

New examples of lanthanide(II) phosphides and arsenides with planar coordination at the heteroatom: crystal structures of $[(\text{Mesityl})_2\text{P}]_2\text{Sm}(\text{THF})_4$ and of $[(\text{Mesityl})_2\text{As}]_2\text{Sm}(\text{THF})_4$

François Nief^{*}, Louis Ricard

Laboratoire hétéroéléments et coordination, CNRS URA 1499, DCPH, Ecole Polytechnique, 91128 Palaiseau, France

Received 1 April 1996; accepted 10 May 1996

Abstract

Reaction of potassium bis(tetramesitylphosphide) or potassium bis(tetramesitylarsenide) with samarium diiodide in THF afforded the title compounds, $[(\text{Mesityl})_2\text{P}]_2\text{Sm}(\text{THF})_4$ and $[(\text{Mesityl})_2\text{As}]_2\text{Sm}(\text{THF})_4$ respectively. The crystal structures of the two title compounds have been determined, and are similar to that of the already described $[(\text{Mesityl})_2\text{P}]_2\text{Yb}(\text{THF})_4$: in all of these compounds the coordination around the heteroatom (P or As) is planar. $[(\text{Mesityl})_2\text{As}]_2\text{Sm}(\text{THF})_4$ is the first structurally described compound with an Sm–As bond.

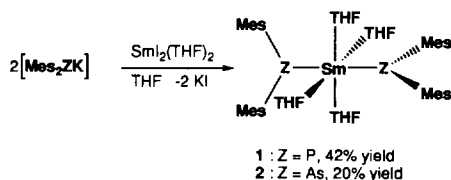
Keywords: Samarium; Phosphide; Arsenide

1. Introduction

Chemistry of the lanthanides in the +II oxidation state is expected to be dominated by the ionic character of their molecular compounds, because of the similarity of these elements with the heavier alkaline-earth elements such as strontium or barium. A recent statistical study of structural data by Sockwell and Hanusa concluded that the description of the M(II)–Cp interaction was consistent with the ionic model [1] (also, see Ref. [2] for a recent comprehensive survey of lanthanide compounds and properties). The Ln(II) ions usual behaviour is that of hard electrophiles that prefer coordination with hard Lewis bases such as oxygen or nitrogen. However, there are noticeable exceptions to this rule: for instance, Yb(II) has been shown to coordinate with phosphines [3], olefins [4] and acetylenes [5]. Moreover, quite recently, a growing number of publications have described stable compounds of these metals with soft second and third row elements such as sulphur and selenium [6], and more examples with phosphorus [7–

10]. In the field of divalent lanthanide chemistry, a few examples of Yb(II) or Sm(II) diorganophosphides exist, of general formula $(\text{R}_2\text{P})\text{M}(\text{THF})_4$, in which the environment around phosphorus can be pyramidal or planar. The quite unusual planar environment of the phosphorus atom in $(\text{Mes}_2\text{P})_2\text{Yb}(\text{THF})_4$ [9] had been attributed to steric crowding by the mesityl group, since it is not observed in $(\text{Ph}_2\text{P})_2\text{Yb}(\text{THF})_4$ [10], and because the electronic influence of the phenyl and mesityl groups are expected to be similar in these two compounds; planarity at phosphorus had also been attributed to steric crowding in a diphenylphosphido compound of La(III) [11]. In order to gain more insight into this unusual mode of coordination, we decided to synthesise the title compounds for the following reason: the Sm–P and Sm–As bonds in these compounds are expected to be longer than the Yb–P of $(\text{Mes}_2\text{P})_2\text{Yb}(\text{THF})_4$ bond and therefore they should exhibit less steric congestion around the metal, so we wanted to see if coordination around the heteroatom remained planar. From this point of view, Westerhausen recently described the synthesis and crystal structures of two Sr(II) phosphides and arsenides, which are quite similar to the corresponding Ln(II) compounds: whereas the phosphorus atom is planar in $[(\text{Me}_3\text{Si})_2\text{P}]_2\text{Sr}(\text{THF})_4$ [12], one arsenic atom

^{*} Corresponding author.



Scheme 1.

is planar and the other pyramidal in $[(\text{Me}_3\text{Si})_2\text{As}]_2\text{Sr}(\text{THF})_4$ [13].

2. Results and discussion

2.1. Synthesis of $[(\text{Mesityl})_2\text{P}]_2\text{Sm}(\text{THF})_4$, **1**, and of $[(\text{Mesityl})_2\text{As}]_2\text{Sm}(\text{THF})_4$, **2**

Our initial attempt to prepare **1** and **2** was by insertion of Sm metal into the P–P and As–As bonds respectively of $\text{Mes}_2\text{P–PMes}_2$ and $\text{Mes}_2\text{As–AsMes}_2$ in THF. However, no reaction occurred after 1 week of stirring. Therefore, we decided to prepare these compounds by the more traditional anionic route: reaction of Mes_2PK or Mes_2AsK with $\text{SmI}_2(\text{THF})_2$ in THF at room temperature afforded respectively the expected compounds **1** and **2** as dark greenish-brown crystals (Scheme 1).

Although the reaction appeared to proceed satisfactorily, compounds **1** and **2** were contaminated with unidentified brown oily material that could only be eliminated by repeated rinsing with cold THF, and so the isolated yields in pure products are quite low. Unfortunately, no satisfactory microanalytical data could be obtained for **1** or **2**.

Table 2

Selected bond lengths (Å) and bond angles (deg) for compounds **1** and **2**

	1		2
Sm–P	3.034(2)	Sm–As	3.061(3)
Sm–O10	2.564(5)	Sm–O10	2.55(2)
P–C1	1.836(7)	As–C1	1.96(2)
C1–P–C1'	102.4(3)	C1–As–C1'	99.5(8)
C1–P–Sm	128.8(2)	C1–As–Sm	130.3(8)
P–Sm–O10	90.8(1)	As–Sm–O10	92.3(4)
P–Sm–O10''	89.2(1)	As–Sm–O10''	87.7(4)
O10–Sm–O10'	178.3(2)	O10–Sm–O10'	175.3(6)
O10–Sm–O10''	90.0(2)	O10–Sm–O10''	90.1(5)

2.2. Crystal and molecular structures of **1** and **2**

Crystals of **1** and **2** suitable for X-ray analysis could be obtained by crystallisation from warm THF solutions of the compounds. Crystal data and data collection parameters are listed in Table 1, and Table 2 lists selected bond lengths and angles for **1** and **2**. Fig. 1 represents an ORTEP plot of one molecule of **1** together with the numbering scheme used. The most striking features of these two crystal structures is that, overall, they are similar to that of the previously described $(\text{Mes}_2\text{P})\text{Yb}(\text{THF})_4$ (**3**) [9], in that they also crystallise in the tetragonal space group $I4_1/a$; so, **1** and **2**, having S_4 symmetry, display crystallographically imposed planar coordination around phosphorus and arsenic respectively. The Sm–P bond in **2** (3.03 Å) is similar in length to that found in a benzophospholyl π -complex of Sm(II) (3.08 Å) [8] but somewhat shorter than in other σ -complexes of Sm(II): bis(dibenzophospholyl)Sm(THF)₄ (3.19 Å) [8] and $(\text{Ph}_2\text{P})_2\text{Sm}(\text{N–MeIm})_4$ (3.14 Å) [10]. The Sm–As bond in **3** (3.06 Å) is only very slightly

Table 1

Crystal data and data collection parameters

Empirical formula	$\text{C}_{52}\text{H}_{76}\text{O}_4\text{P}_2\text{Sm}$	$\text{C}_{52}\text{H}_{76}\text{As}_2\text{O}_4\text{Sm}$
FW	977.48	1065.38
Space group	tetragonal $I4_1/a$ (no. 88)	tetragonal $I4_1/a$ (no. 88)
a (Å)	16.820(2)	16.852(2)
c (Å)	18.683(2)	18.846(2)
V (Å ³)	5285.9(1.8)	5352.1(1.8)
Z	4	4
Crystal colour, size (mm ³)	dark green, $0.25 \times 0.25 \times 0.25$	dark green, $0.3 \times 0.3 \times 0.3$
D_{calc} (g cm ⁻³)	1.228	1.322
Radiation	Mo K α ($\lambda = 0.71073$ Å)	Mo K α ($\lambda = 0.71073$ Å)
μ (cm ⁻¹)	12.1	23.6
Temperature (°C)	-150 ± 0.5	-150 ± 0.5
Maximum 2θ	60.0	46.8
No. of reflections measured	4209 total, 3856 unique	2090 total, 1938 unique
Reflections included	2355 with $F_o^2 > 3.0\sigma(F_o^2)$	1442 with $F_o^2 > 0.0\sigma(F_o^2)$
Unweighted agreement factor	0.060	0.062
Weighted agreement factor	0.092	0.083
G.O.F.	1.54	0.94
Convergence, largest shift/error	0.00	0.00

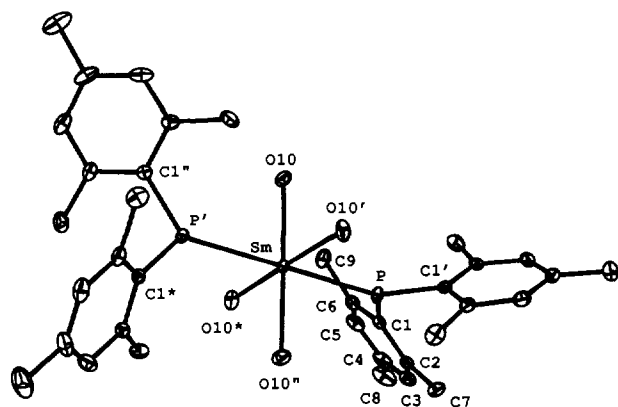


Fig. 1. An ORTEP plot of one molecule of **1**. Ellipsoids are scaled to enclose 50% of the overall electronic density; the carbon atoms of the THF ligands are omitted for clarity.

longer than the Sm–P bond in **2**, but here no direct comparison with existing compounds can be made, since **2** is the first structurally characterised compound with an Sm–As bond. However, Schumann and coworkers have prepared and structurally characterised two homologous compounds: $\text{Cp}_2\text{Lu}(\mu\text{-PPh}_2)_2\text{Li}(\text{TMEDA})$ (**4**) [14] and $\text{Cp}_2\text{Lu}(\mu\text{-AsPh}_2)_2\text{Li}(\text{TMEDA})$ (**5**) [15] with Lu–P and Lu–As bonds also rather similar, at 2.80 Å and 2.88 Å respectively. The C–P bond of the ligand in **1** (1.84 Å), **3** (1.84 Å) and in Schumann's compound **4** (1.84–1.86 Å) are similar and can be characterised as single bonds, while the C–P–C angles in **1** (102.5°), **3** (102.4°) and **4** (101–105°) are also similar. The C–As bond in **2** (1.96 Å), of course longer than a C–P bond, is similar to that found in **5** (1.94–1.97 Å) and can also be characterised as a single bond; likewise, the C–As–C bond (99.5°) is similar to that found by Schumann in **5** (99°).

As far as the non-bonding distances around the lanthanide metal are concerned in compounds **1–3**, the closest atom is found to be a methyl group of the dimesityl-phosphido or -arsenido ligand, which is thought to be responsible for the steric crowding around the metal inducing planarity at the heteroatom. Fig. 2 shows the metal–methyl distance together with the torsion angle around the heteroatom–mesityl bond.

It can be seen that, in this respect, the structures of compounds **1–3** are indeed very similar: for example, in comparing **2** with **3**, despite the fact that the Sm–As

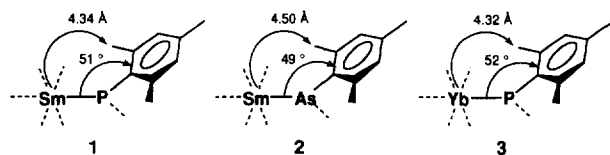


Fig. 2. Steric environment around the metals in compounds **1**, **2** and **3**.

bond, the As–C bond and the Sm–As–C angle of **2** are larger than respectively the Yb–P bond, the P–C bond and the Yb–P–C angle of **3**, the torsion angle around the As–C bond in **2** is smaller than the torsion angle around the P–C bond in **2**, with the result that the metal–methyl close distance in **2** (4.50 Å) is not very much different from that in **3** (4.32 Å). Thus, steric crowding around the metal has not been significantly decreased from **3** to **1** to **2**, and all of these compounds display planar coordination at the heteroatom.

3. Experimental section

All reactions were performed in dry solvents under dry oxygen-free argon in a Braun Labmaster 130 glove box or on a vacuum line. $\text{SmI}_2(\text{THF})_2$ [16], Mes_2AsCl [17] and $\text{Mes}_2\text{P–PMes}_2$ [18] were prepared as previously described. All reagents were used as received from the suppliers. NMR spectra were recorded in $\text{THF-}d_8$ as solvent on a Bruker AC200 spectrometer operating at 200.13 MHz for ^1H , 50.33 MHz for ^{13}C and 81.01 MHz for ^{31}P . Chemical shifts are expressed in parts per million downfield from internal TMS for ^1H and ^{13}C , and from external 85% H_3PO_4 for ^{31}P ; coupling constants are expressed in hertz.

3.1. Potassium tetramesitylphosphide, KPMes_2

In a 100 ml Schlenk vessel, a stirred solution of $\text{Mes}_2\text{P–PMes}_2$ (1.07 g, 2 mmol) in THF (30 ml) was treated with potassium metal (0.2 g, 5.1 mmol) at room temperature for 6 h. The orange solution was then decanted from the potassium residues via cannula transfer into another Schlenk vessel. These residues were carefully destroyed with $^t\text{BuOH}$ and the clear orange solution was evaporated to dryness, leaving KPMes_2 as a yellow powder which was not further purified. (1.12 g, 3.6 mmol, 91%). NMR ^1H : 2.10 (s, 18H, CH_3 ortho and para), 6.51 (s, 4H, H meta). ^{13}C : 20.97 (CH_3 para), 25.25 (d, $J_{\text{PC}} = 15$, CH_3 ortho), 127.11 (d, $J_{\text{PC}} = 2$, C para), 127.28 (C meta), 138.82 (d, $J_{\text{PC}} = 10$, C ortho) 151.52 (d, $J_{\text{PC}} = 55$, C ipso). ^{31}P : –50.03.

3.2. Potassium tetramesitylarsenide, KAsMes_2

In a 100 ml Schlenk vessel, a solution of Mes_2AsCl (3.48 g, 10 mmol) in THF (50 ml) was treated with potassium metal (1.0 g, 25.6 mmol) and the mixture was carefully and progressively heated to reflux for 30 min with efficient magnetic stirring. After cooling to room temperature, the resulting suspension was transferred to a centrifuge tube and centrifuged. After decantation, the residue was carefully destroyed with $^t\text{BuOH}$ and the clear orange-yellow solution was evaporated to dryness,

leaving KAsMes_2 as a yellow powder which was not further purified. (2.53 g, 8.2 mmol, 82%). NMR ^1H : 2.08 (s, 12H, CH_3 ortho), 2.15 (s, 6H, CH_3 para), 6.49 (s, 4H, H meta). ^{13}C : 21.05 (CH_3 para), 26.40 (CH_3 ortho) 126.72 (C meta), 128.16 (C para), 140.74 (C ortho) 153.80 (C ipso).

3.3. $[(\text{Mesityl})_2\text{P}]_2\text{Sm}(\text{THF})_4$, **1**, and $[(\text{Mesityl})_2\text{As}]_2\text{-Sm}(\text{THF})_4$, **2**

On a vacuum line, THF (15 ml) was condensed at -80°C onto an equimolar mixture of KPMe_2 or KAsMes_2 and $\text{SmI}_2(\text{THF})_2$. The reaction mixture was then brought to room temperature and stirred for 1 h. The resulting dark brown mixture was then filtered and the residue repeatedly extracted with warm THF. The filtrate was concentrated to a small volume and the dark green crystalline precipitates of **1** or **2** were filtered, rinsed with cold THF and dried in vacuum. With KPMe_2 (0.66 g, 2.2 mmol) and $\text{SmI}_2(\text{THF})_2$ (0.6 g, 1.1 mmol), 0.44 g of **1** was obtained (0.45 mmol, 42%). With KAsMes_2 (0.47 g, 1.3 mmol) and $\text{SmI}_2(\text{THF})_2$ (0.35 g, 0.64 mmol), 0.14 g of **2** was obtained (0.13 mmol, 20%). **1**. ^1H : 1.59 (s, 6H, CH_3 para), 1.72 (THF), 2.33 (s, 12H, CH_3 ortho), 3.60 (THF), 5.93 (s, 4H, H meta). **2**. NMR ^1H : 1.76 (THF), 1.85 (s, 6H, CH_3 para), 2.42 (s, 12H, CH_3 ortho), 3.61 (THF), 6.30 (s, 4H, H meta).

3.4. X-ray data collection and processing

Crystals of **1** and **2** were grown by slow cooling of a THF solution of the compounds. Data were collected on an Enraf Nonius CAD4 diffractometer using $\text{Mo K}\alpha$ radiation and a graphite monochromator. The crystal structures were solved and refined using the Enraf Nonius MOLEN package. Lorentz-polarisation and absorption corrections (the latter by the psi-scan method) were applied. Direct methods were used to solve the structures and yielded a solution for all atoms. The hydrogen atoms were included as fixed contributions in the final stages of least squares refinement while using

anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a p factor equal to 0.08.

References

- [1] S.C. Sockwell and T.P. Hanusa, *Inorg. Chem.*, **29** (1990) 76.
- [2] T. Edelmann, in E.W. Abel, F.G.A. Stone and G. Wilkinson (eds.), *Comprehensive Organometallic Chemistry II*, Vol. 4, Pergamon, 1995, p. 11.
- [3] T.D. Tilley, R.A. Andersen and A. Zalkin, *J. Am. Chem. Soc.*, **104** (1982) 3725.
- [4] C.J. Burns and R.A. Andersen, *J. Am. Chem. Soc.*, **109** (1987) 941.
- [5] C.J. Burns and R.A. Andersen, *J. Am. Chem. Soc.*, **109** (1982) 915.
- [6] K. Mashima, Y. Nakayama, H. Fukumoto, N. Kanehisa, Y. Kai and A. Nakamura, *J. Chem. Soc. Chem. Commun.*, (1994) 2523. B. Çetinkaya, P.B. Hitchcock, M.F. Lappert and R.G. Smith, *J. Chem. Soc. Chem. Commun.*, (1992) 932. A.R. Strzelecki, P. Timinski, B.A. Hessel and P. Bianconi, *J. Am. Chem. Soc.*, **114** (1992) 3159. F. Nief and L. Ricard, *J. Chem. Soc. Chem. Commun.*, (1994) 2723. M. Brewer, D. Khasnis, M. Buretea, M. Berardini, T.G. Enge and J.G. Brennan, *Inorg. Chem.*, **33** (1994) 2743.
- [7] G.W. Rabe, J. Riede and A. Schier, *Inorg. Chem.*, **35** (1996) 40. H.H. Karsch, G. Ferazin, O. Steigelmann, H. Kooijman and W. Hiller, *Angew. Chem. Int. Ed. Engl.*, **32** (1994) 1739.
- [8] F. Nief and L. Ricard, *J. Organomet. Chem.*, **464** (1994) 149.
- [9] S. Atlan, F. Nief and L. Ricard, *Bull. Soc. Chim. Fr.*, **132** (1995) 649.
- [10] G.W. Rabe, G.P.A. Yap and A.J. Rheingold, *Inorg. Chem.*, **34** (1995) 4521.
- [11] H.C. Aspinall, S.R. Moore and A.K. Smith, *J. Chem. Soc. Dalton Trans.*, (1992) 153.
- [12] M. Westerhausen, *J. Organomet. Chem.*, **479** (1994) 141.
- [13] M. Westerhausen and W. Schwartz, *Z. Naturforsch. Teil B.*, **50** (1995) 106.
- [14] H. Schumann, E. Palamidis, G. Schmid and R. Boese, *Angew. Chem. Int. Ed. Engl.*, **25** (1986) 718.
- [15] H. Schumann, E. Palamidis, J. Loebel and J. Pickardt, *Organometallics*, **7** (1988) 100.
- [16] J.-L. Nanny, P. Girard, H.B. Kagan and P.E. Caro, *Nouv. J. Chim.*, **5** (1981) 479. P.L. Watson, T.H. Tulip and I. Williams, *Organometallics*, **9** (1990) 1999.
- [17] C.G. Pitt, A.W. Purdy, K.T. Hlga and R.L. Wells, *Organometallics*, **5** (1986) 1266.
- [18] S.G. Baxter, A.H. Cowley, R.E. Davis and P.E. Riley, *J. Am. Chem. Soc.*, **103** (1981) 1699.