Synthesis and Reactivity of Organometallic Complexes of Divalent Thulium with Cyclopentadienyl and Phospholyl Ligands

Florian Jaroschik, François Nief,* Xavier-Frédéric Le Goff, and Louis Ricard

Laboratoire Hétéroéléments et Coordination, CNRS, Ecole Polytechnique, Route de Saclay, 91128 Palaiseau, France

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Reaction of sodium 1,2,4-tris(trimethylsilyl)cyclopentadienide [Na(Cp‴)] with [$TmI_2(THF)_3$] afforded the divalent thulium complex [$(Cp‴)_2Tm(THF)$]. Its crystal structure is similar to that of the previously described [$(Cp^{ttt})_2Tm(THF)$] (Cp^{ttt} = 1,2,4-tris(*tert*-butyl)cyclopentadienyl). [$(Cp‴)_2TmI$] was prepared by reaction of TmI_3 with [K(Cp‴)] and could be reduced by KC_8 into a new unsolvated, homoleptic complex, [$(Cp‴)_2Tm$], which was characterized by NMR. [$(Cp‴)_2Tm$] gave [$(Cp‴)_2Tm(THF)$] by interaction with THF. A convenient alternative pathway to [$(Cp^{ttt})_2Tm$] by reduction of [$(Cp^{ttt})_2Tm(BH_4)$] with KC_8 was found: [$(Cp^{ttt})_2Tm(BH_4)$] derives from [$Tm(BH_4)_3(THF)_3$], which can be prepared from the less expensive $TmCl_3$. On the other hand, the dimer [$\{(Cp^{tt})_2TmI\}_2$] (Cp^{tt} = 1,3-bis(*tert*-butyl)-cyclopentadienyl), obtained by reaction of TmI_3 with [$Na(Cp^{tt})$], gave only intractable results by reaction with KC_8. The previously described Tm^{II} complex [$(Dtp)_2Tm$] (Dtp = 2,5-di-*tert*-butyl-3,4-dimethylphospholyl) and the new, homoleptic, structurally characterized Tm^{II} dimer [$\{(Htp)_2Tm\}_2$] (Htp = 2,5-di-*tert*-butylphospholyl) were prepared by KC_8 reduction of [$(Dtp)_2TmI$] and [$\{(Htp)_2TmI\}_2$], respectively. Reaction of [$(Cp^{ttt})_2Tm$] with pyridine resulted in an immediate reduction of pyridine into 1,1′-bis(1,4-dihydropyridylamide) and the formation of the structurally characterized [$\{(Cp^{ttt})_2Tm\}_2\{\mu$-$(NC_5H_5$-$C_5H_5N)\}$], while the reaction of [$(Dtp)_2Tm$] with pyridine gave no isolable complexes. An NMR study suggests that initially a simple Tm^{II} adduct such as [$(Dtp)_2Tm$(pyridine)] is formed in this reaction.

Introduction

Although organothulium(II) complexes can no longer be considered as rarities, the organometallic chemistry of thulium(II) is still in its beginning, as the vast majority of organolanthanide(II) complexes include Sm, Eu, and Yb as metals.[1] This is in part because, until a practical route to the diiodide TmI_2 using solution chemistry was found recently,[2] this useful precursor was available only by high-temperature, solid-state techniques.[3] Also, solvated complexes such as $L_2Ln(Solv)_n$ (L = ligand, Solv = donor solvent), which are so common with Ln = Sm, Eu, and Yb, are not always stable with Ln = Tm: for instance, although [$(Cp^*)_2Tm(DME)_x$] (Cp^* = 1,2,3,4,5-pentamethylcyclopentadienyl, DME = 1,2-dimethoxyethane) may have been observed transiently, it was not isolated.[4] Most likely, the compound decomposed by electron transfer from the highly reducing thulium(II) to the coordinated solvent.[5]

We recently showed that it was not necessary to use TmI_2 as the source of divalent thulium for the synthesis of organothulium(II) complexes: the unsolvated Tm^{II} complex [$(Cp^{ttt})_2Tm$][6] (**1**) [Cp^{ttt} = 1,2,4-$(tBu)_3C_5H_2$] could as well be made by chemical reduction of the Tm^{III} precursor [$(Cp^{ttt})_2TmI$] with KC_8. However, an early attempt to synthesize [$(Cp^R)_2Tm$] [Cp^R = 1,3-$(tBuMe_2Si)_2C_5H_3$] by potassium reduction of [$\{(Cp^R)_2TmI\}_2$] was reported to be unsuccessful.[7]

So, it appears that there are now two distinct methods for the synthesis of organothulium(II) complexes—the simple metathesis technique using TmI_2 as divalent precursor and the reductive pathway as described above—and that the obtaining of stable complexes may depend both on the substitution pattern around Tm and on the choice of the synthetic method.

Therefore, in order to get a better understanding of the factors that govern the stability and reactivity of organothulium(II) complexes, we have undertaken the synthesis of new homoleptic and heteroleptic cyclopentadienyl and phospholyl complexes of Tm^{II}. We also report on the reaction of some of them with pyridine.

Results and Discussion

Cyclopentadienyl Complexes. The stability of most cyclopentadienyl complexes of Tm^{II} prepared so far appears rather limited: [$(Cp^*)_2Tm(THF)_x$] could not be isolated,[5] and, although both [$(Cp″)_2Tm(THF)$] [$Cp″$ = 1,3-$(Me_3Si)_2C_5H_3$][8] and [$(Cp^{tt})_2Tm(THF)$] [Cp^{tt} = 1,3-$(tBu)_2C_5H_3$][9] can be structurally characterized, they quickly decompose in THF solution at room temperature. However, switching from Cp^{tt} to Cp^{ttt} by adding a third tBu group on the ring allowed for the syntheses

* Corresponding author. E-mail: francois.nief@polytechnique.edu.

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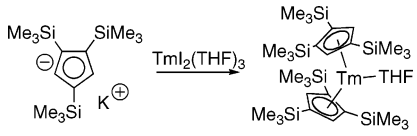
Scheme 1



of $[(Cp^{ttt})_2Tm]$ (**1**) and $[(Cp^{ttt})_2Tm(THF)]$ (**2**), which were both stable at room temperature.[6] Therefore, it seemed likely that a complex of Tm^{II} with the more bulky Cp‴ ligand [Cp‴ = 1,2,4-$(Me_3Si)_3C_5H_2$] would also be more stable than with the Cp″ ligand. Indeed, when [Na(Cp‴)] was reacted with $TmI_2(THF)_3$, a purple solution, stable at room temperature, was obtained, from which crystals were obtained after treatment. Like with other Tm^{II} complexes, we observed in the paramagnetically shifted NMR spectrum of the isolated product three peaks corresponding to two equivalent Me_3Si groups, one distinct Me_3Si group, and the two ring CH's. However, since we could not ascertain from the NMR spectrum whether THF was coordinated to Tm^{II} in the isolated product, we undertook an X-ray crystal analysis, which revealed that the product was in fact the solvated **3**: $[(Cp‴)_2Tm(THF)]$ (Scheme 1 and Figure 1). Note that $[(Cp^{ttt})_2Tm(THF)]$ lost the coordinated THF molecule during workup.[6]

One of the main structural features of **3** is the value of the Tm−O bond distance (Tm1−O11 = 2.457(2) Å). This value is slightly shorter than that previously found in **2** (2.473(2) Å),[6] but, on the whole, the steric bulk of the Cp‴ and that of Cp^{ttt} are quite similar; however, the THF is more tightly held in **3** than in **2**: it was not possible to remove it by pumping, or otherwise without decomposition. This might be due to an electronic effect since the silyl-substituted Cp‴ is less electron-donating than Cp^{ttt} and the Tm^{2+} ion is likely to be more Lewis acidic in **3** than in **2**.

We thus undertook the synthesis of a Tm^{II} complex with the Cp‴ ligand by the reductive pathway, which can be entirely conducted in noncoordinating solvents: reaction of [K(Cp‴)] with TmI_3 afforded $[(Cp‴)_2TmI]$ (**4**), which was characterized by elemental analysis and X-ray. **4** also displayed an NMR spectrum consisting of two peaks at 50 and 160 ppm that could be accurately integrated (in a 2:1 ratio); these peaks correspond to the $SiMe_3$ groups on the ring. This observation prompted us to reinvestigate the spectrum of $[(Cp^{ttt})_2TmI]$, which we previously reported as giving two peaks that were difficult to integrate. A much better spectrum of this compound could be obtained, in which three tBu peaks at −15, 90, and 350 ppm in a 1:1:1 ratio were present. Thus, it appears that the low-field signal at 350 ppm was missed in the previously reported spectrum.[6]

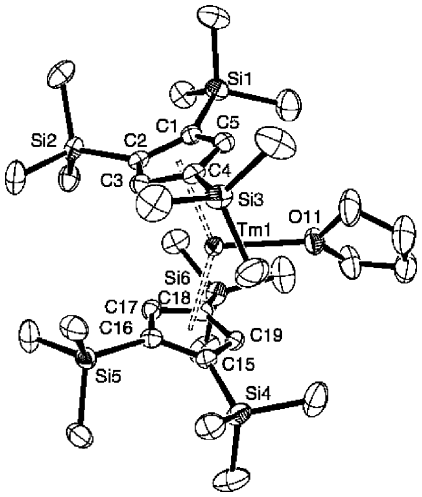
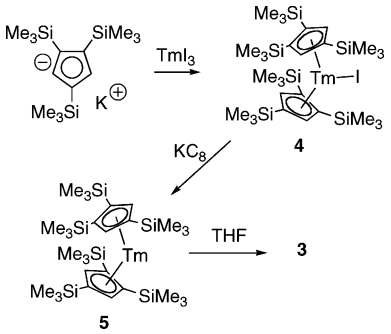


Figure 1. ORTEP plot (50% ellipsoids) of one molecule of $[(Cp‴)_2Tm(THF)]$ (**3**). Hydrogen atoms have been omitted for clarity.

Scheme 2



Reduction of **4** with KC_8 afforded a dark green complex, extremely soluble in *n*-pentane, that unfortunately could not be obtained crystalline. Nonetheless, we could establish its identity as the unsolvated homoleptic $[(Cp‴)_2Tm]$ (**5**) on the following bases: (a) its proton NMR spectrum displays the $SiMe_3$ and ring CH resonances at chemical shifts that are significantly different from that of **3**; (b) after addition of THF to **5**, the color of the solution changed to purple and a purple product was isolated, which was identified as **3** on the basis of its NMR spectrum (Scheme 2 and Figure 2).

A disadvantage of the reductive pathway is the use of the commercially available, but nonetheless very expensive TmI_3, so it appears that another Tm^{III} precursor would be desirable. Unfortunately, reaction of either [Na(Cp^{ttt})] or [K(Cp^{ttt})] with the less expensive $TmCl_3$ failed to give $[(Cp^{ttt})_2TmCl]$. This result can be related to very recent findings by Sitzmann et al., who also failed to obtain by the same route $[(Cp^{ttt})_2LnCl]$, where Ln is a small lanthanide such as Yb or Lu, similar in size to Tm.[10]

However, $TmCl_3$ could be easily transformed into $[Tm(BH_4)_3(THF)_3]$ by reaction with sodium borohydride,[11] and reaction of this thulium(III) borohydride with [K(Cp^{ttt})] gave $[(Cp^{ttt})_2Tm(BH_4)]$ (**6**), which was characterized by elemental

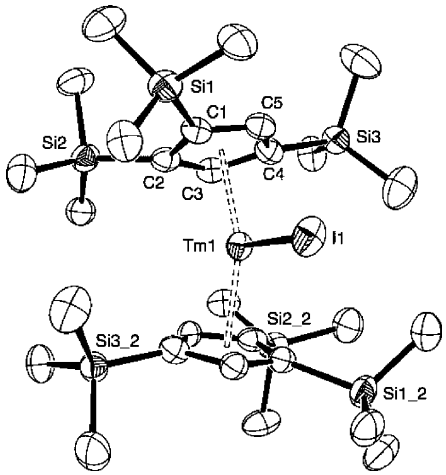
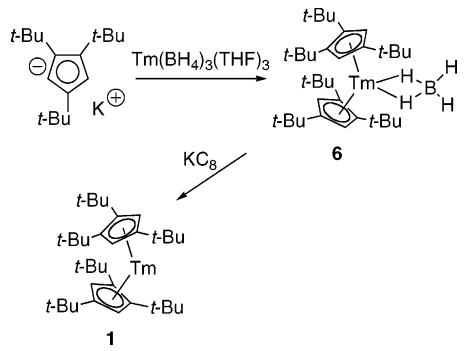


Figure 2. ORTEP plot (50% ellipsoids) of one molecule of $[(Cp‴)_2TmI]$ (**4**). Hydrogen atoms have been omitted for clarity. There are three independent molecules in the unit cell, one of which (represented in the figure) possesses a *C*2 axis along the Tm−I bond.

Scheme 3



analysis and X-ray. Its proton NMR spectrum displays three tBu peaks, at chemical shifts similar to those found in the revised spectrum of $[(Cp^{ttt})_2TmI]$.

Subsequent reduction of **6** with KC_8 proceeded as previously described for $[(Cp^{ttt})_2TmI]$ and also afforded **1**, which was characterized by NMR (Scheme 3 and Figure 3).

We think that this alternative synthesis of **1** is of interest because, since the commercially available $TmCl_3$ can be alternatively obtained from thulium oxide,[12] it can thus be shown that an access to Tm^{II} organometallic chemistry is possible by using Tm_2O_3 as precursor, which is the least expensive source of thulium.

Finally, in order to test the limits of this method, we attempted to synthesize a Tm^{II} complex with a lesser-substituted ligand (Cp^{tt}) by the reductive pathway. Reaction of $[Na(Cp^{tt})]$ with TmI_3 afforded a solid-state centrosymmetric dimer, $[\{(Cp^{tt})_2TmI\}_2]$ (**7**), which was characterized by elemental analysis and X-ray (Figure 4).

The proton NMR of **7** displayed only one peak at 214 ppm for the tBu groups.

The overall structure of **7** is similar to that of the already mentioned $[\{(Cp^R)_2TmI\}_2]$;[7] thus, removal of one tBu group on the cyclopentadienyl ring has diminished steric saturation to such an extent that, while the previously described $[(Cp^{ttt})_2TmI]$ is a solid-state monomer, **7** is now a dimer.

However, all attempts to reduce **7** with KC_8 led to intractable results. Thus, it might be that, even in the absence of polar solvents, $[(Cp^{tt})_2Tm]$ is not sufficiently stable at room temperature to be isolated.

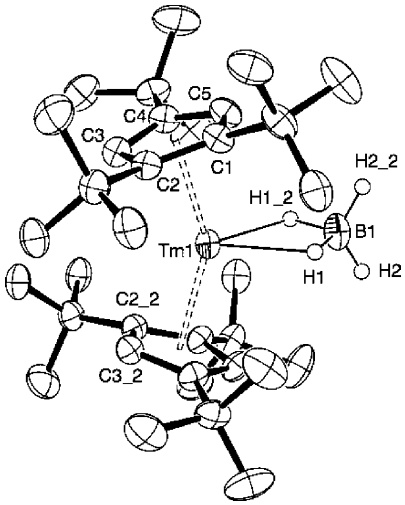


Figure 3. ORTEP plot (50% ellipsoids) of one molecule of $[(Cp^{ttt})_2Tm(BH_4)]$ (**6**). Hydrogen atoms (except those on the borohydride) have been omitted for clarity.

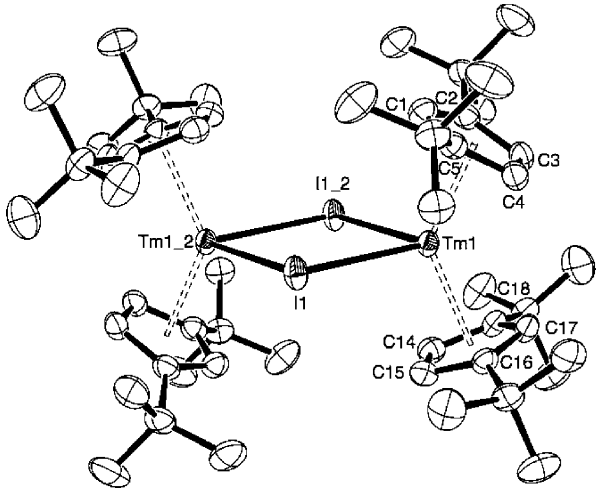
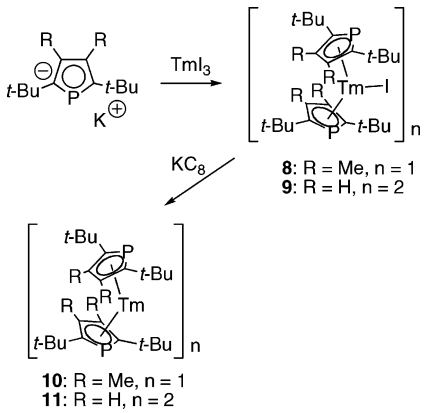


Figure 4. ORTEP plot (50% ellipsoids) of one molecule of $[\{(Cp^{tt})_2TmI\}_2]$ (**7**). Hydrogen atoms have been omitted for clarity.

Scheme 4



Phospholyl Complexes. Our purpose was to establish the feasibility of the synthesis of Tm^{II} phospholyl complexes by the reductive pathway. Like their cyclopentadienyl counterparts, phospholylthulium(III) complexes can be made by reaction of potassium phospholides with TmI_3. Thus, the reaction of $[K(Dtp)]$[13] (Dtp = 2,5-tBu_2-3,4-Me_2C_4P) or $[K(Htp)]$ (Htp = 2,5-tBu_2-H_2C_4P) with TmI_3 respectively afforded $[(Dtp)_2TmI]$ (**8**) and an axially symmetric dimer: $[\{(Htp)_2TmI\}_2]$ (**9**) (Scheme 4 and Figures 5 and 6). As for **7**, the proton NMR spectrum of **9** shows again only one peak for the tBu groups (85 ppm).

Depending on the substitution pattern on the phospholyl ring, a monomeric (**8**) or a dimeric (**9**) Tm^{III} iodide complex can be obtained.

Reduction of **8** with KC_8 was successful: the reaction mixture gradually turned emerald green and the known $[(Dtp)_2Tm]$[13] (**10**) was formed, which was identified by its proton and phosphorus NMR spectra. When **9** was submitted to the same reaction conditions, a new homoleptic complex of Tm^{II}, the centrosymmetric dimer $[\{(Htp)_2Tm\}_2]$ (**11**), was obtained, which was characterized by its X-ray crystal structure (Figure 7).

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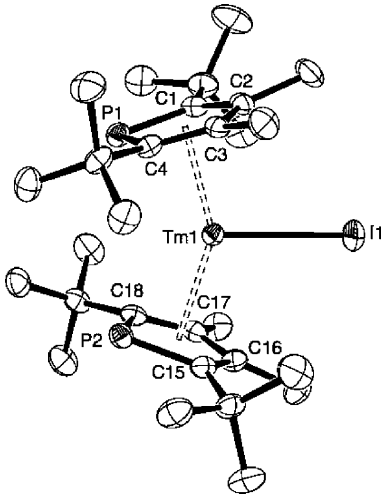

Figure 5. ORTEP plot (50% ellipsoids) of one molecule of $[(Dtp)_2TmI]$ (**8**). Hydrogen atoms have been omitted for clarity.

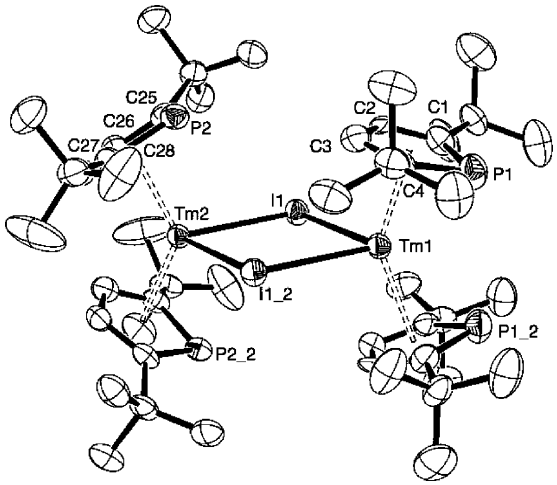

Figure 6. ORTEP plot (50% ellipsoids) of one molecule of $\{[(Htp)_2TmI]\}_2$ (**9**). Hydrogen atoms have been omitted for clarity.

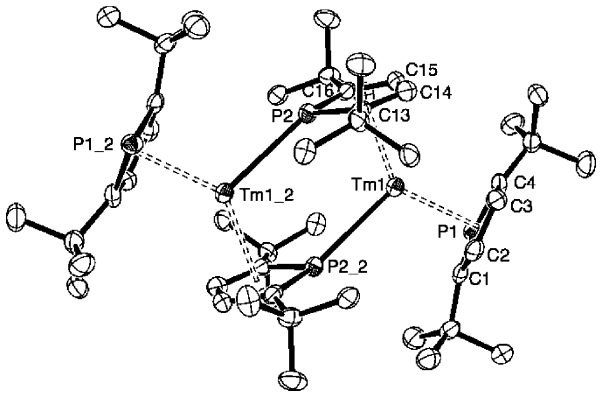

Figure 7. ORTEP plot (50% ellipsoids) of one molecule of $[\{(Htp)_2Tm\}_2]$ (**11**). There are two independent dimers in the unit cell; only one is represented in the figure. Hydrogen atoms have been omitted for clarity.

This structure is strikingly similar to that of the previously described $[\{(Dtp)_2Sm\}_2]$.[13] Just like in this complex, $\sigma-\pi$ bonding of one phospholyl ligand to Tm leads to the dimeric formulation of **11**, and there is also an interaction between thulium and a methyl group belonging to one of the tBu groups α to phosphorus (Tm1−C18_2 = 3.20 Å in **11** versus Sm1−C20_2 = 3.25 Å in $[\{(Dtp)_2Sm\}_2]$[13]). Like with $[\{(Dtp)_2Sm\}_2]$, the proton NMR spectrum of **11** suggests that this compound is monomeric in solution. We could not observe the ^{31}P resonance of **11**; however, upon addition of THF, we observed a peak at the chemical shift of $[(Htp)_2Tm(THF)]$ (−290 ppm).[9]

This result supplements those obtained previously in the field of homoleptic Ln^{II} phospholyl complexes: by switching from the big Sm^{II} to the smaller Tm^{II}, the structure of the bis(Dtp)-lanthanide complex changes from dimeric to monomeric,[13] while by switching from the big Dtp ligand to the smaller Htp, the structure of the bis(phospholyl)thulium complex changes from monomeric to dimeric. Note that **11** is only the second structurally characterized homoleptic complex of Tm^{II} and that it could not be obtained by desolvation of the known $[(Htp)_2Tm(THF)]$:[9] all attempts to remove the solvent by pumping or otherwise were unsuccessful or resulted in decomposition.

Reactivity with Pyridine. The reactivity of bis(phospholyl)- versus that of bis(cyclopentadienyl)thulium(II) homoleptic complexes is likely to be sensitive to the relative steric bulk of the π-ligands. Since the crystal structures of four complexes, $[L_2TmI]$ and $[L_2Tm(THF)]$ (L = Dtp or Cp^{ttt}), are available, it is possible to compare the steric bulk of the Dtp and Cp^{ttt} ligands by examination of the Tm−O(THF) bond distance in the Tm^{II} complexes, the Tm−I bond distance in the Tm^{III} complexes, and the dihedral angle between the two planar Cp^{ttt} or Dtp π-ligands (Table 2). From this table it is clear that the Dtp and Cp^{ttt} ligands are sterically very similar. In the Tm^{II} complexes, the Cp^{ttt} ligand might be a little bigger than the Dtp ligand, as indicated by the slightly longer Tm−O bond and smaller dihedral angle in $[(Cp^{ttt})_2Tm(THF)]$; however, these differences become insignificant in the Tm^{III} complexes.

Bochkarev and Schumann have recently described the reductive dimerization of pyridine with thulium diiodide,[15] and we felt that this reaction would constitute a good test of the respective reducing power of the phospholyl and the cyclopentadienyl complexes of Tm^{II}. We had previous evidence that the phospholyl complexes are more stable than their cyclopentadienyl counterparts,[9] and thus we expected the reactivity of the phospholyl complexes to be weaker.

Reaction of **1** with pyridine resulted in an instantaneous color change from purple to orange, and like in Bochkarev's case, we were able to isolate crystals of a product containing the 1,1′-bis(1,4-dihydropyridylamide) ligand: $[\{(Cp^{ttt})_2Tm\}_2\{\mu\text{-}(NC_5H_5\text{-}C_5H_5N)\}]$ (**12**) (Scheme 5 and Figure 8). However, when unsolvated $[(Dtp)_2Tm]$ (**10**) was treated with pyridine, the reaction mixture turned deep red and we were unable to obtain any tractable material after workup; we therefore decided to investigate the reaction between **10** and pyridine by NMR. Initially, the proton spectrum of an equimolecular mixture of **10** and pyridine displayed two peaks corresponding respectively to the tBu protons at 45 ppm and to the Me protons at −22 ppm; additionally, a broad signal at 3 ppm that was attributed to pyridine was observed. The chemical shift of the tBu and Me protons are similar to that found in $[(Dtp)_2Tm(THF)]$[14] (59 and −23 ppm, rspectively). The phosphorus spectrum of the **10**/pyridine mixture was found at −270 ppm, in the range of other solvated Tm^{II} species such as $[(Dtp)_2Tm(THF)]$[14] (−338 ppm) and $[(Htp)_2Tm(THF)]$[9] (−290 ppm). However, after 5 min at room temperature, the proton spectrum began to degrade and after 30 min the tBu and Me protons could no longer be detected. On these bases, we postulate that the initial species present in the **10**/pyridine mixture was still a Tm^{II} complex,

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Table 1. Crystal Data and Data Collection Parameters for Compounds 3, 4, 6, 7, 8, 9, 11, and 12

	3	4	6	7	8	9	11	12
molecular formula	$C_{32}H_{66}OSi_6Tm$	$C_{28}H_{58}ISi_6Tm$	$C_{34}H_{62}BTm$	$C_{52}H_{84}I_2Tm_2$	$C_{28}H_{48}IP_2Tm$	$C_{48}H_{80}I_2P_4Tm_2$	$C_{48}H_{80}P_4Tm_2$	$C_{78}H_{126}N_2Tm_2$
molecular weight	804.32	859.11	650.58	1300.85	742.43	1372.66	1118.86	1302.66
cryst habit	purple plate	yellow plate	yellow block	pale yellow plate	yellow block	yellow plate	olive-green plate	orange plate
cryst dimens (mm)	$0.20 \times 0.20 \times 0.12$	$0.20 \times 0.18 \times 0.11$	$0.20 \times 0.20 \times 0.15$	$0.22 \times 0.16 \times 0.10$	$0.12 \times 0.08 \times 0.08$	$0.18 \times 0.10 \times 0.04$	$0.10 \times 0.10 \times 0.03$	$0.20 \times 0.14 \times 0.02$
space group	$P2_1/n$	$C2/c$	$C2/c$	$P\bar{1}$	$P2_1/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.348(1)	40.915(2)	10.450(1)	10.492(1)	10.787(1)	27.944(1)	10.730(1)	10.447(1)
b (Å)	22.120(1)	18.358(1)	16.293(1)	10.550(1)	16.997(1)	13.034(1)	11.957(1)	10.865(1)
c (Å)	16.841(1)	32.965(2)	20.077(1)	12.863(1)	16.458(1)	20.208(1)	20.320(1)	18.222(1)
α (deg)	90	90	90	81.180(1)	90	90	88.780(1)	106.818(1)
β (deg)	97.750(1)	125.593(1)	102.619(1)	72.891(1)	91.982(1)	133.686(1)	79.279(1)	91.546(1)
γ (deg)	90	90	90	78.824(1)	90	90	74.166(1)	94.519(1)
V (Å^3)	4188.8(5)	20134.6(2)	3335.8(4)	1327.9(2)	3015.7(2)	5322.4(5)	2463.1(3)	1971.0(3)
Z	4	20	4	1	4	4	2	1
d (g cm^{-3})	1.275	1.417	1.295	1.627	1.635	1.713	1.509	1.097
F(000)	1676	8640	1360	640	1472	2688	1132	620
μ (cm^{-1})	2.311	3.164	2.678	4.512	4.086	4.622	3.738	2.270
maximum θ	30.03	26.37	30.03	30.03	30.03	27.48	27.47	27.50
no. of reflns measd	20 064	33 924	10 296	10 657	15 828	23 040	25 589	16 977
no. of unique data	12 187	20 023	4805	7739	8782	6066	11 211	8955
R_{int}	0.0350	0.0458	0.0229	0.0201	0.0371	0.0471	0.0624	0.0349
no. of reflns used	8702	12 878	4284	7241	6653	4164	7492	6672
wR2	0.0772	0.1138	0.0870	0.1080	0.0920	0.0906	0.1333	0.1513
R1	0.0364	0.0433	0.0328	0.0390	0.0374	0.0354	0.0528	0.0537
GoF	0.998	1.015	1.052	1.004	0.994	1.019	1.067	0.988

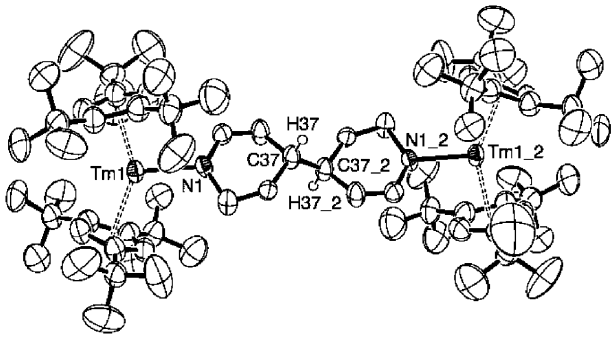
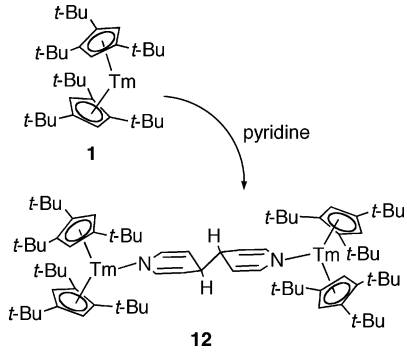


Figure 8. ORTEP plot (50% ellipsoids) of one molecule of $[\{(Cp^{ttt})_2Tm\}_2\{\mu\text{-}(NC_5H_5\text{-}C_5H_5N)\}]$ (**12**). Hydrogen atoms (except those at the bipyridyldiamide junction) have been omitted for clarity; the bipyridine ligand is disordered over two positions; only one is presented in the figure.

Table 2. Comparison of Selected Geometrical Parameters in [(Dtp)$_2$TmI] (8), [(Cp^{ttt})$_2$TmI], [(Dtp)$_2$Tm(THF)], and [(Cp^{ttt})$_2$Tm(THF)]

compound	Tm−I (Å)	Tm−O (Å)	π-ligand dihedral angle (deg)	ref
[(Dtp)$_2$TmI] (**8**)	2.8864(8)		35.3	this work
[(Cp^{ttt})$_2$TmI]	2.8999(5)		35.1	6
[(Dtp)$_2$Tm(THF)]		2.455(2)	33.6	14
[(Cp^{ttt})$_2$Tm(THF)]		2.473(3)	31.8	6

Scheme 5



most likely a simple adduct of **10** with pyridine such as [(Dtp)$_2$Tm(pyridine)], which further decomposed at room temperature, presumably into unidentified Tm^{III} species.

We thus believe that the difference in reactivity toward pyridine between homoleptic Tm^{II} complexes with cyclopentadienyl and phospholyl ligands confirms the higher stability and lower reactivity of the phospholylthulium(II) complexes. Since we have established that the Dtp and Cp^{ttt} ligands are sterically very similar, this difference is likely of electronic origin: in related uranium chemistry, Gradoz et al. have shown that phospholyl ligands are less electron-donating than cyclopentadienyl ligands of similar steric bulk.[16]

Conclusion

There are now two well-established synthetic methods for the preparation of organothulium(II) complexes: the first one, which was originally proposed by Evans et al.,[8] involves the metathesis of an anionic ligand precursor with TmI_2; we have extended its scope to the synthesis of several other cyclopentadienyl and phospholyl complexes,[6,9,13,14] and we now report

(16) Gradoz, P.; Baudry, D.; Ephritikhine, M.; Lance, M.; Nierlich, M.; Vigner, J. *J. Organomet. Chem.* **1994**, *466*, 107−118.

the synthesis of $[(Cp'''')_2Tm(THF)]$ (**3**), stable at room temperature in THF solution. The second approach concerns the chemical reduction of an organothulium(III) precursor: with the use of KC_8 as the reducing agent in nonpolar solvents, we were able to transform $[(Cp^{ttt})_2TmI]$ into $[(Cp^{ttt})_2Tm]$,[6] and we now describe the conversion of the Tm^{III} iodides $[(Cp'''')_2TmI]$ (**4**) and $[\{(Htp)_2TmI\}_2]$ (**9**) respectively into the new homoleptic Tm^{II} complexes $[(Cp'''')_2Tm]$ (**5**) and $[\{(Htp)_2Tm\}_2]$ (**11**). Additionally, we have shown that the known $[(Dtp)_2Tm]$ and $[(Cp^{ttt})_2Tm]$ could also be obtained by reduction of $[(Dtp)_2TmI]$ (**8**) and $[(Cp^{ttt})_2Tm(BH_4)]$ (**6**), respectively. The use of an organothulium(III) borohydride as precursor is interesting because it can be ultimately obtained from Tm_2O_3, the least expensive source of thulium, through its described transformation into $TmCl_3$ and further into $Tm(BH_4)_3(THF)_3$.

We have investigated the reactivity of the sterically equivalent $[(Cp^{ttt})_2Tm]$ and $[(Dtp)_2Tm]$ with pyridine. With $[(Cp^{ttt})_2Tm]$, an immediate reaction occurred and we obtained a Tm^{III} complex with a reductively coupled bipyridinyl ligand: $[\{(Cp^{ttt})_2Tm\}_2\{\mu\text{-}(NC_5H_5\text{-}C_5H_5N)\}]$ (**12**). With $[(Dtp)_2Tm]$, although no complex could be isolated, an NMR study suggests that initially a simple Tm^{II} adduct of $[(Dtp)_2Tm]$ with pyridine such as $[(Dtp)_2Tm(pyridine)]$ was formed. These findings confirm the higher stability and lower reactivity of phospholylthulium(II) complexes compared to that of cyclopentadienylthulium(II) of similar steric bulk.

We will now attempt to expand the reactivity pattern of the Tm^{II} complexes, by allowing them to react with small molecules such as carbon monoxide.

Experimental Section

General Procedures. All reactions were performed under an inert atmosphere with purified dry, deoxygenated solvents by using vacuum line and drybox techniques. The following compounds were prepared according to literature procedures: $[Na(Cp'''')]$,[17] $[K(Cp'''')]$,[18] $[K(Cp^{ttt})]$,[19] [K(Dtp)],[13] [K(Htp)],[9] $[TmI_2(THF)_3]$,[9] KC_8.[20] $[K(Cp^{tt})]$ was prepared with KH and HCp^{tt} [21] according to the procedure reported for $[K(Cp^{ttt})]$. $[Tm(BH_4)_3(THF)_3]$ was prepared from $TmCl_3$ and $NaBH_4$ according to the method described for the synthesis of $[Nd(BH_4)_3(THF)_3]$.[11] All other materials were commercially available and used without further purification. Elemental analyses were performed at the "Service de Microanalyse de l'Université de Dijon", Dijon (Bourgogne), France.

General Procedure (GP) for the Synthesis of the Tm^{III} Complexes L_2TmX (L = Cp‴, Cp^{ttt}, Cp^{tt}, Dtp, Htp; X = I, BH_4). In the glovebox a mixture of $[TmX_3(THF)_y]$ (for X = I, y = 0; for X = BH_4: y = 3) (1.0 equiv) and K(L) (2.2 equiv) was prepared in a Schlenk tube fitted with a J. Young valve. Toluene (20 mL) was condensed onto this mixture at −78 °C, and the suspension was allowed to warm to room temperature. Under stirring the reaction was heated to reflux for 48 h. After that time the yellow solution was cooled to room temperature and centrifuged. The solvent was evaporated and the crude product was recrystallized from pentane at −30 °C.

$[(Cp^{ttt})_2Tm]$[6] (1). To a solution of $[(Cp^{ttt})_2Tm(BH_4)]$ (50 mg, 0.08 mmol) in pentane (4 mL) was added KC_8 (104 mg, 0.77 mmol), and the reaction was left for 48 h. The resulting violet solution was centrifuged and evaporated. After washing with cold pentane, pure **1** was obtained in 48% yield (23 mg, 0.04 mmol). The ^1H NMR spectrum was identical to the one previously reported.[6]

$[(Cp'''')_2Tm(THF)]$ (3). Onto a mixture of $[TmI_2(THF)_3]$ (0.10 g, 0.16 mmol) and $[Na(Cp'''')]$ (0.09 g, 0.31 mmol), diethyl ether (10 mL) was condensed at −78 °C, and the reaction was allowed to warm to room temperature under stirring. After 2 h the resulting violet solution was filtered and evaporated. Recrystallization from pentane at −30 °C led to the isolation of the pure **3** as a violet crystalline solid in 32% yield (0.04 g, 0.05 mmol). ^1H NMR (300 MHz, C_6D_6): δ (ppm) 53 (br s, 18H, $w_{1/2} \approx 1$ kHz, $Si(CH_3)_3$), 14 (br s, 36H $w_{1/2} \approx 1$ kHz, $Si(CH_3)_3$), −23 (br s, 4H, $w_{1/2} \approx 1$ kHz, CH). $\mu_{eff} = 5.0\ \mu_B$ (Evans' NMR method).

$[(Cp'''')_2TmI]$ (4). From the reaction of TmI_3 (0.30 g, 0.55 mmol) and $[K(Cp'''')]$ (0.38 g, 1.2 mmol) according to the GP, **4** was obtained as a yellow powder in 53% yield (0.25 g, 0.29 mmol). ^1H NMR (300 MHz, C_6D_{12}): δ (ppm) 157 (br s, 18H, $w_{1/2} \approx 2$ kHz, $Si(CH_3)_3$), 48 (br s, 36H, $w_{1/2} \approx 4$ kHz, $Si(CH_3)_3$). Anal. Calcd for $C_{28}H_{58}ISi_6Tm$ (859.11): C, 39.15; H, 6.80. Found: C, 39.52; H, 6.54. Crystals suitable for X-ray analysis were obtained from sublimation at 220 °C and 10^{-3} mbar.

$[(Cp'''')_2Tm]$ (5). To a solution of $[(Cp'''')_2TmI]$ (0.10 g, 0.11 mmol) in cyclohexane (6 mL) was added KC_8 (0.16 g, 1.2 mmol) in small portions. After 48 h the dark green solution was centrifuged and evaporated. Addition of some drops of cyclohexane to the oily residue led to the precipitation of pure **5** as a dark green solid in 42% yield (0.03 g, 0.05 mmol). ^1H NMR (300 MHz, C_6D_{12}): δ (ppm) 24 (br s, 18H, $w_{1/2} \approx 60$ Hz, $Si(CH_3)_3$), 21 (br s, 36H $w_{1/2} \approx 90$ Hz, $Si(CH_3)_3$), −54 (br s, 4H, $w_{1/2} \approx 600$ Hz, CH).

$[(Cp^{ttt})_2Tm(BH_4)]$ (6). From the reaction of $[Tm(BH_4)_3(THF)_3]$ (0.30 g, 0.70 mmol) and $[K(Cp^{ttt})]$ (0.42 g, 1.54 mmol) according to the GP, **6** was obtained as a yellow powder in 73% yield (0.33 g, 0.51 mmol). ^1H NMR (300 MHz, C_6D_{12}): δ (ppm) 279 (br s, 18H, $w_{1/2} \approx 3$ kHz, tBu), 107 (br s, 18H, $w_{1/2} \approx 3$ kHz, tBu), −26 (br s, 18H, $w_{1/2} \approx 2$ kHz, tBu). Anal. Calcd for $C_{34}H_{62}BTm$ (650.60): C, 62.77; H, 9.61. Found: C, 62.79; H, 9.69. Crystals suitable for X-ray analysis were obtained from pentane at −30 °C.

$[\{(Cp^{tt})_2TmI\}_2]$ (7). From the reaction of TmI_3 (0.30 g, 0.55 mmol) and $[K(Cp^{tt})]$ (0.26 g, 1.2 mmol) according to the GP, **7** was obtained as a yellow powder in 66% yield (0.23 g, 0.18 mmol). ^1H NMR (300 MHz, C_6D_{12}): δ (ppm) 214 (br s, $w_{1/2} \approx 3$ kHz, tBu). Anal. Calcd for $C_{52}H_{84}I_2Tm_2$ (1300.90): C, 48.01; H, 6.51. Found: C, 47.99; H, 6.69. Crystals suitable for X-ray analysis were obtained from pentane at −30 °C.

$[(Dtp)_2TmI]$ (8). From the reaction of TmI_3 (0.40 g, 0.72 mmol) and [K(Dtp)] (0.42 g, 1.58 mmol) according to the GP, **8** was obtained as a yellow powder in 78% yield (0.42 g, 0.56 mmol). ^1H NMR (300 MHz, C_6D_6): δ (ppm) 167 (br s, $w_{1/2} \approx 9$ kHz, tBu). Anal. No correct analysis could be obtained. Crystals suitable for X-ray analysis were obtained from sublimation at 190 °C and 10^{-3}mbar.

$[\{(Htp)_2TmI\}_2]$ (9). From the reaction of TmI_3 (0.20 g, 0.36 mmol) and [K(Htp)] (0.18 g, 0.79 mmol) according to the GP, **9** was obtained as a yellow powder in 45% yield (0.11 g, 0.16 mmol). ^1H NMR (300 MHz, C_6D_{12}): δ (ppm) 85 (br s, $w_{1/2} \approx 3$ kHz, tBu). Anal. Calcd for $C_{48}H_{80}I_2P_4Tm_2$ (1372.72): C, 42.00; H, 5.87. Found: C, 42.11; H, 5.89. Crystals suitable for X-ray analysis were obtained from pentane at −30 °C.

$[(Dtp)_2Tm]$[12] (10). To a solution of $[(Dtp)_2TmI]$ (37 mg, 0.05 mmol) in pentane (4 mL) was added KC_8 (67 mg, 0.50 mmol), and the reaction was left for 48 h. The resulting dark green solution was centrifuged, and the volume was reduced to 2 mL under vacuum. From the solution pure **10** crystallized as a dark green solid in 67% yield (20 mg, 0.03 mmol). The NMR spectra (^1H, ^{31}P) were identical to those previously reported.[12]

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[{(Htp)$_2$Tm}$_2$] (11). To a solution of [{(Htp)$_2$TmI}$_2$] (25 mg, 0.018 mmol) in hexanes (2 mL) was added KC_8 (50 mg, 0.36 mmol), and the reaction was shaken for 1 h. The resulting green solution was centrifuged and transferred to a crystallization tube. From this solution pure **11** crystallized at −30 °C as green solid in 15% yield (3 mg, 0.003 mmol). ^{1}H NMR (300 MHz, C_6D_{12}): δ (ppm) 40 (br s, 36H, $w_{1/2} \approx 1$ kHz, tBu), −26 (br s, 4H, $w_{1/2} \approx 1$ kHz, C*H*).

[{(Cp^{ttt})$_2$Tm}$_2${μ-(NC$_5$H$_5$-C$_5$H$_5$N)}] (12). Addition of pyridine (2.5 μL, 0.03 mmol) to a solution of [(Cp^{ttt})$_2$Tm] (20 mg, 0.03 mmol) in toluene (2 mL) at room temperature led to an immediate color change to orange. After evaporation of the solvent, the residue was dissolved in THF and crystals suitable for X-ray analysis were grown from this solution at −30 °C, yielding red **12** in 10% yield (4 mg, 0.003 mmol).

Reaction of [(Dtp)$_2$Tm] (10) with Pyridine. Addition of pyridine (2.5 μL, 0.03 mmol) to a solution of [(Dtp)$_2$Tm] (19 mg, 0.03 mmol) in C_6D_6 (0.5 mL) led to the formation of a dark red solution, which was stable for 30 min at room temperature. ^{1}H NMR (300 MHz, C_6D_6): δ (ppm) 45 (br s, 36H, $w_{1/2} \approx 300$ Hz, tBu), 3 (br s, py), −22 (br s, 12H, $w_{1/2} \approx 600$ kHz, CH_3). ^{31}P NMR (120 MHz, C_6D_6): δ (ppm) −260 (br s).

X-ray Experimental Section. All measurements were made with a Nonius KappaCCD diffractometer with a graphite-monochromated Mo Kα source ($\lambda = 0.71069$ Å) at 150 K. Further details are presented in the .cif file (see Supporting Information).

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Supporting Information Available: NMR spectra of compounds **3**, **4**, **5**, **6**, **7**, **8**, [(Cp^{ttt})$_2$TmI], and [(Dtp)$_2$Tm] and of the 1:1 mixture of [(Dtp)$_2$Tm] and pyridine, and a crystallographic cif file for all structurally described compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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