1306 *Inorg. Chem.* **1995**, *34*, 1306−1307

Phospholylsamarium(III) Complexes

Hans-Jürgen Gosink, François Nief,* Louis Ricard, and François Mathey

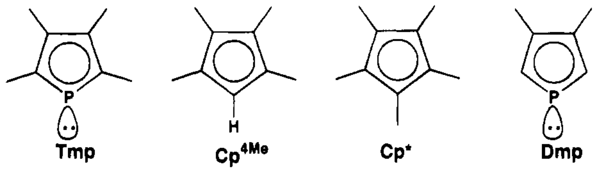
Laboratoire Hétéroéléments et Coordination, CNRS URA 1499, DCPH, Ecole Polytechnique, 91128 Palaiseau, France

Received October 25, 1994

The phospholyl group, a phosphorus analogue of cyclopentadienyl, has recently been characterized as a η^5 π ligand in lanthanide[1] and actinide[2] chemistry. Of special interest to us is the 2,3,4,5-tetramethylphospholyl (Tmp) ligand, which can be compared to the 1,2,3,4-tetramethylcyclopentadienyl (Cp^{4Me}) ligand and to the 1,2,3,4,5-pentamethylcyclopentadienyl (Cp*) ligand, as far as steric bulk is concerned (Chart 1). As an example, in actinide chemistry, very recently both $[(\eta^5\text{-Tmp})_3UCl]$[3] and $[(\eta^5\text{-Cp}^{4Me})_3UCl]$[4] were prepared, whereas $[(\eta^5\text{-Cp}^*)_3UCl]$ is so far unknown, presumably for steric reasons,[5] which seems to indicate that the Tmp ligand is more akin to Cp^{4Me} than to Cp*. Interestingly, in lanthanide chemistry, the only $[(\eta^5\text{-Cp}^*)_3Ln]$ compound known to date is $[(\eta^5\text{-Cp}^*)_3Ln]$ which Evans et al. discovered in 1985.[6] On the other hand, Schumann et al. have described a range of $[(\eta^5\text{-Cp}^{4Me})_3Ln]$ compounds (Ln = La, Sm, Tb)[7] by the straightforward reaction of $NaCp^{4Me}$ with $LnCl_3$ in tetrahydrofuran (THF). Therefore, it seemed interesting to assess the potential of the Tmp ligand with samarium(III). We hereafter report the synthesis and crystal structures of the first phospholylsamarium(III) complexes.

Reaction of KTmp[2] with $SmCl_3$ (3:1 molar ratio) in toluene at 110 °C over 24 h resulted in the formation of an orange solution, which, after filtration, deposited crystals at room temperature. X-ray crystallography[8] revealed the structure of a polymeric product **1**, of formula $[(Tmp)_6Sm_2(KCl)_2(C_7H_8)_3]_n$. Figure 1 represents part of the supramolecular structure of **1**, where only the heteroatoms are depicted for the sake of clarity. This structure is made up of two similar, but crystallographically different eight-membered rings: $[Sm1{-}P11{-}K1{-}Cl1]_2$ (unit A) and $[Sm2{-}P45{-}K2{-}Cl2]_2$ (unit B), each with a crystallographic inversion center in the middle; the connections between units A and B are secured by [Sm1−P6−K2] and [Sm2−P40−K1] links. Unit A is detailed in Figure 2. Samarium atom Sm1 is in a pseudotetrahedral environment: it is coordinated to one Tmp ligand through phosphorus atom P11, two other Tmp ligands through their π-systems (P1, C2 to C4 and P6, C7 to C10), and a bridging chlorine atom Cl1. Potassium atom K1 is also in a pseudo-tetrahedral environment, being coordinated to the bridging chlorine atom Cl1, one π-Tmp ligand (through P11, C12 to C15), and one π-toluene molecule, and also with phosphorus atom P40 belonging to unit B; likewise, in unit B, potassium atom K2 is also bonded to P6 belonging to unit A. There is also a loose toluene molecule in the unit cell. So, there are three types of differently coordinated Tmp ligands: one is only η^5-bonded to samarium (type 1: P1 to C5 and P35 to C39), one is η^1-bonded to samarium and η^5-bonded to potassium (type 2: P11 to C15 and P45 to C49), and one is η^5-bonded to samarium and η^1-bonded to potassium (type 3: P6 to C10 and P40 to C44). Tmp ligands of type 3 thus make the link between units A and B and bring about the supramolecular structure of **1**.

Chart 1



Sm−P bond distances in **1** (2.92−2.95 Å) are comparable to those in $[Sm^{III}_2Cp^*_4(\mu\text{-}t\text{BuCPPC}t\text{Bu})]$,[9] but larger than in $[Sm^{III}(Ph_2PCHPPh_2)_3]$.[10] The unusual η^6-coordination of toluene to potassium has also been found in $[Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)K(\eta^6\text{-toluene})_2]$.[11] The K−C(toluene) and K−Cl distances in this compound (3.21−3.56 and 3.00 Å, respectively) are

---

(1) Nief, F.; Mathey, F. *Synlett* **1991**, 745.

(2) Gradoz, P.; Baudry, D.; Ephritikhine, M.; Nief, F.; Mathey, F. *J. Chem. Soc., Dalton. Trans.* **1992**, 3047.

(3) Gradoz, P.; Boisson, C.; Baudry, D.; Ephritikhine, M.; Lance, M.; Nierlich, M; Vigner, J. *J. Chem. Soc., Chem. Commun.* **1992**, 1720.

(4) Cloke, F. G. N.; Hawkes, S. A.; Hitchcock, P. B.; Scott, P. *Organometallics*, **1994**, *13*, 2895.

(5) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650.

(6) Evans, W. J.; Gonzales, S. L.; Ziller, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 7423.

(7) Schumann, H.; Glanz, M.; Hemling, H. *J. Organomet. Chem.* **1993**, *445*, C1.

(8) X-ray structures (Enraf-Nonius CAD4 diffractometer, $T = -150 \pm 0.5$ °C): **1** : $C_{69}H_{88}Cl_2P_6K_2Sm_2$, M = 1561.18 triclinic space group $P\bar{1}$ (No. 2), $a = 15.484(2)$ Å, $b = 16.674(2)$ Å, $c = 17.335(2)$ Å, $\alpha = 84.99(1)°$, $\beta = 66.32(1)°$, $\gamma = 72.89(1)°$, $V = 3662.63(75)$ Å^3, $Z = 2$, Mo Kα radiation, $\lambda = 0.710\,73$ Å, μ(Mo Kα) = 19.5 cm^{-1}, final $R = 0.073$, $R_w = 0.101$, g.o.f. = 2.04 for 13 383 unique [of which 8327 had $F^2 \geq 3.0\sigma(F^2)$] reflections collected up to $2\theta = 50°$; **2** : $C_{36}H_{48}P_6Sm_2$, triclinic space group $P\bar{1}$ (No. 2), $a = 8.829(1)$ Å, $b = 9.799(1)$ Å, $c = 12.306(1)$ Å, $\alpha = 97.43(1)°$, $\beta = 97.25(1)°$, $\gamma = 114.43(1)°$, $V = 941.95(43)$ Å^3, $Z = 1$, Mo Kα radiation, $\lambda = 0.710\,73$ Å, μ(Mo Kα) = 33.7 cm^{-1}, final $R = 0.017$, $R_w = 0.024$, g.o.f. = 1.10 for 5821 unique [of which 5055 had $F^2 \geq 3.0\sigma(F^2)$] reflections collected up to $2\theta = 60°$. Both structures were solved by the Patterson method and refined by least-squares methods with the MOLEN software.

(9) Recknagel, A.; Stalke, D.; Roesky, H. W.; Edelmann, F. T. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 445.

(10) Hao, S.; Song, J.-I.; Aghabozorg, H.; Gambarotta, S. *J. Chem. Soc., Chem. Commun.* **1994**, 157.

(11) Schaverien, C. J.; Van Mechelen, J. B. *Organometallics* **1991**, *10*, 1704. A pyrrolylneodymium(III) complex also containing an alkali halide (NaCl) in a dimeric structure has recently been described : Schumann, H.; Winterfeld, J.; Hemling, H.; Kuhn, N. *Chem. Ber.*, **1993**, *126*, 2657. Salt-binding solvate complexes of type $[Cp^*_2LnCl{\cdot}MCl{\cdot}L_2]$ are known for virtually all lanthanides; *e.g.* for a recent review see: Schaverien, C. J. *Adv. Organometal. Chem*, **1994**, *36*, 335.

(12) Rabe, G.; Roesky, H. W.; Stalke, D.; Pauer, F.; Sheldrick, G. M. *J. Organomet. Chem.* **1991**, *403*, 11.

(13) Maigrot, N.; Ricard, L.; Charrier, C.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1031.

(14) **1**: a mixture of KTmp (0.36 g, 2.0 mmol) and $SmCl_3$ (0.18 g, 0.7 mmol) in toluene (15 mL) was refluxed for 24 h while the dispersion turned orange. After filtration and extraction of the residue with hot toluene, **1** precipitated as orange crystals upon cooling. The crystals were filtered and washed with hexane (5 mL), and dried under vacuum. Yield: 0.12 g (22%). NMR (C_7D_8, relative intensity in brackets): ^{1}H : $\delta = 4.75$ (s, $w_{1/2} = 35$ Hz, [1]), 4.20 (s, $w_{1/2} = 40$ Hz, [1]), 2.71 (s, $w_{1/2} = 2.5$ Hz, [3]), 2.16 (s, $w_{1/2} = 2.5$ Hz, [3]), 2.01 (s, $w_{1/2} = 24$ Hz, [3]), 1.19 (s, $w_{1/2} = 4$ Hz, [1]), 1.08 (s, $w_{1/2} = 6$ Hz, [3]), 0.91 (s, $w_{1/2} = 6$ Hz [1]), −0.25 (s, $w_{1/2} = 6$ Hz [3]), −0.65 (s, $w_{1/2} = 6$Hz [3]), −2.13 (s, $w_{1/2} = 53$ Hz [1]), −2.90 (s, $w_{1/2} = 59$ Hz [1]). ^{31}P : $\delta = 52.3$ (s, $w_{1/2} = 61$ Hz [3]), 50.1 (s, $w_{1/2} = 38$ Hz [3]), 47.7 (s, $w_{1/2} = 109$ Hz [1]), 44.5 (s, $w_{1/2} = 79$ Hz [0.2]), 41.4 (s, $w_{1/2} = 18$ Hz [2]), 34.1 (s, $w_{1/2} = 12$ Hz [1]). ^{31}P relative intensities are approximative due to overlap and a noisy spectrum. Anal. Calcd for $C_{62}H_{88}Cl_2K_2P_6Sm_2{\cdot}{}^1/_2C_7H_8$: C, 51.9; H, 6.1; P, 12.3; K, 5.2; Sm, 19.8. Found: C, 51.4; H, 5.7; P, 11.7; K, 4.5; Sm, 19.6. A half-equivalent of toluene of crystallization was presumably lost upon drying.

0020-1669/95/1334-1306$09.00/0

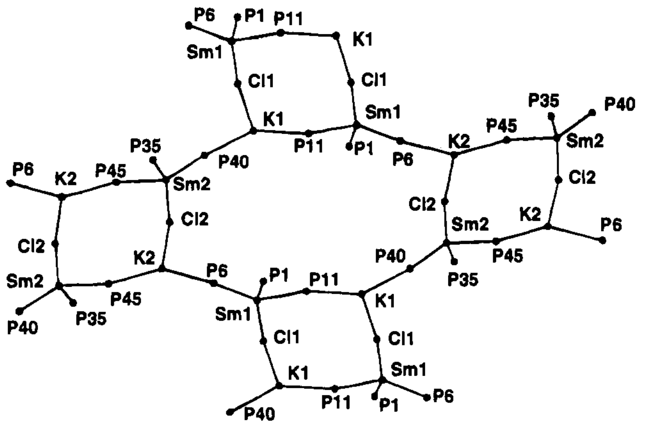


Figure 1. A sketch of the supramolecular structure of **1**.

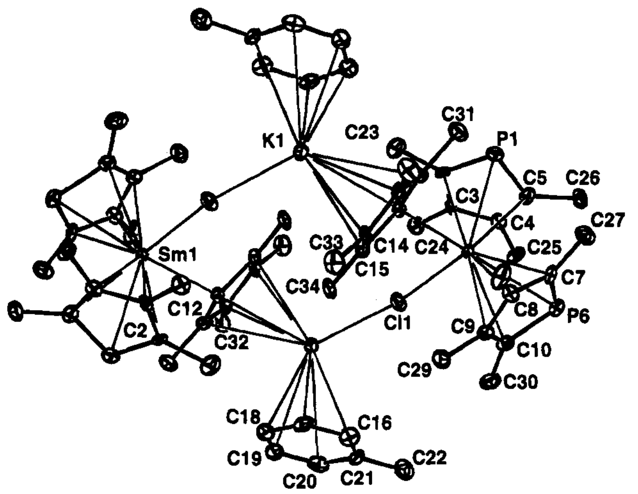


Figure 2. ORTEP plot of the $[Sm1-P11-K1-Cl1]_2$ ring structure of **1** (unit A). Ellipsoids are scaled to enclose 50% of the overall electronic density. Selected distances (Å) and angles (deg) are as follows: Sm1−Cl1, 2.632(3), Sm1−P1, 2.953(3), Sm1−P6, 2.924(4), Sm1−P11, 2.931(4), Sm−C(av) = 2.79, K1−Cl1 = 2.988(4), K1−P11 = 3.263(5), K1−P40 = 3.383(5), K−C(Tmp) = from 3.02(1) to 3.20(1), K−C(toluene) = from 3.21(2) to 3.55(1); Cl1−Sm1−P11 = 89.4(1), Sm1−P11−K1 = 163.1(1), P11−K1−Cl1 = 110.0(1), K1−Cl1−Sm1 = 169.9(1).

similar to those found in **1** (3.17−3.55 and 3.00 Å, respectively). The K−C(Tmp) and K−P(Tmp) distances are like those found in $[Cp^*K(C_5H_5N)_2]$[12] and in $[K_2(\mu\text{-DME})_2(\text{tetraphenyldiphosphafulvalene}]_n$[13] respectively. In the bridging phospholyl ligands of types 2 and 3, the η^1-coordinated metals (Sm and K) are bent away from the phospholyl plane by angles of 53 and 45° respectively.

The solution behavior of **1** is not clearly understood. It is not very soluble in toluene, and NMR spectra[14] in this solvent are complex: several peaks, of unequal intensity, appear in the ^1H spectrum between −2.90 and 4.95 ppm (attributable to methyl groups) and in the ^{31}P spectrum between 34.1 and 52.3 ppm. Presumably the supramolecular structure of **1** breaks up in solution into several oligomers. **1** is more soluble in THF, but the NMR spectra are again complex.

Elimination of the last equivalent of KCl in **1** could not be achieved by further heating of the reaction mixture over several days.

We next decided to attempt trisubstitution of Sm by the less bulky 3,4-dimethylphospholyl (Dmp) ligand. When KDmp[15] and $SmCl_3$ were reacted together in the same conditions as above (3:1 molar ratio, 110 °C, toluene, 24 h), a red solution was obtained, which after filtration deposited crystals at room temperature. X-ray crystallography[8] revealed the structure of a product, **2**,[16] of formula $[(\eta^5\text{-Dmp})_4\{\mu\text{-}(\eta^5,\eta^1)\text{-Dmp}\}_2Sm_2]$. The dimeric structure is thus generated by two $(\eta^5\text{-Dmp})_2Sm$ units bridged by two μ-(η^5,η^1)-Dmp ligands, the samarium atoms being in a pseudotetrahedral environment. The bonding pattern of this compound is similar to that of the actinide (IV) complex $[(\eta^5\text{-Cp})_4\{\mu\text{-}(\eta^5,\eta^1)\text{-}C_5H_4\}_2Th_2]$.[17] The Sm−P bond distances are similar to those found in complex **1** while Sm−C bonds are slightly longer. The centroid−Sm−centroid angles (mean value = 117.7°) are quite similar to those found in $[Cp_3SmL]$ (L being a donor molecule) such as in the recently prepared $[Cp_3Sm(THF)]$.[18] The P−Sm η^1-bond is almost in the Dmp ring plane, as indicated by the sum of angles around P6 (356,7°).

Dimer **2** is only slightly soluble in toluene at room temperature so interpretable NMR spectra could only be obtained in THF-d_8. The simplicity of the spectra suggests transformation of **2** into $[(Dmp)_3Sm(THF\text{-}d_8)]$.

On the whole, compound **1** can be thought of as a product of incomplete trisubstitution of the chlorine atoms of $SmCl_3$ by Tmp ligands: although three Tmp ligands are indeed bonded to Sm, only 2 equiv of KCl have been eliminated. The last KCl equivalent is still present in the crystal, so the last substitution step of Sm−Cl bonds by Tmp is stopped halfway, as in a reaction intermediate. In the same reaction conditions, in **2**, three less bulky Dmp ligands are π-coordinated to Sm(III) and do not even saturate its coordination sphere, since samarium can accept an additional phosphorus lone pair from the bridging Dmp ligand.

Work on other complexes of samarium(III) with phospholyl is in progress.

Acknowledgment. The authors wish to thank CNRS and Ecole Polytechnique for financial support. H.-J.G. thanks the Alexander von Humboldt foundation for a fellowship.

Supplementary Material Available: ORTEP plot of one molecule of **2** and text describing the structure determination and tables of X-ray crystallographic data, atomic coordinates, thermal parameters, and bond lengths and angles for **1** and **2** (29 pages). Ordering information is given on any current masthead page.

IC9412320

---

(15) KDmp was prepared as described by: Charrier, C.; Mathey, F. *Tetrahedron Lett.* **1987**, *28*, 5025. NMR (THF-d_8) : ^1H : $\delta = 6.40$ (d, $^2J_{H-P} = 41$ Hz, CH), 2.12 (d, $^3J_{H-P} = 1$ Hz, CH_3). ^{13}C : $\delta = 133.4$ (d, $^1J_{C-P} = 43$ Hz, C2), 131.0 (d, $^2J_{C-P} = 3$ Hz, C3), 20.7 (s, CH_3). ^{31}P : $\delta = 64.9$ (s).

(16) **2** : Similarly, KDmp (0.30 g, 2.0 mmol) and $SmCl_3$ (0.18 g, 0.7 mmol) were heated in toluene (15 mL) for 24 h. **2** could be isolated as red crystals by the above-described workup. Yield: 0.09 g (28%). NMR (THF-d_8): ^1H $\delta = 11.03$ (s, $w_{1/2} = 53$ Hz, CH), −0.213 (s, $w_{1/2} = 13$ Hz, CH_3). ^{13}C $\delta = 137.6$ (s, $w_{1/2} = 20$ Hz, C2 or C3), 131.1 (s, $w_{1/2} = 55$ Hz, C2 or C3), 25.0 (s, $w_{1/2} = 14$ Hz, CH_3); ^{31}P NMR $\delta = 9.3$ (s, $w_{1/2} = 120$ Hz). Anal. Calcd for $C_{36}H_{48}P_6Sm_2$: C, 44.7; H, 5.0; Sm, 31.1. Found: C, 44.3; H, 5.2; Sm, 31.4. Selected bond lengths (Å) and angles (deg): Sm−P1 = 2.9003(5), Sm−P6 = 2.9978(5), Sm−P6′ = 2.9862(5), Sm−P11 = 2.9270(5), Sm−C(av) = 2.88; P6−Sm−P6′ = 72.10(1), Sm-P6-Sm′ = 107.90(1).

(17) Baker, E. C.; Raymond, K. N.; Marks, T. J.; Wachter, W. A. *J. Am. Chem. Soc.* **1974**, *96*, 7586.

(18) Wang, S.; Yu, Y.; Ye, Z.; Qian, C.; Huang, X. *J. Organomet. Chem.* **1994**, *464*, 55.