New Complexes of Divalent Thulium with Substituted Phospholyl and Cyclopentadienyl Ligands

François Nief,*[a] Brice Tayart de Borms,[a] Louis Ricard,[a] and Duncan Carmichael[a]

Keywords: Phosphorus heterocycles / Lanthanides / Subvalent compounds / Thulium / Cyclopentadienyl ligands

In order to try to stabilise the Tm^{II} ion with phospholyl ligands lacking methyl groups at the 3 and 4 positions, the following ligand precursors were prepared: sodium 2,5-di-*tert*-butylphospholyl [Na(Htp)] (**3**) and sodium 2,5-bis(trimethylsilyl)phospholyl [Na(Hsp)] (**8**). Because of its similar steric bulk, we also decided to use sodium di-*tert*-butylcyclopentadienyl [$NaCp^{tt}$] (**9**) as a ligand precursor. Compound **3** was obtained by sodium cleavage of the P–P bond of 2,5,2′,5′-tetra-*tert*-butyl-1,1′-diphosphole (**2**). Halogen-lithium exchange in 1,4-diiodo-1,4-bis(trimethylsilyl)buta-1,3-diene (**4**) followed by reaction with $PhPCl_2$ afforded 1-phenyl-2,5-bis(trimethylsilyl)phosphole (**5**). Treatment of **5** with lithium metal followed by oxidative treatment with iodine gave 2,5,2′,5′-tetrakis(trimethylsilyl)-1,1′-diphosphole (**7**) which could be transformed into **8** by treatment with sodium. Treatment of **3**, **8** and **9** with $[TmI_2(THF)_3]$ in diethylether yielded three new organothulium(II) complexes $[Tm(Htp)_2(THF)]$ (**10**), $[Tm(Hsp)_2(THF)]$ (**11**) and $[Tm(Cp^{tt})_2(THF)]$ (**12**), respectively, which could be isolated pure as crystalline solids in low to moderate yields. Complexes **10**, **11** and **12** were studied by X-ray crystallography and their structures compared with those of two previously described complexes, $[Tm(Cp'')_2(THF)]$ **1** [Cp′′ = 1,3-bis(trimethylsilyl)cyclopentadienyl] and $[Tm(Dtp)_2(THF)]$ (**13**) (Dtp = 3,4-dimethyl-2,5-di-*tert*-butylphospholyl). Although the phospholyl ligands may be slightly more bulky than their cyclopentadienyl counterparts, the structures of **1**, **10**, **11** and **12** are remarkably similar and are substantially different from that of the more bulky **13**.

Introduction

For a long time, the coordination chemistry of divalent lanthanide (Ln) ions has been limited to the classical Eu^{II}, Yb^{II} and Sm^{II}.[1] Although other Ln^{II} species can exit in the solid state, these ions were until recently considered too reactive to be isolated as molecular compounds.[2]

However, this statement has been challenged very recently by the isolation of molecular solvates of the type $[MI_2(solv.)_n]$ where M = Nd, Dy or Tm and solv. is a donor solvent such as THF or dimethoxyethane (DME).[3–7] As expected, these species are highly reducing. While solvated TmI_2[3,4] is reasonably stable, solvated DyI_2[6] and NdI_2[7] are highly reactive complexes which are only stable below room temperature.

In coordination chemistry, no other complexes of Nd^{II} and Dy^{II} have been isolated up to now although their transient nature has been postulated in trapping reactions. Likewise, some transient Tm^{II} complexes have also been observed this way. For instance the M^{II} cations can be trapped with nitrogen, forming [μ-(N_2^{2-})] complexes[8–10] or by oxidative splitting of the coordinated solvent[8,11] or the ligand[12] thus yielding M^{III} complexes. They are also able to reduce aromatic hydrocarbons[6,13] or acetonitrile.[14] Interestingly, reduction of Ho^{III} or Y^{III} amides in the presence of nitrogen also yields products in which N_2 has been activated.[15]

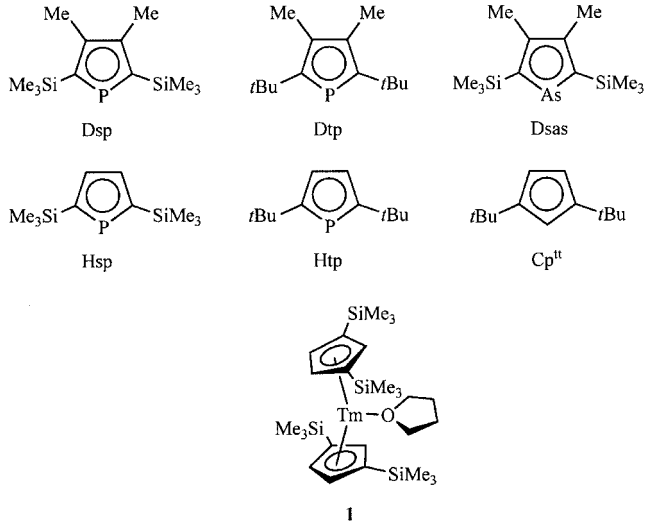
In the case of Tm^{II}, however, after some unsuccessful attempts, Evans et al. isolated the first structurally characterised organometallic complex of thulium(II), $[TmCp''_2(THF)]$ (**1**) [Cp′′ = $C_5H_3(SiMe_3)_2$].[8] Since then, by using very bulky phospholyl or arsolyl ligands, we have been able to isolate several other Tm^{II} compounds[16,17] including a homoleptic complex.[17] The chemistry of the "new" divalent lanthanides has been very recently reviewed.[18]

The phospholyl and arsolyl ligands appear particularly suitable for the stabilisation of low-valent complexes because of their reduced π-donating ability. So far, we have used the following ligands around Tm^{II}: Dsp = $PC_4Me_2(Tms)_2$, Dsas = $AsC_4Me_2(Tms)_2$ and Dtp = $PC_4Me_2tBu_2$. These ligands differ from the Cp′′ ligand by the presence of the heteroatom in the ring but also by their higher bulkiness due to the presence of two extra methyl groups as substituents.

At this point, we wanted to expand the scope of Tm^{II} chemistry by synthesising new complexes which would be sterically more similar to that of Evans (**1**).[8] Thus, we decided to attempt to stabilise the Tm^{II} ion with phospholyl

[a] Laboratoire Hétéroéléments et Coordination, CNRS UMR 7653, DCPH, Ecole Polytechnique,
91128 Palaiseau, France
Fax: +33-1-69333990
E-mail: nief@poly.polytechnique.fr

ligands lacking the two methyl groups on the rings which are present in Dsp and Dtp. These ligands are Hsp = $PC_4H_2(Tms)_2$ and Htp = $PC_4H_2tBu_2$. In order to have a complete picture, we also decided to use the well known Cp^{tt} ligand [Cp^{tt} = $C_5H_3tBu_2$] (Scheme 1). Interestingly, Lappert has recently characterised an unusual La^{II} anionic complex with this ligand, namely [K(18-crown-6)(η-$C_6H_6)_2$][$(LaCp^{tt}_2)_2$(μ-C_6H_6)] by reduction of the trivalent precursor [$(LaCp^{tt}_2)_3$].[19]



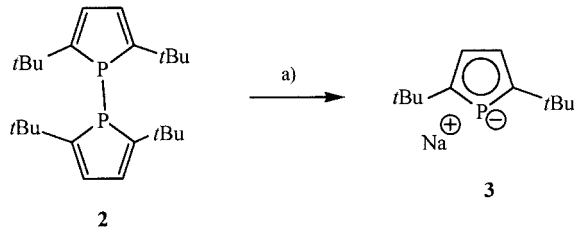
Scheme 1. Ligands and complexes in Tm^{II} chemistry

In this paper we report the synthesis of the new ligand Hsp, the synthesis of three new Tm^{II} complexes with the Hsp, Htp and Cp^{tt} ligands, and a structural study of these complexes by comparison with that of **1**.

Results and Discussion

Ligands

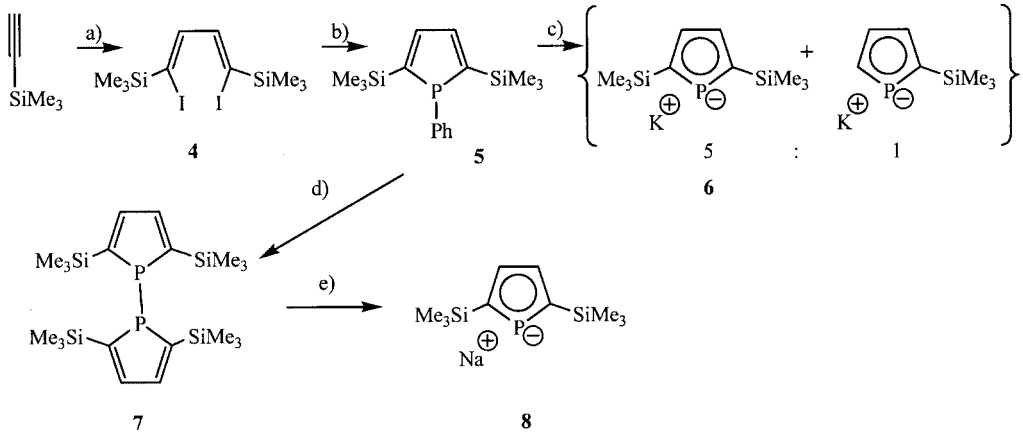
The synthesis of 2,5,2′,5′-tetra-*tert*-butyl-1,1′-diphosphole $(Htp)_2$ (**2**) has been described in the literature.[20] The new ligand precursor [Na(Htp)] (**3**) was simply obtained in good yield by sodium cleavage of the P–P bond in **2** (Scheme 2).



Scheme 2. Synthesis of Na(Htp) (**3**); reagents and conditions: a) excess Na, THF, room temp., 85%

The Hsp ring has not been described in the literature although Sato et al. have recently described a silole (silacyclopentadiene) possessing the same substituents on the heterocyclic ring. These authors, using trimethylsilylacetylene as a starting material, employed Ti^{II}-based chemistry in order to prepare 1,4-diiodo-1,4-bis(trimethylsilyl)buta-1,3-diene (**4**) as a key intermediate. Further iodine-lithium exchange followed by treatment with $Si(OEt)_4$ allowed them to isolate 1,1-dimethoxy-2,5-bis(trimethylsilyl)silole.[21]

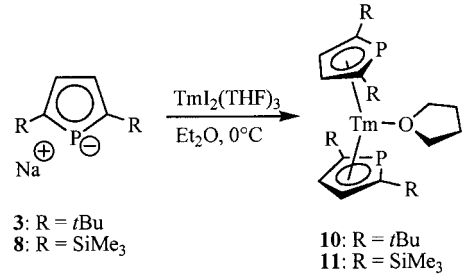
Compound **4** was prepared with slight modifications to the original procedure due to scale-up. Iodine-lithium exchange in **4** with *n*BuLi in Et_2O followed by treatment with $PhPCl_2$ gave 1-phenyl-2,5-bis(trimethylsilyl)phosphole (**5**) in fair yield. Further treatment of **5** with potassium metal under the conditions previously used for the synthesis of [K(Dsp)][16] was less satisfactory and although [K(Hsp)] (**6**) was obtained as the major product, it was invariably contaminated with up to 20% of a product resulting from desilylation, i.e. [K{$PC_4H_3(SiMe_3)$}] (^{31}P NMR: δ = 116 ppm). Although repeated extraction of the crude solid with Et_2O could reduce the side product content of **6** to less than 10%, we nevertheless sought a better synthesis of the Hsp anion. We found that no concomitant desilylation took place when **4** was treated with lithium instead of potassium and the



Scheme 3. Synthesis of Na(Hsp) (**8**); reagents and conditions: a) $Ti(OiPr)_4$ + *i*PrMgCl, Et_2O, –78 °C to –50 °C, 2 h, then I_2, –50 °C to room temp., 2 h, 67%; b) 2 *n*BuLi, Et_2O, –78° to room temp., 1h, then $PhPCl_2$, –78° to room temp., 30 min, 42%; c) excess K, DME, 70 °C, 2h; d) excess Li, THF, room temp., 3 h, then $AlCl_3$, 0 °C, 30 min, then I_2, room temp., 15min, 66%; e) excess Na, THF, room temp., 79%

resultant [Li(Hsp)] could be transformed, in situ, into $(Hsp)_2$ (**7**) by treatment with iodine. Pure [Na(Hsp)] (**8**) was then obtained by treatment of **7** with sodium in THF (Scheme 3).

Finally, 1,3-di-*tert*-butylcyclopentadiene (HCp^{tt}) was prepared by literature methods[22] and transformed into [$NaCp^{tt}$] (**9**) by treatment with $NaNH_2$ in THF.[23]



Scheme 4. Synthesis of Tm^{II} phospholyl complexes

New Complexes of Thulium(II)

We then tried to synthesise Tm^{II} complexes of the Htp, Hsp and Cp^{tt} ligands by utilising their sodium salts (**3**, **8**, and **9**, respectively) in reactions with [$TmI_2(THF)_3$], in a 2:1 mole ratio, at 0 °C and with diethylether as a solvent. With the phospholyl anions **3** and **8**, the reaction mixtures quickly turned dark green. After 1 hour, the solutions were checked by ^{31}P NMR spectroscopy and the spectra showed complete disappearance of the starting anions and the presence of two new, broad peaks at δ = –290 and –235 ppm, respectively, with Htp and Hsp as the ligands. These signals provided good evidence for the presence of Tm^{II} phospholyl complexes, their chemical shifts being similar to those of the already described [$Tm(Dtp)_2(THF)$] and [$Tm(Dsp)_2$-(THF)].[16] Complexes formulated as [$Tm(Htp)_2(THF)$] (**10**) and [$Tm(Hsp)_2(THF)$] (**11**) could be subsequently isolated as dark green crystalline powders from pentane at –30 °C (Scheme 4).

Complexes **10** and **11** exhibit reasonably well-resolved (and quite similar) proton NMR spectra in C_6D_6. Whilst the methyl groups could be clearly identified at low field (δ = 57 ppm for **10** and 43 ppm for **11**), the remaining signals (corresponding to the coordinated THF and the β-protons on the ring) were present as three sets of broad humps at high field which were difficult to integrate accurately due to their large width and baseline roll. In order to simplify this situation, we decided to prepare an analogue of **10** in which the THF was replaced by perdeuterated THF. This was accomplished by allowing **3** to react with unsolvated TmI_2 in diethylether in the presence ofca. 0.1 mL of [D_8]THF. Afterstandard workup, [$Tm(Htp)_2$([D_8]THF)] (**10-d**) could be isolated and its proton spectrum is presented below together with that of **10** (Figure 1).

A comparison of these spectra suggests that the signals around –30 ppm and –45 ppm in **10** belong to the THF solvent and that the peak at highest field around –70 ppm corresponds to the β-protons on the phospholyl ring. The assignment of the high-field signals in the spectrum of **11** was inferred accordingly (see experimental section). Finally, magnetic susceptibility measurements confirmed the +II oxidation state of thulium in **10** and **11**.

The reaction of **9** with [$TmI_2(THF)_3$] proceeded similarly to those described above but the solution colour was purplish-red. Evaporation to dryness of the filtered solution induced some apparent decomposition of the product since further extraction with pentane invariably resulted in the

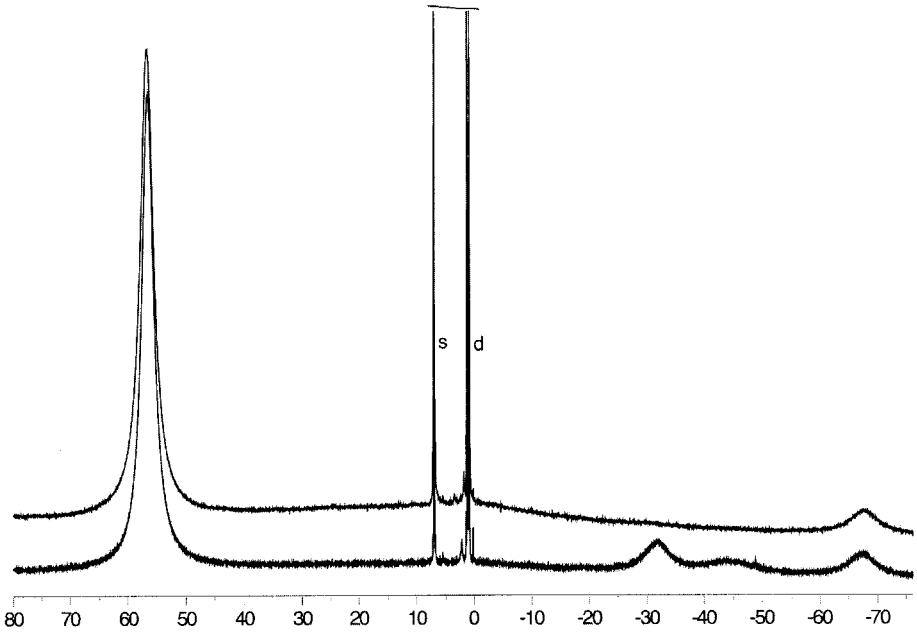
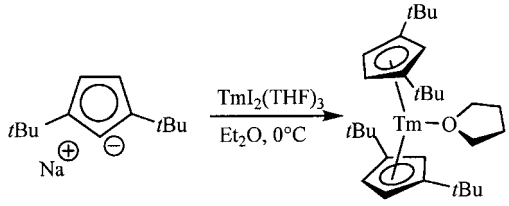


Figure 1. Proton NMR spectra (C_6D_6 solutions, ppm values) of **10**–**d** (upper trace) and **10** (lower trace) (s = C_6D_5H, d = diamagnetic impurities)

precipitation of large amounts of white, insoluble material (this was not the case with the phospholyl compounds). We found that a red crystalline solid, formulated as [Tm(Cp^{tt})$_2$(THF)] (**12**) could be obtained in low yield by concentrating the filtered reaction mixture by evaporation of diethylether and allowing the solution to stand at –30 °C for two days. The proton NMR spectra of a solution of these crystals in [D_6]benzene or [D_{12}]cyclohexanedisplayed a peak at δ = 63 ppm which can reasonably be attributed to the methyl groups but the other parts of the spectra were less clear. We found that for **12** μ_{eff}= 4.6 μ_B, a value which is compatible with Tm^{II} (Scheme 5).



9 **12**

Scheme 5. Synthesis of a Tm^{II} cyclopentadienyl complex

Diethyl ether solutions of **10**, **11** and **12** were then exposed to 1atm. of nitrogen. In the case of **10** and **11**, no reaction had taken place after 24h at room temperature. In contrast, in the case of **12**, a colour change to light brown occurred within a few minutes. Unfortunately, however, despite several attempts, we could not isolate any crystalline product from this reaction mixture. Thus, no definite compounds could be isolated from the reaction of our new Tm^{II} complexes with N_2. Nevertheless, we can confirm that coordination of the phospholyl ligand considerably lessens the reactivity of thulium(II).

X-ray Crystal Structures

Suitable crystals of **10**, **11** and **12** were obtained by low-temperature crystallisation. A summary of the X-ray data is presented in Table 1 and Figure 2 shows ORTEP plots of one molecule each of **10**, **11** and **12**, respectively.

In the structures of **11** and **12**, the Tm–O bond coincides with a crystallographic symmetry axis. In addition, in **12**, the coordinated THF molecule is disordered over two positions and only one is presented in Figure 2. Table 2 displays relevant distances and angles for **10**, **11** and **12** together with relevant data for **1**[8] (the trimethylsilyl analogue of **12**) and [Tm(Dtp)$_2$(THF)] **13**[16] (analogue of **10** with two methyl substituents on the phospholyl ring).

The structures of **1**, **10**, **11** and **12** are strikingly similar. The Tm–O bond lengths and the ligand bending, as indicated by both the centroid-Tm-centroid angles and the dihedral angles between the mean planes of the π-ligands (referred to as ligand plane angles in Table 2), are almost identical in these four complexes. The main difference between the phospholyl complexes **10** and **11** and their cyclopentadienyl analogues (**12** and **1**, respectively) is that in **10** and **11** the C–Tm bonds are longer. This is probably due to the fact that the phospholyl complexes have to accommodate a long P–Tm bond in the Tm^{II} coordination sphere. Incidentally, this bond length in **10** and **11** falls in the range of the tabulated values for Yb^{II}–P bonds[24] (the ionic radii of Yb^{II} and Tm^{II} are similar). On these grounds, the steric bulk of the Hsp and Htp ligands should be larger than their all-carbon counterparts (Cp'' and Cp^{tt}, respectively). However, this is not reflected by the Tm–O distances and ligand bending in **1**, **10**, **11** and **12**. On the contrary, in **13**, all parameters relevant to steric crowding (Tm–O and Tm–C bond lengths, cnt–Tm–cnt and ligand plane angles) are higher than in **1**, **10**, **11** and **12**. This is most likely due to inter-

Table 1. Crystallographic data and data collection parameters

Compound	**10**	**11**	**12**
Mol. formula	$C_{28}H_{48}OP_2Tm$	$C_{24}H_{48}OP_2Si_4Tm$	$C_{30}H_{50}OTm$
Mol. mass	631.53	695.85	595.63
Crystal habit	green block	green block	deep red block
Crystal size [mm]	0.20 × 0.18 × 0.18	0.20 × 0.20 × 0.20	0.18 × 0.16 × 0.16
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$ (No.14)	$C2/c$ (No.15)	$Pbcn$ (No.60)
a [Å]	11.2140(10)	20.2000(10)	10.9610(10)
b [Å]	17.0150(10)	11.1120(10)	15.2930(10)
c [Å]	15.4690(10)	14.9950(10)	17.1860(10)
β [°]	91.0540(10)	98.7800(10)	90
V [Å^3]	2951.1(4)	3326.4(4)	2880.8(4)
Z	4	4	4
d [g cm^{-3}]	1.421	1.389	1.373
F(000)	1292	1420	1228
μ [cm^{-1}]	3.132	2.922	3.098
Maximum θ [°]	30.00	30.03	30.03
Reflections measured	14403	13656	7936
Unique data	8577	4849	4221
R_{int}	0.0176	0.0663	0.0279
Reflections used	7111	3826	2778
wR_2 (all data)	0.0714	0.0912	0.1549
R_1	0.0275	0.0374	0.0544
GoF	1.034	0.965	1.102

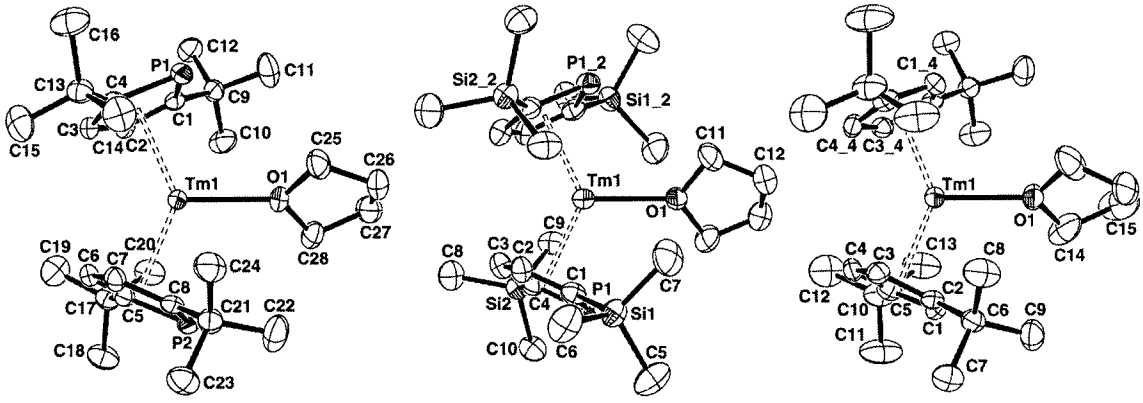


Figure 2. ORTEP plots of **10**, **11** and **12** together with the numbering schemes used (50% probability ellipsoids, H atoms omitted)

Table 2. Selected distances [Å] and angles [°] for complexes **1**, **10**, **11**, **12** and **13**

Distances [Å]	**1**[8]	**10**	**11**	**12**	**13**[16]
Tm–O	2.365(5)	2.393(2)	2.398(3)	2.388(7)	2.455(2)
Tm–C (min./av./max.)	2.65/2.68/2.71	2.72/2.76/2.80	2.72/2.75/2.79	2.65/2.68/2.74	2.77/2.83/2.90
Tm–P	–	2.941(2) (av.)	2.921(1)	–	2.95(1) (av.)
Tm–centroid (cnt)	2.39	2.45 (av.)	2.46	2.40	2.53 (av.)
Angles [°]					
Cnt–Tm–cnt	135	135	130	136	145
Ligand planes	133	131	128	131	146

ring steric repulsion of the methyl groups in **13**. Thus, adding methyl groups to the ring induces more structural changes than a CH ↔ P substitution.

Conclusions

In this report, we have described access to the new 2,5-bis(trimethylsilyl)phospholyl (Hsp) ring system and the successful isolation of two new Tm^{II} phospholyl complexes, [$Tm(Htp)_2(THF)$] (**10**) and [$Tm(Hsp)_2(THF)$] (**11**) as well as the second Tm^{II} cyclopentadienyl complex, [$Tm(Cp^{tt})_2$-(THF)] (**12**). Preliminary studies seem to indicate that the reactivity of **12** is higher than that of **10** and **11**.

We feel that organothulium(II) π complexes can no longer be considered as rarities. They are not especially difficult to isolate as long as the ligands provide adequate steric protection of the Tm^{II} environment and oxygen, nitrogen and water are excluded during their synthesis. We are convinced that many more Tm^{II} compounds can be made, thus opening the way to more studies of the chemistry of divalent thulium.

Experimental Section

General Remarks: All manipulations involving lanthanide complexes were performed on a vacuum line or in a drybox under argon using dry, oxygen-free solvents. All other reactions were performed in Schlenk glassware under nitrogen. Diphosphole (**2**)[20] and TmI_2[17] were prepared as described previously. [$TmI_2(THF)_3$] was obtained by extraction of TmI_2 with THF. 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 de microanalyse du CNRS, Gif-sur-Yvette, France, and at the Service de microanalyse de l′université de Dijon, Dijon, France.

Phospholyl 3: To a solution of diphosphole **2**[20] (1.5 g, 3.84 mmol) in THF (30 mL) at room temperature was added excess sodium in small pieces (0.35 g). After 3 h, the remaining sodium was removed from the reaction mixture which was then evaporated to dryness under vacuum. The residue was rinsed with hexane and sodium 2,5-di-*tert*-butylphospholyl (**3**) was obtained as an air-sensitive white powder which was dried in vacuo (1.43 g, 6.55 mmol, 85%). ^{1}H NMR (300 MHz, [D_8]THF): δ = 1.32 (s, 18 H, CH_3), 6.47 ppm (d, J_{HP} = 4 Hz, 2 H, CH). ^{13}C NMR (75.5 MHz, [D_8]THF): δ = 35.2 (d, J_{CP} = 18 Hz, C), 35.3 (d, J_{CP} = 8 Hz, CH_3), 113.1 (d, J_{CP} = 2 Hz, C3), 160.3 ppm (d, J_{CP} = 47 Hz, C2). ^{31}P NMR (122 MHz, [D_8]THF): δ = 56 ppm.

Diiodide 4:[21] This was prepared by a modification of the literature procedure. To a diethylether (300 mL) solution of $Ti(OiPr)_4$ (18 mL, 17.28 g, 60.7 mmol) and TmsCCH (14 mL, 9.94 g, 103 mmol) at –70 °C was added an ether solution of *i*PrMgCl (60 mL of 2 M soln., 120 mmol) The mixture was warmed to –50 °C over 1 h. After stirring for an additional 1 h, I_2 (31.75g, 125 mmol) was added as a solid to the mixture at –50 °C. The mixture was warmed to room temperature and stirred for 2 h. A saturated aqueous solution of $Na_2S_2O_3$ was then added and the mixture was extracted with hexane. The extract was dried with $MgSO_4$, filtered and evaporated whereupon the resultant oil partially crystallised. The residue was recrystallised from methanol at 0 °C and 1,4-diiodo-1,4-bis(trimethylsilyl)buta-1,3-diene (**4**) (15.15g, 33.6 mmol, 67%) was obtained as tan crystals. ^{1}H NMR (300 MHz, C_6D_6): δ = 0.14 (s, 18 H, CH_3), 7.31 ppm (s, 2 H, CH).

Phosphole 5: A solution of diiodide **4** (9 g, 20 mmol) in diethylether (80 mL) was cooled to –78 °C and a solution of *n*BuLi in hexane (30 mL of 1.33 M soln., 40 mmol) was added dropwise. After 1 h stirring at this temperature, a solution of $PhPCl_2$ (4.5 g, 25 mmol)

in hexane (20 mL) was added dropwise and the reaction mixture was allowed to warm to room temperature. The solution was then evaporated to dryness and taken up in a 1:1 hexane/satd. aq. $NaHCO_3$ mixture (200 mL). This mixture was decanted, the aqueous phase extracted with hexane, the combined organic phases dried with $MgSO_4$ and the solvents evaporated to dryness. The residue was chromatographed on silica gel using hexane as the eluent. The compound 1-phenyl-2,5-bis(trimethylsilyl)phosphole (**5**) was obtained as a colourless oil (2.55 g, 8.37 mmol, 42%). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.11 (s, 18 H, CH_3) 6.95 (m, 3 H, Ph), 7.21 (d, J_{HP} = 19.5 Hz, 2 H, CH), 7.25 ppm (m, 2 H, Ph). ^{13}C NMR (75.5 MHz, C_6D_6): δ = 0.18 (d, J_{CP} = 2.5 Hz, CH_3), 128.4 (d, J_{CP} = 9.0 Hz, C *meta*-Ph), 129.8 (d, J_{CP} = 1.5 Hz, C *para*-Ph), 131.0 (d, J_{CP} = 8.5 Hz, C *ipso*-Ph), 135.0 (d, J_{CP} = 20.5 Hz, C *ortho*-Ph), 144.9 (d, J_{CP} = 10.5 Hz, C3), 158.4 ppm (d, J_{CP} = 31.5 Hz, C2). ^{31}P NMR (122 MHz, C_6D_6): δ = 38.5 ppm. MS (70 eV, CI/NH_3): *m*/*z* (%) 305 $[M + H]^+$ (100). $C_{16}H_{25}PSi$ (304.5): calcd. C 63.1, H 8.3; found C 63.0, H 8.3.

Diphosphole 7: A solution of phosphole **5** (1 g, 3.28 mmol) in THF (30 mL) was treated with lithium metal (0.18 g, excess). After 3 h at room temperature, the excess lithium was removed and the solution was treated with $AlCl_3$ (0.15 g, 1.1 mmol). After 30min at room temperature, solid iodine (0.42 g, 1.64 mmol) was added to the reaction mixture which was then evaporated to dryness under vacuum. The crystalline residue was dissolved in hexane, the solution was evaporated and the resultant solid recrystallised from methanol. The product 2,5,2′,5′-tetrakis(trimethylsilyl)-1,1′-diphosphole (**7**) was obtained as pale yellow crystals (0.49 g, 2.16 mmol, 66%). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.27 (s, 36 H, CH_3), 7.22 ppm (pseudo-t, $J_{HP(app.)}$ = 22 Hz, 4 H, CH). ^{13}C NMR (75.5 MHz, C_6D_6): δ = 0.63 (s, CH_3) 144.6 (pseudo-t, $J_{CP(app.)}$ = 16 Hz, C3), 152.1 ppm (pseudo-t, $J_{CP(app.)}$ = 37 Hz, C2). ^{31}P NMR (122 MHz, C_6D_6): δ = –3 ppm. MS (70 eV, CI/NH_3) *m*/*z* (%) 455 $[M + H]^+$ (100). $C_{20}H_{40}P_2Si_4$ (454.8): calcd. C 52.8, H 8.9; found C 52.7, H 9.0.

Phospholyl 8: This was prepared similarly to **3** by cleavage of diphosphole **7** (0.3 g, 0.66 mmol) with sodium (0.15 g, excess) in THF solution (10 mL). Yield: 0.26 g (1.04 mmol, 79%) of sodium 2,5-bis(trimethylsilyl)phospholyl (**8**) as an air-sensitive white powder. ^{1}H NMR (300 MHz, [D$_8$]THF): δ = 0.19 (s, 18 H, CH_3), 7.14 ppm (d, J_{HP} = 8.5 Hz, 2 H, CH). ^{13}C NMR (75.5 MHz, [D$_8$]THF): δ = 2.50 (d, J_{CP} = 2 Hz, CH_3) 127.5 (d, J_{CP} = 2 Hz, C3), 144.4 ppm (d., J_{CP} = 67.5 Hz, C2). ^{31}P NMR (122 MHz, [D$_8$]THF): δ = 145 ppm. $C_{10}H_{20}NaPSi_2$ (250.4): calcd. C 48.0, H 8.0; found C 48.0, H 7.6.

General Method for the Synthesis of the Tm^{II} Complexes: Dry diethylether was condensed at –78 °C onto a mixture of $TmI_2(THF)_3$ (1 equiv.) and the anions **3**, **8** or **9** (2 equiv.). The reaction mixture was stirred at 0 °C for 2 h then worked up as described below.

Complex 10: This was prepared from $TmI_2(THF)_3$ (0.150 g, 0.23 mmol) and **3** (0.102 g, 0.47 mmol). The dark green solution was evaporated to dryness and the residue extracted with pentane. The pentane solution was evaporated to dryness and the residue rinsed with cold pentane. Yield 0.056 g of **6** as dark green crystals (0.089 mmol, 38%). ^{1}H NMR (300 MHz, C_6D_6): δ = –68 (br., 4 H, CH), –44 (br., 4 H, THF), –32 (br., 4 H, THF), 57 ppm (br., 36 H, CH_3). ^{31}P NMR (122 MHz, C_6D_6): δ = –290 ppm (br). μ_{eff} = 4.7 μ_B.

Complex 11: This was prepared from $TmI_2(THF)_3$ (0.128 g, 0.200 mmol) and **8** (0.100 g, 0.40 mmol). The dark green solution was filtered, evaporated to dryness and the residue dissolved in pentane. The pentane solution was filtered, concentrated to a small volume and cooled to –30 °C whereupon the product crystallised. Complex **11** was obtained as dark green crystals (0.067 g, 0.096 mmol, 48%). ^{1}H NMR (300 MHz, C_6D_6): δ = –63 (br., 4 H, CH), –52 (br., 4 H, THF), –34 (br., 4 H, THF), 43 ppm (br., 36 H, CH_3). ^{31}P NMR (122 MHz, C_6D_6): δ = –240 ppm (br. s). μ_{eff} = 4.7 μ_B.

Complex 12: This was prepared from $TmI_2(THF)_3$ (0.200 g, 0.31 mmol) and **9** (0.26 g, 0.62 mmol). The purplish-red solution was filtered and concentrated to a small volume and this solution was kept for 2 days at –30 °C whereupon the product crystallised. Complex **11** was obtained as a dark reddish-purple powder (0.036 g, 0.06 mmol, 19%). ^{1}H NMR (300 MHz, C_6D_6): δ = 63 ppm (br. s, CH_3). Other small peaks were present at 89, 83 and –77 ppm. μ_{eff}= 4.6 μ_B.

X-ray Crystallographic Study: Suitable single-crystals of **10** and **11** were obtained from saturated pentane solutions at –30 °C and those of **12** were obtained from a saturated diethylether solution at –30 °C. X-ray intensities were measured with a Nonius KappaCCD diffractometer at 150(1) K using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). A summary of the crystal structure determinations is presented in Table 1. CCDC-250697–250699 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

Financial support from CNRS and Ecole Polytechnique is gratefully acknowledged.

[1] F. T. Edelmann, in *Comprehensive Organometallic Chemistry II*, vol. 4 (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon Press, Oxford (UK), **1995**, pp. 12–130.
[2] S. A. Cotton, in *Encyclopaedia of Inorganic Chemistry, vol. 7* (Editor in chief: R. B. King), John Wiley & Sons, Chichester (UK), **1994**, pp. 3595–3619.
[3] M. N. Bochkarev, I. L. Fedushkin, A. A. Fagin, T. V. Petrovskaia, J. W. Ziller, R. N. R. Broomhall-Dillard, W. J. Evans, *Angew. Chem.* **1997**, *109*, 123–124; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 133–135.
[4] W. J. Evans, N. T. Allen, *J. Am. Chem. Soc.* **2000**, *122*, 2118–2119.
[5] M. N. Bochkarev, A. A. Fagin, *Chem. Eur. J.* **1999**, *5*, 2990–2992.
[6] W. J. Evans, N. T. Allen, J. W. Ziller, *J. Am. Chem. Soc.* **2000**, *122*, 11749–11750.
[7] M. N. Bochkarev, I. L. Fedushkin, S. Dechert, A. A. Fagin, H. Schumann, *Angew. Chem.* **2001**, *113*, 3268–3270; *Angew. Chem. Int. Ed.* **2001**, *40*, 3176–3178.
[8] W. J. Evans, N. T. Allen, J. W. Ziller, *Angew. Chem.* **2002**, *114*, 369–371; *Angew. Chem. Int. Ed.* **2002**, *41*, 359–361.
[9] W. J. Evans, N. T. Allen, J. W. Ziller, *J. Am. Chem. Soc.* **2001**, *123*, 7927–7928.
[10] W. J. Evans, G. Zucchi, J. W. Ziller, *J. Am. Chem. Soc.* **2003**, *125*, 10–11.
[11] I. L. Fedushkin, F. Girgsdies, H. Schumann, M. N. Bochkarev, *Eur. J. Inorg. Chem.* **2001**, 2405–2410.
[12] I. Korobkov, G. Aharonian, S. Gambarotta, G. P. A. Yap, *Organometallics* **2002**, *21*, 4899–4901.
[13] I. L. Fedushkin, M. N. Bochkarev, S. Dechert, H. Schumann, *Chem. Eur. J.* **2001**, *7*, 3558–3563.
[14] M. N. Bochkarev, G. V. Khoroshenkov, H. Schumann, S. Dechert, *J. Am. Chem. Soc.* **2003**, *125*, 2894–2895.

[15] W. J. Evans, D. S. Lee, J. W. Ziller, *J. Am. Chem. Soc.* **2004**, *126*, 454–455.
[16] F. Nief, D. Turcitu, L. Ricard, *Chem. Commun.* **2002**, 1646–1647.
[17] D. Turcitu, F. Nief, L. Ricard, *Chem. Eur. J.* **2003**, *9*, 4916–4923.
[18] M. N. Bochkarev, *Coord. Chem. Rev.* **2004**, *248*, 835–851.
[19] M. C. Cassani, D. J. Duncalf, M. F. Lappert, *J. Am. Chem. Soc.* **1998**, *120*, 12958–12959.
[20] D. Carmichael, L. Ricard, F. Mathey, *J. Chem. Soc., Chem. Commun.* **1994**, 1167–1168.
[21] S. Yamaguchi, R.-Z. Jin, K. Tamao, F. Sato, *J. Org. Chem.* **1998**, *63*, 10060–10062.
[22] R. Riemschneider, *Z. Naturforsch., Teil B* **1963**, *18*, 641–645.
[23] M. Schultz, C. J. Burns, D. J. Schwartz, R. A. Andersen, *Organometallics* **2000**, *19*, 781–789.
[24] F. Nief, *Coord. Chem. Rev.* **1998**, *178–180*, 13–81.

Received: September 22, 2004

