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Synthesis of mixed phospholyl/cyclooctatetraenyl–lanthanide complexes. Crystal and molecular structure of (cyclooctatetraenyl)[3,4-dimethyl-2,5-bis(trimethylsilyl)-phospholyl]-(tetrahydrofuran)neodymium

Marc Visseaux [a],*, François Nief [b], Louis Ricard [b]

[a] *Laboratoire de Synthèse et Electrosynthèse Organométalliques, CNRS UMR 5632, Université de Dijon, 9 Avenue Savary, 21000 Dijon, France*
[b] *Laboratoire Hétéroéléments et Coordination, CNRS UMR 7653, DCPH, Ecole Polytechnique, 91128 Palaiseau, France*

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Abstract

New mixed phospholyl/cyclooctatetraenyl lanthanide complexes have been prepared by metathesis of phospholylpotassium salts with cyclooctatetraenyllanthanide halide precursors: [(cot)Sm(Tmp)(THF)] (**5**), [(cot)Sm(Dsp)] (**6**), and [(cot)Nd(Dsp)(THF)] (**7**) have been thus prepared (cot = cyclooctatetraenyl, Tmp = 2,3,4,5-tetramethylphospholyl, Dsp = 3,4-dimethyl-2,5-bis(trimethylsilyl)-phospholyl). Complex **7** has been structurally characterised. Formation of **5** has also been observed in the reaction of $[(Tmp)_2Sm]$ with cyclooctatetraene. An alternative synthesis of the $[\{(cot)SmCl(THF)\}_2]$ precursor has been reported, and the X-ray crystal structure of this complex determined. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cyclooctatetraene; Neodymium; Samarium; Phosphole

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1. Introduction

The implication of organolanthanides—particularly in the early series—in the field of homogeneous catalysis is well documented [1], and since potentially active compounds must be coordinatively unsaturated, organolanthanide complexes containing the C_8H_8 (cot) ligand, which is dianionic, are well suited for this purpose: only one additional anionic ligand (such as cyclopentadienyl, halide, thiolate…) is sufficient to ensure electroneutrality [2]. However, the rules of stability of organolanthanides, and especially active species, are not well established [3,4] and it was of interest to synthesise new cyclooctatetraenyl complexes of early lanthanides to compare their electronic and steric behaviour. In order to prepare soluble complexes, especially in non-polar solvents, the second ligand is usually chosen among the substituted cyclopentadienyl-type series.

The phospholyl (phosphacyclopentadienyl) and arsolyl (arsacyclopentadienyl) ligands are now well-established alternatives to the ubiquitous cyclopentadienyl group in organolanthanide chemistry [5]. Earlier experiments involved the 2,3,4,5-tetramethylphospholyl (Tmp) ligand, which can be seen as an analogue to the pentamethylcyclopentadienyl (Cp*) ligand. We recently prepared new complexes featuring differently substituted phospholyl and arsolyl ligands around a Cp^*_2Sm residue, and we showed that the substitution pattern and the steric bulk on the phospholyl ligand had a marked influence on the solid-state structure of the complexes [6].

Thus, in order to extend the range of lanthanide phospholyl complexes, we wished to prepare and study mixed cyclooctatetraenyl(phospholyl)lanthanide compounds. We also wished to introduce the 3,4-dimethyl-2,5-bis(trimethylsilyl)-phospholyl (Dsp) ligand in lanthanide chemistry because of its very large steric bulk and ease of synthesis: this ligand has been recently developed by Westerhausen et al. and successfully employed in alkaline-earth chemistry [7]. We report here

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* Corresponding author. Tel.: + 33-380-396-061; fax: + 33-380-396-084.
E-mail address: mvisseau@u-bourgogne.fr (M. Visseaux).

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on the synthesis of the new potassium 3,4-dimethyl-2,5-bis(trimethylsilyl)phospholide [K(Dsp)] (**1**), of several cyclooctatetraenyl(phospholyl)lanthanide complexes together with the crystal structure of one of them, and on a new synthesis and crystal structure of the known precursor cyclooctatetraenyl(chloro)samarium.

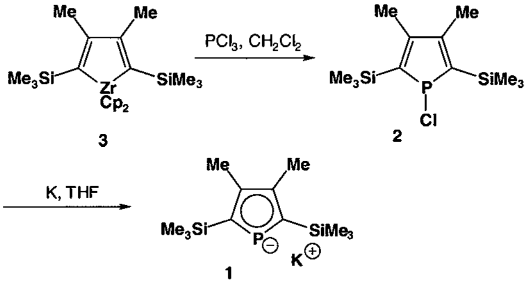
2. Results and discussion

2.1. Syntheses

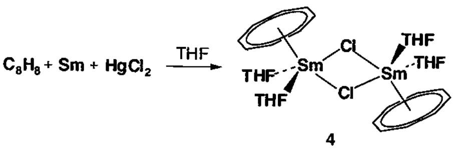
Westerhausen [7] reported difficulties in the synthesis of pure 1-chloro-3,4-dimethyl-2,5-bis(trimethylsilyl)phosphole (**2**) by the metathesis of 3,4-dimethyl-2,5-bis(trimethylsilyl)-zirconacyclopentadiene (**3**) with PCl_3 in THF. Almost at the same time, it was found [8] that 1-bromo-3,4-dimethyl-2,5-bis(trimethylsilyl)phosphole could be made in reasonable yield similarly from **3** and PBr_3 but with the use of dichloromethane as solvent; a 2,5-disilyl-substituted 1-chlorophosphole was also reported in the same paper. We reinvestigated Westerhausen's results for the reaction of **3** with PCl_3 but using dichloromethane as solvent and a higher concentration. We found that the reaction, which can be monitored by the progressive precipitation of dichlorozirconocene and by ^{31}P-NMR, was complete after 2 h. Crude **2** could even be purified by short-path distillation (Kugelrohr). Subsequent treatment of **2** with potassium metal afforded a fair yield of potassium 3,4-dimethyl-2,5-bis(trimethylsilyl)phospholide (**1**) (Scheme 1).

The proton and ^{31}P-NMR characteristics of the Dsp ligand in **1** are quite similar to those in $[Cp(Dsp)_2Ca_2Cl(THF)_2]$ [7], in accordance with the probably similar (ionic) metal–Dsp ligand interactions in these two compounds.

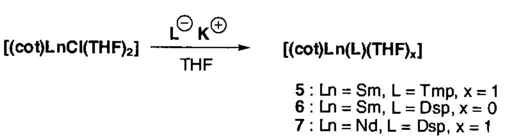
The (cyclooctatetraenyl)lanthanide chloride precursors were also prepared according to known procedures [9]. However, we found an alternative preparation of cyclooctatetraenyl(chloro)samarium. When 1,3,5,7-cyclooctatetraene (cot), samarium metal and mercuric chloride were stirred together in THF, a fair yield of $[\{(cot)SmCl(THF)_2\}_2]$ (**4**) was isolated. This method is advantageous because it avoids the use of potentially explosive $[K_2(cot)]$ [10] and also because it is a one-pot procedure (Scheme 2). This compound had been previously prepared similarly by Mashima et al. using Ph_3PCl_2 as the oxidant [11].



Scheme 1.



Scheme 2.



Scheme 3.

An analogous procedure was used by Edelmann et al. [12] to synthesise [(cot*)Ln(DAD)(THF)] (Ln = Yb, Sm; cot* = $1,4\text{-}(Me_3Si)_2C_8H_6$; DAD = 1,4-diazadienes). Very recently, $[(cot)TmI(THF)_2]$ could be similarly obtained by reduction of 1,3,5,7-cyclooctatetraene by TmI_2 [13].

The [(cot)Ln(Phospholyl)] complexes were then prepared in good yield by the standard metathetical reaction of the [(cot)LnCl] precursors with the potassium phospholides [K(Dsp)] (**1**) and [K(Tmp)] (Scheme 3).

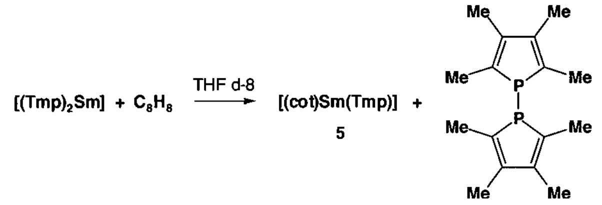
After the usual work-up, **6** and **7** were crystallised in toluene. According to NMR analysis, **6** did not contain any coordinated THF. A slight pressurisation of the NMR tube led to a THF adduct (paramagnetic THF signals), but this ligand could be reversibly decoordinated by pumping off the solvents. Complex **7** showed a different behaviour, the crystals were isolated as a solvate. Concerning **5**, after reaction in THF, the black–green solid obtained after evaporation was poorly soluble in toluene (and insoluble after evaporation of this toluene solution). It was then extracted once again with THF, and concentration of that solution led to violet crystals unfortunately not suitable for X-ray analysis. Elemental analysis and NMR data are consistent with the formula [(cot)Sm(Tmp)(THF)].

^{1}H-NMR data of the complexes **5**–**7** are reported in Table 1. It is noteworthy that the proton NMR signal of the cot ligand in **5** appears in the same range as $[(cot)Sm(C_5Me_4PPh_2)(THF)]$ [14] and [(cot)Sm(2,5-di-*tert*-butylpyrrolyl)(THF)] [15] (10.24 and 10.45 ppm in C_6D_6, respectively), which bear electron-deficient cyclopentadienyl or pyrrolyl ligands, whereas in unsolvated **6**, this signal is shifted upfield, in a region where the signals of unsolvated cyclooctatetraenyl complexes such as [(cot)SmCp*] [16] or $[(cot)Sm(C_5H^{i}Pr_4)]$ [4] (8.88 and 8.64 ppm in C_6D_6, respectively) appear.

Table 1
^{1}H-NMR data for complexes **5**, **6**, and **7** (δ, C_6D_6, 300 K)

Compound	**5** [a]	**6**	**6** [a]	**7**
C_8H_8	10.59	9.65	9.95	−15.93
CH_3 (phospholyl)	3.79; 0.67	4.01	4.38	15.58
$Si(CH_3)_3$	–	0.16	−0.03	−7.52
THF	4.39; 1.76	–	4.93; 1.99	5.45; 6.60

[a] In the presence of THF vapour.



Scheme 4.

Nevertheless, **6** is not too sterically crowded: pressurisation with two equivalents of THF afforded an adduct showing paramagnetic signals for the THF ligand. Easy and reversible decoordination of the THF ligand has already been observed with the related [(cot)Sm($C_5Me_4PPh_2$)(THF)] [14], contrarily to [(cot)SmCp*(THF)] [17]. In complex **7**, desolvation is no longer possible because of the more electrophilic character of the larger neodymium atom. Such a behaviour is indicative of the difference of reactivity which may exist in the early series: the steric aspect is more pronounced in the case of neodymium while, in the case of samarium, the coordinative behaviour of the metal may also be sensitive to electronic factors.

In a NMR experiment, a solution of [$(Tmp)_2Sm$] [18] in THF d-8 was treated with an excess of 1,3,5,7-cyclooctatetraene. In the proton NMR of the reaction mixture, **5** could be detected together with signals corresponding to $(Tmp)_2$ (Scheme 4).

Such a behaviour parallels that found in Cp* chemistry, where Edelmann et al. [19] have also found that [$Cp^*_2Sm(THF)_2$] could be oxidised with 1,3,5,7-cyclooctatetraene into [(cot)SmCp*(THF)] and bis(pentamethylcyclopentadienyl) (Cp^*_2).

2.2. Crystal structures

Crystal data and data collection parameters for **4** and **7** are listed in Table 2, and selected bond lengths and angles are presented in Table 3. Figs. 1 and 2, respectively, represent ORTEP plots of **4** and **7** together with the numbering scheme used.

The whole [(cot)LnCl$(THF)_2$] family was synthesised by Streitwieser et al. [9] and by Wayda [20], but only [{(cot)CeCl$(THF)_2$}$_2$] has been structurally characterised [21]. Like this complex, **4** is a dimer in which the two samariums are bridged by two chlorine atoms. The differences between the two Ln–Cl bridge distances in [(cot)CeCl$(THF)_2$] (0.08 Å) and **4** (0.07 Å) are comparable, and so are the Cl–Ln–Cl′ angles (73.4 and 73.6°, respectively). The smaller ionic radius of Sm^{3+} with respect to that of Ce^{3+} due to the lanthanide

Table 2
Crystal data and data collection parameters for **4** and **7**

Compound	**4**	**7**
Empirical formula	$C_{16}H_{24}ClO_2Sm$	$C_{24}H_{40}NdOPSi_2$
Formula weight	434.15	575.95
Crystal habit	Purple cube	Emerald green plate
Crystal size (mm)	0.20 × 0.20 × 0.20	0.22 × 0.20 × 0.10
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (#14)	$P2_1/m$ (#11)
a (Å)	11.6570(5)	8.412(5)
b (Å)	12.7970(4)	17.983(5)
c (Å)	11.7340(5)	8.949(5)
β (°)	113.1440(16)	96.310(5)
V (Å^3)	1609.54(11)	1345.5(12)
Z	4	2
D_{calc} (g cm^{-3})	1.792	1.422
$F(000)$	860	590
μ (cm^{-1})	3.813	2.090
Maximum θ	26.35	29.93
Independent reflections	3286	3994
Reflections used	2920 with $I > 2\sigma(I)$	3722 with $I > 2\sigma(I)$
wR_2 (all data)	0.0706	0.0598
R_1	0.0220	0.0233
Goodness-of-fit	1.041	1.011

Table 3
Selected bond lengths (Å) and angles (°) for compounds **4** and **7**

Compound **4**			
Bond lengths			
Sm(1)–O(2)	2.524(2)	Sm(1)–O(1)	2.528(2)
Sm(1)–C(5)	2.651(4)	Sm(1)–C(6)	2.653(4)
Sm(1)–C(4)	2.656(4)	Sm(1)–C(3)	2.665(3)
Sm(1)–C(8)	2.666(3)	Sm(1)–C(2)	2.668(3)
Sm(1)–C(1)	2.676(3)	Sm(1)–C(7)	2.679(4)
Sm(1)–Cl(2)	2.8135(8)	Sm(1)–Cl(2) # 3	2.8804(8)
C–C(COT) (av.)	1.401(16)		
Bond angles			
O(2)–Sm(1)–O(1)	68.87(7)	Cl(2)–Sm(1)–Cl(2) # 3	73.62(3)
C–C–C(COT) (av.)	134.9(12)		
Compound **7**			
Bond lengths			
Nd(1)–O(1)	2.518(2)	Nd(1)–C(7)	2.632(2)
Nd(1)–C(8)	2.655(2)	Nd(1)–C(9)	2.710(2)
Nd(1)–C(10)	2.659(2)	Nd(1)–C(1)	2.866(2)
Nd(1)–C(2)	2.853(2)	Nd(1)–P(1)	3.0195(4)
P(1)–C(1)	1.766(2)	C(1)–C(2)	1.424(2)
C(2)–C(2) # 4	1.411(4)	C–C(COT) (av.)	1.38(2)
Bond angles			
C(1)–P(1)–C(1) # 4	91.9(1)	Cnt–Nd(1)–Cnt	144.1
C–C–C(COT) (av.)	135.7(16)		

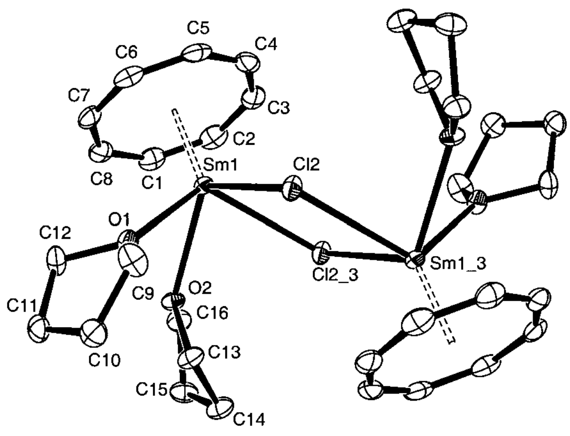


Fig. 1. An ORTEP plot of the dimeric structure of **4** together with the numbering scheme used (50% ellipsoids).

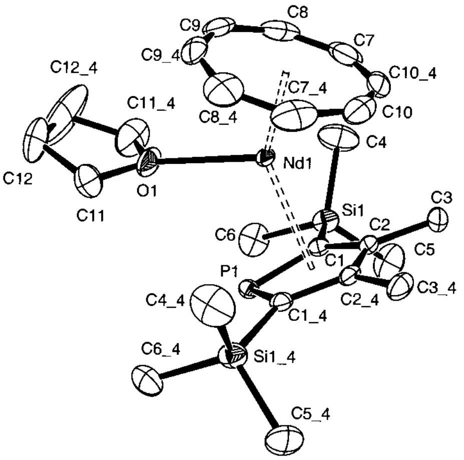


Fig. 2. An ORTEP plot of one molecule of **7** together with the numbering scheme used. (50% ellipsoids).

contraction [22] is evidenced by the Ln–centroïd(cot) distance (Ln = Ce, Sm) which is smaller in **4** (1.94 Å) than in [{(cot)CeCl(THF)$_2$}$_2$] (2.01 Å).

The structure of **7** shows the Nd atom coordinated η^8- to the cot ligand, η^5- to the Dsp ligand and solvated with just one molecule of THF; **7** can thus be compared to another mixed cot/heterocyclopentadienyl complex, the already mentioned [(cot)Sm(2,5-di-*tert*-butylpyrrolyl)(THF)] [15]. In this complex, the following distances: Sm–cnt(cot) (1.91 Å) (cnt = centroïd), Sm–cnt(Pyr) (2.46 Å) (Pyr = pyrrolyl) and angle: cnt(cot)–Sm–cnt(Pyr) (144.48°) can be, respectively, compared to Nd–cnt(cot) (1.94 Å), Nd–cnt(Dsp) (2.57 Å) and cnt(cot)–Nd–cnt(Dsp) (144.1°), for complex **7**; the THF ligand is in both complexes on the same side as the heteroatom. The longer Nd–cnt distance is probably due to the long Nd–P bond; this bond is longer than in the only other compound displaying a Nd–P bond: [{(SiMe$_3$)$_2$P}$_3$Nd(THF)$_2$] [23], but similar to the Sm–P bonds of several π-phospholyl samarium complexes [5]. It can also be noted that the Nd–cnt(cot) distance (1.94 Å) is equivalent to that found in [(cot)Nd(C$_5$H^{i}Pr$_4$)] (1.90 Å), despite the presence of a THF molecule in **7**. Finally, the geometric parameters of the Dsp ligand in **7** and in [Cp(Dsp)$_2$Ca$_2$Cl(THF)$_2$] [7] are not significantly different. In particular, the average C–P bond distances and C–P–C bond angles in [Cp(Dsp)$_2$Ca$_2$Cl(THF)$_2$] (1.776(11) Å and 91.7(3)°, respectively) are comparable to that in **7** (see Table 3).

Most structurally characterised mixed cyclooctatetraenyl–cyclopentadienyl complexes of early lanthanides (III) (from La to Gd) either have two molecules of THF coordinated to the metal, such as in [(cot)SmC$_5$H$_4$PPh$_2$(THF)$_2$] [14], [(cot)LaC$_5$Me$_4$H(THF)$_2$] [24], [(cot)PrCp(THF)$_2$], [(cot)Pr(indenyl)(THF)$_2$] [25], and [(cot)Nd(cpnCp)(THF)$_2$] (cpn = (cyclopentyl)cyclopentadienyl) [26], or none, like [(cot)SmCp*] [27] and [(cot)Ln(C$_5$H^{i}Pr$_4$)] (Ln = Nd, Sm) [4]; however, there is one gadolinium complex which crystallises as both monosolvated and disolvated species in the unit cell: [(cot)Gd(cpnCp)(THF)$_2$] and [(cot)Gd(cpnCp)(THF)$_2$] [26]. In this sense, complex **7**, together with its analogue: [(cot)Sm(2,5-di-*tert*-butylpyrrolyl)(THF)] [15], with just one mole of THF, are atypical.

3. Experimental

All reactions were performed in dry solvents under dry oxygen-free Ar in Braun Labmaster 130 or Jacomex glove boxes or on a vacuum line. NMR spectra were recorded on Bruker AC200 or ARX300 spectrometers. [K(Tmp)] [28], [K$_2$(cot)] [10] and [{(cot)NdCl(THF)$_2$}$_2$] [9] were prepared as previously described. Chemical shifts are expressed in parts per millions downfield from internal TMS for ^{1}H and ^{13}C, and from external 85% H_3PO_4 for ^{31}P. Elemental analyses were obtained at the Service d'Analyses de l'Université de Dijon.

3.1. *1-Chloro-3,4-dimethyl-2,5-bis(trimethylsilyl)-phosphole (**2**)*

To a solution of bis(cyclopentadienyl)[3,4-dimethyl-2,5-bis(trimethylsilyl)zircona-cyclopentadiene (5.02 g, 11.26 mmol) in CH_2Cl_2 (20 ml) was added phosphorus trichloride (1 ml, 1.57 g, 11.46 mmol), and the reaction mixture was stirred for 2 h, while Cp_2ZrCl_2 progressively precipitated. The reaction mixture was filtered and evaporated to dryness and the residue was extracted into hexane and evaporated, leaving a yellow oil that was short-path-distilled at 110 °C/0.1 torr (1.72 g, 5.9 mmol, 52%).

NMR: ^{1}H (CDCl$_3$): 0.30 (s, 18H, (CH_3)$_3$Si), 2.16 (d, J_{PH} = 6.5, 6H, CH_3–C3). ^{13}C{^{1}H} (CDCl$_3$): 0.12 (d, J_{PC} = 3.5, (CH$_3$)$_3$Si), 18.14 (d, J_{PC} = 4, CH$_3$–C3), 145.99 (d, J_{PC} = 51, C2), 159.48 (d, J_{PC} = 11, C3). ^{31}P{^{1}H} (CDCl$_3$): 93.9.

*3.2. Potassium 3,4-dimethyl-2,5-bis(trimethylsilyl)-phospholide (**1**)*

A solution of **1** (0.650 g, 2.23 mmol) and potassium metal (400 mg, 10.2 mmol) in THF (25 ml) was stirred and progressively heated to reflux. The solution was then stirred for 30 min at reflux and slowly cooled to room temperature (r.t.). The residue was filtered and evaporated to dryness under vacuum and continuously extracted with warm Et_2O for 24 h. The ether extract was evaporated to dryness, filtered and rinsed with hexane, to yield **2** as a white solid (0.45 g, 1.53 mmol, 68%).

NMR: ^1H (C_4D_8O): 0.31 (s, 18H, $(CH_3)_3Si$), 2.36 (s, 6H, CH_3–C3). $^{13}C\{^1H\}$ (C_4D_8O): 2.54 (d, $J_{PC} = 7$, $(CH_3)_3Si$), 17.72 (s, CH_3–C3), 136.64 (s, C3), 140.50 (d, $J_{PC} = 64$, C2). $^{31}P\{^1H\}$ (C_4D_8O): 150.0. Anal. Calc. for $C_{12}H_{24}KPSi_2$: C, 48.93; H, 8.21. Found: C, 48.88; H, 8.08%.

*3.3. Cyclooctatetraenylbis(tetrahydrofuran)samarium (**4**)*

A solution of cyclooctatetraene (420 mg, 4 mmol) in THF (15 ml) was stirred at r.t. with samarium (600 mg, 4 mmol) and mercuric chloride (540 mg, 2 mmol) for 48 h. The resulting violet solution was filtered and the precipitate continuously extracted with warm THF for 12 h. The reaction mixture was then evaporated to dryness, and the resulting violet powder rinsed with Et_2O and dried under vacuum (854 mg, 1.97 mmol, 49%).

NMR: ^1H (C_4D_8O) 1.78 (THF), 3.62 (THF), 11.16 (cot).

*3.4. Cyclooctatetraenyltetramethylphospholyl-(tetrahydrofuran)samarium (**5**)*

THF (30 ml) was condensed at −80 °C onto a mixture of tetramethylphospholyl–potassium (175 mg, 0.99 mmol) and $[(cot)SmCl(THF)_2]_2$ (430 mg, 0.49 mmol), and the solution was allowed to warm at r.t. After 12 h of stirring, the solvent was evaporated off and the residue extracted twice with toluene. The resulting purple–red solution was filtered and slowly concentrated to give, after washing with pentane and drying under vacuum, 295 mg (0.49 mmol, 51%) of small green–black crystals.

NMR: ^1H (C_4D_8O) 0.66 (6H, CH_3), 3.18 (6H, CH_3), 10.46 (8H, cot). $^{31}P\{^1H\}$ (C_4D_8O): no signal detected. Anal. Calc. for $C_{20}H_{28}OPSm$: C, 51.50; H, 6.01. Found: C, 51.36; H, 5.92%. The crystals were soluble in C_6D_6 only in the presence of THF (ca. 2–3 equivalents): 0.67 (6H, CH_3), 1.76 (THF-β), 3.79 (6H, CH_3), 4.39 (THF-α), 10.59 (8H, cot).

3.5. Reaction of $[(Tmp)_2Sm]$ with 1,3,5,7-cyclooctatetraene (NMR experiment)

In an NMR tube, $[(Tmp)_2Sm]$ (21 mg, 0.05 mmol) was dissolved in C_4D_8O (0.5 ml), and the solution was checked by ^{31}P-NMR; the spectrum displayed a characteristic signal at −580 ppm [18]. Cyclooctatetraene (one drop, 10 mg, excess) was then added to this solution. ^{31}P-NMR showed complete disappearance of the $[(Tmp)_2Sm]$ signal and a new peak at −8.5 ppm, characteristic of $(Tmp)_2$ [29]. In the ^1H-NMR spectrum, the resonances of **5** and those of $(Tmp)_2$ [1.78(m); 1.88(s)] were observed.

*3.6. Cyclooctatetraenyl3,4-dimethyl-2,5-bis(trimethylsilyl)phospholylsamarium (**6**)*

THF (30 ml) was condensed at −80 °C onto a mixture of $[(cot)SmCl(THF)_2]_2$ (429 mg, 0.49 mmol) and a stoichiometric amount of **1**, and the solution was allowed to warm at r.t. After 8 h of stirring, the solvent was evaporated off and the residue extracted twice with toluene. The resulting purple–blue solution was filtered and slowly concentrated to give, after decantation and drying under vacuum, 240 mg (0.47 mmol, 48%) of a microcrystalline purple–black powder.

NMR: ^1H (C_6D_6) 0.16 (18H, $(CH_3)_3Si$), 4.01 (6H, CH_3), 9.65 (8H, cot). $^{31}P\{^1H\}$ (C_6D_6): 134.1. Anal. Calc. for $C_{20}H_{32}PSi_2Sm$: C, 47.10; H, 6.32. Found: C, 45.96; H, 6.14%.

*3.7. Cyclooctatetraenyl3,4-dimethyl-2,5-bis(trimethylsilyl)phospholylneodymium (**7**)*

Same procedure as for **6**, starting from $[(cot)NdCl(THF)_2]_2$ (125 mg, 0.15 mmol) with solid $K_2(cot)$ reagent and a stoichiometric amount of **1**, leading to a light green microcrystalline powder (100 mg, 0.17 mmol, 58%).

NMR: ^1H (C_6D_6) −15.93 (8H, cot), −7.52 (18H, $(CH_3)_3Si$), 5.45 (THF), 6.60 (THF), 15.58 (6H, CH_3). Despite repeated attempts, no meaningful analyses could be obtained for this compound.

3.8. X-ray data collection and processing

Complex **4** was recrystallised from warm THF, and **7** was recrystallised from toluene at r.t. Data were collected on an Enraf Nonius KappaCCD diffractometer using Mo–K_α radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The crystal structures were solved by direct methods using maXus. While initial refinements were performed with the latter, final least-squares were conducted with SHELXL97 (full-matrix on F^2). No absorption corrections were applied. A mixed model was used for the treatment of the hydrogen atoms, while using anisotropic temperature factors for all other atoms.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 170640 for compound **4** and 170639 for compound **7**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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