}]\mathrm{MgSeH}$. The presence of terminal –SH and –SeH moieties in these complexes provides an interesting and marked contrast with the hydroxide derivative $\{[\mathrm{Tp}^{\mathrm{Ar,Me}}]\mathrm{Mg}(\mu\text{-OH})\}_2$ (Ar = $\mathrm{C_6H_4Bu^t}$-*p*) in which the hydroxide ligand prefers to bridge two metal centres.

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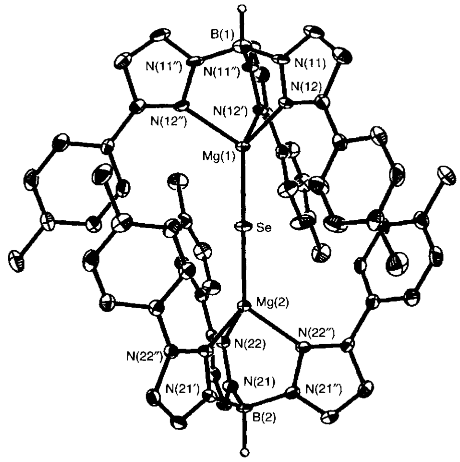

Fig. 2 ORTEP drawing of $\{[\mathrm{Tp}^{p\text{-Tol}}]\mathrm{Mg}\}_2\mathrm{Se}$

Footnotes

† Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/62.

‡ This classification is obviously not appropriate for complexes with M–Se–M interactions in which the two metal centres are linked *via* additional interactions.

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6 Such a method has been used previously for the synthesis of related hydrosulfido complexes, *e.g.* $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{BeSH}$, $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{MgSH}$ and $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{ZnSH}$. See G. Parkin, *Adv. Inorg. Chem.*, 1995, **42**, 291.

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