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Effects of metal-size and auxiliary ligand on the alkylation of lanthanide–halide with $Li[(CH_2)(CH_2)PPh_2]$. X-ray crystal structures of $[Me_2PPh_2][Sm(\eta^5\text{-}C_5H_4Bu^t)_3Cl]$ and $[Li(C_4H_8O)_4][Er(NPh_2)_4]$

Wai-Kwok Wong,[a]* Lilu Zhang,[a] Feng Xue[b] and Thomas C. W. Mak[b]

[a]Department of Chemistry, Hong Kong Baptist University, 224 Waterloo Road, Kowloon, Hong Kong;
[b]Department of Chemistry, The Chinese University of Hong Kong, Shatin, N. T., Hong Kong

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Abstract—The interaction of $Li[(CH_2)(CH_2)PPh_2]$ in tetrahydrofuran with one equivalent of $[(\eta^5\text{-}C_5H_4Bu^t)_2LnCl\cdot LiCl]$ (Ln = Sm, Yb) gave the anionic lanthanide *ate* complex $[Me_2PPh_2][Ln(\eta^5\text{-}C_5H_4Bu^t)_3Cl]$ (**1**, Sm) or the neutral lanthanide-ylide complex $[(\eta^5\text{-}C_5H_4Bu^t)_2Ln(Cl)CH_2P(Me)Ph_2]$ (**3**, Yb). The interaction of $LnCl_3$ (Ln = Er, Yb) in tetrahydrofuran with two equivalents of $NaNPh_2$ followed by one equivalent of $Li[(CH_2)(CH_2)PPh_2]$ gave the unexpected anionic homoleptic tetra-coordinate lanthanide–amide *ate* complex, $[Li(C_4H_8O)_4][Ln(NPh_2)_4]$ (**4**, Er; **5**, Yb). All of these complexes have been characterized by analytical and spectroscopic methods. The structures of **1** and **4** have been established by X-ray diffraction. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: samarium; erbium; ytterbium; lanthanide-amide *ate* complexes; ylide; structure.

Phosphorus ylides have been shown to possess an extensive coordination chemistry with main group, *d*-block and *f*-block metal atoms and to form metal–carbon σ-bonds of unusual stability [1–3]. With actinide metals, depending on the reaction conditions, phosphorus ylidic ligand can act either as a monodentate or a bidentate ligand, as shown below [3].

We are interested in examining the factors that affect the mode of coordination of phosphorus ylidic ligands, particularly the steric and electronic effects of substituents of the cyclopentadienyl rings. Recently, we have shown that the interaction of $Cp'_2LnCl\cdot LiCl$ (Ln = Nd, Sm) with $Li[(CH_2)(CH_2)PPh_2]$ gives the cyclic ylidic complex when Cp′ is the sterically bulky C_5Me_5 ring [4] and the ylide complex when Cp′ is the sterically less demanding C_5H_5 and $C_5H_4Bu^t$ rings [5]. We have examined the effect of the size of lanthanide metals and the nature of the auxiliary ligands of the lanthanide complexes on the mode of coordination of the phosphorus ylidic ligand. Herein we report the results of the interaction of $[(\eta^5\text{-}C_5H_4Bu^t)_2LnCl\cdot LiCl]$ (Ln = Sm, Yb) and $Ln(NPh_2)_2Cl$ (Ln = Er, Yb) with the ylidic ligand $Li[(CH_2)(CH_2)PPh_2]$.

RESULTS AND DISCUSSION

Interaction of $[(\eta^5\text{-}C_5H_4Bu^t)_2LnCl\cdot LiCl]$ *with* $Li[(CH_2)(CH_2)PPh_2]$

Ln = Sm. Interaction of $[(\eta^5\text{-}C_5H_4Bu^t)_2SmCl\cdot LiCl]$ with one equivalent of $Li[(CH_2)(CH_2)PPh_2]$ in tetrahydrofuran at room temperature for 16 h, after work up gave light yellow crystals of stoichiometry $[Me_2PPh_2][Sm(\eta^5\text{-}C_5H_4Bu^t)_3Cl]$ (**1**) in 20% yield after recrystallization from toluene solution. The structure of **1**

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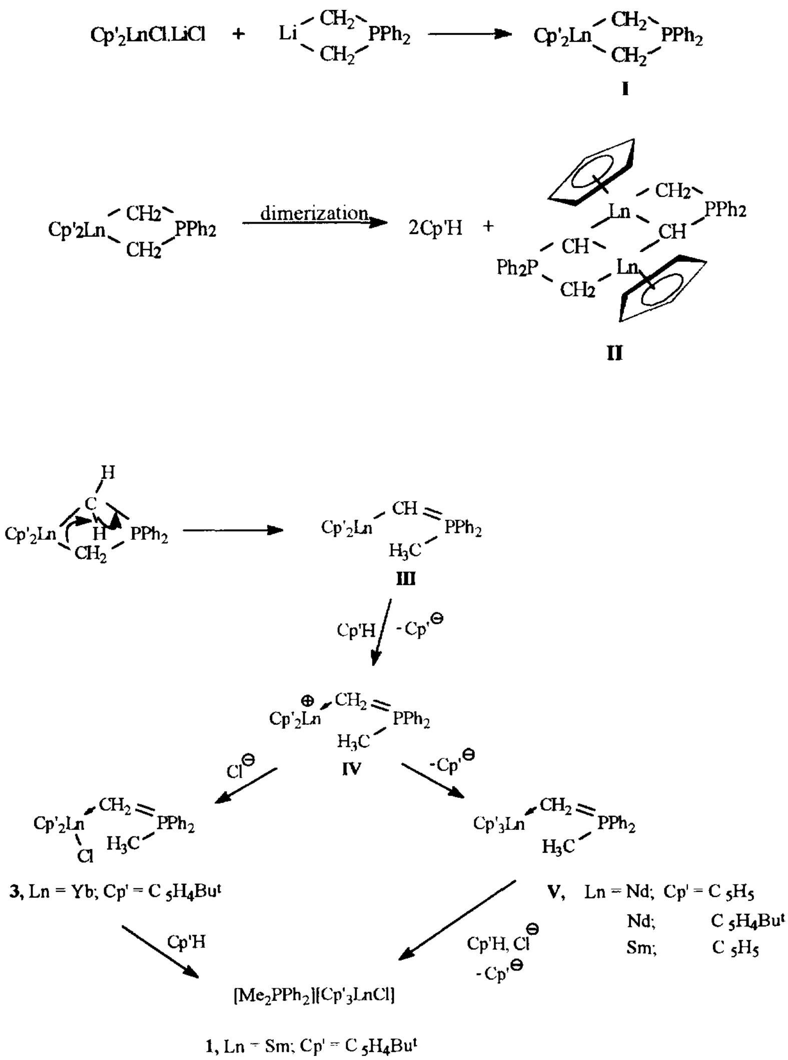
*Author to whom correspondence should be addressed.



Scheme 1. A possible mechanism for the formation of **1** and **3**.

was established by X-ray crystallography. Crystals suitable for X-ray diffraction study were grown from a solution in toluene. A perspective drawing of **1** is shown in Fig. 1. Selected bond lengths and bond angles are given in Table 1.

The crystal structure analysis revealed that **1** is composed of a discrete cation and a discrete anion. The cation $[Me_2PPh_2]^+$ exists as a discrete moiety with the phosphorus adopting a tetrahedral geometry. The P—C distances and C—P—C angles are normal and range from 1.774(7) to 1.800(7) Å and 106.8(4) to 111.5(4)°, respectively. The anion $[Sm(\eta^5\text{-}C_5H_4Bu^t)_3Cl]^-$ can be described as a distorted tetrahedron if one considers that the metal is coordinated to the centroid of each cyclopentadienyl ring. The cyclopentadienyl rings are bonded in a η^5-fashion with Sm—C (ring) distances ranging from 2.693(6) to 3.001(7) Å with the longest distances being those carbon atoms bonded to *tert*-butyl groups. Similar observations have been reported for $[(\eta^5\text{-}C_5H_4Bu^t)_3NdCH_2P(Me)Ph_2]$ [5b] and $[(\eta^5\text{-}C_5H_4Bu^t)_2NdMe]_2$ [6]. The mean Sm—C distances for the three cyclopentadienyl rings are 2.82, 2.85 and 2.85 Å which are slightly longer than that of $[(\eta^5\text{-}C_5H_5)_3SmCH_2P(Me)Ph_2]$ [5a] (2.75, 2.78 and 2.79 Å). This is consistent with the fact that *tert*-butyl group is an electron-donating group and in agreement with a negative charge delocalized on to the samarium metal. The Sm—Cl(1) distance of 2.719(2) Å is comparable to that of $[(\eta^5\text{-}C_5Me_5)_2Sm(Cl)(THF)]$ [2.709 (8) Å] [7].

Ln = *Yb*. Interaction of $[(\eta^5\text{-}C_5H_4Bu^t)_2YbCl \cdot LiCl]$ with one equivalent of $Li[(CH_2)(CH_2)PPh_2]$ in tetrahydrofuran at room temperature for 16 h, work up gave white crystals of stoichiometry $[Me_2PPh_2][(\eta^5\text{-}C_5H_4Bu^t)_2Li]$ (**2**) and yellow crystals of stoichiometry $[(\eta^5\text{-}C_5H_4Bu^t)_2Yb(Cl)CH_2P(Me)Ph_2]$ (**3**) in 10% and 30% yield, respectively, after successive recrystallization from a tetrahydrofuran/toluene mixture. Both structures were established by X-ray diffraction studies [8]. **2** has a sandwich structure for the discrete

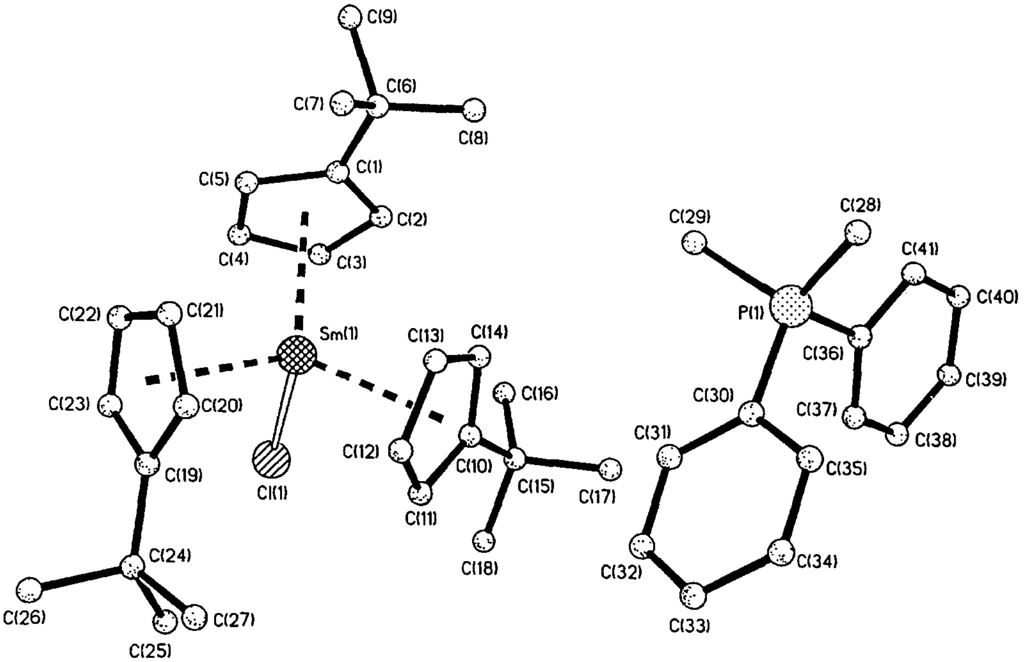


Fig. 1. A perspective drawing of Compound **1**, $[MePPh_2][Sm(\eta^5\text{-}C_5H_4Bu^t)_3Cl]$.

$[(C_5H_4Bu^t)_2Li]^-$ anion with the Li atom coordinated to the centroid of the two parallel *tert*-butylcyclopentadienyl rings. **3** is a distorted tetrahedron if one considers that the metal is coordinated to the centroid of the *tert*-butylcyclopentadienyl rings. Their spectroscopic data were consistent with their solid state structures [8].

The results of our study on the interaction of $[(\eta^5\text{-}C_5H_4R)_2LnCl\cdot LiCl]$ with $Li[(CH_2)(CH_2)PPh_2]$ show that with a relatively large metal such as Nd, the product is the neutral lanthanide–ylide complex $[(\eta^5\text{-}C_5H_4R)_3NdCH_2P(Me)Ph_2]$ (R = H, *t*-Bu) [5b], with smaller metals such as Sm, the product is the neutral lanthanide–ylide complex $[(\eta^5\text{-}C_5H_5)_3SmCH_2P(Me)Ph_2]$ [5a] if R is H, and the anionic lanthanide complex $[Me_2PPh_2][Sm(\eta^5\text{-}C_5H_4Bu^t)_3Cl]$ if R is the steric demanding *tert*-butyl group; with a relatively small metal such as Yb, the product is the neutral lanthanide–ylide complex $[(\eta^5\text{-}C_5H_4Bu^t)_2Yb(Cl)CH_2P(Me)Ph_2]$. This suggests that the nature of the alkylation products of the interaction of $[(\eta^5\text{-}C_5H_4R)_2LnCl\cdot LiCl]$ with $Li[(CH_2)(CH_2)PPh_2]$ is influenced by the size of the lanthanide metals as well as the size of the substituents R of the cyclopentadienyl rings. A possible mechanism for the formation of the products is shown in Scheme 1.

Compounds **1** and **4** are probably formed *via* the cyclic ylidic intermediate **I**, which may either undergo dimerization to give **II** and CpH or under rearrangement to give **III** which reacts with CpH to give the intermediate **IV**. Uranium compounds analogous to the dimerization intermediate **II** [9] and the rearrangement intermediate **III** [10] have been isolated. With relatively large lanthanide metals such as Nd and Sm, **IV** reacts with the cyclopentadienyl anion to give the neutral *tris*(cyclopentadienyl)lanthanide-ylide complex $[(\eta^5\text{-}C_5H_4R)_3LnCH_2P(Me)Ph_2]$, **V**; however, with the bulkier *tert*-butylcyclopentadienyl anion and smaller metal Sm, **V** further undergoes dissociation to give the *tris*(*tert*-butyl-cyclopentadienyl)lanthanide complex and the uncoordinated ylide to relieve the steric congestion. Such an equilibrium has been previously reported [5b]. The free ylide then reacts with a proton source such as CpH to give the phosphonium salt; and the *tris*(*tert*-butyl-cyclopentadienyl)lanthanide complex reacts with a chloride ion, a smaller nucleophile, to give the lanthanide *ate* anion $[Sm(\eta^5\text{-}C_5H_4Bu^t)_3Cl]^-$ resulting in the formation of **1**. With a small lanthanide metal such as Yb, **IV** then reacts with a chloride ion to give the neutral chloro-lanthanide-ylide complex **3**. However, one cannot rule out the possibility that **1** may be formed *via* the chloro-lanthanide-ylide complex which may react with *tert*-butyl-cyclopentadiene to give the chloro-*tris*(*tert*-butylcyclopentadienyl)lanthanide *ate* complex.

Preparation of $[Li(C_4H_8O)_4][Ln(NPh_2)_4]$

Ln = *Er*. The interaction of $Er(NPh_2)_2Cl$, generated *in situ* from the reaction of $ErCl_3$ with two equivalents of $NaNPh_2$, with one equivalent of $Li[(CH_2)(CH_2)PPh_2]$ in tetrahydrofuran for 16 h, work up gave the unexpected yellow crystals of stoichiometry $[Li(C_4H_8O)_4][Er(NPh_2)_4]$ (**4**) in 20% yield after recrystallization from a toluene solution. The structure of **4** was established by an X-ray diffraction study. A perspective drawing of **4** is shown in Fig. 2. Selected bond lengths and bond angles are given in Table 2.

Table 1. Selected bond lengths (Å) and angles (°) for compound **1**

Sm(1)—Cl(1)	2.719(2)	Sm(1)—C(1)	2.953(6)
Sm(1)—C(2)	2.907(7)	Sm(1)—C(3)	2.767(7)
Sm(1)—C(4)	2.747(7)	Sm(1)—C(5)	2.863(6)
Sm(1)—C(10)	2.956(6)	Sm(1)—C(11)	2.877(7)
Sm(1)—C(12)	2.758(7)	Sm(1)—C(13)	2.693(6)
Sm(1)—C(14)	2.823(6)	Sm(1)—C(19)	3.001(7)
Sm(1)—C(20)	2.892(7)	Sm(1)—C(21)	2.723(7)
Sm(1)—C(22)	2.756(7)	Sm(1)—C(23)	2.883(7)
C(1)—C(2)	1.403(10)	C(1)—C(5)	1.422(9)
C(1)—C(6)	1.519(10)	C(2)—C(3)	1.430(10)
C(3)—C(4)	1.393(10)	C(4)—C(5)	1.400(10)
C(10)—C(11)	1.416(10)	C(10)—C(14)	1.400(10)
C(10)—C(15)	1.505(10)	C(11)—C(12)	1.373(12)
C(12)—C(13)	1.420(11)	C(13)—C(14)	1.418(11)
C(19)—C(20)	1.432(11)	C(19)—C(23)	1.411(9)
C(19)—C(24)	1.493(10)	C(20)—C(21)	1.406(10)
C(21)—C(22)	1.414(11)	C(22)—C(23)	1.389(11)
P(1)—C(28)	1.782(9)	P(1)—C(29)	1.774(7)
P(1)—C(30)	1.791(7)	P(1)—C(36)	1.800(7)

C(1)—Sm(1)—C(2)	27.7(2)	C(1)—Sm(1)—C(5)	28.3(2)
C(2)—Sm(1)—C(3)	29.1(2)	C(3)—Sm(1)—C(4)	29.3(2)
C(4)—Sm(1)—C(5)	28.8(2)	C(10)—Sm(1)—C(11)	28.1(2)
C(10)—Sm(1)—C(14)	27.9(2)	C(11)—Sm(1)—C(12)	28.1(2)
C(12)—Sm(1)—C(13)	30.2(2)	C(13)—Sm(1)—C(14)	29.7(2)
C(19)—Sm(1)—C(20)	28.1(2)	C(19)—Sm(1)—C(23)	27.7(2)
C(20)—Sm(1)—C(21)	28.8(2)	C(21)—Sm(1)—C(22)	29.9(2)
C(22)—Sm(1)—C(23)	28.4(2)	C(1)—C(2)—C(3)	107.4(6)
C(2)—C(3)—C(4)	108.6(7)	C(3)—C(4)—C(5)	107.9(6)
C(4)—C(5)—C(1)	108.7(6)	C(5)—C(1)—C(2)	107.5(6)
C(10)—C(11)—C(12)	109.3(7)	C(11)—C(12)—C(13)	108.8(7)
C(12)—C(13)—C(14)	106.1(7)	C(13)—C(14)—C(10)	109.3(6)
C(14)—C(10)—C(11)	106.5(6)	C(19)—C(20)—C(21)	108.5(6)
C(20)—C(21)—C(22)	107.6(7)	C(21)—C(22)—C(23)	108.1(6)
C(22)—C(23)—C(19)	109.6(7)	C(28)—P(1)—C(29)	106.8(4)
C(28)—P(1)—C(30)	111.5(4)	C(28)—P(1)—C(36)	110.9(3)
C(29)—P(1)—C(30)	110.4(3)	C(29)—P(1)—C(36)	108.9(3)
C(30)—P(1)—C(36)	108.4(3)		

The crystal structure analysis revealed that **4** is composed of a discrete cation and a discrete anion. In $[Li(C_4H_8O)_4]^+$, the Li atom adopts a tetrahedral geometry with four molecules of tetrahydrofuran coordinated to the Li atom *via* the oxygen atoms. The Li—O distances and the O—Li—O angles are normal and lie in the range 1.904(23)–1.933(29) Å and 105.5(13)–113.8(13)°, respectively. The anion $[Er(NPh_2)_4]^-$ can be described as a distorted tetrahedron with the Er atom coordinated by four terminal NPh_2 groups. The Er—N distances ranging from 2.243(16)–2.276(16) Å. The N—Er—N angles ranging from 100.0(6)–115.7(5)° are typical of a slightly distorted tetrahedron. The N atoms of the amide groups adopt a planar geometry with C—N—C angles ranging from 112.8(13)–127.7(12)° and can be considered as sp^2 hybridized. There is very little structural information on Er-amide complexes [11], and **4** is the first structurally characterized Er-amide *ate* complex to comprise of a discrete cation and a discrete homoleptic tetra-coordinate Er-amide anion.

Ln = Yb. The interaction of $Yb(NPh_2)_2Cl$, generated *in situ* from the reaction of $YbCl_3$ with two equivalents of $NaNPh_2$, with one equivalent of $Li[(CH_2)(CH_2)PPh_2]$ in tetrahydrofuran for 16 h, work up gave the unexpected dark red crystals of stoichiometry $[Li(C_4H_8O)_4][Yb(NPh_2)_4]$ (**5**) in 22% yield after recrystallization from a toluene solution. The structure of **5** was established by an X-ray diffraction study [12]. **5** is *iso*-structural with **4** and is composed of a discrete $[Li(C_4H_8O)_4]^+$ cation and a discrete $[Yb(NPh_2)_4]^-$ anion. The anion $[Yb(NPh_2)_4]^-$ can be described as a distorted tetrahedron with the Yb atom coordinated by four terminal NPh_2 groups. The N atoms of the amide groups adopt a planar geometry with C—N—C angles ranging from 115.0(9)–119.9(9)° and can be considered as sp^2 hybridized.

Lanthanide *ate* complexes with homoleptic NR_2 groups have been structurally characterized recently [13,14]. However, in all of them the cation and the anion moieties of the complexes are linked together *via*

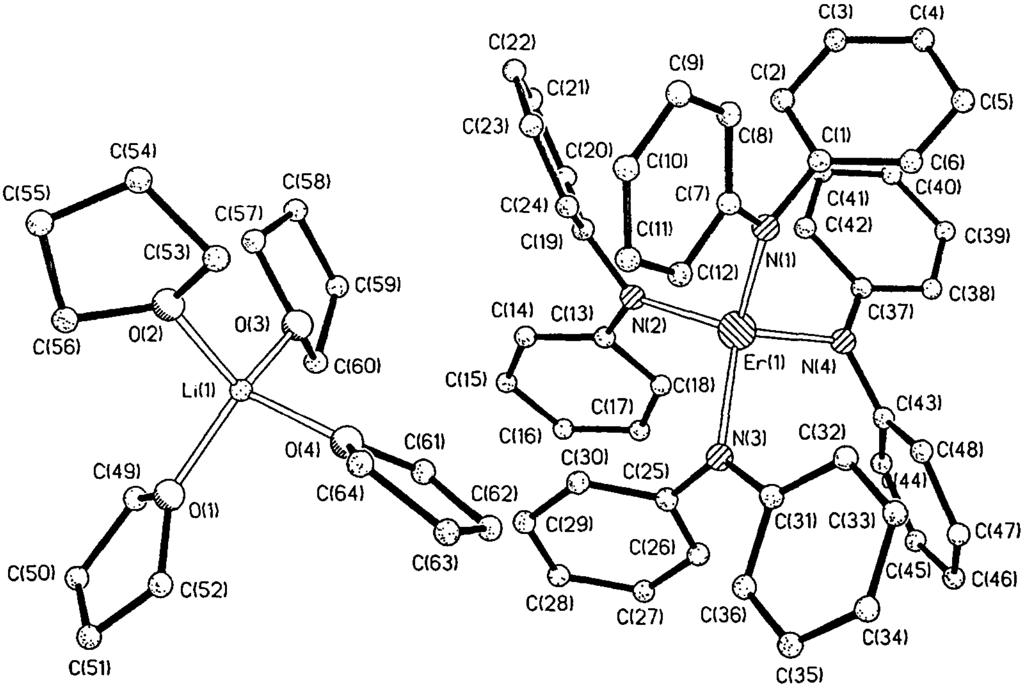


Fig. 2. A perspective drawing of Compound **4**, $[Li(C_4H_2O)_4][Er(NPh_2)_4]$.

Table 2. Selected bond lengths (Å) and angles (°) for compound **4**

Er(1)—N(1)	2.243(16)	Er(1)—N(2)	2.251(12)
Er(1)—N(3)	2.276(16)	Er(1)—N(4)	2.273(18)
N(1)—C(1)	1.431(20)	N(1)—C(7)	1.320(21)
N(2)—C(13)	1.350(19)	N(2)—C(19)	1.433(19)
N(3)—C(25)	1.383(18)	N(3)—C(31)	1.367(18)
N(4)—C(37)	1.395(21)	N(4)—C(43)	1.419(17)
Li(1)—O(1)	1.933(27)	Li(1)—O(2)	1.933(29)
Li(1)—O(3)	1.931(29)	Li(1)—O(4)	1.904(23)
N(1)—Er(1)—N(2)	113.5(5)	N(1)—Er(1)—N(3)	105.2(6)
N(1)—Er(1)—N(4)	111.3(6)	N(2)—Er(1)—N(3)	115.7(5)
N(2)—Er(1)—N(4)	100.0(6)	N(3)—Er(1)—N(4)	111.3(5)
Er(1)—N(1)—C(1)	111.7(10)	Er(1)—N(1)—C(7)	133.5(11)
C(1)—N(1)—C(7)	112.8(13)	Er(1)—N(2)—C(13)	130.4(9)
Er(1)—N(2)—C(19)	111.4(9)	C(13)—N(2)—C(19)	117.1(10)
Er(1)—N(3)—C(25)	99.8(9)	Er(1)—N(3)—C(31)	129.0(10)
C(25)—N(3)—C(31)	127.7(12)	Er(1)—N(4)—C(37)	128.5(10)
Er(1)—N(4)—C(43)	117.3(10)	C(37)—N(4)—C(43)	113.3(13)
O(1)—Li(1)—O(2)	113.8(13)	O(1)—Li(1)—O(3)	112.1(14)
O(1)—Li(1)—O(4)	105.5(13)	O(2)—Li(1)—O(3)	110.8(14)
O(2)—Li(1)—O(4)	107.5(12)	O(3)—Li(1)—O(4)	106.7(12)

two bridging amide groups. Lanthanide *ate* complexes with a discrete cation and a discrete heteroleptic lanthanide-amide anion have also been reported [15]. Nevertheless, **4** and **5** are the very first structurally characterized anionic lanthanide-amide *ate* complexes to comprise of a discrete cation and a discrete homoleptic tetra-coordinate lanthanide-amide anion.

In this paper, we have demonstrated that the nature of the reaction products of the alkylation of Ln—Cl with $Li[(CH_2)(CH_2)PPh_2]$ depends on the size of the lanthanide metals, the nature of the auxiliary ligands, and the size of the substituent R on the cyclopentadienyl rings if the auxiliary ligand is cyclopentadienyl ring.

EXPERIMENTAL

All operations were carried out under dry nitrogen or *in vacuo*. Solvents were dried by standard procedures, distilled and deaerated prior to use. All chemicals used were of reagent grade, obtained from the Aldrich Chemical Company and, where appropriate, degassed before use. The compounds $[(\eta^5\text{-}C_5H_4Bu^t)_2LnCl\cdot LiCl]$ (Ln = Sm, Yb) [16], $NaNPh_2$ [15] and $Li[(CH_2)(CH_2)PPh_2]$ [17] were prepared according to literature methods. Carbon, hydrogen and nitrogen analyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, China. Analyses of metal was carried out by complexometric titration, and of chloride by Volhard's method. IR spectra (KBr pellets) were recorded on a Nicolet Nagna-IR 550 spectrometer; data are given in cm^{-1}. NMR spectra were recorded on a JEOL EX270 spectrometer. Chemical shifts of ^1H and ^{13}C-$\{^1H\}$ NMR spectra were referenced to internal deuterated solvents and then recalculated to TMS = δ 0.00 ppm. Chemical shifts of ^{31}P-$\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4.

Interaction of $[(\eta^5\text{-}C_5H_4Bu^t)_2LnCl\cdot LiCl]$ *with* $Li[(CH_2)(CH_2)PPh_2]$

Ln = Sm. To a cooled (−15°C) solution of $Li[(CH_2)(CH_2)PPh_2]$ (0.59 g, 2.7 mmol) in tetrahydrofuran (20 cm^3) was added a solution of $[(\eta^5\text{-}C_5H_4Bu^t)_2SmCl\cdot LiCl]$ (1.27 g, 2.7 mmol) in tetrahydrofuran (20 cm^3) dropwise over 10 min. The reaction mixture was stirred at −15°C for 2 h before warming up to room temperature to give a red solution. The resultant red solution was stirred at room temperature for another 10 h. The solution was filtered and the solvent of the filtrate was removed *in vacuo* to give a red residue. The residue was extracted with toluene (3 × 10 cm^3) to give a light orange solution. The toluene solution was concentrated to *ca* 10 cm^3 and cooled to −20°C to give light yellow crystals of **1** which were filtered and dried *in vacuo*. Yield: 0.41 g, 20%. Yellow crystals, m.p. 156–158°C. Found: C, 64.5; H, 7.1; Cl, 4.6; Sm, 19.6. Calc. for $C_{41}H_{55}PSmCl$: C, 64.4; H, 7.2; Cl, 4.6; Sm, 19.7%. IR (cm^{-1}, in KBr): 2964 w, 2942 m, 2890 m, 1593 w, 1491 m, 1438 s, 1388 m, 1302 w, 1156 w, 1124 s, 1117 s, 977 m, 942 s, 890 m, 791 w, 748 vs, 689 s, 492 m, 478 m, 449 m. ^{31}P-$\{^1H\}$ NMR (toluene-d_8): δ 27.8 (s) ppm.

Ln = Yb. To a cooled (−15°C) solution of $Li[(CH_2)(CH_2)PPh_2]$ (0.53 g, 2.3 mmol) in tetrahydrofuran (20 cm^3) was added a solution of $[(\eta^5\text{-}C_5H_4Bu^t)_2YbCl\cdot LiCl]$ (2.3 mmol) in tetrahydrofuran (20 cm^3) dropwise over 10 min. The reaction mixture was stirred at −15°C for 2 h before warming up to room temperature to give an orange solution. The resultant orange solution was stirred at room temperature for another 10 h. The solution was filtered and the solvent of the filtrate was removed *in vacuo* to give an orange residue. The residue was washed with hexane (2 × 5 cm^3) and diethyl ether (2 × 5 cm^3), and redissolved in tetrahydrofuran (2 × 10 cm^3) to give an orange solution. The solution was filtered and concentrated to *ca* 10 cm^3. Toluene (10 cm^3) was added to the orange tetrahydrofuran solution. The resultant mixture was then concentrated to *ca* 15 cm^3 and cooled to −20°C to give white crystals of **2** which were filtered and dried *in vacuo*. Yield: 0.11 g, 10%. White crystals, m.p. 170–172°C dec. Found: C, 82.7; H, 9.2. Calc. for $C_{32}H_{42}PLi$: C, 82.8; H, 9.1%. IR (cm^{-1}, in KBr): 3566 m, 2989 w, 2952 w, 1676 m, 1602 m, 1441 m 1256 vs, 1169 s, 1119 m, 1030 s, 963 w, 945 m, 873 w, 751 m, 692 m, 639 s, 578 w, 520 m, 498 m, 483 m. ^{31}P-$\{^1H\}$ NMR (THF-d_8): δ 26.3 (s) ppm. ^1H NMR (THF-d_8): δ 7.61–7.88 (10H, m), 5.40 (4H, m), 5.31 (4H, m), 2.27 (6H, d, J = 14.0 Hz), 1.18 (18H, s) ppm. ^{13}C-$\{^1H\}$ NMR (THF-d_8): δ 135.0 (s), 134.0 (s), 133.2 (m), 132.6 (s), 131.6 (m), 130.7 (m), 129.4 (m), 129.0 (s), 124.4 (s), 123.5 (s), 122.9 (s), 122.0 (s), 102.6 (s), 100.6 (s), 41.4 (s), 40.6 (s), 33.9 (s), 31.3 (s), 30.1 (s), 8.6 (d, J = 56.1 Hz) ppm.

The solvent of the orange filtrate was removed *in vacuo* to give an orange residue. The residue was redissolved in tetrahydrofuran (5 cm^3) and filtered. Toluene (15 cm^3) was added to the orange tetrahydrofuran solution. The resultant mixture was then concentrated to *ca* 15 cm^3 and cooled to −20°C to give yellow crystals of **3** which were filtered and dried *in vacuo*. Yellow crystals, m.p. 175–178°C dec. Yield: 0.46 g, 30%. Found: C, 58.1; H, 6.4; Cl, 5.2. Calc. for $C_{32}H_{41}PYbCl$: C, 57.8; H, 6.2; Cl, 5.3%. IR (cm^{-1}, in KBr): 2940 m, 2878 m, 2804 w, 1603 w, 1438 s, 1320 w, 1302 w, 1265 m, 1166 w, 1119 s, 982 m, 944 s, 891 s, 794 m, 748 vs, 687 vs, 492 m, 478 s, 452 m. ^{31}P-$\{^1H\}$ NMR (toluene-d_8): δ 62.1 (s) ppm.

Preparation of $[Li(C_4H_8O)_4][Ln(NPh_2)_4]$

Ln = Er. A solution of $NaNPh_2$ (2.48 g, 13.0 mmol) in tetrahydrofuran (20 cm^3) was added dropwise over a period of 10 min to a cooled (−15°C) suspension of $ErCl_3$ (1.78 g, 6.5 mmol) in tetrahydrofuran (30 cm^3). The reaction mixture was allowed to stir at −15°C for 2 h, warmed up to room temperature and stirred for another 24 h. The resultant solution was centrifuged and filtered. The solvent of the filtrate was removed *in vacuo* to give a pink residue. The residue was then extracted with tetrahydrofuran (3 × 10 cm^3) to give a clear pink solution. The lanthanide metal and chloride concentration of the tetrahydrofuran solution was determined by complexometric titration and Volhard's method, respectively. The erbium to chloride mole ratio was found to be 1 : 1. The resultant $Er(NPh_2)_2Cl$ solution was then used for subsequent reaction. To a cooled (−15°C) solution of $Li[(CH_2)(CH_2)PPh_2]$ (0.60 g, 2.7 mmol) in tetrahydrofuran (20 cm^3) was added a solution of $Er(NPh_2)_2Cl$ (1.45 g, 2.7 mmol) in tetrahydrofuran (13.0 cm^3) dropwise over 10 min. The reaction mixture was stirred at −15°C for 2 h before warming up to room temperature to give a pink solution. The resultant pink solution was allowed to stir at room temperature for another 48 h.

The solution was filtered and the solvent of the filtrate was removed *in vacuo* to give a pink residue. The residue was washed with hexane (2 × 5 cm^3), extracted with toluene (2 × 10 cm^3) and filtered to give a pink solution. The filtrate was concentrated to *ca* 10 cm^3 and cooled to -20°C to give light yellow crystals of **4** which were filtered and dried *in vacuo*. Yield: 0.64 g, 20%. Light yellow crystals, m.p. 148–150°C. Found: C, 67.5; H, 6.2; N, 4.9; Cl, <0.1. Calc. for $C_{64}H_{72}LiN_4O_4Er$: C, 67.7; H, 6.3; N, 4.9; Cl, 0.0%. IR (cm^{-1}, in KBr): 3046 w, 1597 vs, 1520 vs, 1495 vs, 1458 s, 1417 s, 1319 vs, 1246 m, 1219 w, 1172 m, 1086 w, 1025 w, 994 w, 876 m, 745 vs, 701 m, 689 vs, 640 w, 618 w, 569 w, 507 m, 431 w.

Ln = Yb. To a cooled (-15°C) solution of $Li[(CH_2)(CH_2)PPh_2]$ (0.64 g, 2.9 mmol) in tetrahydrofuran (20 cm^3) was added dropwise over 10 min a solution of $Yb(NPh_2)_2Cl$ (1.58 g, 2.9 mmol) in tetrahydrofuran (14.0 cm^3), generated *in situ* as described above for $Er(NPh_2)_2Cl$ solution. The reaction mixture was stirred at -15°C for 2 h before warming up to room temperature to give a deep red solution. The resultant deep red solution was stirred at room temperature for another 48 h. The solution was filtered and the solvent of the filtrate was removed *in vacuo* to give a dark red residue. The residue was washed with hexane (2 × 5 cm^3), extracted with toluene (2 × 10 cm^3) and filtered to give a deep red solution. The filtrate was concentrated to *ca* 10 cm^3 and cooled to -20°C to give dark red crystals of **5** which were filtered and dried *in vacuo*. Yield: 0.72 g, 22%. Dark red crystals, m.p. 188–190°C dec. Found: C, 66.8; H, 6.0; N, 4.9; Cl, <0.1. Calc. for $C_{64}H_{72}LiN_4O_4Yb$: C, 67.3; H, 6.3; N, 4.9; Cl, 0.0%. IR (cm^{-1}, in KBr): 3038 w, 1596 vs, 1520 vs, 1495 vs, 1458 s, 1418 s, 1320 vs, 1240 w, 1173 m, 1080 w, 1031 w, 991 w, 877 m, 745 vs, 701 m, 690 vs, 504 w, 431 w. ^{1}H NMR (C_6D_6): δ 7.23 (16H, br, s), 6.92 (8H, br, s), 4.90 (8H, br, s), 4.43 (16H, br, s), 2.21 (8H, br, s), 1.36 (8H, br, m), 1.02 (8H, br, s) ppm.

X-ray crystallography

Crystals of **1** and **4** suitable for X-ray diffraction study were grown from toluene solution. The crystals are exceedingly air-sensitive and were sealed in Lindeman glass capillaries in an argon atmosphere. Information concerning crystallographic data and structure refinement of **1** and **4** are summarized in

Table 3. Data collection and processing parameters for **1** and **4**

	1	**4**
Empirical formula	$C_{41}H_{55}PSmCl$	$C_{64}H_{72}ErN_4LiO_4$
Colour; habit	Light yellow prism	Yellow block
Crystal size (mm)	0.10 × 0.20 × 0.22	0.20 × 0.32 × 0.40
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1$ (No. 4)
a (Å)	11.503(2)	10.916(2)
b (Å)	12.229(2)	14.130(4)
c (Å)	13.707(3)	19.364(7)
α (°)	82.08(3)	
β (°)	88.18(3)	96.62(1)
γ (°)	87.46(3)	
V (Å^3)	1907.3(10)	2966.8(13)
Z	2	2
Formula weight	764.7	1135.5
Density (calc.) (g cm^{-3})	1.332	1.271
Absorption coefficient	16.78 cm^{-1}	14.62 cm^{-1}
F(000)	790	1174
Diffractometer	Rigaku RAXIS IIc	Siemens P4
Radiation	Mo-K_α (λ = 0.71073 Å)	Mo-K_α (λ = 0.71073 Å)
Temperature (K)	294	294
Collection range	$-14 \leqslant h \leqslant 14$; $-15 \leqslant k \leqslant 0$; $-15 \leqslant l \leqslant 15$	$-12 \leqslant h \leqslant 12$; $-16 \leqslant k \leqslant 0$; $0 \leqslant l \leqslant 22$
2θ range	3.0–55.0°	3.0–50.0°
Independent reflections	7130 (R_{int} = 2.1%)	4808
Observed reflections	5891 [$F_0 > 6.0\sigma(F_0)$]	2083 [$F_0 > 4.0\sigma(F_0)$]
R_F	0.059	0.063
wR	0.065	0.054
Goodness-of-fit, S	2.21	1.37
Largest & mean Δ/σ	0.034, 0.001	0.069, 0.006
Number of parameter, p	453	574
Residual extrema	0.75 to -1.40 e Å^{-3}	0.98 to -0.69 e Å^{-3}

$R_F = \Sigma\Delta/\Sigma|F_0|$, $wR = [\Sigma w\Delta^2/\Sigma|F_0|^2]^{1/2}$ and $S = [\Sigma w\Delta^2/(n-p)]^{1/2}$ where $\Delta = ||F_0|-|F_c||$, $w = [\sigma^2(F_0) + K|F_0|^2]^{-1}$, $K = 0.0001$.

Table 3. Intensity data of **1** were collected at 294 K on a MSC/Rigaku RAXIS IIc imaging plate system with a rotating-anode X-ray source (Mo K_α radiation, $\lambda = 0.71073$ Å, 50 kV, 90 mA, 45 4° oscillation frames in the range of 0–180°, exposure 8 min per frame) [18], and corrected for absorption using the ABSCOR program [19]. Intensity data of **4** were collected at 294 K on a Siemens P4 four-circle diffractometer in the variable ω-scan mode using Mo K_α radiation [$\lambda = 0.71073$ Å, 4.0 to 40.0° per min in ω, $\omega = (0.60 + 0.35 \tan \theta)$°]. The determination of the crystal class, orientation matrix, and unit-cell dimensions was performed according to established procedures [20], parameters were calculated from least-squares fitting of 2θ angles for 20–25 reflections. Crystal stability was monitored by recording three check reflections at intervals of 97 data measurements, and no significant variation was detected. The raw data were processed with a learn-profile procedure [21], and empirical absorption corrections were applied by fitting a pseudo-ellipsoid to the ψ-scan data of selected strong reflections over a range of 2θ angles [22].

The structures of **1** and **4** were solved by the direct method, and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated in their idealized positions (C—H bond fixed at 0.96 Å), assigned appropriate isotropic thermal parameters and allowed to ride on their respective parent carbon atoms. All the hydrogen atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinements. All computations were performed on a IBM compatible 486 PC with the SHELXTL-PLUS program package [23]. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [24].

Two of the three *tert*-butyl groups in **1** were positional disordered. The atomic positional and thermal parameters of the methyl carbons of the disordered *tert*-butyl groups were refined with occupancy 0.5.

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