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Synthesis and structure of phospholyl- and arsolylthulium(II) complexes

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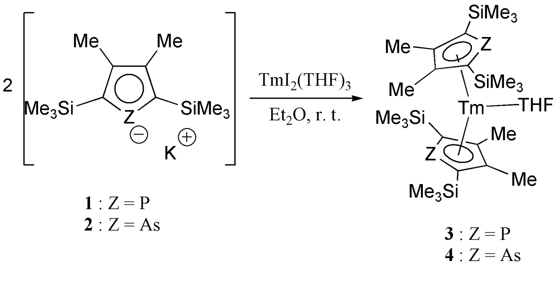
Reaction of thulium diiodide with substituted phospholide and arsolide salts respectively afforded stable bis(phospholyl)- and bis(arsolyl)thulium(II) complexes, that were characterised by multinuclear NMR and X-ray crystal structures, thus showing the beneficial effects of the steric and electronic properties of crowded phospholyl and arsolyl ligands for the stabilisation of divalent thulium.

Until very recently, the organometallic and coordination chemistry of divalent lanthanides was traditionally restricted to three 'classical' elements: europium, ytterbium, and samarium.[1] However, in the last few years, several molecular coordination complexes of lanthanide diiodides with ethers have been structurally characterised with the 'non-classical' Tm,[2,3] Dy[4] and Nd.[3] As expected, these compounds have very high reducing power.[4–6] To date, although several transient 'non-classical' divalent organolanthanides have been detected by trapping experiments,[4,7,8] only two such compounds have been isolated and structurally characterised: $[(\mathrm{Cp''}_2\mathrm{Tm(thf)}]$[9] ($\mathrm{Cp''} = \mathrm{C_5H_3(SiMe_3)_2}$) and $[\mathrm{K(18\text{-}C\text{-}6)}(\eta\text{-}\mathrm{C_6H_6})_2][(\mathrm{LaCp^{tt}}_2)_2(\mu\text{-}\mathrm{C_6H_6})]$[10] ($\mathrm{Cp^{tt}} = \mathrm{C_5H_3(CMe_3)_2}$); thus the successful isolation of such 'non-classical' complexes would depend on the proper combination of ligand, solvents and reaction conditions.[9,11] The phospholyl and arsolyl ligands appear well qualified for this purpose: their reduced π-donating ability[12] is well suited to the very electron-rich 'non-classical' divalent lanthanides, while steric protection can also be achieved with phospholes and arsoles bearing bulky substituents.[13–15] We report hereafter on the synthesis, structure and stability of three new phospholyl- and arsolylthulium(II) complexes.

Initial reactions of potassium 2,5-bis(trimethylsilyl)-3,4-dimethylphospholide: [K(Dsp)] (**1**) with $\mathrm{TmI_2(THF)_3}$ in THF under argon did not give products of definite composition. However, treatment of a solution of $\mathrm{TmI_2(THF)_3}$ in $\mathrm{Et_2O}$ with 2 equivalents of **1** or of potassium 2,5-bis(trimethylsilyl)-3,4-dimethylarsolide: [K(Dsas)] (**2**) under argon resulted in the formation of dark green solutions from which green solids (**3** and **4** respectively) could be isolated by crystallisation from pentane (Scheme 1).

The dark green colour of the solutions was a good indication that **3** and **4** were Tm(II) species, and a definitive proof was obtained by the crystal structure of **4**, which can thus be formulated as $[(\eta^5\text{-}(\mathrm{Dsas})_2\mathrm{Tm(THF)}]$ (Fig. 1); By analogy, **3** is formulated as $[(\eta^5\text{-}(\mathrm{Dsp})_2\mathrm{Tm(THF)}]$.†



Scheme 1

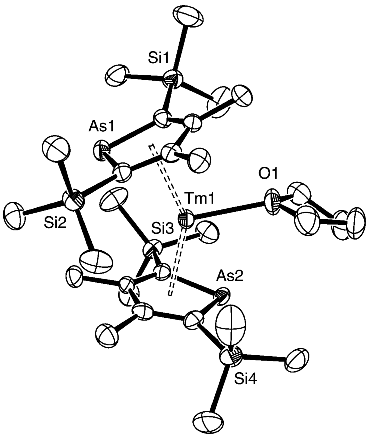
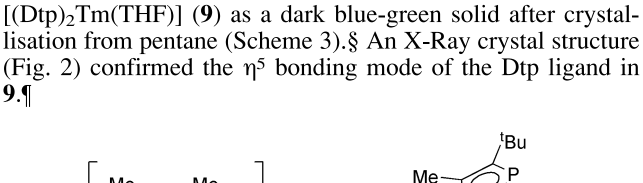


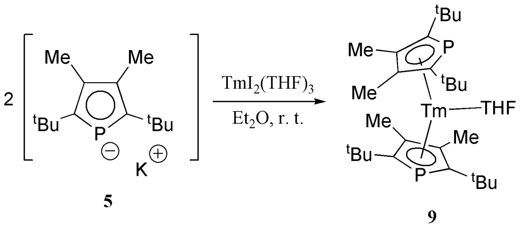
Fig. 1 An ORTEP plot of **4** (50% ellipsoids). Selected distances (Å) and angles (°): Tm1–As1: 2.968(1), Tm1–As2: 2.9759(8), Tm1–O1: 2.410(4), Tm1–C(av.): 2.79(1), cnt–Tm1–cnt: 146.

Next, the trimethylsilyl substituents were replaced by *tert*-butyls in order to increase the π-donating ability of the ring[10] while keeping the steric properties similar. The new potassium 2,5-di-*tert*-butyl-3,4-dimethylphospholide: [K(Dtp)] (**5**) was thus prepared (Scheme 2): Iodinolysis of zirconacyclopentadiene **6**[16] afforded diiodide **7**, iodine–lithium exchange in **7** followed by reaction with $\mathrm{PhPCl_2}$[17] afforded phosphole **8**, which after potassium cleavage in DME afforded the desired **5** (direct treatment of **6** with either $\mathrm{PhPCl_2}$ or $\mathrm{PCl_3}$ was unsuccessful in producing phospholes).‡



Scheme 2 *Reagents and conditions* : a, $\mathrm{I_2}$, THF, 0 °C, 2 h, 75%; b, 2 n-BuLi, $\mathrm{Et_2O}$, −78 °C to r.t., 1 h, then $\mathrm{PhPCl_2}$, −78 °C to r.t., 30 min, 79%; c, 4 eq. K, DME, 70 °C, 2 h, 89%.

Reaction of **5** with $\mathrm{TmI_2(THF)_3}$ in $\mathrm{Et_2O}$ afforded $[(\mathrm{Dtp})_2\mathrm{Tm(THF)}]$ (**9**) as a dark blue-green solid after crystallisation from pentane (Scheme 3).§ An X-Ray crystal structure (Fig. 2) confirmed the η^5 bonding mode of the Dtp ligand in **9**.¶



Scheme 3

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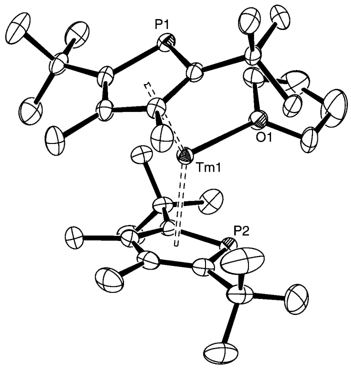

Fig. 2 An ORTEP plot of **9** (50% ellipsoids). Selected distances (Å) and angles (°): Tm1–P1: 2.943(1), Tm1–P2: 2.967(1), Tm1–O1: 2.455(2), Tm1–C(av.): 2.83(2), cnt–Tm1–cnt: 144.5.

Steric crowding in **4** and **9** can be assessed by the value of the Tm–C bond distances. In **4**, they extend from 2.759(4) to 2.824(5) Å, and, in **9**, from 2.766(3) to 2.899(4) Å with two other Tm–C bonds at 2.883(3) and 2.884(3) Å. This can be attributed to a higher steric congestion in **9** than in **4**. One can also note the differences between the Tm–O distances in [Cp″$_2$Tm(THF)]: 2.365(5) Å,[9] **4**: 2.410(4) Å and **9**: 2.455(2) Å.

Multinuclear NMR data at room temperature could be obtained for the three Tm(II) complexes. In the proton spectra, the methyl resonances of the ligands could be clearly assigned and accurately integrated in all cases; one can note that the CH_3 (silyl) signals of **3** (38.8 ppm), **4** (41.6 ppm) in C_6D_6 solution are quite similar to that of the reaction product of KCp″ with TmI_2 in ether under argon (38.4 ppm).[7] In the ^{13}C spectra, the functionality of all ring atoms could not be clearly ascertained either by DEPT, Jmod or proton-coupled experiments, presumably because of relaxation problems, and the β-CH_3 *vs.* C(ring) assignments is only tentative. Reproducible ^{31}P spectra could be obtained for **3** and **9**. Finally, magnetic susceptibility measurements (Evans' NMR method) were performed on **3**, **4** and **9**, and the results ($\mu_{eff} = 4.7\ \mu_B$: same value for the three compounds) are compatible with Tm(II).

The thermal stability of **3**, **4** and **9** in THF solution under argon appears higher than that of [Cp″$_2$Tm(THF)] (30 min at 25 °C),[9] since, after 24 h at room temperature, these solutions are still dark green, and their proton NMR spectra only show minor amounts of impurities. The new Tm(II) complexes appear stable as solids under argon at −30 °C, however they slowly decompose at room temperature in the drybox.

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Notes and references

† **2** was prepared in 71% yield from potassium and DsasCl (ref.13) as described in ref. 15 for **1**. NMR (*d-8* THF): ^1H: 0.21 (s, $Si(CH_3)_3$), 2.23 (s, CH_3). ^{13}C: 2.74 ($Si(CH_3)_3$), 19.81 (CH_3), 138.33 (*C*-C-As), 153.70 (*C*-As). **3** was prepared under argon from $TmI_2(THF)_3$ (0.26 mMole) and **1** (0.51 mMole) in Et_2O (10 ml) and was obtained in 72% yield after filtration and crystallisation from pentane. NMR: $^1H(C_6D_6)$: −28.6 (br.s, THF), −19.6 (br.s, CH_3), −8.6 (br.s, THF), 41.8 (br.s, $Si(CH_3)_3$) (attribution of the THF bands was confirmed by the addition of *d-8* THF). ^{13}C(*d-8* THF): −163.9 (C ring), −98.2 (C ring), −31.4 (CH_3), 32.3 ($Si(CH_3)_3$). ^{31}P (THF) −265.7. **4** was obtained similarly to **3** from $TmI_2(THF)_3$ (0.2 mMole) and **2** (0.4 mMole) in 56% yield. NMR: $^1H(C_6D_6$ + *d-8* THF): −20.3 (br.s, CH_3), 40.5 (br.s, $Si(CH_3)_3$). $^{13}C(C_6D_6$ + *d-8* THF): −161.5 (C ring), −92.7 (C ring), −27.8 (CH_3), 28.2 ($Si(CH_3)_3$).

‡ **7**: NMR ($CDCl_3$): ^1H: 1.32 (s, $C(CH_3)_3$), 1.99 (s, CH_3). ^{13}C: 18.82 (CH_3), 33.08 ($C(\mathit{C}H_3)_3$), 40.41 ($\mathit{C}(CH_3)_3$) 119.07 (*C*-I), 150.19 (*C*-C-I). *m*/*z* 318 ($M^+ - I$, 83%), 136 (100%). **8**: NMR ($CDCl_3$): ^1H: 1.05 (s, $C(\mathit{C}H_3)_3$), 2.05 (d, $J_{PH} = 2.5$, CH_3), 7.2 (br.m, Ph). ^{13}C: 16.81 (d, $J_{PC} = 3$, Me), 32.22 (d, $J_{PC} = 7$, $C(\mathit{C}H_3)_3$), 34.43 (d, $J_{PC} = 16.5$, $\mathit{C}(CH_3)_3$) 128.00 (d, $J_{PC} = 8$, C*meta*), 128.66 (d, $J_{PC} = 1.5$, C*para*), 134.14 (br.s, C*ortho*), 135.12 (d, $J_{PC} = 12$, C*ipso*), 143.26 (d, $J_{PC} = 11.5$, *C*-C-P), 149.94 (d, $J_{PC} = 2.5$, *C*-P). ^{31}P: 4.6. *m*/*z* 299 ($M^+ - H$, 22%), 188 (100%). Calcd for $C_{20}H_{29}P$, C: 79.96, H: 9.73; found, C: 80.02, H: 9.83%. **5**: NMR (*d-8* THF): ^1H: 1.36 (d, $J_{PH} = 1.5$, $C(CH_3)_3$), 2.16 (s, CH_3). ^{13}C: 17.09 (s, CH_3), 33.86 (d, $J_{PC} = 12$, $C(\mathit{C}H_3)_3$), 35.47 (d, $J_{PC} = 19$, $\mathit{C}(CH_3)_3$), 123.71 (s, *C*-C-P), 151.51 (d, $J_{PC} = 41$, *C*-P). ^{31}P: 58.8.

§ **9** was obtained similarly to **3** and **4** from $TmI_2(THF)_3$ (0.23 mMole) and **5** (0.46 mMole) in 52% yield. NMR: $^1H(C_6D_6$ + *d-8* THF): −23.0 (br.s, Me), 59.5 (br.s, $C(CH_3)_3$). $^{13}C(C_6D_6$ + *d-8* THF): −167.0 (C ring), 81.4 (C ring), −31.8 (CH_3) 58.1 ($\mathit{C}(CH_3)_3$), 72.9 ($C(\mathit{C}H_3)_3$). ^{31}P (THF) −338.3.

¶ *Crystallographic data* for **4**: green crystals (pentane, −30 °C), $C_{28}H_{56}As_2OSi_4Tm$, M = 839.86, monoclinic, $a = 10.659(5)$, $b = 17.230(5)$, $c = 20.156(5)$ Å, $\beta = 94.300(5)°$, $V = 3691(2)$ Å^3, $T = 150(1)$ K, space group $P2_1/n$ (no. 14), $Z = 4$, μ(Mo-Kα) = 4.331 cm^{-1}, 17595 reflections measured, 10768 unique ($R_{int} = 0.0275$), 8056 with $I > 2\sigma(I)$, final $R1 = 0.0475$, $wR2 = 0.1204$ (all data), GoF = 1.063, diff. peak/hole (e Å^{-3}): 6.555(0.162)/−4.126(0.162). *Crystallographic data* for **9**: green crystals (ether, −30 °C), $C_{32}H_{56}OP_2Tm$, M = 687.64, tetragonal, $a = 23.589(5)$, $c = 23.060(5)$ Å, $V = 12832(5)$ Å^3, $T = 150(1)$ K, space group $I4_1/a$ (no. 88), $Z = 16$, μ(Mo-Kα) = 2.887 cm^{-1}, 15144 reflections measured, 9370 unique ($R_{int} = 0.0227$), 7089 with $I > 2\sigma(I)$, final $R1 = 0.0367$, $wR2 = 0.0981$ (all data), GoF = 1.055, diff. peak/hole (e Å^{-3}): 2.117(0.135)/−1.611(0.135). CCDC 185425 and 185426. See http://www.rsc.org/suppdata/cc/b2/b204337h/ for crystallographic data in .cif or other electronic format.

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