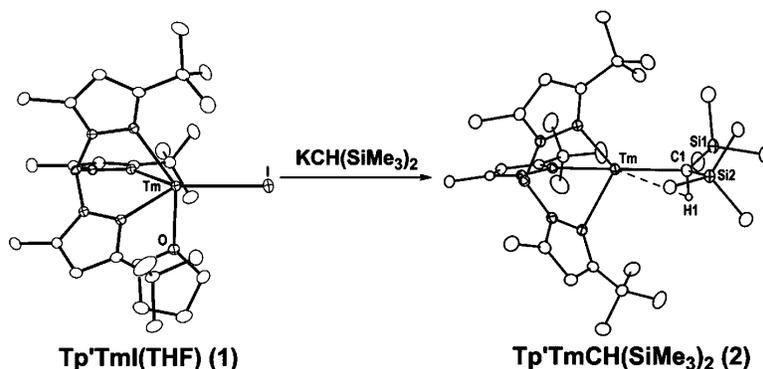


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Heteroleptic Tm(II) Complexes: One More Success for Trofimenko's Scorpionates

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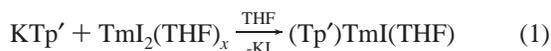
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The emergence of new, and largely unexpected, divalent lanthanides for solution molecular chemistry has been one of the most exciting recent developments in lanthanide chemistry. As pointed out by Evans,¹ since 1997 the number of divalent lanthanides available for the synthetic chemist has doubled from the time tested Eu(II), Yb(II), and Sm(II) to include the much more reducing Tm(II), Dy(II), and Nd(II).

Recent reviews by Bochkarev² and Edelmann³ have catalogued progress in this "new" divalent lanthanide field, including the preparation of organometallic derivatives. However, heteroleptic Tm(II) compounds, except for solvent adducts, have remained elusive as has the synthesis of Tm(II)-hydrocarbyl species. It was quickly established that the outcome of a reaction crucially depended on the choice of ligand, solvent, and even on the nature of the inert atmosphere used.

The bulky hydro-tris(3-*t*Bu-5-Me-pyrazolyl)borate ligand (Tp^{*t*Bu,Me}, Tp'), a second generation Trofimenko "scorpionate",⁴ has been used to prepare heteroleptic "(Tp')LnER" (Ln = Yb(II) and Sm(II)) type complexes,⁵ including hydrocarbyl species. On the basis of these observations, we attempted similar reactions with TmI₂. Here we report our preliminary results on the successful synthesis of the first heteroleptic Tm(II) complexes, including the Tm(II)-hydrocarbyl, (Tp')Tm{CH(SiMe₃)₂}.

Addition of KTp' to a THF solution of TmI₂ at room temperature (rt) in a glovebox (He/N₂ atmosphere), followed by simple work up afforded dark green (Tp')TmI(THF) (**1**) in moderate yield.



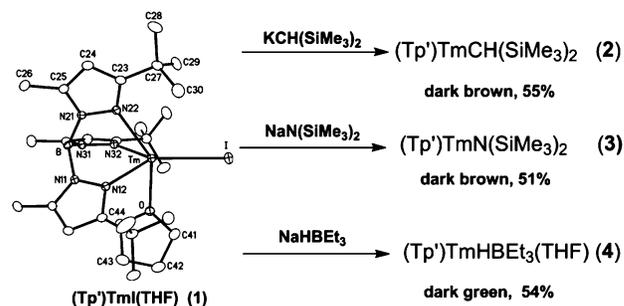
Complex **1** was fully characterized, including the solid-state X-ray structure (Scheme 1). The complex is isostructural with the Yb(II)/Sm(II) analogues,⁵ in particular the metrical parameters are very close to those of the slightly smaller Yb(II) with distances Ln (Tm/Yb) of Ln–N_{ave} = 2.462(3)/2.453(6) Å, Ln–I = 3.0595(4)/3.0536(8) Å, and Ln–O = 2.454(2)/2.447(6) Å. The coordination geometry is distorted trigonal bipyramidal with the THF oxygen and N22 occupying axial sites (O–Tm–N22 = 145.15(9)°) and I, N12, and N32 the equatorial positions.

Although isolable, complex **1** undergoes slow decomposition both in solution and in the solid state,^{6,7} when kept at –30 °C. Pure **1** can be recovered from small amounts of decomposed material (appearance of white solid) by recrystallization from OEt₂.

Despite its delicate nature, complex **1** is a useful starting material for the synthesis of a select number of heteroleptic Tm(II) complexes (Scheme 1). Thus simple salt metathesis gave the dark brown Tm(II)-hydrocarbyl, (Tp')Tm{CH(SiMe₃)₂} (**2**), dark brown (Tp')Tm{N(SiMe₃)₂} (**3**), and the dark green triethylborohydride complex (Tp')Tm(μ-HBEt₃)(THF) (**4**). The complexes were fully characterized, including EA, and the solid-state structures were established by single-crystal X-ray studies.

The most remarkable compound is (Tp')Tm{CH(SiMe₃)₂} (**2**), with a Tm(II)-hydrocarbyl bond, the first time such σ-alkyl species could be isolated. Although Izod has provided evidence for the likely presence of a Tm(II)-σ-carbon bond, these previous attempts

Scheme 1.



led to the isolation of Tm(III)-hydrocarbyl derivatives.⁸ The successful preparation of **2** is yet another demonstration of the remarkable kinetic stabilization conferred on otherwise highly reactive metal centers by Trofimenko's bulky scorpionates. The structure of **2** is shown in Figure 1.

The Tm(II) center is bonded to a classical κ³ scorpionate and an almost planar CH(SiMe₃)₂ hydrocarbyl ligand, with the sum of the angles involving nonhydrogen atoms bonded to C1 being 351°. One hydrocarbyl SiMe₃ group (containing Si2) is wedged between two pyrazolyl ligands (those containing N12 and N22) while the other SiMe₃ points toward the *t*Bu group on the third pyrazole ring. Steric repulsion between the latter two groups certainly contributes to the observed distorted tetrahedral coordination geometry of Tm (the Tm–C1 bond vector is 16.27(10)° off the B–Tm axis), but electronic factors must also play a role. This is evidenced by the vastly different Tm–C1–Si1 (132.18(18)°) and Tm–C1–Si2 (100.84(14)°) angles, the relatively short Tm---C7 distance (3.123(4) Å), the small Tm–C1–H1 angle (100°) and the short Tm---H1 distance (2.90 Å). All are indications of agostic Tm(II)---CH interactions, a common feature with electron deficient lanthanide centers, as is the case with complex **2**. Although comparison to other Tm(II)–C bond lengths is not possible, the Tm–C1 distance of 2.554(3) Å is virtually identical to that of the immediate neighbor Yb(II) analogue, 2.552(5) Å. In view of the isoelectronic nature of the CH(SiMe₃)₂ and N(SiMe₃)₂ ligands, it is not surprising that the coordination geometry of the metal center of (Tp')Tm{N(SiMe₃)₂} (**3**) is a similarly distorted tetrahedron (see Supporting Information). Compounds **2** and **3** are also delicate. Further elaboration of the Tm(II)–C/N bonds is best carried out on freshly prepared materials.

Complex **4** joins the relatively short list of electropositive metal complexes, including lanthanides, which contain an intact alkylborohydride ligand.⁹ Because of the higher precision of the present structure, compared to the Yb(II)/Sm(II) analogues,^{5a,c} the nature of the bonding between the Tm(II) and the (HBEt₃)[–] ligand could be fully established. As shown in Figure 2, in addition to the bridging hydride, the (HBEt₃)[–] ligand has one of its ethyl groups oriented toward thulium and takes part in agostic interactions as evidenced by the severely bent Tm–H2–B2 bridge (113(6)°) and the close contacts between Tm and methylene protons H5A and H5B (2.71 Å and 2.55 Å, respectively).¹⁰ The coordination mode of the (HBEt₃)[–] ligand is thus similar to that observed in (C₅Me₃)₂-La(HBEt₃)(THF).⁹ Compound **4** is the most stable of the heteroleptic

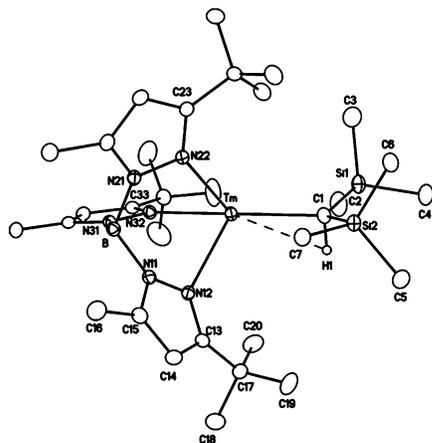


Figure 1. ORTEP plot of $(\text{Tp}')\text{Tm}\{\text{CH}(\text{SiMe}_3)_2\}$ (**2**). Ellipsoids are drawn at the 20% probability level.

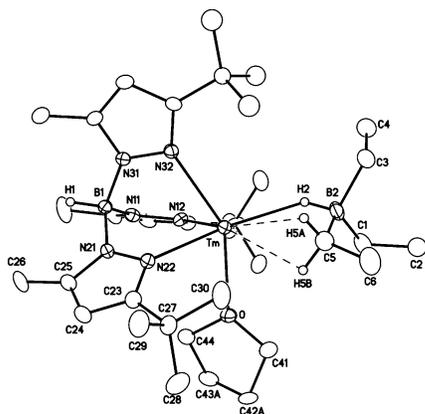


Figure 2. ORTEP plot of $(\text{Tp}')\text{Tm}(\mu\text{-HBtEt}_3)(\text{THF})$ (**4**). Ellipsoids are drawn at the 20% probability level.

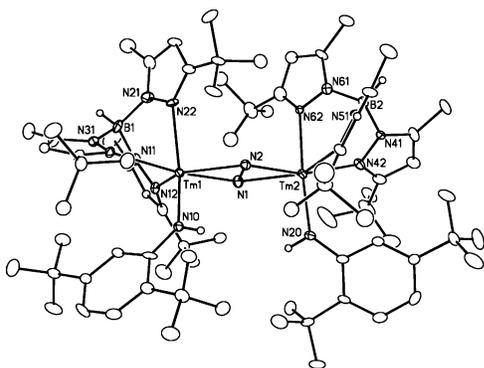
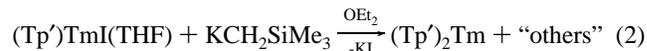


Figure 3. ORTEP plot of **6**. Ellipsoids are drawn at the 20% probability level.

Tm(II) derivatives isolated in this study, showing no sign of decomposition after one week at ambient temperature. Important for enhanced stability, the ethyl groups appeared equivalent in the room temperature ^1H NMR spectrum, indicating that the Tm–Et agostic interactions are insufficiently strong to prevent ligand rearrangement. Lowering the temperature was accompanied by spectral changes and the emergence of a complex spectrum at $-80\text{ }^\circ\text{C}$, with widely separated signals (-90 to 140 ppm) due to the paramagnetic Tm^{2+} center. Unfortunately, the broad signals could not be reliably assigned and hence we were unable to extract the energetics of the Tm–Et agostic interactions.

Wishing to expand the number of Tm(II) hydrocarbyl species, complex **1** was treated with $\text{KCH}_2\text{SiMe}_3$, hoping to obtain the Tm(II) analogue of the versatile and synthetically very useful $(\text{Tp}')\text{-}$

$\text{Yb}(\text{CH}_2\text{SiMe}_3)(\text{THF})$, which allowed the isolation of the unique Ln(II)–hydride, $[(\text{Tp}')\text{Yb}(\mu\text{-H})_2]$.¹¹ Unexpectedly, the reaction was accompanied by ligand redistribution and the only Tm(II) species that could be isolated was $(\text{Tp}')_2\text{Tm}$ (**5**), eq 2. The structure of **5** is identical to that of the Yb(II)/Sm(II) analogues,¹² with a $\kappa^3\text{-N}_3$ and $\kappa^3\text{-N}_2\text{H}$ scorpionate ligands.



Ligand redistribution was also observed when preparation of primary amido derivatives, $(\text{Tp}')\text{Tm}(\text{NHR})$, was attempted via salt metathesis. However the outcome of a protonolysis protocol proved very different. Addition of a 2,5-*t*Bu₂-aniline to a hexane solution of **2** in the drybox (He/N_2 atmosphere) initially gave a dark brown solution, which bleached in 1 h, indicating formation of a Tm(III)–imido species were quickly dashed when the solid-state structure showed that the yellow compound **6** was $[(\text{Tp}')\text{Tm}\{\text{NHC}_6\text{H}_3\text{-}(t\text{Bu})_2\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)]$,¹³ (Figure 3) with similar inner core as the $[(\text{C}_5\text{Me}_5)_2\text{Ln}(\text{THF})_{1,0}]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$ complexes of Evans.¹⁴

In summary, we have shown that the sterically very demanding scorpionate, $\text{Tp}^{\text{tBu,Me}}$, is capable of stabilizing heteroleptic Tm(II) derivatives, including the first Tm(II)–hydrocarbyl species, and this, for complexes **1–5**, even in the presence of dinitrogen. Future studies are aimed at expanding the range of Tm(II) complexes, to study their reactivities and to reinvestigate the synthesis in the absence of dinitrogen with a view to harness possible internal redox behavior to generate Tm(III)–multiple-bonded species, like $(\text{Tp}')\text{-TmNR}$. Extension of the work to the more reducing Dy(II) and Nd(II) is also planned.

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Supporting Information Available: Synthesis and spectroscopic and X-ray diffraction details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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