Journal of Organometallic Chemistry, 464 (1994) 149–154

JOM 23882

Synthesis of η^1 and η^5 complexes of samarium(II) with benzophospholyl ligands

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(Received April 5, 1993)

Abstract

Reaction of bis(cyclopentadienyl)-2,3-dimethylzirconaindole, obtained by addition of 2-butyne to benzynezirconocene, with PCl_3, affords 1-chloro-2,3-dimethylphosphindole (1-chloro 2,3-dimethylbenzophosphole) in a one-pot reaction and in moderate yield. Treatment of this compound with potassium and subsequent reaction with $[SmI_2(THF)_2]$ afforded bis(η^5-2,3-dimethylphosphindolyl)bis(tetrahydrofuran)samarium. Treatment of the P–P bonded bis(dibenzophospholyl) with Sm metal activated by $HgCl_2$ also affords a complex of Sm^{II} that was shown to be bis(η^1-dibenzophospholyl) tetrakis(tetrahydrofuran)samarium, a σ-Sm phosphide complex. Both complexes were analysed by X-ray crystallography.

Key words: Samarium; Heterocycles

1. Introduction

Organosamarium(II) compounds are receiving much attention because of their unusual reactivity [1], they have recently been found to activate CO [2], transform olefins into π-allyl systems [3], and form π-complexes with N_2 [4]; they are also used as reducing agents in organic chemistry [5]. Their reactivity seems to be dependent on the ligand environment and the coordination at the metal centre. We recently introduced the phospholyl ligand (L) as an analogue of the cyclopentadienyl ligand in this chemistry, and we have shown that complexes of composition $[(\eta^5\text{-L})_2M(THF)_2]$ can be obtained [6]. At this point, we were interested in using phosphindolyl (**A**) and dibenzophospholyl (**B**) as analogues of indenyl and fluorenyl ligands (Scheme 1).

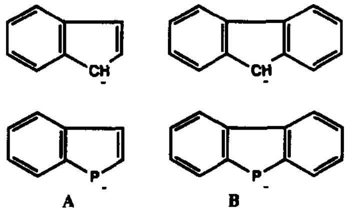
Indeed, η^5-indenyl and -fluorenyl complexes can generally undergo ring slippage to η^3 or η^1 more easily than η^5-cyclopentadienyl complexes [7] and thus have higher reactivity as far as ligand substitution is concerned. We thus wanted first to study which compounds could be made with **A** and **B** in samarium(II) chemistry.

2. Results and discussion

2.1. *Synthesis of phosphindolyl complex 4*

Although there are several known syntheses of the phosphindole ring system, these methods are generally long [8]. Taking advantage of the recently introduced zirconacyclopentadiene method [9], we were able to prepare 1-chloro-2,3-dimethylphosphindole (**1**) by reaction of PCl_3 with the known bis(cyclopentadienyl)-2,3-dimethylzirconaindole (**2**) [10] in fair yield; **2** need not even be isolated, and thus **1** can be conveniently prepared from Cp_2ZrPh_2, 2-butyne and PCl_3 in a one-pot reaction according to Scheme 2.

Subsequent reaction of **1** with potassium metal in dimethoxyethane (DME) afforded potassium 2,3-dimethylphosphindolide (**3**); ^1H NMR spectroscopy showed that the isolated orange powder contained *ca.* 0.75 mol of DME per mol of anion **3**. ^{13}C and in



Scheme 1.

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0022-328X/94/$7.00
SSDI 0022-328X(93)23882-X

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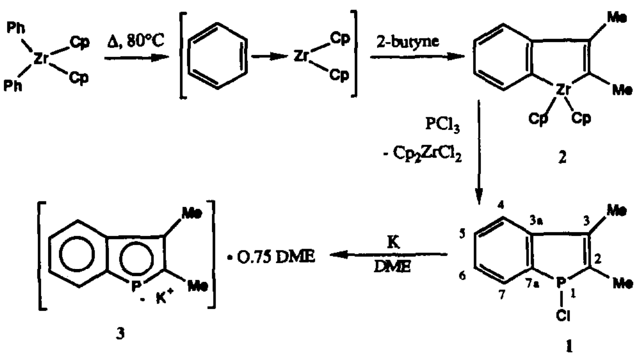
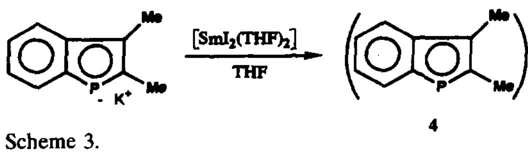


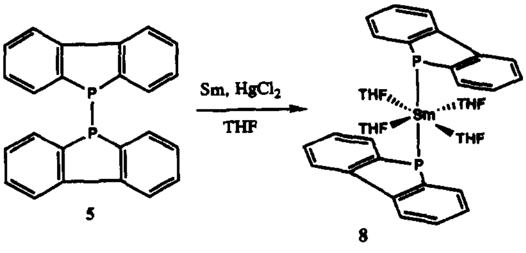
Scheme 2.

particular ^{31}P NMR spectra confirm the structure of **3**; the ^{13}C signals of C2 and C7a are split with a characteristic ^{1}J(PC) coupling constant of about 40 Hz [6]; the ^{31}P resonance of **3** at 46 ppm is very similar to that of the parent phosphindolyl anion, about 30 ppm upfield from the resonance of phospholyl anions; this has been attributed to a loss of aromaticity within the phosphole ring due to benzoannelation [11].

At this point, two synthetic routes to the desired samarium complexes could be considered: either a direct reaction of anion **2** with a Sm^{II} precursor, or by cleavage of a P–P bond of a biphosphindolyl with Sm^{0}. Reaction of anion **3** with I_2 did produce such a biphosphindolyl, but because the P atoms are pyramidal in this molecule, it was obtained as a mixture of two diastereomers (*meso* and racemic); ^{31}P NMR spectroscopy indicated that this mixture was approximatively 1 : 1. Because of the expected difficulties in purifying this mixture, the anionic route was preferred; thus, reaction of **3** with [$SmI_2(THF)_2$] afforded a brown reaction mixture from which we could isolate crystals of bis (2,3-dimethylphosphindolyl) bis(tetrahydrofuran)samarium (**4**) (Scheme 3). We suspected that complex **4** had an η^5-structure because of the similarity of its NMR data with those of η^5-phospholyl samarium(II) complexes. Indeed, integration of the ^{1}H NMR spectrum indicates one mole of THF per mol of phosphindole, and a very large upfield paramagnetic shift of the ^{31}P resonance ($\delta^{31}P = -694$ ppm) is observed. One of the C atoms α to phosphorus displays a characteristic coupling constant of 43 Hz; the other Cα atom was not detected in the otherwise well-resolved ^{13}C spectrum and may be obscured by a solvent resonance. However, the NMR spectra did not reveal the presence of two different isomers **41** (racemic) or **4b** (*meso*) that might be observed owing to the dissymetric nature of the ligand (Scheme 4). When we measured the ^{1}H NMR spectra of **4** at low temperatures, we observed large variations of the chemical shift with temperature, as expected for a paramagnetic compound, and a gradual broadening of the lines, but even at −80°C we did not observe splitting of the signals. These experiments are consistent with an exchange process having a coalescence temperature below −80°C.



Scheme 3.



Scheme 4.

2.2. *Crystal and molecular structure of 4*

A suitable crystal was obtained by crystallization in THF at room temperature. Crystal data and data collection parameters are listed in Table 1 and Table 2 lists selected bond lengths and angles of **4**. Figure 1 represents an ORTEP plot of one molecule of **4**. Struc-

TABLE 1. X-Ray experimental data for **4** and **8**

Empirical Formula	$C_{28}H_{26}O_2P_2Sm$	$C_{40}H_{40}O_4P_2Sm$
FW	606.82	805.12
Space group	$C2/c$ (no. 15)	$C2/c$ (no. 15)
a (Å)	17.156(1)	17.913(2)
b (Å)	10.794(1)	9.152(1)
c (Å)	15.552(1)	21.956(3)
β (°)	113.71(1)	96.32(1)
Z	4	4
Crystal size (mm)	0.15 × 0.22 × 0.25	0.40 × 0.40 × 0.25
ρ calcd. (g cm^{-1})	1.529	1.495
Radiation	Mo Kα	Mo Kα
Monochromator	Graphite	Graphite
Temperature (°C)	-150 ± 0.5	-150 ± 0.5
2θ max (°)	60	60
Scan type	ω–2θ	ω–2θ
Unique reflections	3845	5203
Reflections with $F^2 > 3\sigma(F^2)$	3399	4438
R	0.019	0.028
R_w	0.028	0.051
Largest shift/error	0.00	0.00
GOF	1.04	1.16

TABLE 2. Selected bond distances (Å) and angles (°) for **4** [a]

Distances			
Sm–P	3.0775(1)	Sm–C2	2.970(1)
Sm–C3	2.941(2)	Sm–C4	2.917(2)
Sm–C9	2.912(2)	Sm–O	2.531(1)
P1–C2	1.780(2)	P1–C9	1.776(2)
C2–C3	1.386(3)	C3–C4	1.442(3)
C4–C5	1.413(3)	C4–C9	1.437(3)
C5–C6	1.372(3)	C6–C7	1.411(3)
C7–C8	1.377(3)	C8–C9	1.418(3)
Angles			
C2–P1–C9	89.31(9)	P1–C2–C3	114.4(1)
C2–C3–C4	111.9(2)	C3–C4–C9	112.1(2)
C9–C4–P1	112.3(1)	C(ring)–C(ring)–C(ring)	120 (mean)
O12–Sm–O12′	84.24(7)	Cnt–Sm–Cnt	139.6

[a] C(ring) are the atoms of the benzo ring. Cnt is the centroid of the 5 membered heterocyclic ring.

tural data confirm the η^5-co-ordination mode of the complex and indicate that the structure is indeed that of **4a** (racemic) since the molecule has a crystallographically imposed C_2 axis. The geometry around the samarium atom is pseudo-tetrahedral if one considers the values of the centroid–Sm–centroid and O–Sm–O angles (136.9° and 84°, respectively). The phosphindolyl is planar and its heterocyclic part appears quite similar to that of other phospholyl ligands, as far as the P–C bonds (1.78 Å) and P–C–P angles (89.3°) are concerned. Although the Sm–C bond distances are slightly different, this is not considered as significant, and, in particular, the ligand does not show any tendency towards η^3-co-ordination as in several π-indenyl complexes [12], including the recently described [tris(π-indenyl)Nd(THF)] [13]. In **4**, the Sm–C bond lengths are longer, and the Sm–O bond lengths shorter, than in [$(C_5Me_5)_2Sm(THF)_2$] [14]; this may reflect the lower π-basicity of the phosphindolyl ligand relatively to that of the C_5Me_5 ligand.

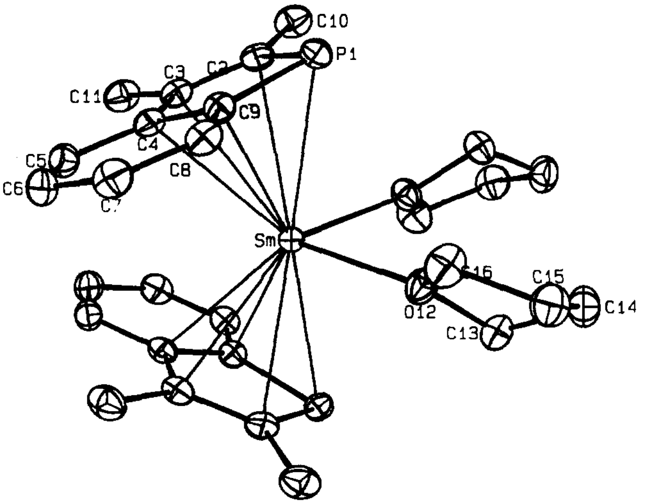
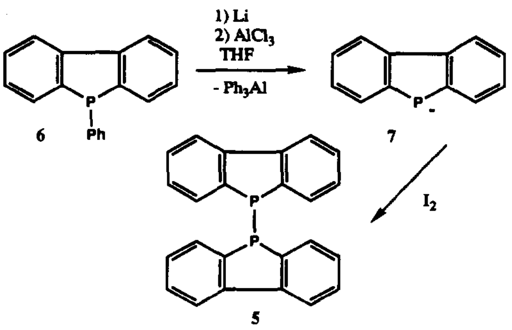


Fig. 1. An ORTEP plot of one molecule of **4**. Ellipsoids are scaled to include 50% of the overall electronic density.



Scheme 5.

2.3. *Synthesis of a dibenzophospholyl complex*

We next turned our attention towards dibenzophospholyl **B**. This time, we decided to use bis(dibenzophospholyl) (**5**) as a precursor, although this compound had only been described in the literature as a by-product [15], it had been found quite stable. We were able to improve its synthesis as follows (Scheme 5); lithium cleavage of the P–C bond of **6** followed by neutralization of phenyllithium with $AlCl_3$ yielded anion **7**, which was not isolated, but oxidized *in situ* with I_2, affording a fair yield of **5**, which was easily isolated from the reaction mixture by filtration, since it is only slightly soluble in THF. The chemical shift of anion **7** (14.3 ppm) is intermediate between that of **3** and that of other organophosphides such as $LiPPh_2$ ($\delta^{31}P = -23$ ppm), which indicates a further loss of aromaticity of the heterocyclic ring in **7** as compared to **3**.

The P–P bond of **5** could be cleaved by metallic samarium; at first, an equimolecular mixture of **5** and Sm metal (activated by $HgCl_2$) at room temperature in THF did not react. However, after an induction period the reaction mixture gradually turned green and dark olive-green crystals began to separate from solution. These crystals were isolated by repeated extraction with warm THF. NMR spectra of a saturated solution of the isolated product **8** in THF-d_8 was not very informative; we failed to detect any ^{31}P and ^{13}C resonances, but the ^1H spectrum revealed four broad ($w_{1/2} \approx 25$ Hz) peaks between 7.9 and 12.2 ppm corresponding to the four non-equivalent protons of the benzo ring, and resonances of the methylene groups of THF. However, it was not possible to determine accurately the THF-to-phospholyl ratio; the low solubility of the product in THF-d_8 induces a relative enhancement of the signal coming from THF-d_7 in the NMR solvent, and an artificial increase in the integral of the THF

TABLE 3. Selected bond distances (Å) and angles (°) for **8** [a]

Distances			
Sm–P	3.1908(6)	Sm–O14	2.574(3)
Sm–O19	2.501(1)	P1–C2	1.791(2)
P1–C13	1.791(2)	C2–C7	1.426(3)
C7–C8	1.456(3)	C8–C13	1.415(3)
C2–C3	1.413(3)	C3–C4	1.374(3)
C4–C5	1.403(3)	C5–C6	1.378(3)
C6–C7	1.400(3)	C8–C9	1.404(3)
C9–C10	1.382(3)	C10–C11	1.397(4)
C11–C12	1.381(3)	C12–C13	1.418(3)
Angles			
C2–P1–C13	89.16(9)	P1–C2–C7	113.5(1)
C2–C7–C8	111.6(2)	C7–C8–C13	112.2(2)
C8–C13–P1	113.6(1)	C(ring)–C(ring)–C(ring)	120 (mean)
O14–Sm–O14′	180	O19–Sm–O19′	180
P1–Sm–P1′	180	O14–Sm–P1	82.91(4)
O19–Sm–P1	95.48(4)	O14–Sm–O19	92.06(7)
Sm–P1–C2	95.78(6)	Sm–P1–C13	105.83(6)

[a] C(ring) are the atoms of the benzo rings.

signals. Therefore we decided to undertake an X-ray crystallographic study on this compound.

2.4. *Crystal and molecular structure of 8*

A suitable crystal of **8** was obtained by slow cooling of a sealed tube containing a hot (80°C) saturated solution of **8** in THF. Crystal data and data collection parameters are listed in Table 1, and Table 3 lists selected bond lengths and angles of **8**. Figure 2 represents an ORTEP plot of one molecular of **8**. The structure confirms that **8** is a complex of dibenzophospholyl with Sm^{II}, but the co-ordination mode of this ligand is now η^1 (Scheme 6), and the P–Sm bond a σ bond.

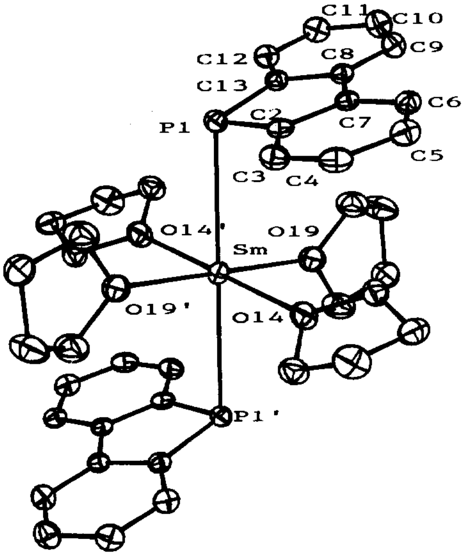
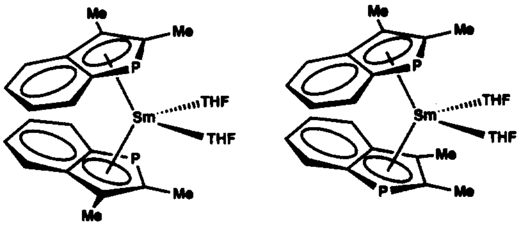


Fig. 2. An ORTEP plot of one molecule of **8**. Ellipsoids are scaled to include 50% of the overall electronic density.



4a (racemic) **4b** (meso)

Scheme 6.

The geometry around Sm, which sits on an inversion centre, is now that of a distorted octahedron, the L–Sm–L angles varying from 83° to 97°. The dibenzophosphole rings are planar and parallel, and the P atom is pyramidal; the mean value of the Sm–P1–C (ring) angles is 100.5°, very similar to that of normal tertiary phosphines, and so cyclic delocalization of the phosphorus lone pair into the heterocyclic ring is less efficient in **8** than in other σ-phospholyl complexes, where the phosphorus atom is less pyramidal [16]. The P–C ring distance in **8** (1.79 Å) is longer than in other π- or σ-phospholyl complexes (≈ 1.76 Å)[17], which may also indicate lower delocalization. Loss of aromaticity within the heterocyclic part of the dibenzophospholyl anion might thus be responsible for the monohapto-bonding with Sm^{II}.

3. Experimental section

Because of the extreme air-sensitivity of the complexes, all operations were performed under dinitrogen with the use of a vacuum line and dry box, with dry, carefully degassed solvents. $[SmI_2(THF)_2]$ [18], $[Cp_2ZrPh_2]$ [19], and 1-phenyldibenzophosphole [20] were prepared as previously described. All reagents were used as received from the commercial suppliers. NMR spectra (^1H, ^{13}C, ^{31}P) were measured on a Bruker AC 200 instrument. Chemical shifts are expressed in δ units downfield from internal TMS (^1H, ^{13}C) and external H_3PO_4 (^{31}P); coupling constants are expressed in Hz. Mass spectra were obtained at 70 eV on a Shimadzu GC-MS 1000 spectrometer. We failed to obtain meaningful microanalyses for recrystallized **8** and **4**.

3.1. *1-Chloro-2,3-dimethylphosphindole (1)*

In a 500-ml thick-wall pressure flask, a solution of Cp_2ZrPh_2 (11.36 g, 30.24 mmol) and 2-butyne (1.8 g, 33 mmol) in THF (20 ml) was heated with stirring at 80°C for 16 h and subsequently at 100°C for 1 h. The reaction mixture was then cooled to room temperature and the vessel carefully opened; there was no excess of pressure. To the resulting red solution was then added an excess of PCl_3 (5 ml, 7.9 g, 57.3 mmol), and the reaction mixture was stirred for 1 h at room temperature and evaporated to dryness. The residue was taken up in pentane and filtered and the filtrate evaporated to dryness. The residue was bulb-to-bulb distilled under reduced pressure. A yellow oil was obtained (3.10 g, 15.77 mmol, 52%). NMR (CD_2Cl_2) ^{1}H: 2.12 (d, J(PH) = 5, CH_3–C2); 2.18 (d, J(PH) = 9, CH_3–C3); 7.31 (m, 2H); 7.44 (t, J = 7, 1H); 7.59 (m, 1H). ^{13}C{^{1}H}: 12.56 (d, J(PC) = 26, CH$_3$–C2); 12.6 (s, CH$_3$–C3); 122.0 (s, CH); 127.1 (d, J(PC) = 6, CH); 130.1 (d, J(PC) = 24, CH); 131.1 (s, CH); 139.4 (d, J(PC) = 25, C); 141.0 (d, J(PC) = 20, C); 144.3 (d, J(PC) = 6, C); 147.6 (d, J(PC) = 3, C). ^{31}P{^{1}H}: 78.0. Mass. spec. m/z 198 (M$^+$[^{37}Cl], 31%), 196 (M$^+$[^{35}Cl], 89%), 129 (100%).

3.2. Potassium 2,3-dimethylphosphindolide (3)

A solution of 1-chloro-2,3-dimethylphosphindole (1) (980 mg, 5 mmol) in 1,2-dimethoxyethane (DME) (20 ml) containing potassium pieces (400 mg, 10.25 mmol) was heated at 70°C with vigorous stirring in order to disperse the molten potassium. The solution became progressively yellow and eventually dark red after 1 h. The reaction mixture was then cooled to room temperature and filtered under a positive pressure of argon; the residue was rinsed with DME (5 ml) and carefully destroyed with ^{t}BuOH, and the orange filtrate was evaporated to dryness. The resulting solid was triturated with pentane and decanted several times, then dried under vacuum. A yellow solid of approximate composition **3** · 0.75 DME was obtained (510 mg, 1.90 mmol, 38%). NMR (C_4D_8O) ^{1}H: 2.27 (s, CH_3–C3); 2.47 (d, J(PH) = 11.5, CH_3–C2); 3.27 (DME); 3.39 (DME); 6.47 (m, 1H); 6.63 (m, 1H); 7.26 (m, 1H); 7.65 (m, 1H); 7.65 (m, 1H). ^{13}C{^{1}H}: 12.2 (s, CH$_3$–C3); 16.8 (d, J(PC) = 32, CH$_3$–C2); 58.8 (DME); 72.5 (DME); 115.1 (d, J(PC) = 11.5, CH); 116.1 (s, CH); 119.1 (d, J(PC) = 1.5, CH); 127.1 (d, J(PC) = 23.5, CH); 128.9 (s, C3 or C3a); 139.6 (s, C3 or C3a); 150.1 (d, J(PC) = 40, C2 or C7a); 147.58 (d, J(PC) = 38, C2 or C7a) ^{31}{^{1}H}: 46.2.

3.3. Bis(η^5-2,3 dimethylphosphindolyl)bis(tetrahydrofuran)samarium(II) (4)

On a vacuum line, THF (20 ml) was condensed onto a mixture of **3** · 0.75 DME (500 mg, 1.84 mmol) and [$SmI_2(THF)_2$] (500 mg, 0.91 mmol). The reaction mixture immediately became dark reddish-brown. After 1 h of stirring at room temperature, the reaction mixture was evaporated to dryness and the solid residue thoroughly extracted with toluene. The toluene extract was then evaporated to dryness and the residue dissolved in a small amount (≈ 1 ml) of THF, whereupon the product crystallized. The dark red crystalline product (310 mg, 0.50 mmol, 55%) was then dried under vacuum and recrystallized in THF. NMR (C_4D_8O) ^{1}H ($w_{1/2} \approx 5$ Hz): 1.01 (s, CH_3–C3); 1.63 (THF); 3.60 (THF); 6.45 (d, J(PH) = 11, CH_3–C2); 7.05 (d, J(HH) = 7, 1H); 7.55 (t, J(HH) = 7, 1H); 8.32 (d, J(HH) = 7, 1H); 8.47 (t, J(HH) = 7, 1H). ^{13}C{^{1}H} ($w_{1/2} \approx 5$ Hz): 14.9 (s, C3 or C3a); 26.3 (THF); 48.9 (d, J(PC) = 43.5, C2 or C7a); 63.5 (s, CH$_3$–C3); 69.5 (THF); 71.3 (d, J(PC) = 30, CH$_3$–C2); 72.6 (s, C3 or C3a); 127.8 (s, CH); 135.4 (d, J(PC) = 11, CH); 162.5 (s, CH); 173.5 (d, J(PC) = 22, CH). One of the C2 or C7a atoms was not detected; the ^{13}C spectrum was edited by a DEPT sequence. ^{31}P{^{1}H} ($w_{1/2} \approx 150$ Hz): −694.

3.4. Bis(1.1'-dibenzophospholyl) (5)

A solution of 1-phenyldibenzophosphole (**6**) (2.60 g, 10 mmol) in THF (25 ml) containing lithium pieces (200 mg, 28 mmol) was stirred at room temperature for 3 h. The excess of lithium was then removed, and $AlCl_3$ (450 mg, 3.33 mmol) was added to the red reaction mixture. After 30 min of stirring, I_2 (1.27 g, 5 mmol) was gradually added. The solution turned colourless, an after 10 min a precipitate began to separate. After a further 10 min, the reaction mixture was filtered, washed successively with water, methanol and pentane, and dried under vacuum; **5** was obtained as yellow microcrystals, m.p. 230°C [15] (1.27 g, 3.47 mmol, 69%). NMR (C_4D_8O) ^{1}H: 6.88 (m, 1H); 7.03 (m, 1H); 7.26 (m, 1H); 7.64 (m, 1H). ^{31}P{^{1}H}: −21.5. Mass spec. m/z 366 (M$^+$, 20%), 183 ([M/2]$^+$, 100%).

3.5. Bis(η^1-1.1'-dibenzophospholyl) tetrakis(tetrahydrofuran)samarium(II) (8)

On a vacuum line, THF (20 ml) was condensed onto a mixture of **5** (500 mg, 1.37 mmol), Sm powder (150 mg, 1 mmol), and $HgCl_2$ (20 mg). The resulting slurry was allowed to stand at room temperature with intermittent stirring. Within 24 h, the reaction mixture turned olive-green and crystals began to separate from solution. After another 24 h of stirring, the reaction mixture was evaporated to dryness and the residue thoroughly extracted with warm THF and the extract concentrated, yielding dark olive-green microcrystals of **8** which were then filtered, rinsed with cold THF and dried (350 mg, 0.43 mmol, 63%). NMR (C_4D_8O) ^{1}H ($w_{1/2} \approx 25$ Hz): 1.7 (THF); 3.6 (THF); 7.9 (1H); 9.9 (1H); 10.0 (1H); 12.2 (1H). No resonances were detected in the ^{13}C and ^{31}P spectra.

3.6. X-Ray data

Crystals of **4** and **8** were obtained by recrystallization in THF in a sealed tube, at room temperature for **4** and from a hot (80°C) solution for **8**. Data were collected on an Enraf Nonius CAD4 diffractometer. The crystal structures were solved and refined using the Enraf Nonius MOLEN software package. In both cases, the samarium atoms were located on a Patterson map and the models were completed by successive difference Fourier maps. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinements while using anisotropic temperature factors for all other atoms. Non-Poisson weighting schemes were applied with *p*-factors equal to 0.04 and 0.08 for **4** and **8**, respectively. X-Ray data will be deposited at the Cambridge Crystallographic Data Centre.

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