Formation and Structure of Thulium(III) Cyclopentadienides as Products of Reactions Directed Towards the Synthesis of Thulium(II) Cyclopentadienides

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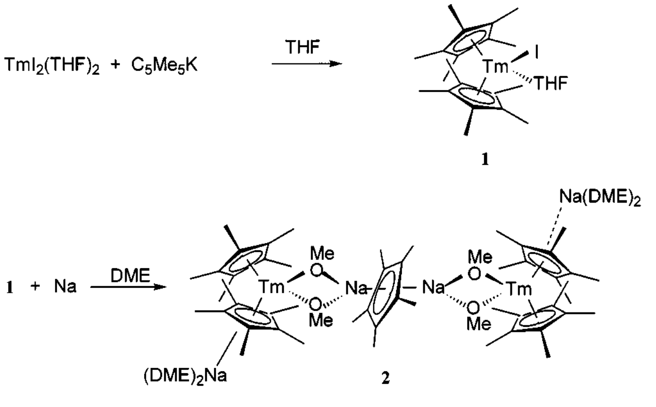
$TmI_2(THF)_2$ and $[C_5Me_5]K$ react in THF to yield the Tm^{III} complex $(C_5Me_5)_2TmI(THF)$ (**1**). The reaction of **1** with excess sodium in 1,2-dimethoxyethane (DME) leads, through Tm^{II} intermediates and a reductive splitting of DME solvent molecules, to the trisodium dithulium(III) complex $[(DME)_2Na(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)Tm(\eta^5\text{-}C_5Me_5)(\mu_2\text{-}OMe)_2(Na\text{-}\mu\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)\text{-}Na(\mu\text{-}OMe)_2Tm(\eta^5\text{-}C_5Me_5)_2]$ (**2**). Treatment of $TmI_2(THF)_2$ with $[(Me_3Si)_2C_5H_3]MgCl$ (**3**) in THF yields the dimeric Tm^{III} complex $[\{1,3\text{-}(Me_3Si)_2C_5H_3\}_2TmCl]_2$ (**4**), while $TmI_3(THF)_3$ reacts with $[C_5H_4CH_2CH_2NMe_2]K(THF)$ (**5**) to yield solvent-free $(C_5H_4CH_2CH_2NMe_2)_2TmI$ (**6**). The new Tm^{III} compounds have been characterized by elemental analysis, IR spectroscopy, and mass spectrometry. The molecular structures of **2**, **4**, **5**, and **6** have been determined by single-crystal X-ray diffraction analysis.

Introduction

We recently reported on the first molecular thulium(II) complex, $TmI_2(DME)_3$, which was prepared by reduction of TmI_3 with metallic thulium in DME.[1] Analogous organic solvent adducts of neodymium and dysprosium diiodide were obtained by high-temperature reactions (> 200 °C) of the respective metal powders with iodine in sealed glass ampoules followed by treatment of the reaction products with DME or THF.[2] The molecular lanthanide(II) diiodides characterized to date include those of samarium, europium, ytterbium, thulium, neodymium, and dysprosium. According to their standard potentials, the stability of the divalent oxidation state decreases in the order $Eu^{II} > Yb^{II} > Sm^{II} > Tm^{II} > Dy^{II} > Nd^{II}$.[3] Whereas organometallic complexes of divalent europium, ytterbium, and samarium are well known and syntheses of the first organolanthanum(II) complex, $[K(18\text{-crown-6})(C_6H_6)_2][(Cp^{tt}{}_2La)_2(C_6H_6)]_2\text{-}C_6H_6$ ($Cp^{tt} = 1,3\text{-}t\text{Bu}_2C_5H_3$),[4a] and of the first organoscandium(II) complex, $[\{(P_3C_2t\text{Bu}_2)Sc\}_2(P_3C_3t\text{Bu}_3)]$,[4b] have recently been reported, organometallic derivatives of divalent thulium, dysprosium, and neodymium are still unknown. Therefore, we have tried to synthesize organothulium(II) complexes, in the knowledge that they would be very reactive towards organic substrates.[5] Thulium(II) iodide promised to be a suitable starting material. However, as demonstrated by the experiments described below, we were not successful in isolating organothulium(II) complexes, but isolated some interesting new thulium(III) complexes instead. Their formation and structures are reported herein.

Results and Discussion

Malachite-green $TmI_2(THF)_2$ reacts with $[C_5Me_5]K$ (molar ratio 1:2) in THF at −30 to +20 °C; the color of the reaction mixture changes first to brownish-green and finally to light-brown. After removal of the solvent, extraction of the remaining solid with toluene, and concentration of the toluene extract, yellow needle-shaped crystals precipitate. These were found to be composed of the thulium(III) complex $(C_5Me_5)_2TmI(THF)$ (**1**) rather than the expected $(C_5Me_5)_2Tm^{II}$ compound (Scheme 1). Compound **1** melts at 285 °C without decomposition; the high relative intensities of the molecular fragment ions $[(C_5Me_5)_2TmI]^+$ (49.86%), $[(C_5Me_5)TmI]^+$ (50.27%), and $[(C_5Me_5)_2Tm]^+$ (100%) in the EI mass spectrum at 241 °C confirm its remarkable thermal stability. The IR spectrum of **1** is rather uninformative, allowing only a clear assignment of the



Scheme 1

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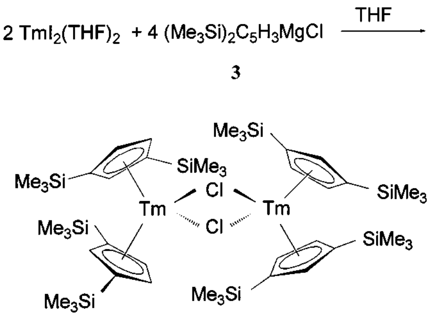
strong THF absorptions at 1010 and 860 cm^{-1}. We have previously observed a similar oxidation of Tm^{II} to Tm^{III} in the reaction of $TmI_2(DME)_3$ with $[Me_2Si(3\text{-}t\text{Bu-5-Me-}C_5H_3)(C_9H_6CH_2CH_2NMe_2)]Na_2$, which afforded the thulium(III) complex *ansa*-$[Me_2Si\text{-}(3\text{-}t\text{Bu-5-Me-}C_5H_3)\text{-}(C_9H_6CH_2CH_2NMe_2)]TmI$.[6]

In a subsequent experiment, we tried to obtain the bis(pentamethylcyclopentadienyl)thulium(II) complex by reducing compound **1** with sodium. At the start of the reaction of **1** with excess sodium in DME at 20 °C, a green coating appeared on parts of the metal surface indicating the formation of a thulium(II) species. However, this green coating disappeared very quickly and after stirring for 1 h, a light-yellow reaction mixture was obtained. Filtration and concentration of the solution afforded an oily residue, which partly redissolved in diethyl ether. From the concentrated clear ethereal solution, colorless crystals precipitated, which were found to contain thulium, but were free of iodine and melted at 68−72 °C with decomposition. The IR spectrum of these crystals shows an absorption band attributable to coordinated DME, together with a very strong, broad band at 1100 cm^{-1} indicating the presence of methoxide groups, these arising from cleavage of the DME solvent molecules. Such C−O activation has previously been observed by Lappert et al.,[7] who studied the reactions of $[1,3\text{-}(SiMe_3)_2C_5H_3]_3Nd$ and $(1,3\text{-}t\text{Bu}_2C_5H_3)_3Ce$ with lithium in DME yielding the corresponding methoxide complexes $[1,3\text{-}(Me_3Si)_2C_5H_3]_2Nd(\mu\text{-}OMe)_2Li(DME)$ and $[(1,3\text{-}t\text{Bu}_2C_5H_3)_2Ce(\mu\text{-}OMe)]_2$, respectively. The isolated crystals were characterized by single-crystal X-ray diffraction analysis. Whereas the data from a first diffraction experiment[8] implied some intrinsic contradictions, a second X-ray analysis of a crystal of the same crop afforded precise structural data, from which the formula of the compound formed in the reaction of **1** with sodium in DME could be assigned as $[(DME)_2Na(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_5Me_5)Tm(\eta^5\text{-}C_5Me_5)(\mu_2\text{-}OMe)_2\text{-}(Na\text{-}\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_5Me_5)Na(\mu\text{-}OMe)_2Tm(\eta^5\text{-}C_5Me_5)_2]$ (**2**), i.e. one containing only thulium(III) ions. The first step in the reaction is the expected reduction of **1** with the formation of green Tm^{II} species, which, because of their high reduction potential and high oxophilicity, attack DME solvent molecules with reductive splitting of MeO−C bonds and the formation of thulium(III) methoxide units. The generation of the four methoxide groups of **2** requires four electrons. Since two of the intermediately formed thulium(II) species provide only two electrons, the sodium metal must also take part in the reductive cleavage of DME. At this point, it should be noted that sodium metal does not react with DME in the absence of lanthanide compounds, not even on prolonged reflux. The organic products formed in the DME splitting process could not be identified.

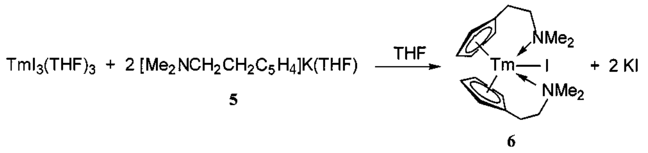
From the results reported above, we conclude that the possibility of synthesizing a stable organothulium(II) compound will probably arise by the use of space-demanding substituted cyclopentadienyl ligands or of cyclopentadienyl ligands containing nitrogen as a strong donor atom in the side chain, thus stabilizing the complex by additional intramolecular metal coordination. Lappert et al.[4a] have previously demonstrated that bulky cyclopentadienyl ligands are effective in stabilizing Ln^{II} ions. Therefore, we studied the interactions of $TmI_2(THF)_2$ with $[1,3\text{-}(Me_3Si)_2C_5H_3]M$ [M = K[9] or MgCl (**3**)]. Since only intractable product mixtures were obtained using the potassium cyclopentadienide, which can only be recovered from organic media in an impure state, we turned our attention to the corresponding cyclopentadienylmagnesium chloride, $[1,3\text{-}(Me_3Si)_2\text{-}C_5H_3]MgCl$ (**3**), which can be obtained from $[1,3\text{-}(Me_3Si)_2C_5H_3]K$ and $MgCl_2$ (1:1 molar ratio) in diethyl ether as a pure crystalline solid. Addition of **3** to a solution of $TmI_2(THF)_2$ in THF (2:1 molar ratio) led to the immediate formation of a highly dispersed dark-grey solid, which reacted readily with water and was found to consist of metallic magnesium formed by reduction of MgICl by intermediately formed organothulium(II) species. As a consequence, workup of the reaction mixture again afforded only an organothulium(III) derivative, the dimeric compound $[\{1,3\text{-}(Me_3Si)_2C_5H_3\}_2TmCl]_2$ (**4**) (Scheme 2). Compound **4** was isolated in 67% yield and did not melt below 280 °C. Its mass spectrum shows ion peaks of a fragment of the dimer, $[M - 2\ CH_3 - (CH_3)_3Si]_2^+$ (0.5%), of the monomeric unit $[Cp^{\#}{}_2TmCl]^+$ (8%), and of fragments predominantly formed by cleavage of Si−C bonds. The MS data indicate that the metallocene structure of **4** is thermodynamically rather stable.



Scheme 2

The [2-(dimethylamino)ethyl]cyclopentadienyl ligand, which has already been used successfully for the synthesis of the ytterbium(II) complex $(Me_2NCH_2CH_2C_5H_4)Yb$,[10] should offer another possible means of obtaining a stable organothulium(II) complex. The corresponding potassium salt, $[Me_2NCH_2CH_2C_5H_4]K(THF)$ (**5**), was prepared from $Me_2NCH_2CH_2C_5H_5$ [11] and KH in THF according to literature methods (Scheme 3).[12] It forms long needle-shaped crystals, the structure of which we determined by X-ray diffraction analysis (Figure 3). Once again, compound **5** and $TmI_2(THF)_2$ did not react to form a Tm^{II} derivative. Indeed, in this case, workup of the reaction mixture did not even allow the isolation of a Tm^{III} complex, which we expected to be formed by oxidation of a Tm^{II} intermediate. However, the expected thulium(III) complex $(Me_2NCH_2CH_2C_5H_4)_2TmI$ (**6**) could be isolated as solvent-free colorless needles in 74% yield by treating **5** with

$TmI_3(THF)_3$ (2:1 molar ratio) in THF at 20 °C (Scheme 3). The crystals melt at 109−111 °C without decomposition. The EI mass spectrum of **6** shows no molecular ion peak at temperatures up to 220 °C. The most intense molecular fragments, $[(DoCp)_2Tm]^+$ (9%) and $[(DoCp)TmI]^+$ (4%), were detected at 158 °C (DoCp = $C_5H_4CH_2CH_2NMe_2$).



Scheme 3

Again, at the initial stage of the reaction of **6** with excess sodium in diethyl ether, the intermediate formation of a Tm^{II} compound was indicated by a light-green color of the mixture. However, this coloration disappeared within a few minutes and workup of the reaction mixture did not afford any well-defined products. This is in accordance with previously reported attempts[13] to synthesize cyclopentadienylthulium(II) complexes by reduction of the corresponding Tm^{III} compounds with alkali metals.

Molecular Structures of 2, 4, 5, and 6

Crystals suitable for single-crystal X-ray diffraction studies were obtained from diethyl ether (**2**), hexane (**4**), or THF (**5** and **6**). The crystal and structure refinement data for **2**, **4**, **5**, and **6** are listed in Table 1.

The molecule of **2** (Figure 1) contains two regions of disorder, both located around centers of symmetry. In the center of the molecule, a pentamethylcyclopentadienyl unit is statistically distributed between two symmetry-related alternative orientations. Since the centroid positions of the two orientations are different, the adjacent sodium position is split. At the ends of the molecule, the fragment $[Na(DME)_2]$ has a statistical occupancy of 50%. Due to overlap of the DME regions of neighboring molecules, at first glance the structure seems to be polymeric. However, two different DME molecules may not occupy the same space simultaneously, hence only one orientation can be realized between a given pair of molecules. Consequently, the structure consists of discrete isolated units. The picture given in Figure 1 (top) can be viewed in two ways. The open ellipsoids, together with their filled counterparts, represent the disordered parts of the structure. These atoms have crystallographic occupancies of 50%, resulting in an averaged structure corresponding to $[(DME)_2Na]_{1/2}$(μ-

Table 1. Crystal data and structure refinement for **2**, **4**, **5**, and **6**

	2	**4**	**5**	**6**
Empirical formula	$C_{62}H_{107}Na_3O_8Tm_2$	$C_{44}H_{84}Cl_2Si_8Tm_2$	$C_{13}H_{22}KNO$	$C_{18}H_{28}IN_2Tm$
M_r [g mol^{-1}]	1387.31	1246.59	247.42	568.25
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1/n$	$P2_1/c$	$P2_12_12_1$	$Pcnb$
Unit cell dimensions				
a [Å]	10.1900(11)	10.694(2)	9.7254(1)	10.7653(2)
b [Å]	20.158(3)	14.429(3)	10.6654(2)	13.0419(1)
c [Å]	16.8410(19)	19.980(6)	14.0639(2)	13.5427(2)
β [°]	103.921(12)	104.35(2)	90	90
V [Å^3]	3357.7(7)	2986.8(13)	1458.78(4)	1901.39(5)
Z	2	2	4	4
$\rho_{calcd.}$ [g/cm^3]	1.372	1.386	1.127	1.985
μ [mm^{-1}]	2.692	3.227	0.347	6.289
F(000)	1428	1264	536	1088
Crystal dimensions [mm]	0.54 × 0.46 × 0.36	0.48 × 0.48 × 0.42	0.66 × 0.35 × 0.08	0.30 × 0.24 × 0.12
Data collection θ range [°]	1.60−30.00	2.10−27.46	2.40−27.50	2.42−27.50
h	−14/14	0/13	−7/12	−13/+10
k	−28/28	0/18	−13/13	−16/16
l	−18/+23	−25/25	−18/18	−17/17
Collected/unique reflections	30283/9790	7174/6812	11095/3351	13319/2188
R_{int}	0.0389	0.0748	0.0626	0.0397
Absorption correction	SADABS	none	SADABS	SADABS
Max./min. transmission	0.4278/0.2945	−	0.9774/0.3639	0.3852/0.2426
Data/restraints/parameters	9790/0/440	6802/0/265	3351/0/148	2188/0/104
Goodness-of-fit on F^2	1.051	1.054	1.019	1.075
R_1 [$I > 2\sigma(I)$]	0.0262	0.0498	0.0539	0.0260
wR_2 [$I > 2\sigma(I)$]	0.0517	0.1279	0.1181	0.0507
R_1 (all data)	0.0445	0.0583	0.0904	0.0498
wR_2 (all data)	0.0579	0.1398	0.1339	0.0591
Largest diff. peak and hole [e/Å^3]	0.689/−0.738	3.039/−2.610	0.235/−0.262	1.008/−1.067

$C_5Me_5)Tm(C_5Me_5)(\mu\text{-}OMe)_2[Na(\mu\text{-}C_5Me_5)Na]_{2/2}(\mu\text{-}OMe)_2\text{-}Tm(C_5Me_5)(\mu\text{-}C_5Me_5)[Na(DME)_2]_{1/2}$. Alternatively, ignoring the open ellipsoids and taking the filled ones as complete atoms leads to one possible structure of an actual molecule, which may be described as $[(DME)_2Na(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)Tm(\eta^5\text{-}C_5Me_5)(\mu_2\text{-}OMe)_2(Na\text{-}\mu\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)Na(\mu\text{-}OMe)_2Tm(\eta^5\text{-}C_5Me_5)_2]$ [Figure 1 (bottom)]. The relevant bond lengths and angles fall within the characteristic ranges for the various fragments.[13,14]

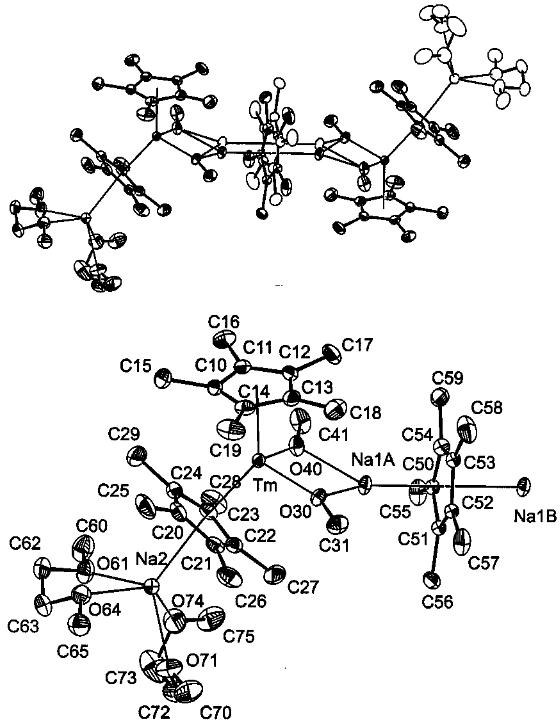


Figure 1. Molecular structure of **2** with 30% probability thermal ellipsoids: representation of a molecule including disorder (see text for details) (top); asymmetric unit showing the atom numbering scheme (bottom); all hydrogen atoms have been omitted for clarity; selected bond lengths [Å] and angles [°]: Tm−Cp(1) 2.4010(14) [Tm−C 2.669(2)−2.703(3)], Tm−Cp(2) 2.4159(13) [Tm−C 2.672(3)−2.732(3)], Tm−O 2.1062(17)−2.1184(17), Na(1A)−Cp(3) 2.328(10) [Na(1A)−C 2.601(11)−2.639(12)], Na(1B)−Cp(3) 2.364(10) [Na(1B)−C 2.606(11)−2.685(11)], Na(1A)−O 2.210(11)−2.350(10), Na(1B)′−O 2.191(10)−2.331(11), Na(2)−Cp(2) 2.620(2) [Na(2)−C 2.656(3)−3.098(4)], Na(2)−O 2.370(8)−2.450(5); Cp(1)−Tm−Cp(2) 135.79(4), O(30)−Tm−O(40) 86.60(7), Cp−Tm−O 105.72(6)−106.17(6), Tm−Cp(2)−Na(2) 166.33(8), Tm−O−Na(1) 93.8(2)−99.2(3), O(30)−Na(1)−O(40) 78.8(3)−79.6(4), O−Na(1)−Cp(3) 137.2(5)−141.6(5), Na(1A)−Cp(3)−Na(1B) 179.2(3); Cp(1), Cp(2), and Cp(3) represent the centroid positions of the rings C(10)−C(14), C(20)−C(24), and C(50)−C(54), respectively; symmetry transformation (′) used to generate equivalent atoms: 1 − *x*, 1 − *y*, 1 − *z*

The X-ray crystal structure of $[\{1,3\text{-}(Me_3Si)_2C_5H_3\}_2\text{-}TmCl]_2$ (**4**) shows this complex to be a centrosymmetric, chloro-bridged dimer (Figure 2). Compound **4** crystallizes in the monoclinic space group $P2_1/c$ with two dimers in the unit cell. The bond lengths and bond angles estimated for **4** are in the characteristic ranges for the various fragments.[13,14]

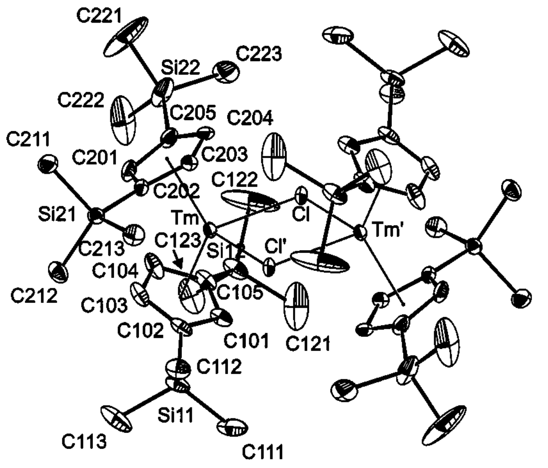


Figure 2. Molecular structure of **4** showing the atom numbering scheme (30% probability thermal ellipsoids); all hydrogen atoms have been omitted for clarity; selected bond lengths [Å] and angles [°]: Tm−Cp(1) 2.314(3) [Tm−C 2.582(6)−2.642(5)], Tm−Cp(2) 2.316(3) [Tm−C 2.604(6)−2.618(5)], Tm−Cl 2.6829(15), Tm−Cl′ 2.6883(13); Cp(1)−Tm−Cp(2) 130.08(10), Cp(1)−Tm−Cl 110.60(7), Cp(1)−Tm−Cl′ 111.03(8), Cp(2)−Tm−Cl 106.82(8), Cp(2)−Tm−Cl′ 106.46(8), Cl−Tm−Cl′ 80.85(4), Tm−Cl−Tm′ 99.15(4); Cp(1) and Cp(2) represent the centroid positions of the rings C(101)−C(105) and C(201)−C(205), respectively; symmetry operation (′) used to generate equivalent atoms: 1 − *x*, 1 − *y*, 1 − *z*

$[Me_2NCH_2CH_2C_5H_4]K(THF)$ (**5**) (Figure 3) is polymeric and crystallizes in the chiral orthorhombic space group $P2_12_12_1$ with four formula units per unit cell. The structure consists of infinite one-dimensional chains extending parallel to the *b* axis. Each potassium atom is coordinated by one THF molecule, the C_5H_4 aromatic ring system, the nitrogen atom of the 2-(dimethylamino)ethyl side chain, and, additionally, by the C_5H_4 ring system of a neighbouring molecule. The $\mu_2\text{-}\eta^5{:}\eta^5$ coordination of the cyclopentadienyl moi-

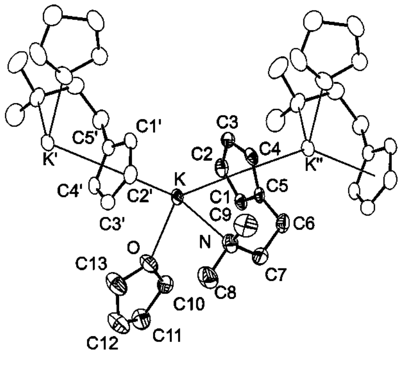


Figure 3. Section of the polymeric structure of **5** showing the atom numbering scheme (30% probability thermal ellipsoids); symmetry-equivalent atoms are represented by open ellipsoids to emphasize the asymmetric unit; all hydrogen atoms have been omitted for clarity; selected bond lengths [Å] and angles [°]: K−Cp 2.8082(16) [K−C 3.007(3)−3.097(3)], K−Cp′ 2.8183(16) [K−C 3.007(3)−3.119(3)], K−N 2.867(3), K−O 2.734(3); Cp−K−Cp′ 143.23(5), O−K−N 88.01(10), Cp−K−N 85.38(7), Cp−K−O 109.43(6), Cp′−K−N 115.23(8), Cp′−K−O 101.76(6), K−Cp−K″ 174.56(6); Cp represents the centroid position of the ring C(1)−C(5); symmetry transformations used to generate equivalent atoms: (′) 1 − *x*, 1/2 + *y*, 1/2 − *z*; (″) 1 − *x*, −1/2 + *y*, 1/2 − *z*

ety is characterized by only small differences in the K−C bond lengths (3.007−3.119 Å) and an almost linear K−Cp−K arrangement (174.56°).

The complex $(Me_2NCH_2CH_2C_5H_4)_2TmI$ (**6**) crystallizes in the orthorhombic space group *Pcnb*. The molecules possess a twofold rotational axis containing the thulium and iodine atoms (Figure 4). Consequently, the asymmetric unit comprises half a molecule for a total of two formula units per unit cell. In **6**, both donor atoms are intramolecularly coordinated to the thulium atom. As for other donor-functionalized bis(cyclopentadienyl)lanthanide(III) halides having a formal coordination number of 9,[15] the coordination geometry around the thulium atom is that of a distorted trigonal bipyramid with the two cyclopentadienyl rings and the iodine atom occupying the equatorial positions and the two nitrogen atoms of the cyclopentadienyl side chains in the axial positions forming an N−Tm−N angle of 157.9°. The distance from the thulium atom to the ring centers is 2.352 Å and the Tm−I and Tm−N distances of 3.014 and 2.789 Å, respectively, are within the ranges found for other thulium(III) complexes.[13,14]

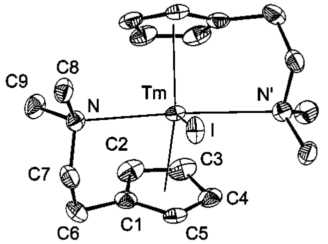


Figure 4. Molecular structure of **6** showing the atom numbering scheme (50% probability thermal ellipsoids); all hydrogen atoms have been omitted for clarity; selected bond lengths [Å] and angles [°]: Tm−Cp 2.352(2) [Tm−C 2.627(5)−2.650(4)], Tm−I 3.0145(4), Tm−N 2.789(4); I−Tm−Cp 114.27(6), I−Tm−N 78.97(8), Cp−Tm−Cp′ 131.46(8), Cp−Tm−N 90.91(11), Cp−Tm−N′ 98.12(11), N−Tm−N′ 157.94(16); Cp represents the centroid position of the ring C(1)−C(5); symmetry transformation (′) used to generate equivalent atoms: 1 − *x*, 1/2 − *y*, *z*

Conclusion

Reactions of thulium(II) iodide with cyclopentadienylpotassium or -magnesium derivatives do not yield stable cyclopentadienylthulium(II) complexes. Under the conditions used, only thulium(III) derivatives are formed. Neither the C_5Me_5 ligand nor the donor-functionalized $Me_2NCH_2CH_2C_5H_4$ or the bulky $1,3\text{-}(Me_3Si)_2C_5H_3$ ligand are able to stabilize organothulium(II) complexes in coordinating ether solvents.

Experimental Section

General Remarks: All manipulations were carried out either in vacuo or under nitrogen using standard Schlenk techniques. The solvents used were dried with sodium/benzophenone and were condensed in vacuo prior to use. − Melting points and decomposition temperatures were determined for samples sealed in capillaries in vacuo. − Elemental analyses were performed on a Perkin−Elmer Series II CHNS/O Analyser 2400. − IR spectra were recorded with a Specord M-80 spectrometer. The samples were prepared as mulls in Nujol. − Mass spectra (EI, 70 eV) were recorded with a Varian MAT 311A spectrometer. Only characteristic fragments and highest-abundance isotope peaks are listed. Relative intensities (%) are given in parentheses. − Informative NMR spectra of the thulium(III) complexes could not be obtained due to the strong paramagnetism of thulium(III) (μ_{eff} = 7.0−7.5 B.M.). $TmI_2(THF)_5$ formed in the reaction of $TmI_3(THF)_3$ with metallic thulium in THF changes into $TmI_2(THF)_2$ upon drying at 90 °C. The detailed experimental procedure will be published elsewhere. Literature methods were used for the synthesis of $[Me_2NCH_2CH_2C_5H_4]K(THF)$ (**5**),[12] and $[1,3\text{-}(Me_3Si)_2C_5H_3]K$.[9]

$(C_5Me_5)_2TmI(THF)$ (1): To a stirred suspension of $(C_5Me_5)K$ (1.12 g, 6.42 mmol) in THF (25 mL), precooled to −30 °C, was added $TmI_2(THF)_2$ (1.84 g, 3.24 mmol). The brownish-green mixture was allowed to warm to ambient temperature over a period of 2 h and then stirred for a further 1 h. The solvent was then removed in vacuo and the remaining solid was extracted with toluene (3 × 15 mL). Concentration of the combined toluene extracts to a volume of 8−10 mL led to the deposition of **1** (0.69 g, 34%) as yellow needle-shaped crystals; m.p. 285 °C. − IR (Nujol): $\tilde{\nu}$ = 1230 (w), 1190 (m), 1010 (vs), 965 (w), 920 (m), 860 (vs), 670 cm^{-1} (w). − MS (241 °C, ^{169}Tm): *m*/*z* (%) = 565.8 (49.86) $[M - THF]^+$, 439.0 (100) $[M - THF - I]^+$, 430.8 (50.27) $[M - THF - C_5Me_5]^+$, 295.8 (43.39) $[M - THF - 2\ C_5Me_5]^+$. − μ_{eff} (295 K) = 7.7 B.M. − $C_{24}H_{38}IOTm$ (638.40): calcd. I 19.88, Tm 26.46; found I 21.02, Tm 26.54.

$[(DME)_2Na][(C_5Me_5)_2Tm(OMe)_2\{Na(C_5Me_5)Na\}(OMe)_2Tm(C_5Me_5)_2]$ (2): A mixture of $(C_5Me_5)_2TmI(THF)$ (1.61 g, 2.52 mmol) and sodium (0.3 g, 13.04 mg-atom) in DME (10 mL) was stirred for 1 h at ambient temperature. The light-yellow solution was then decanted from the excess sodium, the solvent was removed under reduced pressure, and the oily residue was dried in vacuo. Treatment of this residue with diethyl ether (15 mL) led to the precipitation of NaI. The ether solution was centrifuged and decanted from the precipitate. Within 1 d, colorless crystals of **2** had precipitated from the concentrated (5 mL) ether solution. Yield 0.51 g (29%); m.p. 68−72 °C (decomp). − IR (Nujol): $\tilde{\nu}$ = 1300 (m), 1250 (m), 1160 (m), 1100 (vs), 1030 (s), 980 (m), 920 (w), 870 cm^{-1} (s). − μ_{eff} (295 K) = 7.4 B.M. − $C_{62}H_{107}Na_3O_8Tm_2$ (1387.36): calcd. C 53.68, H 7.77, Tm 24.35; found C 53.87, H 6.41, Tm 24.77.

$[1,3\text{-}(Me_3Si)_2C_5H_3]MgCl$ (3): To a stirred suspension of $MgCl_2$ (0.77 g, 8.08 mmol) in diethyl ether (50 mL), $[1,3\text{-}(Me_3Si)_2C_5H_3]K$ (1.95 g, 7.84 mmol) was added. After 2 h, the mixture was filtered. The ether solution was concentrated in vacuo and the remaining waxy solid was washed with hexane (20 mL). Recrystallization of the solid from diethyl ether gave **3** (1.12 g, 53%). − MS (73 °C, ^{24}Mg): *m*/*z* (%) = 442.2 (78.31) $[Cp^{\#}_2Mg]^+$, 427.3 (84.16) $[Cp^{\#}_2Mg - CH_3]^+$, 339.1 (16.14) $[Cp^{\#}_2Mg - 2\ CH_3 - TMS]^+$, 268.1 (1.02) $[Cp^{\#}MgCl]^+$, 251.0 (9.76) $[Cp^{\#}_2Mg - 3\ CH_3 - 2\ TMS]^+$, 233.2 (9.95) $[Cp^{\#}Mg]^+$, 210.2 (5.84) $[Cp^{\#}]^+$, 195.2 (8.91) $[Cp^{\#} - CH_3]^+$, 73.0 (100) $[TMS]^+$, 59.0 (5.07) $[MgCl]^+$. − $C_{11}H_{21}ClMgSi_2$ (269.22): calcd. C 49.08, H 7.86; found C 49.44, H 8.27.

$[\{1,3\text{-}(Me_3Si)_2C_5H_3\}_2TmCl]_2$ (4): Addition of $[1,3\text{-}(Me_3Si)_2C_5H_3]MgCl$ (0.84 g, 3.13 mmol) to a solution of $TmI_2(THF)_2$ (0.95 g, 1.67 mmol) in THF (40 mL) led to an immediate darkening of the reaction mixture. The solvent was removed in vacuo and the residual solid was extracted with hexane at 50 °C. The colorless compound **4** (0.65 g, 67%) crystallized on cooling of the hexane extract; m.p. > 280 °C. − IR (Nujol): $\tilde{\nu}$ = 1440 (s), 1400 (m), 1320 (m), 1250 (vs), 1095 (vs), 985 (w), 930 (s), 845 (vs), 800 (s), 765 (s), 700 (m), 640 (m), 620 cm^{-1} (m). − MS [$Cp^{\#}$ = 1,3-$(Me_3Si)_2C_5H_3$, 207 °C, ^{169}Tm]: *m/z* (%) = 622.4 (8.22) $[M]^+$, 607.4 (100) $[M - CH_3]^+$, 587.1 (10.99) $[M - Cl]^+$, 518.9 (15.92) $[M - 2\ CH_3 - TMS]^+$, 499.2 (24.31) $[M - CH_3 - (CH_3)_3Si - Cl]^+$, 413.0 (6.45) $[M - Cp^{\#}]^+$, 397.0 (9.83) $[M - Cp^{\#} - CH_3]^+$, 210.2 (8.20) $[Cp^{\#}]^+$, 195.2 (10.92) $[Cp^{\#}\ CH_3]^+$, 73.0 (97.51) $[TMS]^+$. − μ_{eff} (295 K) = 7.2 B.M. − $C_{22}H_{42}ClSi_4Tm$ (623.30): calcd. C 42.38, H 6.79, Tm 27.19; found C 41.11, H 6.55, Tm 27.95.

$(C_5H_4CH_2CH_2NMe_2)_2TmI$ (6): To a suspension of $TmI_3(THF)_3$ (1.9 g, 2.48 mmol) in THF (35 mL) was added $(C_5H_4CH_2CH_2NMe_2)K(THF)$ (1.25 g, 5.06 mmol). The mixture was stirred for 1 h at room temperature. Evaporation of the solvent and extraction of the residual solid with toluene (3 × 10 mL) gave **6** (1.05 g, 74%) as colorless crystals; m.p. 109−111 °C. − MS (DoCp = $C_5H_4CH_2CH_2NMe_2$, 158 °C, ^{169}Tm): *m/z* (%) = 440.9 (9.09) $[M - I]^+$, 431.8 (4) $[M - DoCp]^+$, 295.7 (1.71) $[M - 2\ DoCp]^+$, 58.2 (100) $[CH_2NMe_2]^+$. − $C_{18}H_{28}IN_2Tm$ (568.27): calcd. C 38.02, H 4.97, N 4.93; found C 37.53, H 4.33, N 5.14.

Crystal Structure Determinations: Data were collected with a Siemens SMART CCD area detector diffractometer (ω scans, T = 173 K) for **2**, **5**, **6** or with an Enraf−Nonius CAD4 diffractometer (ω−2θ scans, T = 163 K) for **4**. Both diffractometers were equipped with low-temperature devices and were operated with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97[16] (**2**, **5**, **6**) or SHELXS-86[17] (**4**) and were refined against F^2 using SHELXL-97[18] (**2**, **5**, **6**) or SHELXL-93[19] (**4**). In the case of **2**, **5**, and **6**, an empirical absorption correction was applied using the program SADABS.[20] All non-hydrogen atoms were refined with anisotropic thermal parameters, except for the ring atoms of the disordered C_5Me_5 ligand in **2**. Hydrogen atoms were placed in idealized positions with fixed isotropic temperature factors (U_{iso} = 0.08 Å^2). Crystal and structure refinement data are given in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-158695 (**2**), -158696 (**4**), -158697 (**5**), and -158698 (**6**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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