Structure and Reactivity of Homoleptic Samarium(II) and Thulium(II) Phospholyl Complexes

Daniela Turcitu, François Nief,* and Louis Ricard[a]

Abstract: Potassium 2,5-di-*tert*-butyl-3,4-dimethylphospholide K(dtp) (**9**) was synthesised in 45% yield from commercially available starting materials by using zirconacyclopentadiene chemistry. Reaction of the K salt of this bulky anion and of the previously described potassium 2,5-bis(trimethylsilyl)-3,4-dimethylphospholide K(dsp) (**8**) with SmI_2 in diethyl ether afforded the homoleptic samarium(II) complexes **7** and **6**, respectively, whose solid-state structures, $[\{Sm(dtp)_2\}_2]$ (**7a**) and $[\{Sm(dsp)_2\}_2]$ (**6a**), are dimeric owing to coordination of the phosphorus lone pairs to samarium, as shown by X-ray crystallography. Reaction of **8** with TmI_2 in diethyl ether afforded $[Tm(dsp)_2(Et_2O)]$, which could not be desolvated without decomposition. In contrast, the coordinated ether group of the solvate $[Tm(dtp)_2(Et_2O)]$, obtained from **9** and TmI_2, could easily be removed by evaporation of the solvent and extraction with pentane at room temperature, and the monomer $[Tm(dtp)_2]$ (**5**) could be isolated and was characterised by X-ray crystallography. Presumably, steric crowding in **5** is too high for dimerisation to occur. Compound **5**, the first Tm^{II} homoleptic sandwich complex, is remarkably stable at room temperature in solution and did not noticeably react with nitrogen, in sharp contrast with other thulium(II) species. As expected, **5**, **6** and **7** all reacted with azobenzene to give the trivalent complexes $[Tm(dtp)_2(N_2Ph_2)]$ (**13**), $[Sm(dsp)_2(N_2Ph_2)]$, (**14**) and $[Sm(dtp)_2(N_2Ph_2)]$ (**15**), respectively; **13** and **14** were characterised by X-ray crystallography. Complex **5** immediately reacted with triphenylphosphane sulfide at room temperature to give $[\{Tm(dtp)_2\}_2(\mu\text{-}S)]$ (**16**), which was characterised by X-ray crystallography, whereas samarium(II) complexes **6** and **7** did not noticeably react with Ph_3PS over 24 h under the same conditions.

Keywords: low-valent compounds · metallocenes · P ligands · samarium · thulium

Introduction

The molecular chemistry of low-valent lanthanide (Ln) complexes has long been restricted to europium, ytterbium and samarium, that is, to the elements of the lanthanide series that have an accessible +II oxidation state and for which precursors such as LnI_2 are easily available by solution chemistry near room temperature.[1] Although other lanthanide(II) diiodides,[2] namely, NdI_2, DyI_2 and TmI_2, were first described some time ago, their chemistry has not been much developed, probably because their synthesis involved high-temperature, solid-state techniques.[3, 4]

However, this situation recently changed when Evans and Bochkarev et al.[5, 6] described the solution synthesis and isolation of TmI_2 solvated with dimethoxyethane (DME) or THF by the direct reaction of thulium metal with iodine. Shortly afterwards, Bochkarev and Fagin[7] and Evans et al.[8, 9] showed that unsolvated NdI_2, DyI_2 and TmI_2 could be made by a method that, while still using a high-temperature reaction of the lanthanide elements with iodine, could nevertheless be conducted in the laboratory in ordinary glassware or silica apparatus. Solvated NdI_2[10] and DyI_2[8] (with DME or THF) are highly reactive complexes that are only stable below room temperature.

As far as organometallic and coordination chemistry is concerned, other complexes of neodymium(II), dysprosium(II) and thulium(II) are generally too reactive to be isolated. For instance, they react with nitrogen to give interesting μ-N_2^{2-} complexes,[11–13] undergo oxidative cleavage of the coordinated solvent[11, 14] or ligand[15] to give lanthanide(III) complexes, and can reduce aromatic hydrocarbons[8, 16] and acetonitrile.[17] Nevertheless, Evans et al. were able to isolate the first structurally characterised organometallic complex of thulium(II), $[Cp''_2Tm(thf)]$ (**1**; $Cp'' = C_5H_3(SiMe_3)_2$), which has limited stability at room temperature, and thus showed that, by careful selection of the ligand and reaction conditions, "nonclassical" lanthanide(II) complexes can be obtained.[11] In another approach, Lappert et al. recently characterised the unusual lanthanum(II) anionic complex [K([18]crown-6)(η-

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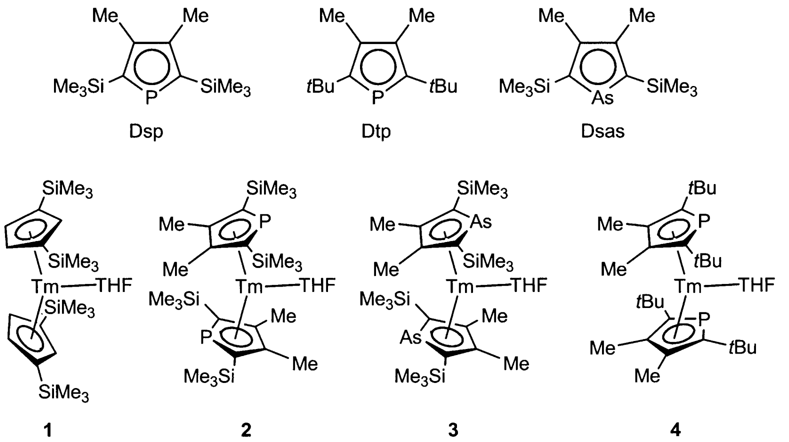
$C_6H_6)_2][(LaCp^{tt}_2)_2(\mu\text{-}C_6H_6)]$ ($Cp^{tt} = C_5H_3(tBu)_2$) by reduction of the trivalent precursor $[(LaCp^{tt}_2)_3]$.[18]

The phospholyl (phosphacyclopentadienyl) ligand has been successfully used in organolanthanide and organoactinide chemistry.[19] It appears particularly well suited for the stabilisation of low-valent complexes because of its reduced π-donor capability; thus, we described in a previous communication three new complexes of thulium(II) with bulky phospholyl and arsolyl ligands: $[Tm(dsp)_2(thf)]$ (**2** (dsp = $PC_4Me_2(SiMe_3)_2$), $[(dsas)_2Tm(thf)]$ (**3**, dsas = $AsC_4Me_2(SiMe_3)_2$), and $[Tm(dtp)_2(thf)]$ (**4**; dtp = $PC_4Me_2tBu_2$), and we found that the stability of these compounds in solution was improved with respect to that of **1**[20] (Scheme 1).



Scheme 1. Ligands and complexes in thulium(II) chemistry.

We now report the synthesis of a new unsolvated metallocene-like thulium(II) sandwich complex: $[Tm(dtp)_2]$ (**5**). Since we thought that a comparison of **5** with homologous samarium(II) complexes would be useful, we also describe the syntheses of the homoleptic complexes $[Sm(dsp)_2]$ (**6**) and $[Sm(dtp)_2]$ (**7**). Finally, the reactivity of **5** is compared to those of **6** and **7**.

Abstract in Romanian: *Anionul fosfolil K(dtp) (**9**) a fost obtinut pe baza chimiei zirconiului din materii prime comerciale cu un randament total de 45 %. Reactia acestuia cat si cea a anionului K(dsp) (**8**), descris anterior, cu* SmI_2 *in* Et_2O *au condus la izolarea a doi complecsi homoleptici dimeri ai* Sm^{II} *(raze X) prin coordinarea perechii libere a fosforului de Sm. Complexul solvatat* $[Tm(dtp)_2(Et_2O)]$*, obtinut din (**9**) in aceleasi conditii, pierde usor solventul coordinat prin extractie cu hexan, rezultand un complex monomer* $[Tm(dtp)_2]$ *(**5**) (raze X). Probabil ca acest compus nu se prezinta sub forma unui dimer din cauza impiedicarii sterice. (**5**), primul complex sandwich homoleptic al* Tm^{II}*, prezinta stabilitate termica in solutie si este inert fata de* N_2*, contrar altor specii ale* Tm^{II}*. Compusii homoleptici ai Sm si Tm divalenti reactioneaza cu azobenzenul, obtinandu-se speciile trivalente corespunzatoare,* $[Tm(dtp)_2(N_2Ph_2)]$ *(**13**) si* $[Sm(dsp)_2(N_2Ph_2)]$ *(**14**) (raze X). Compusul (**5**) reactioneaza instantaneu cu* $Ph_3P{=}S$*, la temperatura camerei, formand* $[Tm(dtp)_2(\mu\text{-}S)]$ *(**16**), a carui structura a fost determinata, in timp ce complecsii* Sm^{II} *nu au dat nici un rezultat dupa 24 h in aceleasi conditii.*

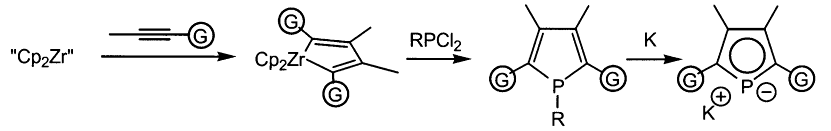
Results and Discussion

Ligands: A general method for constructing symmetrical phospholes uses zirconium chemistry: zirconacyclopentadienes, which are readily available by oxidative coupling of two equivalents of an alkyne around a transient zirconocene, can directly afford phospholes by metathesis with phosphorus dihalides.[21] Large substituents G in the alkyne regiospecifically end up in the position α to zirconium, and thus phospholes bearing bulky groups in the 2,5-positions are obtained;[22, 23] the corresponding phospholides, equivalents of cyclopentadienide, are then obtained by treatment with an alkali metal (Scheme 2). Using this method, we successfully isolated K(dsp) (**8**).[24]

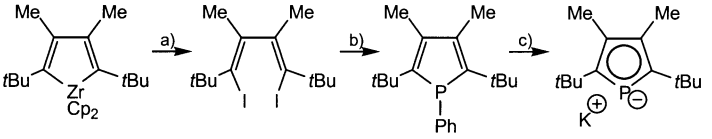
Potassium 2,5-bis(*tert*-butyl)-3,4-dimethylphospholide K(dtp) (**9**) was obtained by a similar route. Iodinolysis[25] of the known $[Cp_2Zr\{C_4Me_2tBu_2\}]$ (**10**)[26] gave diiodide **11**, which could be transformed into a dilithium salt by standard halogen/lithium exchange; treatment of this salt in situ with $PhPCl_2$ afforded the corresponding 1-phenyl-2,5-di-*tert*-butyl-3,4-dimethylphosphole **12**, which could be converted to **9** by treatment with an excess of potassium in DME. (Scheme 3)

Compound **9** can thus be satisfactorily obtained in about 45 % yield from commercially available $[Cp_2ZrCl_2]$ and $tBuC{\equiv}CMe$ (yield of isolated **10** is ca. 90 %).

Homoleptic complexes of samarium(II): We described some time ago the synthesis of samarium(II) and ytterbium(II) complexes of the tetramethylphospholyl (tmp = C_4Me_4P) ligand: $[Sm(tmp)_2(thf)_2]$ and $[Yb(tmp)_2(thf)_2]$, and found that the coordinated THF in these complexes was labile and could be removed by evaporation of toluene solutions of the compounds. However, the resulting $[Sm(tmp)_2]$ and $[Yb(tmp)_2]$ were amorphous insoluble solids for which no solution NMR spectra could be obtained.[27] We suspected that this insolubility was due to intermolecular contacts in the solid state, maybe involving coordination of the phosphorus lone pair to the lanthanide(II) ions. Interestingly, it has been shown that, in the three-dimensional crystal structure of the highly insoluble $[Yb(C_5Me_4H)_2]$, the C_5Me_4H ligand of which is sterically very similar to tmp, short intermolecular contacts are present between a CH unit of one molecule and the ytterbium atom of another.[28]



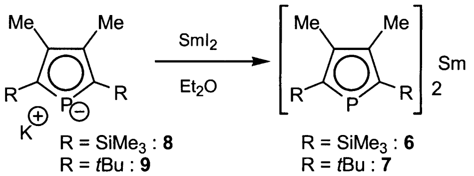
Scheme 2. The zirconacyclopentadiene synthesis of phospholes and phospholides.



10 11 12 9

Scheme 3. a) I_2, THF, 0 °C, 2 h, 75 %; b) 2*n*BuLi, Et_2O, −78 °C to RT, 1 h, then $PhPCl_2$, −78 °C to RT, 30 min, 79 %; c) K (4 equiv), DME, 70 °C, 2 h, 89 %.

We thought that dtp or dsp, which have bulky substituents α to phosphorus, would offer a better better chance of obtaining more soluble material, and that using diethyl ether as solvent instead of the more basic THF would make desolvation easier. Reaction of **8** or **9** with unsolvated SmI_2 in diethyl ether afforded solutions which, after stripping of the solvent and treatment with pentane, yielded green solids of respective compositions $[Sm(dsp)_2]$ (**6**) and $[Sm(dtp)_2]$ (**7**) (Scheme 4).



Scheme 4. Synthesis of **6** and **7**.

Compounds **6** and **7** are moderately soluble in toluene and could be recrystallised from this solvent. ^1H NMR spectra in C_6D_6 gave very broad signals both for **6** and **7**, and no phosphorus signals were observed; however ^{31}P spectra could be recorded in THF. X-ray crystal structures were obtained (a summary of the X-ray data is presented in Table 1).

Complexes **6** and **7** are centrosymmetric dimers in the solid state: $[\{Sm(dsp)_2\}_2]$ (**6a**) and $[\{Sm(dtp)_2\}_2]$ (**7a**), composed of two metallocene-like moieties linked by additional P–Sm dative bonds (Figure 1). Thus, the bulky substituents α to phosphorus in the dsp and dtp ligands do not prevent coordination of the lone pair of the phosphorus atom in the similar dimeric structures of **6a** and **7a**. Furthermore, although the Sm–P dative bonds are long, they fall in the range of those already found for samarium(II) complexes.[29] In both compounds, there is an additional short contact between the samarium atom of one metallocene moiety and a methyl group of an $SiMe_3$ substituent (C17 2 in **6a**) or a *t*Bu group (C20 2 in **7a**) of the other, thus approaching the optimum coordination number of eight for samarium(II). Compound **7a** looks slightly more crowded than **6a**, as evidenced by the fact that all bond lengths involving Sm are longer. Finally, the singlet ^1H NMR signals of the phospholyl substituents in **6** and **7** suggest that these compounds are monomeric in C_6D_6 solution.

Sandwich complex of thulium(II): Having successfully isolated homoleptic complexes of samarium(II), we treated unsolvated TmI_2 with two equivalents of **8** or **9** in Et_2O. After 24 h at room temperature, ^{31}P NMR spectra of the reaction mixtures displayed broad high-field signals at $\delta = -273$ (for **8**) and −310 ppm (for **9**), chemical shifts which are respectively similar to those of the previously reported THF solvates **2** ($\delta = -266$ ppm) and **4** ($\delta = -338$ ppm).[20] Consequently, complexes such as $[Tm^{II}L_2(Et_2O)]$ (L = phospholyl) are probably present in solution at that point. After evaporation to dryness and extraction of the residue with pentane, dark green solids were obtained in both cases. With the dsp ligand, the ^1H and ^{31}P data of the isolated thulium(II) complex are very similar to those of **2**; the presence of coordinated solvent was revealed by ^1H NMR spectroscopy. By contrast, with the dtp ligand, the ^{31}P signal had experienced a substantial shift after the pentane extraction step (from $\delta = -310$ to −257 ppm). In the ^1H spectrum in C_6D_6 solution, no signals that could correspond to coordinated solvent were apparent, and the ligand signals were significantly shifted with respect to

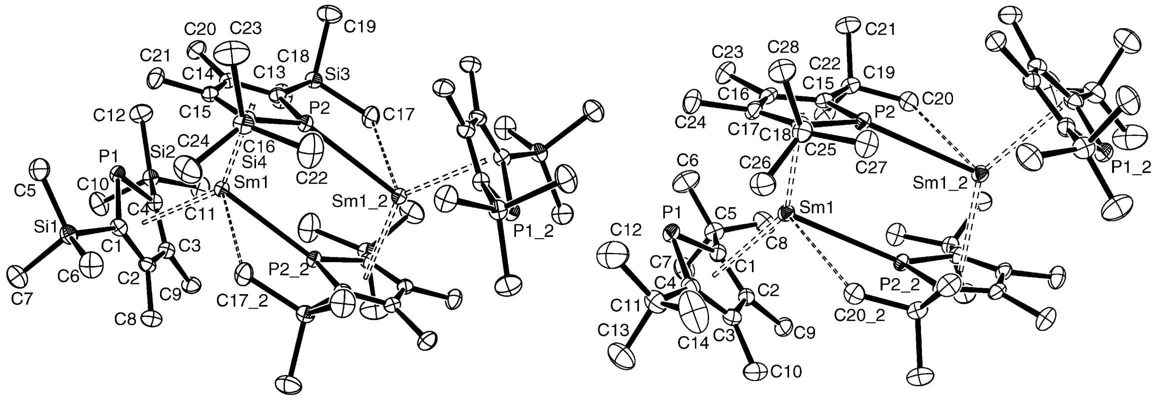
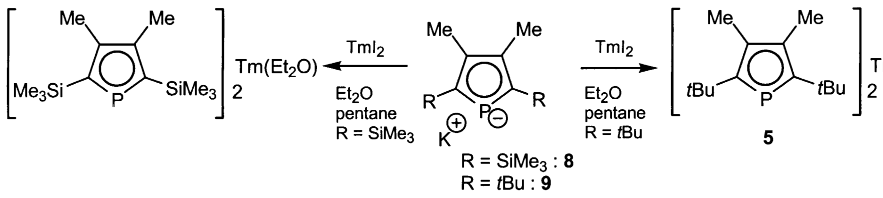


Figure 1. ORTEP plots of **6a** and **7a** (50 % ellipsoids, H atoms omitted). Selected distances [Å] and angles [°]: **6a**: Sm1–P1 3.023(1), Sm1–P2 3.113(1), Sm1–C_{ring} (av) 2.95(2), Sm1–P1 2 3.168(1), Sm1-C17 2 3.25; Cnt-Sm1-Cnt 138. **7a**: Sm1–P1 3.045(1), Sm1–P2 3.148(1), Sm1–C_{ring} (av) 2.97(3), Sm1-P1 2 3.197(1), Sm1-C20 2 3.25, Cnt-Sm1-Cnt 143.

Table 1. Crystal data and data collection parameters.

Compound	**5**	**6a**	**7a**	**13**	**14**	**16**
molecular formula	$C_{28}H_{48}P_2Tm$	$C_{48}H_{96}P_4Si_8Sm_2 \cdot 2\,C_7H_8$	$C_{56}H_{96}P_4Sm_2 \cdot 3\,C_7H_8$	$C_{40}H_{58}N_2P_2Tm$	$C_{36}H_{58}N_2P_2Si_4Sm$	$C_{56}H_{60}P_4STm_2$
molecular weight	615.53	1506.82	1470.31	797.75	843.52	1226.84
crystal habit	block	plate	cube	plate	plate	plate
crystal colour	dark green	emerald green	dark green	emerald green	dark green	pale yellow
crystal dimensions [mm]	0.16 × 0.16 × 0.16	0.22 × 0.22 × 0.03	0.16 × 0.16 × 0.16	0.18 × 0.18 × 0.08	0.20 × 0.20 × 0.14	0.22 × 0.22 × 0.08
crystal system	monoclinic	triclinic	triclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)	$Pbcn$ (no. 60)	$P2_1/c$ (no. 14)
a [Å]	25.0660(10)	11.843(5)	12.195(5)	16.5740(10)	14.9990(10)	12.9980(10)
b [Å]	14.4460(10)	12.994(5)	13.418(5)	13.1900(10)	13.6930(10)	14.9560(10)
c [Å]	24.0510(10)	14.366(5)	13.659(5)	18.3560(10)	20.2920(10)	30.0730(10)
α [°]	90	109.140(5)	106.410(5)	90	90	90
β [°]	95.4150(10)	97.680(5)	106.540(5)	112.0000(10)	90	92.839(4)
γ [°]	90	110.240(5)	110.620(5)	90	90	90
V [Å^3]	8670.1(8)	1881.9(13)	1813.7(12)	3720.6(4)	4167.6(5)	5839.0(7)
Z	12	1	1	4	4	4
ρ [g cm^{-3}]	1.415	1.330	1.346	1.424	1.344	1.437
$F(000)$	3780	780	766	1644	1744	2584
μ [cm^{-1}]	3.193	1.791	1.731	2.500	1.627	3.198
max. θ	25.00	30.03	30.03	30.02	30.03	26.37
refl. measured	59267	15674	14895	8791	20244	11141
unique data	15194	10976	10545	5402	6094	7881
R_{int}	0.0812	0.0332	0.0256	0.0269	0.0242	0.0315
refl. used ($I > 2\sigma(I)$)	10095	9161	9091	4489	4531	6091
$wR2$ (all data)	0.1415	0.0873	0.0775	0.0933	0.0989	0.1842
$R1$	0.0530	0.0368	0.0328	0.0375	0.0327	0.0704
GoF	1.005	1.028	1.038	1.009	1.033	1.086

those of **4**. This suggested that the isolated product was a thulium(II) dtp complex of composition $[\mathrm{Tm(dtp)_2}]$ (**5**; Scheme 5).



Scheme 5. Synthesis of **5**.

An X-ray crystal structure of **5** (Table 1) confirmed that it is indeed an unsolvated complex, but, unlike **6a** and **7a**, **5** is monomeric in the solid state and is thus the first homoleptic sandwich complex of thulium(II). There are three independent molecules in the unit cell, which are not significantly different from one another, so only molecule 1 is shown (Figure 2)

In **5**, the thulium atom is sandwiched between two phospholyl planes that are not rigorously parallel, but the dihedral angles are small (molecule 1: 6.1°, molecule 2: 2.8°, molecule 3: 5.5°). Lanthanide(II) metallocenes are generally more bent than **5**,[28, 30–34] although the rings of $[(C_5i\mathrm{Pr}_5)_2\mathrm{Eu}]$ are parallel.[34]

It is interesting to compare the structure of **5** with that of the monomeric $[\mathrm{Cp}^{\mathrm{tt}}_2\mathrm{Yb}]$,[28] because $\mathrm{Cp^{tt}}$ and dtp both have two *tert*-butyl substituents and the ionic radii of ytterbium(II) and thulium(II) are similar. Both compounds are free of short intermolecular contacts, yet they display intramolecular contacts between the lanthanide(II) ion and two methyl carbon atoms of *tert*-butyl groups. In $[\mathrm{Cp}^{\mathrm{tt}}_2\mathrm{Yb}]$ these methyl groups belong to the *tert*-butyl groups of one $\mathrm{Cp^{tt}}$ ligand, while in **5** they are located on two different dtp ligands (C13 and C21 in Figure 2).

As expected, the average Tm–C and Tm–P bonds are shorter than the Sm–C and Sm–P bonds in the Sm analogue **7a**. Presumably, the more compact **5** remains a monomer because coordination of another phosphorus lone pair to thulium is prevented for steric reasons.

The ease of desolvation of the intermediate $[\mathrm{Tm(dtp)_2(Et_2O)}]$ to give **5** (by simple evaporation of the ether solvent and extraction with pentane at room temperature) is quite remarkable. By contrast, $[\mathrm{Tm(dsp)_2(Et_2O)}]$ under the same conditions is not desolvated, and attempts to use more forcing conditions (evaporation of warm toluene solutions or heating the solid at 50 °C under vacuum) led to decomposition. We already noted that the Tm–O bond in $[\mathrm{Tm(dtp)_2(thf)}]$ (**4**) is significantly longer than that in **1**[11] or **3**,[20] and this suggests a relative weakness of this bond in $[\mathrm{Tm(dtp)_2(Et_2O)}]$, too.

Reactivity of the thulium(II) and samarium(II) complexes: Complex **5** is quite stable; pentane solutions of this compound appear unchanged for days at room temperature under dry argon. However, since **1** is known to react with dinitrogen,[11]

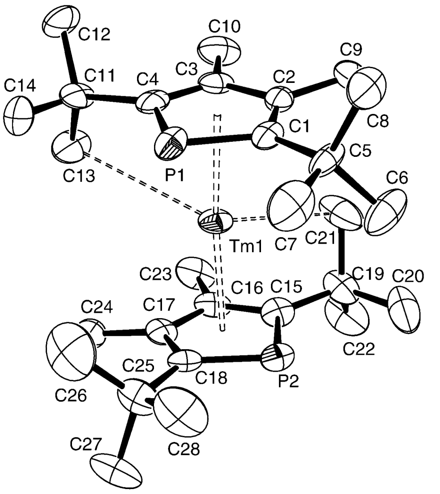
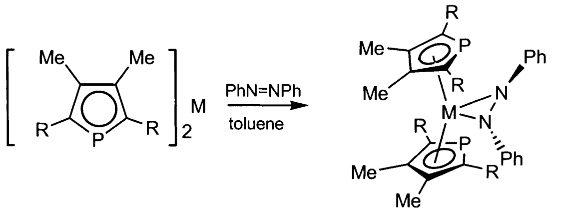


Figure 2. Structure of **5** (ORTEP plot; molecule 1, 50% ellipsoids, H atoms omitted). Selected distances [Å] and angles [°]: Tm1−P1 2.875(2), Tm1−P2 2.867(2), Tm1−C_{ring} (av) 2.73(3); Cnt-Tm1-Cnt 170, Tm1-C13 3.29, Tm1-C21 3.43.

we exposed pentane solutions of **5** and THF solutions of **2** and **4** to 1 atm of dinitrogen gas. After 8 h, no apparent change occurred in the colours of the reaction mixtures, which remained dark green, and the ^{31}P NMR spectra of the solutions were unchanged and still indicated the presence of the starting materials. Thus, under these conditions, no noticeable reaction of our thulium(II) complexes with nitrogen took place.

Another possibility to test the reactivity of thulium(II) complex **5** is reaction with an aromatic hydrocarbon such as anthracene, which is known to oxidise $[(C_5Me_5)_2Sm]$.[35] Thus, this hydrocarbon was added to toluene solutions of **5**, and of the samarium complexes **6** and **7**, and again no reaction took place after 8 h at room temperature.

Thus, it seems that the dsp and dtp ligands impart considerable stability to the lanthanide(II) centres. We thought that our samarium(II) and thulium(II) complexes should react with azobenzene, which is known to oxidise even ytterbium(II).[36] Addition of one equivalent of azobenzene to toluene solutions of **5**, **6** and **7** at room temperature resulted in the immediate formation of dark blue solutions from which we could respectively isolate $[Tm(dtp)_2(N_2Ph_2)]$ (**13**), $[Sm(dsp)_2(N_2Ph_2)]$ (**14**) and $[Sm(dtp)_2(N_2Ph_2)]$ (**15**) (Scheme 6). Complexes **13** and **14** were characterised by X-ray crystallography (Figure 3 and Table 1)



5: R = *t*Bu, M = Tm
6: R = $SiMe_3$, M = Sm
7: R = *t*Bu, M = Sm

13: R = *t*Bu, M = Tm
14: R = $SiMe_3$, M = Sm
15: R = *t*Bu, M = Sm

Scheme 6. Synthesis of azobenzene complexes.

The overall structure of these two complexes is similar to that of $[(C_5Me_5)_2Sm(N_2Ph_2)(THF)]$[36] in the sense that they all show η^2 coordination of the N_2Ph_2 ligand, and the C(Ph)-N-N′-C′(Ph) dihedral angle, which indicates the degree of bending of the ligand, is similar in **13** (41°), **14** (39°), and $[(C_5Me_5)_2Sm(N_2Ph_2)(THF)]$ (36°). In these three complexes, the N−N bond is substantially elongated relative to free azobenzene (**13** and **14**: 1.35 Å; $[(C_5Me_5)_2Sm(N_2Ph_2)(THF)]$: 1.32 and 1.39 Å), and thus indicates reduction of the ligand, so that the metal is in the trivalent state. This was confirmed by magnetic susceptibility measurements (Evans method), which gave the expected value for thulium(III) in **13** (μ_{eff} = 7.6 μ_B) and for samarium(III) in **14** (μ_{eff} = 1.9 μ_B) and **15** (μ_{eff} = 2.1 μ_B). Finally, the Sm−C and Sm−N bonds in **14** and $[(C_5Me_5)_2Sm(N_2Ph_2)(THF)]$ are similar, while these bonds

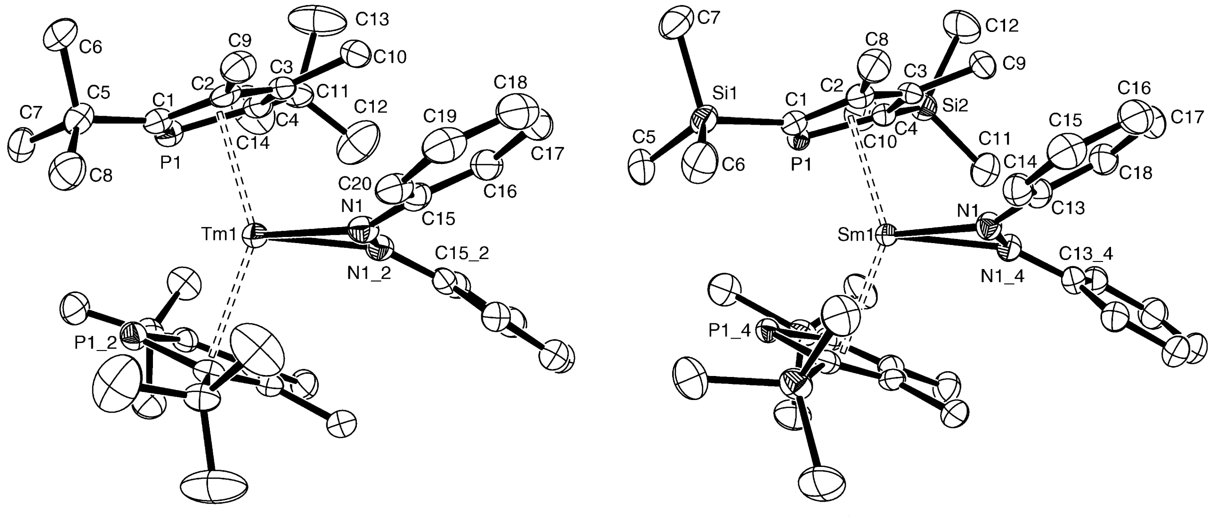
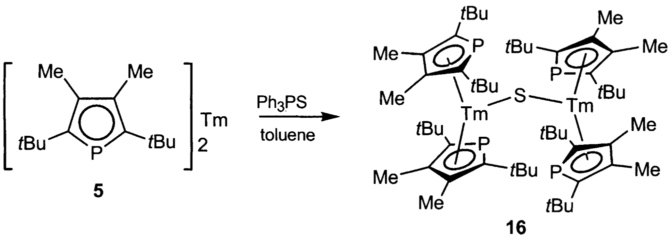


Figure 3. Structures of **13** and **14** (ORTEP plots; 50% ellipsoids, H atoms omitted). Selected distances [Å] and angles [°]: **13**: Tm1−P1 2.869(1), Tm1−C_{ring} (av) 2.75(1), Tm1−N1 2.292(3), N1−N1 2 1.351(5); N1-Tm1-N1 2 34.3(1), Cnt-Tm1-Cnt 143, C15-N1-N1 2-C13 2 41. **14**: Sm1−P1 2.9484(6), Sm1−C_{ring} (av) 2.80(1), Sm1−N1 2.364(2), N1−N1 4 1.351(4); N1-Sm1-N1 4 33.3(1), Cnt-Sm1-Cnt 140, C13-N1-N1 4-C13 4 39.

are shorter in **13**, a normal consequence of the lanthanide contraction.

Triphenylphosphane sulfide reacts with [$(C_5Me_5)_2$Yb(Et_2O)] and [$(C_5Me_5)_2$Sm(thf)$_2$] to give [{$(C_5Me_5)_2$Yb}$_2$(μ-S)][37] and [{$(C_5Me_5)_2$Sm(THF)}$_2$(μ-S)].[38] When we added Ph_3PS to toluene solutions of **13** at room temperature (Tm/Ph_3PS 2/1), an immediate colour change to yellow occurred, accompanied by the disappearance of the ^{31}P NMR signal of **13** and the appearance of a signal corresponding to Ph_3P. From this mixture, yellow crystals of [{Tm(dtp)$_2$}$_2$(μ-S)] (**16**) could be isolated (Scheme 7).



Scheme 7. Synthesis of the thulium sulfide complex.

By contrast, no noticeable change after 24 h at room temperature occurred when Ph_3PS was added to toluene or diethyl ether solutions of **14** and **15**. Thus, we have been able to find a system in which, in comparable environments, phospholylthulium(II) complexes are more reactive that their phospholylsamarium(II) homologues, as they indeed should be.

The X-ray crystal structure of **16** was determined (Figure 4). The overall structure of **16** is similar to those of [{$(C_5Me_5)_2$Yb}$_2$(μ-Se)][37] and [{$(C_5Me_5)_2$Sm(thf)}$_2$(μ-S)].[38] The Tm-S-Tm angle (165.3(2)°) is similar to the Sm-S-Sm angle (170.0(1)°). The Tm–S bonds (2.575(4) Å and 2.582(4) Å), are, as expected, slightly shorter than the Sm–S bonds in [{$(C_5Me_5)_2$Sm(THF)}$_2$(μ-S)] (2.663(1) Å and 2.665(1) Å). The observed magnetic moment of **16** corresponds to two noninteracting thulium(III) centers.

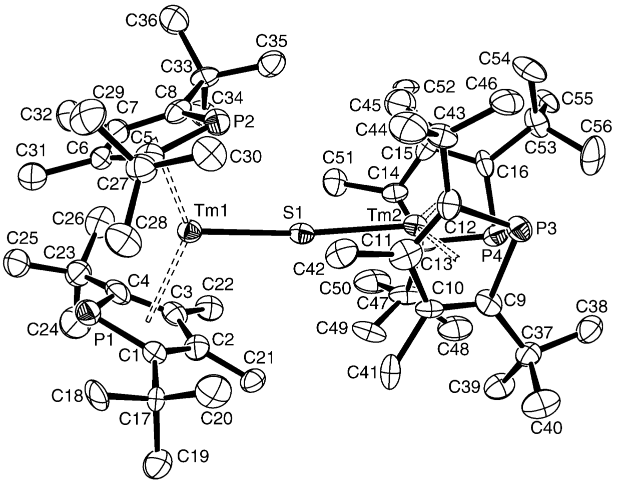


Figure 4. Structure of **16** (ORTEP plot; 50% ellipsoids, H atoms omitted). Selected distances [Å] and angles [°]: Tm1–S1 2.575(4), Tm2–S1 2.582(4), Tm–P(av) 2.875(7); S1-Tm1-S2, 165.3(2) Cnt-Tm-Cnt (av) 139

Conclusion

We have isolated and characterised [Tm(dsp)$_2$], a sandwich compound which is the first homoleptic complex of thulium(II). By contrast, [{Sm(dsp)$_2$}$_2$] and [{Sm(dtp)$_2$}$_2$] are dimers, probably because of the larger ionic radius of samarium(II). Our reactivity study revealed high stability of thulium(II) bound to the dtp ligand and low reactivity of samarium(II) and thulium(II) when coordinated by the dtp and dsp ligands. Our next goal will be to try to stabilise dysprosium(II) and neodymium(II) by interaction with phospholyl ligands, an objective that will certainly prove challenging.

Experimental Section

All manipulations involving lanthanide complexes were performed on a vacuum line or in a drybox under argon with dry, oxygen-free solvents. All other reactions were performed in Schlenk glassware under nitrogen. SmI_2,[37] complex **10**[26] and phospholide **8**[24] were prepared as previously described. TmI_2[7] was prepared by heating thulium metal and iodine in a silica apparatus similar to that described by Evans et al. for the synthesis of DyI_2.[8] For the synthesis of **5**, a small excess of TmI_2 was used to take into account possible contamination of this material by small amounts of residual thulium metal. All other reagents were commercial and used as received from the suppliers. Magnetic susceptibility data were obtained by the Evans NMR method. Elemental analyses were performed at the Service central d'analyses du CNRS, Vernaison, France and at the Service de microanalyse de l'université de Dijon, Dijon, France.

Diiodide 11: Solid iodine (27.26 g, 107 mmol) was added in small portions to an orange solution of zirconacyclopentadiene **10** (22.16 g, 54 mmol) in THF (300 mL) at 0°C. The solution gradually turned brown. After the addition, the reaction mixture was stirred at room temperature for 1 h. The solution was filtered and evaporated to dryness, and the residue was taken up in hexane and purified by chromatography on silica gel (hexane). **11** was obtained as white crystals (17.94 g, 40 mmol, 74%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.32$ (s, 18H), 1.99 ppm (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 18.82$ (CH_3), 33.08 (CH_3), 40.41 (C) 119.07 (C), 150.19 ppm (C); MS (70 eV): *m/z* (%): 318 $[M-I]^+$ (8), 136 (10).

Phosphole 12: A solution of **11** (17.94 g, 40 mmol) in Et_2O (200 mL) was cooled to −78°C and a 1.6 M solution of *n*BuLi (50 mL, 80 mmol) was added dropwise. After 1 h of stirring, the yellow solution was warmed to room temperature, stirred for 15 min, and cooled again to −78°C. $PhPCl_2$ (9.4 mL, 7.16 g, 40 mmol) was then added dropwise. The reaction mixture was warmed to room temperature and evaporated to dryness, and the residue purified by chromatography on silica gel (hexane). **12** was obtained as white crystals (9.57 g, 32 mmol, 79%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.05$ (s, 18H), 1.99 (d, J(H,P) = 2.5 Hz, 6H), 7.2 ppm (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 16.80$ (d, J(C,P) = 3 Hz, CH_3), 32.22 (d, J(C,P) = 7 Hz, CH_3), 34.43 (d, J(C,P) = 16.5 Hz, C), 128.00 (d, J(C,P) = 8 Hz, C), 128.66 (d, J(C,P) = 1.5 Hz, C), 134.14 (C) 135.12 (d, J(C,P) = 12 Hz, C), 143.26 (d, J(C,P) = 11.5 Hz, C), 149.95 ppm (d, J(C,P) = 2.5 Hz, C); ^{31}P NMR (122 MHz, $CDCl_3$) $\delta = 4.6$. MS (70eV): *m/z* (%): 299 $[M-H]^+$ (22), 188 (100); elemental analysis (%) calcd for $C_{20}H_{29}P$ (300.42): C 79.96, H 9.73; found: C 80.02, H 9.83.

Phospholide 9: A solution of **12** (4.0 g, 13.3 mmol) in DME (150 mL) and potassium metal (2.08 g, 53.3 mmol) were heated at 70°C for 1.5 h, during which the potassium melted and the reaction mixture turned dark yellow. The cooled reaction mixture was then filtered by using a positive pressure of argon gas. The filtrate was evaporated to dryness and recrystallised from THF. **9** was obtained as an air-sensitive white powder (3.12 g, 11.9 mmol, 89%). ^1H NMR (300 MHz, $[D_8]$THF): $\delta = 1.36$ (d, J(H,P) = 1.5 Hz, 18H), 2.17 ppm (s, 6H); ^{13}C NMR (75.5 MHz, $[D_8]$THF): $\delta = 17.09$ (CH_3), 33.86

(d, J(C,P) = 17 Hz, CH_3), 35.47 (d, J(C,P) = 19 Hz, C), 123.72 (C), 151.51 ppm (d, J(C,P) = 41 Hz, C); ^{31}P NMR (122 MHz, [D$_8$]THF): δ = 58.8 ppm.

General method for the synthesis of the Sm^{II} complexes: Dry diethyl ether was condensed at −78 °C onto a mixture of SmI_2 (1 equiv) and phospholide **8** or **9** (2 equiv). The reaction mixture was stirred at room temperature for 1 h, filtered and evaporated to dryness. The residue was taken up in pentane, whereupon **6** and **7** precipitated as green powders, which were filtered, rinsed with pentane and dried under vacuum.

Sm^{II} complex 6: From SmI_2 (0.137 g, 0.34 mmol) and **8** (0.200 g, 0.68 mmol): the diethyl ether solution was dark green, and 0.143 g of **8** was obtained (0.22 mmol, 64 %). ^{1}H NMR (300 MHz, C_6D_6): δ = 1.3 (br s, 6 H), 10.6 ppm (br s, 18 H); ^{31}P NMR (122 MHz, THF): δ = −383 ppm (br s); μ_{eff} = 3.6 μ_B; elemental analysis (%) calcd for $C_{24}H_{48}P_2Si_4Sm$ (661.29): C 43.59, H 7.32; found, C 43.52, H 7.31.

Sm^{II} complex 7: From SmI_2 (0.232 g, 0.57 mmol) and **9** (0.300 g, 1.14 mmol), the diethyl ether solution was purple, and 0.230 g of **8** was obtained (0.39 mmol, 67 %). ^{1}H NMR (300 MHz, C_6D_6): δ = −2.2 (br s, 6 H), 14.2 ppm (br s, 18 H); ^{31}P NMR (122 MHz, THF): δ = −519 ppm (br s); μ_{eff} = 3.6 μ_B; elemental analysis (%) calcd for $C_{28}H_{48}P_2Sm$ (596.99): C 56.33, H 8.10; found: C 56.27, H 8.02.

Tm^{II} complex 5: A solution of phospholide **9** (0.330 g, 1.26 mmol) and TmI_2 (0.300 g, 0.71 mmol) in diethyl ether (10 mL) was stirred for 24 h at room temperature. The dark green reaction mixture was filtered and evaporated to dryness. The resulting foam was taken up in pentane and concentrated, whereupon **5** precipitated as dark bluish green crystals, which were collected by filtration and dried under vacuum (0.240 g, 0.39 mmol, 62 %). ^{1}H NMR (300 MHz, C_6D_6): δ = 2.0 (br s, 6 H), 32.1 ppm (br s, 18 H); ^{31}P NMR (122 MHz, C_6D_6): δ = −257 ppm (br s); μ_{eff} = 4.7 μ_B. A correct elemental analysis could not be obtained for this compound.

General method for the synthesis of the azobenzene complexes 13, 14 and 15: A toluene (1 mL) solution of azobenzene (1 equiv) was added dropwise to a toluene (3 mL) solution of the Ln^{II} complex **5**, **6** or **7** (1 equiv). The solution immediately turned dark blue in all cases. The solution was evaporated to dryness, the residue taken up in pentane and the azobenzene complexes precipitated as dark bluish green powders, which were collected by filtration, rinsed with cold pentane, and dried under vacuum.

Tm^{III} complex 13: From **5** (0.075g, 0.12 mmol) and azobenzene (0.022 g, 0,12 mmol), 60 mg of **13** was obtained (0.07 mmol, 65 %). μ_{eff} = 7.6 μ_B; elemental analysis (%) calcd for $C_{40}H_{58}N_2P_2Tm$ (797.78): C 60.22, H 7.33, N 3.51; found: C 60.55, H 7.43, N 3.61.

Sm^{III} complex 14: From **6** (0.050 g, 0.075 mmol) and azobenzene (0.014 g, 0,076 mmol), 54 mg of **14** was obtained (0.064 mmol, 84 %). ^{1}H NMR (300 MHz, C_6D_6): δ = −1.24 (s, 36 H), 3.70 (s, 12 H), 71.9 ppm (br s, 4 H). The other phenyl protons were not detected. ^{31}P NMR (122 MHz, C_6D_6): δ = 148 ppm; μ_{eff} = 1.9 μ_B; elemental analysis (%) calcd for $C_{36}H_{58}N_2P_2Si_4Sm$ (843.51): C 51.26, H 6.93, N 3.32; found: C 51.28, H 6.93, N 3.20.

Sm^{III} complex 15: From **7** (0.075g, 0.12 mmol) and azobenzene (0.023g, 0,12 mmol), 76 mg of **15** was obtained (0.097 mmol, 78 %). ^{1}H NMR (300 MHz, C_6D_6): δ = −1.02 (s, 36 H), 2.70 (s, 12 H), 72.0 ppm (br s, 4 H). The other phenyl protons were not detected. ^{31}P NMR (122 MHz, C_6D_6) δ = 46 ppm; μ_{eff} = 2.1 μ_B; elemental analysis (%) calcd for $C_{40}H_{58}N_2P_2Sm$ (779.21): C 61.66, H 7.50, N 3.60; found: C 61.67, H 7.28, N 3.82.

Tm^{III} complex 16: A toluene (1 mL) solution of triphenylphosphane sulfide (0.012 g, 0.040 mmol) was added dropwise to a toluene (3 mL) solution of **5** (0.049 g, 0.079 mmol). The reaction mixture immediately turned yellow. After 2 h at room temperature, the reaction mixture was evaporated to dryness and taken up in pentane (2 mL), and the precipitate was centrifuged. The solution was evaporated to dryness and yellow crystals of **16** were obtained by crystallisation from pentane at −30 °C (0.020 g, 0.016 mmol, 38 %). μ_{eff} = 10.5 μ_B. A correct elemental analysis could not be obtained for this compound.

X-ray crystallography: Suitable single crystals of **5**, **13** and **14** were obtained from saturated pentane solutions at −30 °C, and of **6** and **7** by slow cooling of hot toluene solutions to room temperature. **16** was crystallised by slow evaporation of a pentane solution at room temperature. X-ray intensities were measured with a Nonius KappaCCD diffractometer at 150(1) K with Mo$_{K\alpha}$ radiation (λ = 0.71073 Å) and a graphite monochromator. A summary of the crystal structure determinations is presented in Table 1. CCDC-209835 – CCDC-209840 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

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