A Chemical Definition of the Effective Reducing Power of Thulium(II) Diiodide by Its Reactions with Cyclic Unsaturated Hydrocarbons

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Abstract: Thulium diiodide reduces cyclic aromatic hydrocarbons that have reduction potentials more positive than -2.0 V versus SCE. Thus, TmI_2 reacts with cyclooctatetraene or acenaphthylene in THF, or with lithium anthracenide in 1,2-dimethoxyethane (DME) to give thulium triiodide and the thulium(III) complexes $[(\eta^8\text{-}C_8H_8)TmI(thf)_2]$ (**1**), *rac*-ansa-$[(\eta^5\text{-}C_{12}H_8)_2TmI(thf)]$ (**2**), or $[(\eta^2\text{-}C_{14}H_{10})TmI(dme)_2]$ (**3**), respectively. The molecular structures of **1**–**3** were determined by single-crystal X-ray diffraction.

Keywords: biaryls • lanthanides • reduction • structure elucidation • thulium

Introduction

Whereas the existence of divalent ions in the lattice of most inorganic compounds of the lanthanides is well ascertained,[1] coordination compounds of divalent lanthanides are only known for the elements europium, samarium, and ytterbium.[2] Within the past two decades numerous efforts have been made to synthesize divalent molecular complexes of the remaining lanthanides.[3] The stability of the divalent oxidation state of the lanthanide metals roughly correlates with their third ionization potentials, thus allowing one to predict that the next stable divalent ions should be those of thulium, dysprosium, and neodymium.[1] In 1997 the first divalent thulium complex, $[TmI_2(dme)_3]$, was synthesized by reduction of thulium(III) iodide with thulium metal in 1,2-dimethoxyethane (DME).[4] Subsequently, the solvated neodymium and dysprosium diiodides were prepared by reacting the corresponding metal powders with iodine followed by treatment with DME or THF.[5] The diiodides $[TmI_2(dme)_3]$[4] and $[DyI_2(dme)_3]$[6] are the first and only examples of crystallographically characterized molecular complexes of divalent thulium and dysprosium.

Preliminary studies showed that thulium diiodide and dysprosium diiodide are far more powerful reducing agents than $[SmI_2(thf)_x]$.[6, 7] The standard potentials E° (M^{3+}/M^{2+}) in aqueous solution could be estimated only for samarium (-1.55 V), ytterbium (-1.15 V), and europium (-0.35 V)[8] and agree quite well with those calculated by indirect methods.[9] The standard potentials E° (M^{3+}/M^{2+}) of thulium (-2.3 V), dysprosium (-2.5 V), and neodymium (-2.7 V) were deduced from both thermodynamic and spectroscopic data.[9] The reduction potentials of Ln^{2+} ions are essentially dependent on the kind of ligand and their arrangement, on the solvents used, and on the reactants or additives present in solution. Thus, the reduction potential of -1.33 V for SmI_2 determined versus an $Ag/AgNO_3$ electrode in THF increases to -2.2 V by using cosolvents and/or additives containing basic oxygen or nitrogen.[10] Apart from Tm^{II}, Nd^{II}, and Dy^{II} molecular species, decamethylsamarocene $[(C_5Me_5)_2Sm]$ has been suggested to be the strongest reducing lanthanide(II) reagent known to date.[11] Its high reactivity arises not only from its strong reduction potential, but also from the sterically unsaturated bent metallocene geometry. To obtain information about the effective reducing power of decamethylsamarocene, Evans et al. examined the reactions of $[(C_5Me_5)_2Sm]$ with a series of polycyclic aromatic compounds in toluene.[12] We decided also to use this chemical approach to define the effective reducing power of thulium diiodide.

Results

We started the evaluation of the reducing power of TmI_2 by addition of the most simple six-membered cyclic compounds benzene and naphthalene to the reducing agent in THF or

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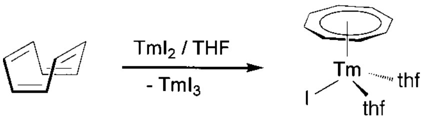
DME. Besides the fact that the addition of increasing amounts of benzene to such THF solutions causes precipitation of [$TmI_2(thf)_x$], no chemical reaction was observed. In contrast to [$(C_5Me_5)_2Sm$], thulium diiodide also proves to be inert towards anthracene, pyrene, and coronene as well as towards stilbene. Since the reduction potentials of these hydrocarbons range from -2.22 V for naphthalene to -1.98 V[13] for anthracene, the effective reduction potential of thulium diiodide in THF must be more positive than -1.98 V. To come to a realistic value, we further examined its reactions with cyclooctatetraene, acenaphthylene, lithium anthracenide, 2,2′-bipyridine, and diphenylacetylene. Whereas the reactions with the three first mentioned reactants afford clear results, the reactions with 2,2′-bipyridine and diphenylacetylene in THF or DME produce complex mixtures of brown-green or purple products from which we could not isolate individual compounds.

Reaction of thulium diiodide with cyclooctatetraene (C_8H_8): The treatment of TmI_2 with equimolar amounts of cyclooctatetraene ($E_{1/2} = -1.83$ V)[13] in THF at room temperature caused a rapid change in the color of the reaction mixture from emerald green to red-orange. Concentration of the filtered THF solution afforded (cyclooctatetraenyl)thulium(III) iodide (**1**) as red crystals in a 75% yield. The formation of the respective amount of [$TmI_3(thf)_3$] could be established [Eq. (1)].

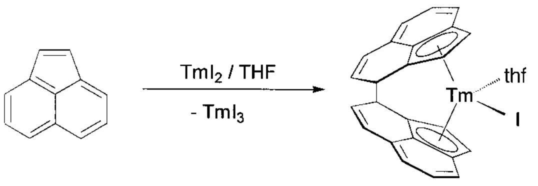


1

(1)

Reaction of thulium diiodide with acenaphthylene ($C_{12}H_8$): Recently we reported on the synthesis of the *rac*-ansa-metalloacenes [$(\eta^5\text{-}C_{12}H_8)_2M(thf)_2$] (M = Yb, Sm,[14a] Ca[14b]) by reductive coupling of acenaphthylene (acene) with activated metallic ytterbium, samarium, or calcium in THF. Whereas the acenyl radical anions formed in the course of these reduction processes undergo coupling to give ansa-biacenyl dianions which stereoselectively coordinate the M^{II} cations, the reduction of acenaphthylene by alkali metals produces adducts of radical anionic acenyl species with the alkali metal cations.[15]

When a solution of acenaphthylene ($E_{1/2} = -1.65$ V)[13] in THF was added to a suspension of equimolar amounts of TmI_2 in THF, the color of the reaction mixture instantly turned deep purple, but changed just as quickly to light orange-brown. Appropriate workup of the mixture allowed the isolation of ansa-[$(\eta^5\text{-}C_{12}H_8)_2TmI(thf)$] (**2**) as orange crystals in yields of 82% [Eq. (2)]. One can suppose that the intense purple color appearing intermediately reflects the initial formation of the radical anionic adduct [$C_{12}H_8TmI_2$] which quickly disproportinates to the final complex **2** and TmI_3.



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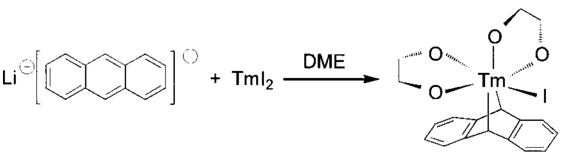
(2)

Reaction of TmI_2 with lithium anthracenide ($LiC_{14}H_{10}$): Looking for suitable methods and reactants for the synthesis of organothulium(II) complexes, we recently investigated the metathetical reactions of thulium diiodide with differently substituted alkali metal cyclopentadienides. However, it turned out that neither the electron-rich C_5Me_5 ligand nor the donor-functionalized or bulky cyclopentadienyl ligands $C_5H_4CH_2CH_2NMe_2$ or 1,3-$(Me_3Si)_2C_5H_3$ provide sufficient stability for thulium(II) cyclopentadienides in coordinating solvents.[16] Likewise, the reaction of TmI_2 with the twofold molar amount of lithium naphthalenide in DME produced the thulium(III) triple-decker complex [$(\eta^2\text{-}C_{10}H_8)_2Tm(\mu_2\text{-}\eta^4{:}\eta^4\text{-}C_{10}H_8)$][3e] instead of a thulium(II) complex. On the other hand, the reactions of europium and ytterbium diiodide with equimolar amounts of lithium naphthalenide in DME afford the europium(II) and ytterbium(II) binuclear complexes [$(\mu_2\text{-}\eta^4{:}\eta^4\text{-}C_{10}H_8)\{LnI(dme)_2\}_2$] (Ln = Eu, Yb)[17] containing naphthalene dianion bridges. The same reaction with thulium diiodide in THF resulted in the formation of a complex mixture of products, the components of which could not be separated.

In the experiment reported here, a freshly prepared solution of lithium anthracenide $C_{14}H_{10}Li$ in THF was added to a suspension of TmI_2 (1:1 molar ratio) in DME. The reaction mixture immediately turned dark red brown. After the filtered and concentrated solution had been stored for one to two days at ambient temperature, red crystals of [$(\eta^2\text{-}C_{14}H_{10})TmI(dme)_2$] (**3**) separated in yields of about 80% [Eq. (3)].



3

(3)

Molecular structures

The crystal and structure refinement data of **1**, **2**, and **3** are listed in Table 1. Crystals suitable for X-ray structure analysis of **1** and **2** were obtained from THF solutions. Because the poor solubility of **3** in DME as well as in THF prevented its recrystallization, the crystals crystallizing directly from the DME reaction solution were used for X-ray diffraction analysis.

[$(\eta^8\text{-}C_8H_8)TmI(thf)_2$] (**1**) crystallizes in the triclinic space group $P\bar{1}$ with four molecules in the unit cell. Only one of the two crystallographically independent molecules which show similar geometric parameters is depicted in Figure 1. The

Table 1. Crystal data and structure refinement for **1**–**3**.

Compound	**1**	**2**	**3**
empirical formula	$C_{16}H_{24}IO_2Tm$	$C_{28}H_{24}IOTm$	$C_{22}H_{30}IO_4Tm$
formula weight	544.18	672.30	654.29
crystal system	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P2_12_12_1$ (no. 19)
unit cell dimensions			
a [Å]	8.4091(1)	21.8563(4)	8.3545(1)
b [Å]	9.5889(1)	13.6689(3)	16.4491(3)
c [Å]	21.6643(4)	15.6112(3)	16.6372(2)
α [°]	86.703(1)	–	–
β [°]	83.989(1)	107.678(1)	
γ [°]	89.336(1)	–	–
V [Å^3]	1734.37(4)	4443.63(15)	2286.35(6)
Z	4	8	4
ρ_{calcd} [g cm^{-3}]	2.084	2.010	1.901
$\mu(Mo_{K\alpha})$ [mm^{-1}]	6.894	5.401	5.254
$F(000)$	1032	2576	1264
crystal size [mm^3]	0.20 × 0.30 × 0.26	0.68 × 0.20 × 0.32	0.74 × 0.36 × 0.10
θ min. θ max [°]	0.95, 27.50.	1.78, 27.50.	2.45, 27.50
index ranges	$-10 \leq h \leq 10$ $-12 \leq k \leq 12$ $-17 \leq l \leq 28$	$-26 \leq h \leq 28$ $-17 \leq k \leq 17$ $-20 \leq l \leq 19$	$-10 \leq h \leq 10$ $-21 \leq k \leq 19$ $-21 \leq l \leq 20$
reflections collected	13177	33050	17524
independent reflections	7860	10189	5225
R(int)	0.0736	0.0434	0.0456
reflections with $I > 2\sigma(I)$	4727	8565	4705
max./min. transmission	0.3867/0.1965	0.4682/0.2334	0.6828/0.1792
goodness-of-fit on F^2	1.010	1.067	1.025
final R indices [$I > 2\sigma(I)$]			
R_1	0.0677	0.0296	0.0295
wR_2	0.1186	0.0630	0.0625
R indices (all data)			
R_1	0.1249	0.0420	0.0364
wR_2	0.1351	0.0674	0.0653
largest diff. peak and hole [e Å^{-3})	4.285 and −1.785	0.782 and −1.813	1.557 and −1.261

molecules adopt a monomeric three-legged piano stool geometry with a capping $C_8H_8^{2-}$ dianion. In contrast to the crystallographically characterized iodo(cyclooctatetraenyl) complexes of the earlier lanthanides [(η^8-C_8H_8)LnI(thf)$_3$][18] (Ln = Sm, Ce), the thulium atom in **1** is coordinated by only two THF molecules, which is consistent with the smaller ionic radius of thulium(III). The Tm–C(C_8H_8) distances range between 2.51 and 2.58 Å. The Tm–I bond length (3.03 Å) is shorter than that in [TmI_2(dme)$_3$][4] (3.14, 3.18 Å), but is consistent with the Tm–I distances in other Tm^{III} iodides.[2c]

[(η^5-$C_{12}H_8$)$_2$TmI(thf)] (**2**) crystallizes in the monoclinic space group $P2_1/c$ with eight molecules in the unit cell. One of the two crystallographically independent molecules which show very similar molecular parameters (occasionally an enantiomeric pair) is depicted in Figure 2. Because of the two different possibilities for the orientation of the two acenyl ring units of the ligand, *meso*- and/or C_2-symmetric *rac*-ansa complexes could be expected. The molecular structure proves that the coupling of the two acenyl radicals occurs selectively with formation of the *rac*-ansa complex. The thulium atom is coordinated by the two cyclopentadienyl units of the dianionic ansa-biacenyl ligand, an iodine atom, and one THF molecule. The iodine atom and the THF ligand slightly deviate from the equatorial wedge of the ansa-ligand framework. With respect to the differences in ionic radii of Yb^{II} and Tm^{III} the

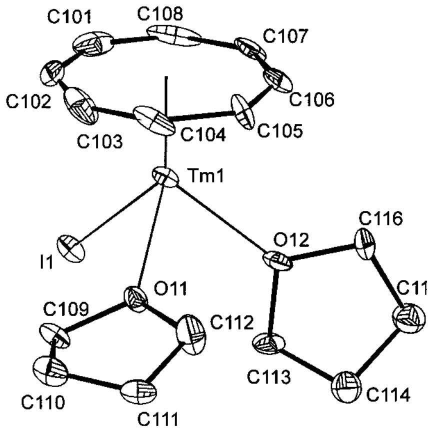


Figure 1. Molecular structure of **1** (ORTEP drawing; thermal ellipsoids drawn at the 30% probability level). Only one of the two crystallographically independent molecules is shown. Hydrogen atoms are omitted. Relevant bond lengths [Å] and angles [°] (Cg was defined by the ring atoms C101–C108): Tm1–Cg 1.750(5), Tm1–I1 3.0338(11), Tm1–O11 2.342(8), Tm1–O12 2.382(9), Tm1–C101 2.525(15), Tm1–C102 2.551(14), Tm1–C103 2.507(18), Tm1–C104 2.577(14), Tm1–C105 2.576(14), Tm1–C106 2.544(13), Tm1–C107 2.541(13), Tm1–C108 2.523(15); Cg1-Tm1-I1 131.06(19), Cg1-Tm1-O11 126.8(3), Cg1-Tm1-O12 129.2(3), I1-Tm1-O11 86.5(2), I1-Tm1-O12 87.1(2).

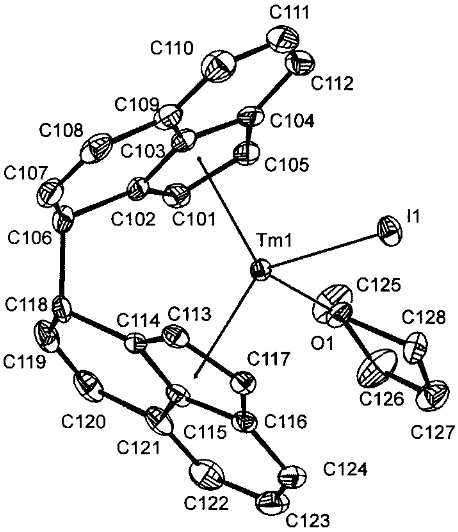


Figure 2. Molecular structure of **2** (ORTEP drawing; thermal ellipsoids drawn at the 50% probability level). Only one of the two crystallographically independent molecules is shown. Hydrogen atoms are omitted. Relevant bond lengths [Å] and angles [°] (Cg1 and Cg2 were defined by the ring atoms C101–C105 and C113–C117): Tm1–Cg1 2.3375(19), Tm1–Cg2 2.3340(15), Tm1–I1 2.9227(3), Tm1–O1 2.301(3), Tm1–C101 2.588(4), Tm1–C102 2.600(4), Tm1–C103 2.641(4), Tm1–C104 2.700(4), Tm1–C105 2.629(4), Tm1–C113 2.594(4), Tm1–C114 2.587(4), Tm1–C115 2.629(4), Tm1–C116 2.697(4), Tm1–C117 2.637(4); Cg1-Tm1-Cg2 123.33(6), Cg1-Tm1-I1 110.67(5), Cg1-Tm1-O1 108.30(9), Cg2-Tm1-I1 110.43(4), Cg2-Tm1-O1 106.65(8), I1-Tm1-O1 93.07(7); ring-slippage [Å]: Cg1 0.111, Cg2 0.113.

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average distance Tm–C(C1–C5, C13–C17) (2.62 Å) is shorter than that in *rac*-ansa-$[(\eta^5\text{-}C_{12}H_8)_2Yb(thf)_2]$ (2.72 Å).[14a] The Cp-Tm-Cp angle (122.4°) is considerably smaller than that in the nonbridged cyclopentadienyl complexes $[Cp_2LnX(thf)]$[2c] (130 to 135°) and in the less constrained five-atom-bridged bis(indenyl)lanthanocenes $[\{O(CH_2CH_2C_9H_6)_2\}LnCl(thf)]$[19] (Ln = Nd, 131.4°; Gd, 132.6°; Ho, 132.6°), but is similar to that in the two-atom-bridged ethylenbis(indenyl) complex *meso*-$[\{(C_9H_6)_2(CH_2)_2\}YbN(SiMe_3)_2]$[20] (122.0°) and in *rac*-ansa-$[(C_{12}H_8)_2Yb(thf)_2]$ (119.2°).[14a] The Tm–I bond lengths (2.92 Å) and Tm–O(thf) (2.30 Å) are somewhat shorter than those in **1** (Tm–I, 3.03 Å; Tm–O(thf), 2.36 Å).

$[(\eta^2\text{-}C_{14}H_{10})TmI(dme)_2]$ (**3**) crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell. The molecular structure of **3** shows the thulium atom coordinated in a tetragonal-bipyramidal fashion with the η^2-bonding $C_{14}H_{10}$ unit and one oxygen atom (O3) of one of the two DME molecules in axial positions and with the iodine atom and the remaining three DME oxygen atoms in equatorial positions (Figure 3). The formal coordination number of the thulium atom is nine. This coordination environment is similar to that in $[(\mu_2\text{-}\eta^4{:}\eta^4\text{-}C_{10}H_8)\{EuI(dme)_2\}_2]$[17a] and $[(\eta^2\text{-}C_{10}H_8)DyI(dme)_2]$.[6] The anthracene ligand is no longer planar. The carbon atoms C1 and C8 exhibit the characteristics of sp^3-hybridization and also the rings formed with the carbons C2–C7 and C9–C14 deviate substantially from planarity. The angle between the average planes of C1-C2-C7-C8 and C1-C14-C9-C8 is 37.8(2)°. The distances of the metal to the bonding anthracene carbon atoms (Tm–C1 2.48 Å; Tm–C8 2.47 Å) are comparable with those in $[(\eta^5\text{-}C_5H_5)Lu(\eta^2\text{-}C_{14}H_{10})(thf)_2]$[21] (2.44 and 2.45 Å) and $[(\eta^2\text{-}C_{10}H_8)DyI(dme)_2]$[6] (2.51 and 2.49 Å) with regard to the differences in ionic radii.[22] The Tm–I bond length (3.03 Å) is similar to that in **1** (3.03 Å). The distance from the thulium atom to the axially positioned DME oxygen atom (Tm–O3 2.57 Å) is significantly longer than the distances to the DME oxygen atoms lying in the equatorial plane (Tm–O1 2.34, Tm–O2 2.36, Tm–O4 2.37 Å). The structural parameters of **3** can also be compared with those of the anthracenyl lanthanide complexes $[(\eta^2\text{-}C_{10}H_8)_2Tm(\mu_2\text{-}\eta^4{:}\eta^4\text{-}C_{10}H_8)]$,[3e] $[(\eta^5\text{-}C_5H_5)Lu(\eta^2\text{-}C_{10}H_8)(dme)]$,[23] and $[(\eta^5\text{-}C_5H_5)_2Lu(\eta^2\text{-}C_{10}H_8)\{Na(diglyme)_2\}]$.[24]

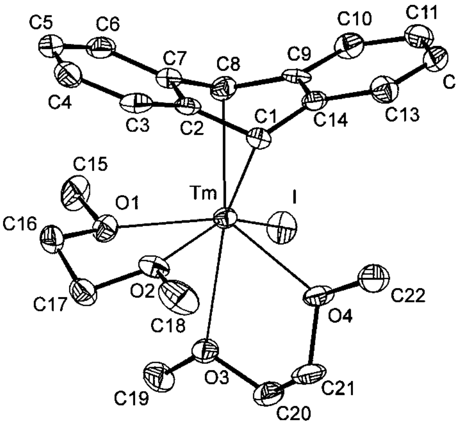

Figure 3. Molecular structure of **3** (ORTEP drawing; thermal ellipsoids drawn at the 50% probability level). Hydrogen atoms are omitted. Relevant bond lengths [Å] and angles [°]: Tm–I 3.0334(3), Tm–O1 2.343(3), Tm–O2 2.359(3), Tm–O3 2.569(4), Tm–O4 2.372(4), Tm–C1 2.479(5), Tm–C2 2.816(5), Tm–C7 2.833(5), Tm–C8 2.471(6), Tm–C9 2.966(5), Tm–C14 2.988(5), C1–C2 1.463(7), C1–C2 1.471(7), C2–C3 1.384(7), C2–C7 1.440(7), C3–C4 1.393(8), C4–C5 1.393(9), C5–C6 1.390(8), C6–C7 1.399(7), C7–C8 1.473(8), C8–C9 1.461(8), C9–C10 1.382(7), C9–C14 1.442(7), C10–C11 1.397(8), C11–C12 1.394(8), C12–C13 1.379(8), C13–C14 1.409(7); O1-Tm-O3 73.13(14), O2-Tm-O4 88.81(14), O2-Tm-O3 74.03(13), O1-Tm-C8 90.33(18), O2-Tm-C1 79.61(14), O4-Tm-C1 87.42(14), C8-Tm-O3 150.76(16), C1-Tm-O3 142.59(15), O1-Tm-I 94.19(7), O2-Tm-I 149.10(9), O3-Tm-I 76.61(10), O4-Tm-I 88.11(9), C1-Tm-I 130.91(11), C8-Tm-I 80.87(14).

Discussion

As shown in Table 2 thulium diiodide reacts in THF only with unsaturated cyclic hydrocarbons that have a reduction potential more positive than −2.0 V, a fact which is not at all consistent with the reduction potential of −2.3 V[9] derived for thulium(II) from spectroscopic data. Based on the assumption that $[TmI_2(thf)_x]$ will be used as a reductive agent in organic synthesis, we believe that its reduction potential must be considered to be very near to −2.0 V. A comparison of the reactivity of $[(C_5Me_5)_2Sm]$, TmI_2, and SmI_2 towards cyclic aromatic hydrocarbons indicates that, under the cited conditions, the reducing power of thulium diiodide is evidently higher than that of samarium diiodide, but lower than that of $[(C_5Me_5)_2Sm]$. In the case of the reactions of $[(C_5Me_5)_2Sm]$

Table 2. Comparison of the reducing power of $[(C_5Me_5)_2Sm]$,[a] TmI_2,[b] and SmI_2 determined from their reactivity with cyclic aromatic hydrocarbons.

Hydrocarbon	$E_{1/2}$[c]	$E_{1/2}'$[c]	Reaction observed and product isolated		
			$[(C_5Me)_2Sm]$	TmI_2	SmI_2
naphthalene	2.6		no	no	–
stilbene	2.22		$[Cp^*Sm]_2(\mu\text{-}\eta^2\text{-}\eta^4\text{-}CH_2CHPh)$	no	–
pyrene	2.10		$[Cp^*Sm]_2(\mu\text{-}\eta^2\text{-}\eta^3\text{-}C_{16}C_{10})$	no	–
coronene	2.05	2.44	no[d]	no	–
2,2′-bipyridine	2.0[e]	–	$[Cp^*Sm(N_2C_{10}H_8)]$[26]	yes[b,f]	yes[b,f]
anthracene	1.98	2.44	$[Cp^*Sm]_2(\mu\text{-}\eta^2\text{-}\eta^3\text{-}C_{14}C_{10})$	no	no[b]
cyclooctatetraene	1.83	1.99	$[Cp^*_2Sm]$ and $[CpSm(C_8H_8)]$	**1**	$[(C_8H_8)SmI(thf)_3]$
acenaphthylene	1.65	1.89	yes[f]	**2**	no[b]
diphenylacetylene	–	–	–	yes[b,f]	no
C_{60}	0.44[g]	0.82[g]		no[d]	–

[a] In toluene.[14] [b] In THF; this work. [c] In Volts relative to the saturated calomel electrode. $E_{1/2}$ and $E_{1/2}'$ describe the first and second reduction potentials of the hydrocarbons, respectively.[19] [d] The low solubility of the substrate may inhibit the reaction.[14] [e] Taken from ref.[27] [f] No individual product was isolated. [g] In CH_2Cl_2.[25]

with aromatic hydrocarbons, the formation of planar hydrocarbon dianions of the dimensions of anthracene or even larger suggests that not only the reduction potential will play an important role, but also the possibility for the respective substrate to have access to the coordination sphere of the metal. Two other important differences between the reductants [$(C_5Me_5)_2Sm$] and TmI_2 must be emphasized: 1) the insolubility of TmI_2 in nonpolar solvents such as toluene or hexane inhibits the performance of reactions in such non-coordinating media, and 2) thulium diiodide exists in THF as a monomer solvated by up to five coordinating THF molecules. Therefore two different electron-transfer processes from the metal to the respective cyclic hydrocarbon substrate will take place, an inner-sphere transfer in the case of [$(C_5Me_5)_2Sm$] and an outer-sphere transfer in the case of [$TmI_2(L)_x$] (L = THF, DME) differing in rate and energy balance. In the case of SmI_2, Skrydstrup and co-workers found out that the electron transfer from SmI_2 to benzophenone in THF is an inner-sphere process, while the electron transfer to benzyl bromide is much closer to an outer-sphere process.[10b] Since cyclic hydrocarbons normally are weak Lewis bases they will not be able to displace the THF ligands bound to the highly oxophilic thulium(II) atom in TmI_2, the reactions of thulium diiodide with cyclooctatetraene or acenaphthylene in THF are suggested to proceed by an outer-sphere electron transfer process.

The reaction of TmI_2 with acenaphtylene suggests that substrates, which after reduction to radical anions by metal-based reductants can strongly coordinate to the metal, will undergo coupling with carbon–carbon bond formation. This supposition is consistent with the reported pinacol coupling reactions promoted by SmI_2 and lanthanoid(II) organometallic reagents.[27]

Experimental Section

All manipulations were done in vacuum. Elemental analyses were obtained on a Perkin-Elmer Series II CHNS/O 2400 Analyzer. Although a special Schlenk tube and small aluminum cans for weighing the samples were used, only reasonably satisfactory C,H analyses could be obtained for the extremely moisture- and air-sensitive complexes. The sublimation of acenaphthylene (75%, Aldrich) at 80/10^{-1} Torr increased the purity to 85% (10 to 15% of acenaphthene as impurity). The given quantity of acenaphthylene was calculated based on pure acenaphthylene. The yields of the compounds **1**–**3** were calculated by assuming that the formation of thulium diiodide from excess thulium metal and iodine according to the procedure given below was quantitative with respect to the amount of iodine used. IR spectra were obtained on a Specord-M80 apparatus.

Synthesis of [$TmI_2(thf)_x$]: A mixture of thulium powder (5.0 g, 29.65 mg-atom) and iodine (1.0 g, 3.94 mmol) in THF (10 mL) was stirred at room temperature until the iodine color had disappeared completely and white powdery thulium triiodide precipitated. Then the mixture was sonicated at 50 °C for 2 h. During sonication the emerald-green microcrystalline powder of [$TmI_2(thf)_x$] precipitated. The precipitate was separated from unreacted metal by extraction with warm THF (240 mL), and the solution of [$TmI_2(thf)_x$] was used for the reactions described below. The unreacted thulium metal can be re-used for the synthesis of thulium diiodide.

[$(\eta^8\text{-}C_8H_8)TmI(thf)_2$] (1): A solution of cyclooctatetraene (0.41 g, 4.03 mmol) in THF (5 mL) was added with stirring to a suspension of thulium diiodide (obtained from 1.0 g, 3.94 mmol of iodine and excess Tm metal) in THF (40 mL). The mixture quickly turned red. After a few minutes the solution was filtered off and concentrated to a volume of 5–7 mL by evaporation of the solvent in vacuum. Red crystals of **1** (0.79 g, 74%) crystallized from the remaining solution and were isolated by decantation. M.p. >255 °C (decomp); elemental analysis calcd (%) for $C_{16}H_{24}IO_2Tm$ (544.2): C 35.31, H 4.45, I 23.32, Tm 31.04; found: C 34.67, H 4.15, I 24.34, Tm 31.11; IR (Nujol): $\tilde{\nu}$ = 1870 w, 1750 w, 1615 w, 1340 m, 1310 w, 1245 w, 1190 m, 1020 vs, 905 s, 865 vs, 780 w, 750 s, 710 vs, 670 s cm^{-1}.

[$(\eta^5\text{-}C_{12}H_8)_2TmI(thf)$] (2): A solution of acenaphthylene (0.62 g, 4.07 mmol) in THF (10 mL) was added with stirring to a suspension of thulium diiodide (obtained from iodine (1.05 g, 4.13 mmol) and excess Tm metal in THF (40 mL). The mixture turned immediately deep purple, but changed color rapidly to light orange-brown. The mixture was concentrated to 30 mL by evaporation of the solvent in vacuum and then filtered off. The solution was concentrated again (ca. 10 mL) and stored at room temperature overnight. Decantation of the solvent left blocklike orange crystals of **2** (1.14 g, 82%). M.p. >160 °C (decomp); elemental analysis calcd (%) for $C_{28}H_{24}IOTm$ (672.3): C 50.02, H 3.60, Tm 25.13; found: C 49.12, H 4.05, Tm 25.37; IR (Nujol): $\tilde{\nu}$ = 1300 w, 1190 m, 1165 m, 1165 m, 1020 s, 855 s, 845 s, 800 vs, 770 s, 750 s cm^{-1}.

[$(\eta^2\text{-}C_{14}H_{10})TmI(dme)_2$] (3): A solution of lithium anthracenide in DME (obtained in situ from lithium (0.031 g, 4.46 mg-atom) and anthracene (0.81 g, 4.54 mmol) in DME (20 mL) was added to a suspension of thulium diiodide (obtained from iodine (1.04 g, 4.09 mmol) in DME (40 mL)) with shaking within a few minutes. The solution was filtered, concentrated to 25 mL and then stored at room temperature. Within 34 h red crystals of **3** separated (2.1 g; 78%). M.p. >90 °C (decomp); elemental analysis calcd (%) for $C_{22}H_{30}IO_4Tm$ (654.3): Tm 25.82; found: Tm 26.74; IR (Nujol): $\tilde{\nu}$ = 1575 w, 1430 s, 1385 m, 1335 m, 1230 vs, 1095 s, 1045 vs, 855 s, 815 s, 875 w, 750 m, 720 s cm^{-1}; $\mu_{eff} = 6.5\,\mu_B$.

Single-crystal X-ray structure determinations of 1–3: The crystal data and the details of the data collection are given in Table 1. The data were collected on a Siemens SMART CCD diffractometer (graphite-monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) with area-detector by using ω scans at 173 K. The structures were solved by direct methods by using the SHELXS-97 program[28] and were refined on F^2 using all reflections with the SHELXL-97 program.[29] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å^2. The calculation of the absolute structure parameter × (according to Flack[30]) for **3** indicated a racemic twinning for the selected crystal. The value of × was refined to 0.517(12); therefore, the ratio of the two enantiomorphs is approximately 52:48. SADABS[31] was used to perform area-detector scaling and absorption corrections. The geometrical aspects of the structures were analyzed by using the PLATON program.[32] 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-159474 (**1**), CCDC-159475 (**2**), CCDC-159476 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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