Synthesis and Reactivity of Bis(phospholyl)neodymium(III) and -samarium(III) Chlorides and Alkyl Derivatives

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The reaction of 2,3,4,5-tetramethylphospholylpotassium [C_4Me_4PK] with [$LnCl_3(THF)_x$] (Ln = Nd, Sm) in a 2:1 ratio gave unsolvated ate complexes of the formula [$(C_4Me_4P)_2LnCl_2K$]. Crystallisation of the samarium complex from ether afforded a polymeric ether solvate: {[(η^5-C_4Me_4P)Sm(μ_3-Cl)$_2$(μ:η^5,η^1-C_4Me_4P)K(Et_2O)]$_\infty$}, which was characterised by X-ray crystallography. Reaction of [$(C_4Me_4P)_2LnCl_2K$] with [$LiCH(SiMe_3)_2$] in toluene gave the alkyl complexes [$(C_4Me_4P)_2LnCH(SiMe_3)_2$]; these complexes were most efficiently prepared from [$LnCl_3(THF)_x$], [KC_4Me_4P] and [$LiCH(SiMe_3)_2$] in a one-pot procedure. Reaction of [$(C_4Me_4P)_2LnCH(SiMe_3)_2$] with molecular hydrogen gave [$(C_4Me_4P)_2NdH$], when Ln = Nd, whereas, when Ln = Sm, reduction occurred and the already known [$(C_4Me_4P)_2Sm$] was isolated instead.

Introduction

Bis(cyclopentadienyl) and substituted bis(cyclopentadienyl) complexes of trivalent lanthanides are interesting because of their structural and mechanistic properties, and also for their catalytic potential.[1] Modification of the parent cyclopentadienyl ligands has been achieved by the introduction of various types of substituents, e.g. those with bulky,[2] chiral and/or bridging properties.[3] A heterocyclopentadienyl ligand such as the 2,3,4,5-tetramethylphospholyl ligand (C_4Me_4P) has been used successfully as an alternative to the cyclopentadienyl ligand in organolanthanide and organoactinide chemistry.[1a] The C_4Me_4P ligand is interesting because it can be considered as relatively bulky, with steric properties resembling that of the ubiquitous C_5Me_5 ligand (in fact very close to that of the tetramethylcyclopentadienyl ligand[4]), while it is much less electron-rich than polyalkylated cyclopentadienyl ligands, and its electronic properties are similar to those of the unsubstituted Cp ring.[5] The authors have described previously (in a communication) the interaction of the C_4Me_4P ligand with the halides of yttrium and lutetium and the synthesis of the ate complexes [$(C_4Me_4P)_2LnCl_2Li(solv.)_2$],[6] and wish to extend these results to the synthesis of bis(tetramethylphospholyl) complexes of samarium and neodymium, because of the more interesting potential of bis(cyclopentadienyl) complexes of the larger Nd^{III} and Sm^{III} ions in catalysis. While catalytic tests on the title compounds are underway, this paper reports on the synthetic part of the work concerning the synthesis of bis(tetramethylphospholyl)neodymium and -samarium chlorides and alkyl derivatives, and the synthesis of a bis(phospholyl)neodymium hydride.

Results

Synthesis of [$(C_4Me_4P)_2SmCl_2K$] (1) and [$(C_4Me_4P)_2NdCl_2K$] (2)

The preparation of [$(C_4Me_4P)_2LnCl_2Li(solv.)_2$] involved the reaction of anhydrous [YCl_3] or [$LuCl_3$] with two equiv. of [C_4Me_4PLi] prepared in situ. Due to the previous development of the use of the potassium salt [C_4Me_4PK],[7] which can be isolated and purified by recrystallization, the reaction of two equiv. of [C_4Me_4PK] with one equiv. of anhydrous [$SmCl_3$] or [$NdCl_3$] in THF was tried initially. No reaction was found to occur even after refluxing overnight: No colour change took place, and examination of the reaction mixture by ^{31}P NMR only showed the [C_4Me_4PK] resonance.

However, when THF-solvated [$LnCl_3(THF)_x$] was substituted for anhydrous [$LnCl_3$], the reaction with two equiv. of [C_4Me_4PK] started immediately (at room temp.), as indicated by a colour change to orange (Ln = Sm) or blue (Ln = Nd), and was completed within 1 h. After evaporation of the solvent, extraction of the residue with ether and drying under vacuum, light orange (Ln = Sm) or light blue (Ln = Nd) powders were obtained in fair to good yield. These products were assigned the formulas of unsolvated ate complexes [$(C_4Me_4P)_2SmCl_2K$] (**1**) and [$(C_4Me_4P)_2NdCl_2K$] (**2**), respectively, on the following grounds: (a) ^{31}P- and ^1H-NMR spectra of the isolated products displayed coordination shifts of the methyl and phosphorus resonances indicating that coordination of the C_4Me_4P ligand around Nd and Sm had indeed occurred, (b) only very small traces of ether or THF were present according to the ^1H-NMR spectra of either the Nd or Sm

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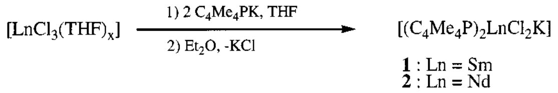
complexes in [D$_8$]THF, (c) elemental analyses were not compatible with the possibility of neutral complexes such as $\{[(C_4Me_4P)_2LnCl]_x\}$ but were in agreement with the formulae given above for **1** and **2** (Scheme 1).



$$[LnCl_3(THF)_x] \xrightarrow[2)\ Et_2O,\ -KCl]{1)\ 2\ C_4Me_4PK,\ THF} [(C_4Me_4P)_2LnCl_2K]$$

1 : Ln = Sm
2 : Ln = Nd

Scheme 1. Synthesis of the complexes **1** and **2**

$[LaCl_3(THF)_x]$ also reacted with $[C_4Me_4PK]$ but the isolated product, presumably $[(C_4Me_4P)_2LaCl_2K]$, was obtained in very low yield because the ether extraction procedure worked poorly for the very insoluble La compound.

Crystal Structure of $\{[(\eta^5\text{-}C_4Me_4P)Sm(\mu_3\text{-}Cl)_2(\mu{:}\eta^5,\eta^1\text{-}C_4Me_4P)K(Et_2O)]_\infty\}$ (3)

In order to gain more insight into the structure of the aforementioned ate complexes X-ray analysis of the crystal structure was carried out. Recrystallization of **1** from diethyl ether gave crystals that were suitable for X-ray analysis. It appears that **1** picked up one diethyl ether molecule in the process, which ended up coordinated to the potassium ion in the crystal, and that the analyzed structure was that of **3**: $\{[(\eta^5\text{-}C_4Me_4P)Sm(\mu_3\text{-}Cl)_2(\mu{:}\eta^5,\eta^1\text{-}C_4Me_4P)K(Et_2O)]_\infty\}$. X-ray details are listed in Table 1, selected bond lengths and angles are collected in Table 2 while ORTEP plots of the asymmetric unit of **3** and of four such repeating units are shown in Figures 1 and 2, respectively. The structure of **3** closely resembles that of $[\{(\eta^5\text{-}C_5Me_5)_2Ce(\mu_3\text{-}Cl)_2K(THF)\}_\infty]$ previously described by Evans:[8] In both cases it is the triply bridging chlorine atoms (between the Ln and K atoms) that are responsible for the polymeric chain that links the organolanthanide residues. However, there are two differences between the structures of **3** and of Evans' cerium complex: (a) in Evans' complex, which is noncentrosymmetric, the $(C_5Me_5)_2CeCl_2K(THF)$ unit repeats itself by a glide plane along the axis of the polymeric chain, whereas in **3**, which is centrosymmetric, the $(C_4Me_4P)_2SmCl_2K(Et_2O)$ units are related by inversion centres on the axis of the chain; (b) in **3** the potassium atom is six-coordinate because of additional bonding with the phosphorus lone pair on one of the C_4Me_4P ligands.

Bond lengths and angles of **3** are listed in Table 2. The Sm−Cl bonds (2.66 and 2.67 Å) are unusually short for a triply bridging chlorine atom bonded to Sm (usually 2.76−2.92 Å).[9] Interestingly, Evans had also noted short Ce−Cl bonds for the triply bridging chlorine atoms in $\{[(\eta^5\text{-}C_5Me_5)_2Ce(\mu_3\text{-}Cl)_2K(THF)]_\infty\}$. The Sm−P bonds are similar to that of other phospholylsamarium(III) complexes.[10] The K−P2 distance is within the recorded bond length-limits (towards the high end, however),[11] denoting K−P electrostatic interaction. The K−O bond length is significantly longer (0.1 Å) than in other K−OEt$_2$ solvates.[12]

Table 1. Table of X-ray data for **3**

Empirical formula	$C_{20}H_{33}Cl_2KOP_2Sm$
Crystal description and size [mm]	orange plate, 0.22 × 0.20 × 0.07
Space group	monoclinic, $P2_1/n$ (no. 14)
a [nm]	1.6145(2)
b [nm]	0.8661(1)
c [nm]	1.8883(2)
β [°]	101.55(2)
V [nm^3]	2.587(1)
Z	4
$d_{calcd.}$ [g·cm^{-3}]	1.570
$F(000)$	1224
Radiation	Mo-K_α (λ = 71.073 pm)
μ [mm^{-1}]	2.778
Temperature [K]	123 ± 0.1
Max. 2θ [°]	60
No. of unique reflections	7514
Reflections included	4755 [$F_o^2 > 3\sigma(F_o^2)$]
Corrections	Lorentz polarisation, absorption (ψ-scans), min. 0.743, max. 1.000
R	0.039
R_w	0.047
G.O.F.	1.008
convergence, largest shift/error	0.00
Minimisation function	$w(\lvert F_o\rvert - \lvert F_c\rvert)^2$, $w = 4F^2/\sigma^2(F^2)$
Least-squares weights	$4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F^2) = \sigma^2(I) + (pF^2)^2$
Instrument instability factor, p	0.06
Largest peak in final diff. map	1.87(16) eÅ^{-3}
Largest hole in final diff. map	−0.32(16) eÅ^{-3}

Table 2. Selected bond lengths [pm] and angles [°] for **3**

Sm−Cl1	266.2(1)	K−P2	346.8(2)
Sm−Cl2	267.1(1)	K−O	282.7(4)
Sm−P1	290.5(2)	P−C(av.)	176.0(7)
Sm−P2	292.6(1)		
Sm−C(av.)	278(2)	Cl1−Sm−Cl2	90.55(4)
Cl1−K	318.8(2)	Cl1−K−Cl2	70.89(4)
Cl2−K	334.4(2)	Cnt−Sm−Cnt[a]	131.6

[a] Cnt denotes the centroid of the phospholyl ligand.

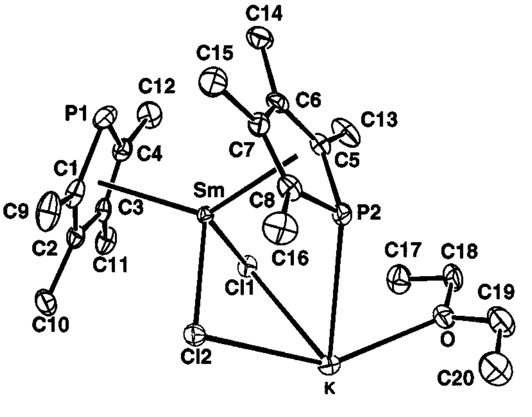


Figure 1. ORTEP plot of **3** (asymmetric unit) together with the numbering scheme used; ellipsoids are scaled to enclose 50% of the electronic density

Synthesis of $[(C_4Me_4P)_2SmCH(SiMe_3)_2]$ (4) and $[(C_4Me_4P)_2NdCH(SiMe_3)_2]$ (5)

Alkyl compounds of organolanthanides are the precursors of organolanthanide hydrides by hydrogenolysis of the lanthanide−carbon σ-bond. [Bis(trimethylsilyl)methyl]lan-

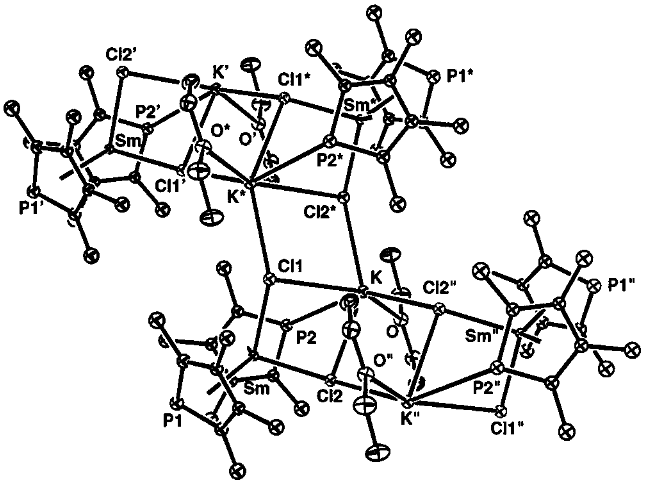
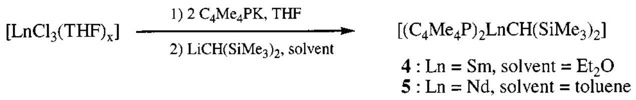


Figure 2. ORTEP plot of **3** (four repeating units); ellipsoids are scaled to enclose 50% of the electronic density

thanide complexes are often used because they are usually hydrocarbon-soluble unsolvated compounds that can be straightforwardly obtained by reaction of organolanthanide halides with $[LiCH(SiMe_3)_2]$.[2g,2i] Initially, small-scale experiments established that reaction of **1** and **2** with $[LiCH(SiMe_3)_2]$ did produce the desired alkyl complexes $[(C_4Me_4P)_2SmCH(SiMe_3)_2]$ (**4**) and $[(C_4Me_4P)_2NdCH(SiMe_3)_2]$ (**5**). However, the overall yields were not especially good and we found that **4** and **5** were best prepared by a one-pot reaction: The crude products from the reaction of $[LnCl_3(THF)_x]$ with $[C_4Me_4PK]$ reacted smoothly with $[LiCH(SiMe_3)_2]$ to give **4** and **5** in fair to good yields. The main advantage was in avoiding the long extraction procedure necessary to isolate pure **1** and **2** (Scheme 2).



Scheme 2. One-pot synthesis of alkyl complexes **4** and **5**

$[(C_4Me_4P)_2LaCH(SiMe_3)_2]$ was also obtained by the same procedure, but the yields were very low and inconsistent. The NMR properties of **4** and **5** are similar to that of their C_5Me_5 analogues:[2g] The steric bulk of the $(C_4Me_4P)_2Ln$ moiety impedes free rotation of the alkyl ligand around the Ln−C σ-bond so that the two C_4Me_4P rings are anisochronous. Thus, **4** and **5** each show four proton signals for the α-, β-, α′- and β′-methyl groups and two phosphorus resonances.

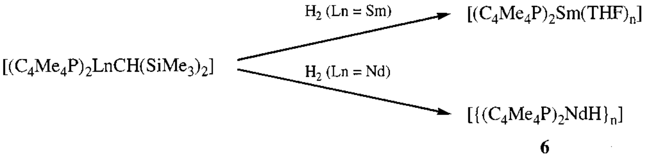
Reaction of $[(C_4Me_4P)_2LnCH(SiMe_3)_2]$ with H_2 (Ln = Sm, Nd) and the Synthesis of $[\{(C_4Me_4P)_2NdH\}_n]$ (6)

Exposure of a benzene solution of **4** to dihydrogen resulted in the formation of a dark black product which gradually separated from solution. ^1H NMR of the reaction mixture indicated the presence of bis(trimethylsilyl)methane. The black product was characterised as $[(C_4Me_4P)_2Sm(THF)_n]$ on the basis of the known high-field position of its ^{31}P resonance in THF solution (δ = −540).[13] Thus, presumably hydrogenolysis of the Sm−C bond occurred, but the hydride $[(C_4Me_4P)_2SmH]$ is unstable and decomposes by disproportionation into $[(C_4Me_4P)_2Sm]$ and H_2.

Hydrogenolysis of **5** under 1 atm of dihydrogen was then attempted in C_6D_6 (NMR experiment) and in pentane (preparative experiment). In the NMR experiment, formation of bis(trimethylsilyl)methane was evident from the ^1H-NMR data of the yellow solution while new resonances (α- and β-methyl groups on the C_4Me_4P ligand) appeared at δ = +17.8 and δ = −17.8; the phosphorus resonance was shifted to δ = 551. Exposure of this reaction mixture to THF vapour caused a colour change to green and a shift in the phosphorus resonance to δ = 377.

In the preparative experiment, a yellow precipitate was isolated, having an elemental analysis compatible with the composition $(C_4Me_4P)_2NdH$. However, this precipitate was sparingly soluble in C_6D_6, and the proton spectrum was complex; exposition of the NMR tube to THF vapour resulted in complete dissolution into a green solution and the appearance of a phosphorus resonance at δ = 377. The yellow precipitate was also soluble in C_4D_8O ($[D_8]$THF) and the proton spectrum displayed resonances at δ = 11.7 and δ = 1.14.

These experiments were interpreted as follows: In the NMR-tube experiment, the new peaks at δ = +17.8 and −17.8 (^1H) and 551 (^{31}P) are attributed to $\{[(C_4Me_4P)_2NdH]_n\}$ (**6**); upon exposure to THF vapour, a shift in the ^{31}P-NMR spectrum and colour change to green are presumably due to the formation of $[(C_4Me_4P)_2NdH(THF)]$. In the preparative experiment **6** was also formed. After precipitation from pentane, it was obtained in a sparingly soluble oligomeric form which converted into $[(C_4Me_4P)_2NdH(THF)]$ upon exposure to THF. The proton spectrum in C_4D_8O shows the resonances of the α- and β-methyl groupss of the C_4Me_4P ligand in $[(C_4Me_4P)_2NdH([D_8]THF)]$ (Scheme 3).



Scheme 3. Reaction of the alkyl complexes **4** and **5** with dihydrogen

Discussion

The reaction of $[C_4Me_4PK]$ with early lanthanide chlorides gives ate complexes containing the $[(C_4Me_4P)_2LnCl_2K]$ unit. The crystal structures of **3** $\{[(\eta^5\text{-}C_5Me_4P)_2Sm(\mu_3\text{-}Cl)_2K(Et_2O)]_\infty\}$ and of its analog $\{[(\eta^5\text{-}C_5Me_5)_2Ce(\mu_3\text{-}Cl)_2K(THF)]_\infty\}$ are closely related to one another. However, the vacuum-dried ate complexes $[(C_4Me_4P)_2LnCl_2K]$ isolated with the phospholyl ligand are desolvated, in contrast with those isolated with the C_5Me_5 ligand; the neutral complex $\{[(C_5Me_5)_2CeCl]_n\}$was obtained upon heating $[(C_5Me_5)_2CeCl_2K(THF)]$ under vacuum.[8] It is to be noted that the K−O(ether) bond in **3** is one of the longest recorded; a weakness of the K−O bond might thus account for the ease of desolvation in the case of the bis(phospholyl) ate complexes.

The one-pot reaction leading to **4** and **5** gives yields comparable to those obtained for the methods used in the preparation of other [bis(trimethylsilyl)methyl]lanthanide complexes, e.g. the analog $[(C_5Me_5)_2LnCH(SiMe_3)_2]$. Like these analogs, the alkyl complexes **4** and **5** are unsolvated, pentane-soluble crystalline powders. Whereas $[(C_5Me_5)_2SmCH(SiMe_3)_2]$ gives the hydride $\{[(C_5Me_5)_2SmH]_2\}$ in the presence of dihydrogen, the reaction of **4** with dihydrogen is different because in this case $[(C_4Me_4P)_2Sm]$ was isolated. The reduction of alkylsamarium(III) to Sm^{II} in the presence of H_2 is unprecedented. It is known in actinide chemistry that the uranium(IV) dihydride $[(C_5Me_5)_2UH_2]$ is unstable and disproportionates into the uranium(III) hydride $\{[(C_5Me_5)_2UH]_n\}$ and H_2, whereas $[(C_5Me_5)_2ThH_2]$ is stable.[14] Likewise, it has been reported that $[(C_4Me_4P)_2UH_2]$ was not detected when $[(C_4Me_4P)_2UR_2]$ (R = CH_3, CH_2SiMe_3) was exposed to dihydrogen; $[(C_4Me_4P)_3U]$ was obtained under these conditions.[15] Although the mechanistic pathway for the reduction to Sm^{II} is unknown, a samarium(III) hydride might be less stabilised with respect to reduction by the relatively poor π-donating C_4Me_4P ligand than by the electron-rich C_5Me_5 ligand.

Similarly to $[(C_5Me_5)_2NdCH(SiMe_3)_2]$, the reaction of **5** with dihydrogen gives the hydride $\{[(C_4Me_4P)_2NdH]_n\}$ (**6**). However, when isolated in pentane, this compound is in a sparingly soluble oligomeric form.

Experimental Section

General: All isolated compounds are air- and moisture-sensitive and were handled in rigourously inert-atmosphere conditions, on a vacuum line, or under argon in a glovebox (Braun Labmaster 130) with H_2O, O_2 < 1 ppm. $[C_4Me_4PK]$[7] was recrystallised from DME/THF. $[LiCH(SiMe_3)_2]$[16] was purified by extraction and crystallisation from hexane. Anhydrous lanthanide trichlorides were used as received from the suppliers and transformed into $[LnCl_3(THF)_x]$[17] according to known procedures. All solvents were dried by vacuum transfer from sodium/benzophenone. − NMR: 200 MHz for ^1H and 80 MHz for ^{31}P. − Elemental analyses: CHN analyser at the Université de Dijon.

General Procedure for the Synthesis of $[(C_4Me_4P)_2LnCl_2K]$: In a glovebox, a mixture of $[LnCl_3(THF)_x]$ (1 equiv.) and $[C_4Me_4PK]$ (2 equiv.) was placed in a vessel fitted to a swivel Schlenk filter. The filter assembly was then taken out of the glovebox, attached to a vacuum line through a vacuum PTFE stopcock and evacuated. THF (20 mL) was then transferred in vacuo onto the solids and the assembly was isolated from the vacuum by closing the stopcock.. The reaction mixture immediately became orange (Ln = Sm) or blue (Ln = Nd). After stirring at room temp. for 1 h, the solution was concentrated to dryness and diethyl ether (20 mL) was transferred in vacuo onto the residue. The filter assembly was then rotated and the solid residue continuously extracted on the frit with warm diethyl ether by placing the receiving flask in a water bath at about 40 °C, whereupon the product precipitated from the diethyl ether solution. The extraction usually took 1−2 d (Ln = Sm) and 4−5 d (Ln = Nd). The swivel filter was then rotated back into its original position and the product filtered, rinsed with cold diethyl ether and dried under vacuum overnight. The filter assembly was then returned to the glovebox and the product collected and weighed.

Isolation of $[(C_4Me_4P)_2SmCl_2K]$ (1): 340 mg (0.63 mmol, 63%) of **1** was isolated from $[SmCl_3(THF)_3]$ (474 mg, 1 mmol) and $[C_4Me_4PK]$ (356 mg, 2 mmol). − ^1H NMR ($[D_8]$THF): δ = 0.87 (s, 12 H), 1.98 (s, 12 H). − ^{31}P NMR: δ = 49.7. − $C_{16}H_{24}Cl_2KP_2Sm$ (538.68): calcd. C 35.68, H 4.49; found C 34.81, H 4.49.

Isolation of $[(C_4Me_4P)_2NdCl_2K]$ (2): 0.680 g (1.28 mmol, 57%) of **2** was isolated from $[NdCl_3(THF)_{1.5}]$ (800 mg, 2.23 mmol) and $[C_4Me_4PK]$ (0.800 g, 4.49 mmol). − ^1H NMR ($[D_8]$THF):δ = 0.66 (s, 12 H), 13.03 (s, 12 H). − ^{31}P NMR: δ = 459. − $C_{16}H_{24}Cl_2KNdP_2$ (532.56): calcd. C 36.09, H 4.54; found C 35.74, H 4.65.

Synthesis of $[(C_4Me_4P)_2SmCH(SiMe_3)_2]$ (4) (One-Pot Procedure): THF (20 mL) was condensed onto a mixture of $SmCl_3(THF)_3$ (474 mg, 1 mmol) and $[C_4Me_4PK]$ (356 mg, 2 mmol). After 1 h at room temp., the solvent was evaporated to dryness in vacuo. Solid $[LiCH(SiMe_3)_2]$ (166 mg, 1 mmol) was added to the residue and 20 mL of diethyl ether condensed onto the mixture. After 2.5 h, the reddish/brown reaction mixture was concentrated to dryness and extracted into 20 mL of hexane. The reaction mixture was concentrated to a small volume whereupon a precipitate appeared, which was filtered and rinsed with cold hexane, leaving **4** as an orange/brown powder (310 mg, 0.53 mmol, 53%) that was recrystallised from hexane. − ^1H NMR (C_6D_6): δ = −4.46 (s, 18 H), −3.02 (s, 6 H), −2.60 (s, 6 H), 2.70 (s, 6 H), 3.11 (s, 6 H), 20.31 (s, 1 H). − ^{31}PNMR: δ = 43.4 (s), 46.7 (s). − $C_{23}H_{43}P_2Si_2Sm$ (588.07): calcd. C 46.98, H 7.37; found C 46.32, H 7.68.

Synthesis of $[(C_4Me_4P)_2NdCH(SiMe_3)_2]$ (5) (One-Pot Procedure): THF (20 mL) was condensed onto a mixture of $[NdCl_3(THF)_{1.5}]$ (490 mg, 1.37 mmol) and $[C_4Me_4PK]$ (490 mg, 2.75 mmol). After 1 h at room temp., the solvent was evaporated to dryness in vacuo. Solid $[LiCH(SiMe_3)_2]$ (0.225 g, 1.35 mmol) was added to the residue and 20 mL of toluene was condensed onto the mixture. After 2.5 h, the green reaction mixture was concentrated to dryness and extracted into 20 mL of pentane. The reaction mixture was concentrated to a small volume whereupon a precipitate appeared, which was filtered and rinsed with cold pentane, leaving **5** as a forest-green powder (0.530 g, 0.91 mmol, 67%) that was recrystallised in pentane. − ^1H NMR (C_6D_6): δ = −11.71 (s, 18 H), −10.55 (s, 6 H), −8.01 (s, 6 H), 12.96 (s, 6 H), 13.34 (s, 6 H), 91.52 (br. s, 1 H). − ^{31}P NMR: δ = 456 (s), 501 (s). − $C_{23}H_{43}NdP_2Si_2$ (581.95): calcd. C 47.47, H 7.45; found C 47.11, H 7.40.

Reaction of $[(C_4Me_4P)_2SmCH(SiMe_3)_2]$ (4) with H_2: Dihydrogen gas was admitted to a solution of **4** (5 mg) in C_6D_6 at 0 °C. The reaction mixture immediately turned dark brown and a black precipitate appeared. While $CH_2(SiMe_3)_2$ was present in the C_6D_6 solution, a ^{31}P-NMR spectrum of the black precipitate in THF showed a signal at δ = −540, characteristic of $[(C_4Me_4P)_2Sm(THF)_x]$.

Reaction of $[(C_4Me_4P)_2NdCH(SiMe_3)_2]$ (4) with H_2 (NMR Scale): An NMR tube containing a solution of $[(C_4Me_4P)_2NdCH(SiMe_3)_2]$ (6 mg, 0.01 mmol) in C_6D_6 (0.5 mL) was exposed to 1 atm of dihydrogen gas. An immediate colour change from green to yellow was observed, $CH_2(SiMe_3)_2$ was detected in the solution, and new signals appeared that were attributed to $\{[(C_4Me_4P)_2NdH]_n\}$ (**6**). − ^{1}H NMR: δ = −17.8 (s, 12 H), 17.8 (s, 12 H); H−Nd signal was not detected. − ^{31}P NMR: δ = 551. − Exposure of the tube to THF vapour caused a colour change to green and a shift in the ^{31}P spectrum to δ = 347.

Synthesis of $[\{(C_4Me_4P)_2NdH\}_n]$ (6): Dihydrogen gas was admitted to a solution of **5** (80 mg, 0.14 mmol) in pentane at 0°C. The reaction mixture turned yellow and a precipitate appeared. This precipitate was filtered, rinsed with pentane and **6** was isolated as a yellow powder (50 mg, 0.12 mmol, 85%). − NMR (C_6D_6): no interpretable spectrum (see text). − ^{31}P NMR (THF):δ = 377. − $C_{16}H_{25}NdP_2$ (423.56): calcd. C 45.37, H 5.95; found C 45.40, H 5.70.

X-ray Crystallographic Study of 3: Crystals of **3**, $C_{20}H_{33}Cl_2KOP_2Sm$ (611.79), were grown at room temp. from a diethyl ether solution of the compound. Data were collected with an Enraf-Nonius CAD4 diffractometer. The compound crystallised in the centrosymmetric space group $P2_1/n$ (no. 14). The crystal structure was solved by direct methods (SIR) and refined using the Enraf-Nonius MOLEN software package. Anisotropic temperature factors were assigned to all non-hydrogen atoms, while hydrogen atoms were included as fixed contributions to the structure factor. A non-Poisson weighting scheme was applied with a p factor equal to 0.06. The final agreement factors were $R = 0.039$, $R_w = 0.047$, G.O.F. = 1.01. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-106502. Copies of the data can be obtained free of charge on application to CCDC, 12 Union road, Cambridge CB2 1EZ [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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