

## ORGANOMETALLIC COMPOUNDS OF THE LANTHANIDES—XL.\* RECENT DEVELOPMENTS IN ORGANOLANTHANIDE CHEMISTRY

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**Abstract**—Lanthanide trichlorides  $\text{LnCl}_3$  react with pentamethylcyclopentadienyl alkali metal derivatives with formation of novel compounds of the type  $\text{C}_5\text{Me}_5\text{LnCl}_3\text{ML}_n$  ( $M$  = alkali metal,  $L$  = donor solvent like  $\text{Et}_2\text{O}$ , THF, DME). X-ray structural investigations showed that  $\text{YbCl}_3$  reacts with  $\text{KC}_5\text{Me}_5$  in THF and DME with formation of  $[\text{K}(\text{DME})_3][\text{K}((\text{C}_5\text{Me}_5\text{Yb})_3\text{Cl}_3\text{K}(\text{DME})_2)_2]$ . Compounds of the type  $\text{Cp}_2\text{Ln}(\mu\text{-CH}_3)_2\text{LiL}_2$  and  $[\text{Li}(\text{TMED})_2][\text{CpLn}(\text{CH}_3)_3]$  are useful starting materials for the synthesis of new organolanthanide derivatives with bonds between the lanthanides and other elements. By their reactions with  $\text{tBuSH}$ ,  $\text{PhSeH}$ ,  $\text{Ph}_2\text{PH}$ , and  $\text{Ph}_2\text{AsH}$ , e.g. the new organolanthanide compounds  $(\text{C}_5\text{Me}_5)_2\text{Lu}(\mu\text{-S}^t\text{Bu})_2\text{Li}(\text{THF})_2$ ,  $(\text{C}_5\text{H}_5)_2\text{Lu}(\mu\text{-SePh})_2\text{Li}(\text{THF})_2$ ,  $(\text{C}_5\text{H}_5)_2\text{Lu}(\mu\text{-PPh}_2)_2\text{Li}(\text{TMED})$ , and  $(\text{C}_5\text{H}_5)_2\text{Lu}(\mu\text{-AsPh}_2)_2\text{Li}(\text{TMED})$  could be synthesized and characterized by X-ray structural analyses. Dicyclopentadienylsamarium chloride reacts with trimethylsilyl lithium in DME with formation of  $[\text{Li}(\text{DME})_3][(\text{C}_5\text{H}_5)_2\text{Sm}(\text{SiMe}_3)_2]$ , whereas in the reaction of  $(\text{C}_5\text{H}_5)_2\text{Sm}(\mu\text{-Cl})_2\text{Na}(\text{DME})$  with  $\text{LiGeMe}_3$  redistribution occurs with formation of hexamethyldigermane and  $[\text{Li}(\text{DME})_3][(\text{C}_5\text{H}_5)_3\text{Sm}-\text{Cl}-\text{Sm}(\text{C}_5\text{H}_5)_3]$ . The same anion is formed in the reaction of  $\text{NaCl}$  with  $(\text{C}_5\text{H}_5)_3\text{Sm}$  in DME. Finally  $\text{LiN}_3$  reacts with  $(\text{C}_5\text{H}_5)_3\text{Sm}$  in DME with formation of the complex  $[\text{Li}(\text{DME})_3][(\text{C}_5\text{H}_5)_3\text{Sm}-\text{NNN}-\text{Sm}(\text{C}_5\text{H}_5)_3]$ .

Organometallic compounds of the lanthanide metals are among the very newest organometallic compounds.<sup>1</sup> With the exception of cerium, which forms dicyclooctatetraenylcerium(IV)<sup>2</sup> and europium, samarium and ytterbium, which form cyclopentadienyl and pentamethylcyclopentadienyl lanthanide(II) derivatives,<sup>3</sup> all the other rare earth metals form only organometallic compounds with the metal in the oxidation state  $\text{Ln}^{3+}$ . Most of them have unsubstituted or substituted cyclopentadienyls bonded to the metal along with hydrogen, halogen, alkyl groups or alkoxides as additional ligands.

Only a few examples of organometallic compounds of the hard Lewis acidic electropositive lanthanide metals with bonds to soft donors such as phosphorus,<sup>4</sup> arsenic<sup>5</sup> and sulphur<sup>6</sup> are known. Organometallic compounds with bonds between the lanthanide metals and metalloids or metals like

germanium, tin or even transition metals have been described in the literature, but they are only very poorly characterized. However, such compounds are of particular interest in organic synthesis because of the high reactivity of the probably covalent  $\text{Ln}-\text{X}$  bonds, as well as for several catalytic processes because of the high degree of unsaturation around the large electropositive lanthanide metals.

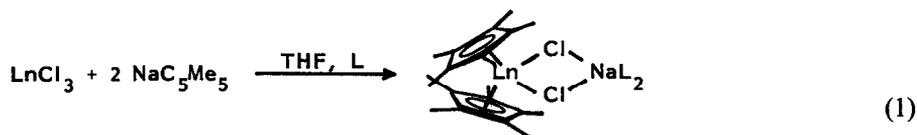
With respect to catalytic activity, organometallic clusters containing lanthanide metals with or without metal-metal bonds should be even much more interesting. Until now, no systematic research has been done in this field.

### PENTAMETHYLCYCLOPENTADIENYL- LANTHANIDE HALIDE CLUSTERS

Lanthanide trichlorides react with pentamethylcyclopentadienylsodium in tetrahydrofuran in the presence of ether or dimethoxyethane with formation of  $(\text{C}_5\text{Me}_5)_2\text{Ln}(\mu\text{-Cl})_2\text{Na}(\text{Et}_2\text{O})_2$  or  $(\text{C}_5\text{Me}_5)_2\text{Ln}(\mu\text{-Cl})_2\text{Na}(\text{DME})_2$ ,<sup>7</sup> see eq. (1).

\* For Part XXXIX, see S. J. Swamy and H. Schumann, *J. Organomet. Chem.*, in press.

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Ln = Sc, Y, La to Lu (except Pm)

L = Et<sub>2</sub>O, DME

The X-ray structural analysis of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Pr(μ-Cl)<sub>2</sub>Na(DME)<sub>2</sub> shows two slightly different independent molecules per asymmetric unit, both with bridging chlorine atoms between praseodymium and sodium<sup>7</sup> (see Structure 1).

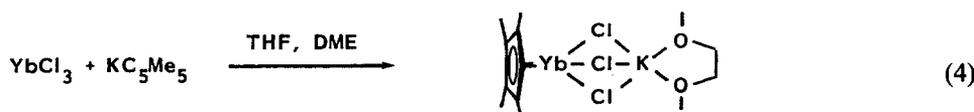
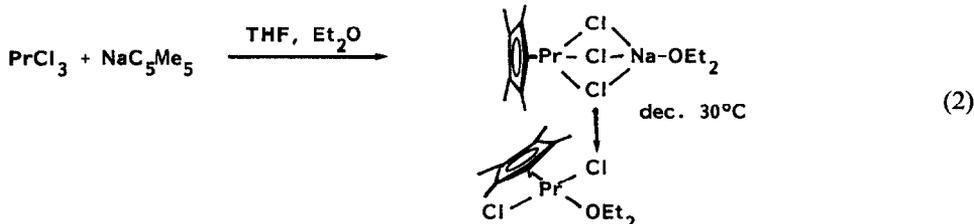
In contrast, compounds of the type C<sub>5</sub>Me<sub>5</sub>LnCl<sub>2</sub> have been only poorly characterized. After the synthesis of the first derivatives of this class, C<sub>5</sub>Me<sub>5</sub>NdCl<sub>2</sub>Na(Et<sub>2</sub>O)<sub>2</sub><sup>8</sup> and C<sub>5</sub>Me<sub>5</sub>YbCl<sub>2</sub>Li(THF)<sup>9</sup> in 1981, we studied the 1 : 1 molar reactions of PrCl<sub>3</sub>, YbCl<sub>3</sub> and LuCl<sub>3</sub> with pentamethylcyclopentadienylsodium and -potassium. PrCl<sub>3</sub> reacts with NaC<sub>5</sub>Me<sub>5</sub> in diethylether with formation of green crystals, the analyses of which agree with the formula C<sub>5</sub>Me<sub>5</sub>PrCl<sub>2</sub>Na(Et<sub>2</sub>O). They decompose during some days with loss of NaCl to give C<sub>5</sub>Me<sub>5</sub>PrCl<sub>2</sub>(Et<sub>2</sub>O). The lutetium complex C<sub>5</sub>Me<sub>5</sub>LuCl<sub>2</sub>Na(Et<sub>2</sub>O)<sub>2</sub> could be isolated in a 37% yield from the reaction of LuCl<sub>3</sub> with NaC<sub>5</sub>Me<sub>5</sub> in ether.

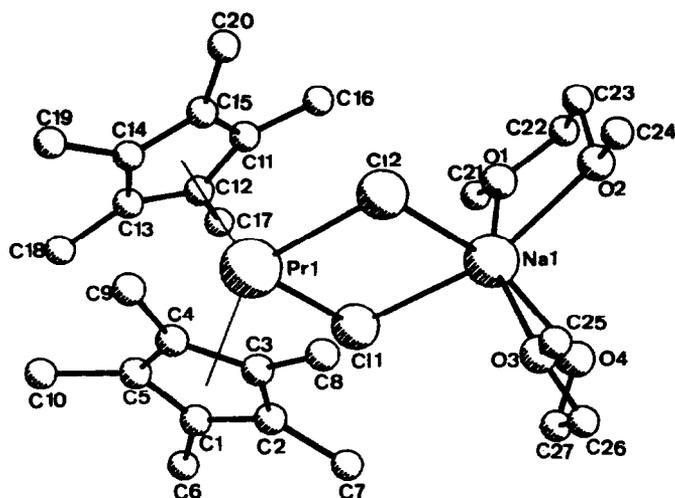
YbCl<sub>3</sub> reacts with KC<sub>5</sub>Me<sub>5</sub> in THF in the presence of DME with formation of blue crystals, which decompose above 250°C. The X-ray structural analysis proves the complex to be built up from six C<sub>5</sub>Me<sub>5</sub>YbCl<sub>2</sub>, four KCl and seven DME units forming a cation-anion pair, [K(DME)<sub>3</sub>]<sup>+</sup>[K((C<sub>5</sub>Me<sub>5</sub>Yb)<sub>3</sub>Cl<sub>8</sub>K(DME)<sub>2</sub>)<sub>2</sub>]<sup>-</sup>, see eqs (2)–(4).

In the anion, two clusters each consisting of three C<sub>5</sub>Me<sub>5</sub>YbCl<sub>2</sub> units and one two-fold coordinated KCl unit are connected symmetrically to a central KCl<sub>2</sub><sup>-</sup> anion. Thus, the central K atom is surrounded octahedrally by six Cl atoms at a distance of 3.11 Å. This distance corresponds with the K—Cl distances in ionic, crystalline potassium chloride (3.14 Å). The Yb—Cl distances are shorter and have values between 2.62 and 2.94 Å (see Structure 2).

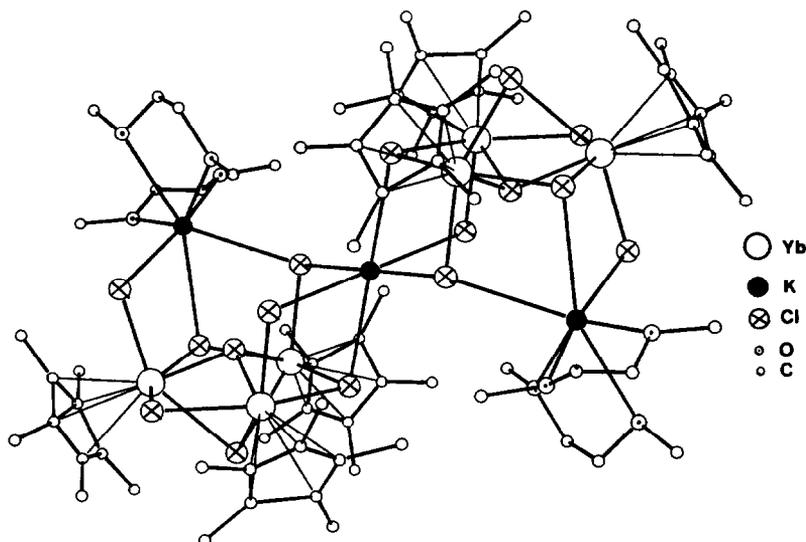
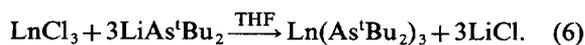
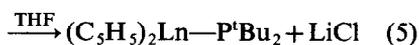
#### ORGANOLANTHANIDE-SULPHUR, -SELENIUM, -PHOSPHORUS AND -ARSENIC COMPOUNDS

The X-ray structural analyses of some of the few organolanthanide compounds containing transition metals prove that there are no direct lanthanide to transition metal bonds. Thus, in (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Yb—OC—Co(CO)<sub>3</sub>(THF)<sup>10</sup> for example, the metals are bridged by a carbonyl group, forming a lanthanide-isocarbonyl linkage. On the other hand the first organolanthanide compounds containing the "soft" elements phosphorus or arsenic, (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>LnP(t-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub><sup>4</sup> or Ln[As(t-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>]<sub>3</sub><sup>5</sup> show real lutetium to phosphorus or lutetium to arsenic bonds, respectively [see eqs (5) and (6)].



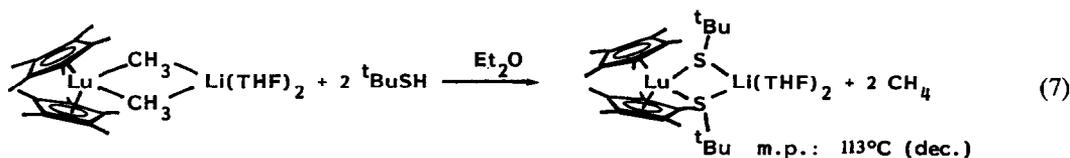


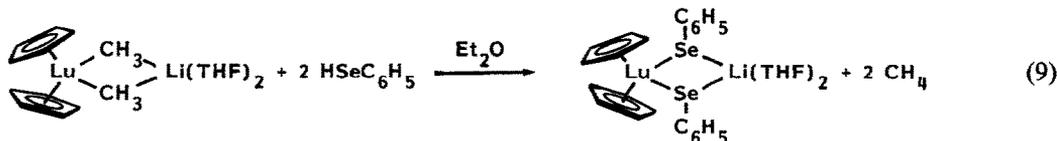
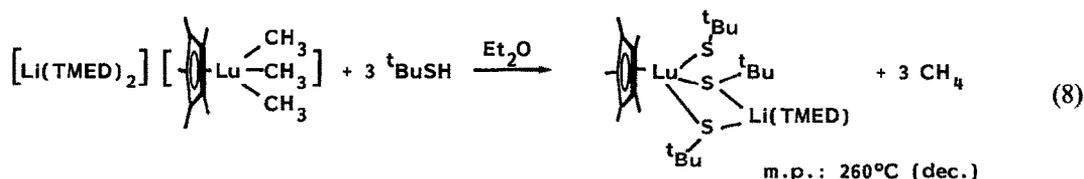
Structure 1.

Structure 2. The anion  $[K((C_5Me_5Yb)_3Cl_8K(DME)_2)_2]^-$ .

We have now found a simple, versatile route to this interesting class of compounds via the elimination of methane from complexes of formulae shown below by acidic compounds like HSR, HSeR, HPR<sub>2</sub> or HASR<sub>2</sub>, see Structure 3.

Bis(pentamethylcyclopentadienyl)lutetiumdi( $\mu$ -methyl)bis(tetrahydrofuran)lithium reacts with *t*-C<sub>4</sub>H<sub>9</sub>SH in ether at  $-78^\circ C$  with formation of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Lu( $\mu$ -SC<sub>4</sub>H<sub>9</sub>-*t*)<sub>2</sub>Li(THF)<sub>2</sub><sup>11</sup> [see eq. (7)]. [Li(TMED)<sub>2</sub>][C<sub>5</sub>Me<sub>5</sub>Lu(CH<sub>3</sub>)<sub>3</sub>] which exists as an ion pair, reacts with *t*-C<sub>4</sub>H<sub>9</sub>SH with formation of a complex, in which the lithium atom is bridged via sulphur to lutetium [see eq. (8)]. The NMR spectrum shows only one signal for the three tert-butyl ligands, proving a rapid exchange between terminal and bridging tert-butylsulphide ligands.





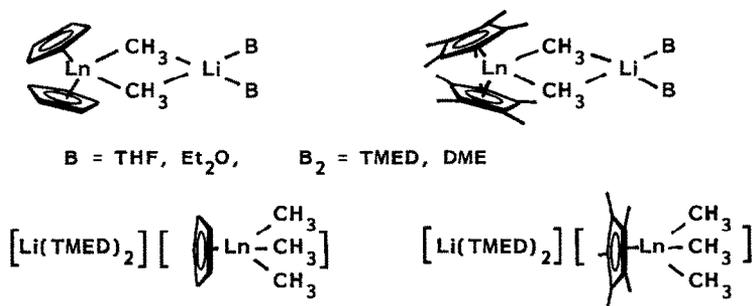
The X-ray structural analysis of the bis-(cyclopentadienyl)lutetium derivative shows the lutetium atom in a distorted tetrahedral environment consisting of the centroids of two cyclopentadienyl rings and the two bridging sulphur atoms. A dihedral angle of 168.7° is found between the S1—Lu—S2 and S1—Li—S2 planes<sup>11</sup> as shown in Structure 4.

Dicyclopentadienyllutetiumdi( $\mu$ -methyl)bis(tetrahydrofuran)lithium reacts with phenylselenol in ether with formation of the first organolanthanide compound containing an Ln—Se bond as shown in eq. (9) The compound darkens on exposure to light with the formation of diphenyldiselenide.

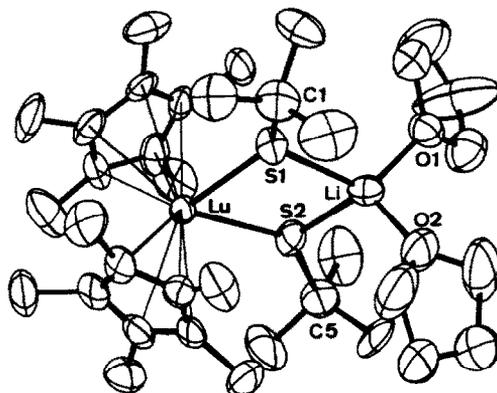
The X-ray structural analysis shows, in analogy

to the above sulphur derivative, a folded four-membered ring with the lutetium and the lithium being bridged by two phenylseleno groups as shown in Structure 5. The dihedral angle is 166.5°. In contrast to the sulphur analogue, both phenylseleno groups are on the same site of the ring. The Lu—Se distances (2.80 Å) are the same order of magnitude as the Lu—S distances (2.72 Å).

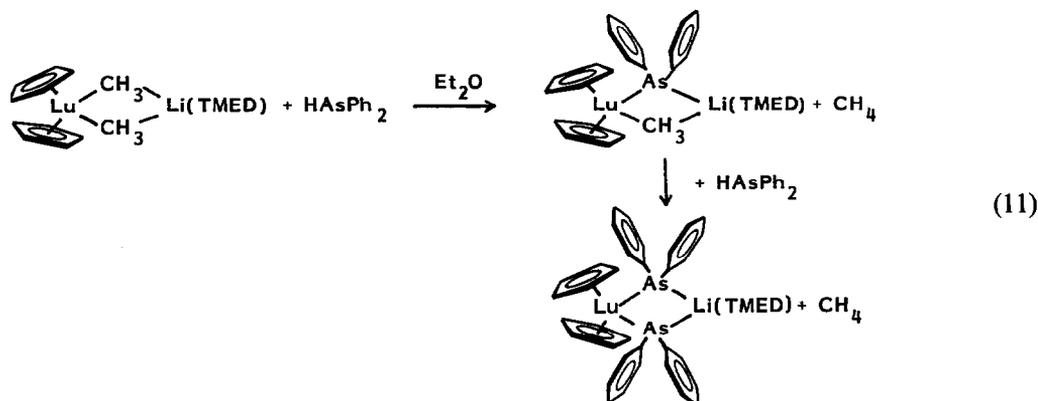
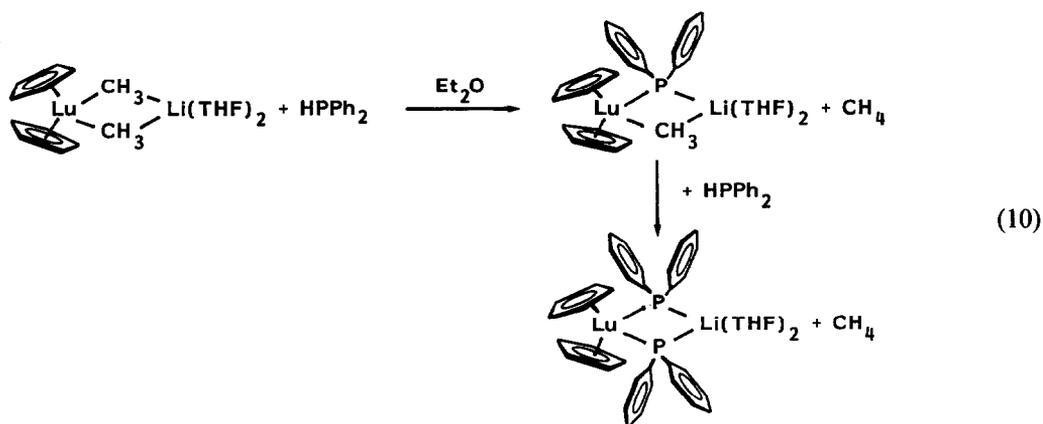
Diphenylphosphine reacts with  $(\text{C}_5\text{H}_5)_2\text{Lu}(\mu\text{-CH}_3)_2\text{Li}(\text{THF})_2$  in ether or toluene at room temperature with elimination of methane yielding the dicyclopentadienyllutetium bis(phosphine) compound.<sup>12</sup> The NMR spectroscopic control of the reaction proves the stepwise  $\text{CH}_3$  substitution, see eq. (10).



Structure 3.

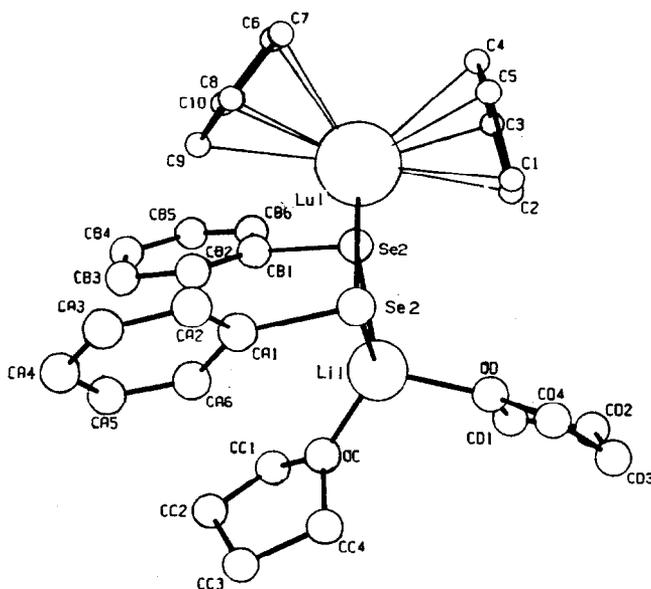


Structure 4.

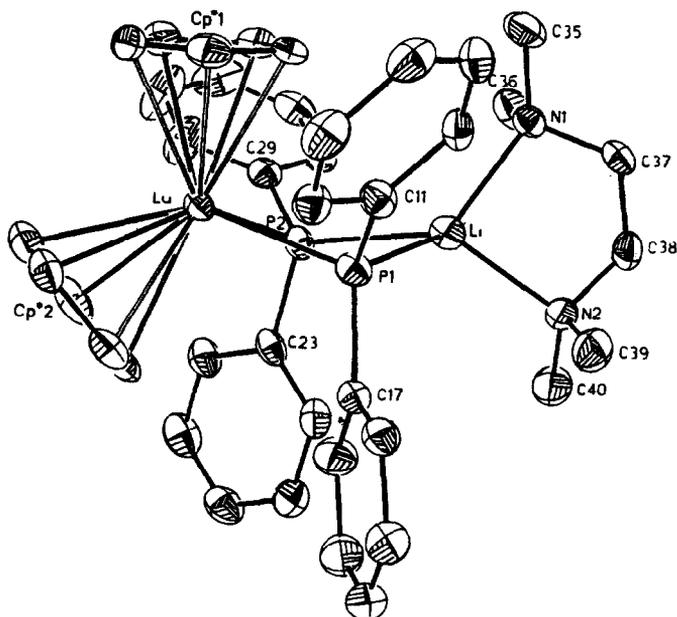


$(\text{C}_5\text{H}_5)_2\text{Lu}(\mu\text{-CH}_3)_2\text{Li}(\text{TMED})$  reacts similarly, the only difference being that the complex formed contains one molecule of toluene per two organo-lutetium molecules in the crystal. In both cases, the P1—Lu—P2 and P1—Li—P2 planes form an angle of  $148.7^\circ$  in the four-membered ring system, see Structure 6.

The same method of preparation led to the successful isolation of the analogous arsenic compound. Via the monosubstitution product, monitored by NMR, dicyclopentadienyllutetium bis(diphenylarsino)lithium (tetramethylethylenediamine) is formed as yellow, air-sensitive crystals [see eq. (11)].



Structure 5.



Structure 6.

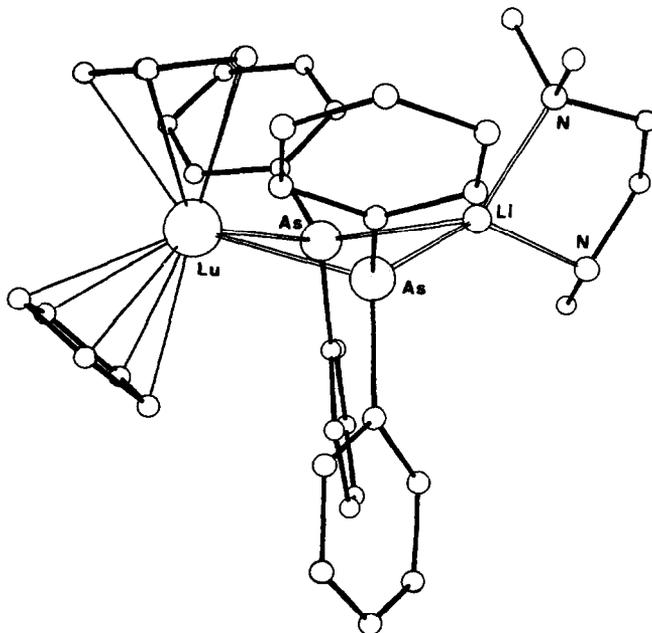
The X-ray structural analysis shows the same ligation system as in the analogous phosphorus complex with an Lu—As distance of 2.88 Å, an Li—As distance of 2.7 Å, and a dihedral angle of the four-membered ring of 152° (see Structure 7 for details).

#### ORGANOLANTHANIDE-SILICON AND -GERMANIUM COMPOUNDS

Some years ago we reported the synthesis of the first lanthanide triphenylgermyl and triphenyl-

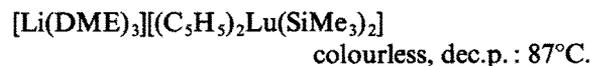
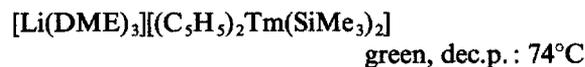
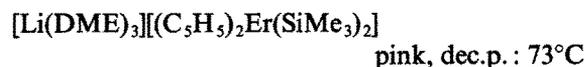
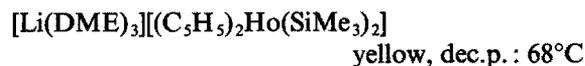
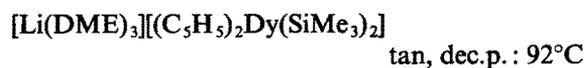
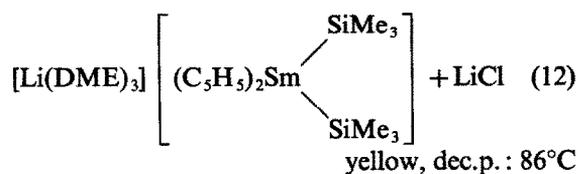
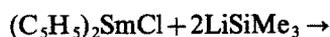
stannyl complexes of the  $\text{Ln}(\text{E}(\text{C}_6\text{H}_5)_3)_3$  and  $(\text{C}_5\text{H}_5)_2\text{Ln}-\text{E}(\text{C}_6\text{H}_5)_3$  type (E = Ge, Sn) from  $\text{LnCl}_3$  (Ln = Pr, Nd, Gd, Er) or  $(\text{C}_5\text{H}_5)_2\text{LnCl}$  (Ln = Er, Yb) and  $\text{LiE}(\text{C}_6\text{H}_5)_3$  (E = Ge, Sn).<sup>13</sup> The purification of these compounds, which contain different amounts of THF, was very difficult and therefore a characterization by X-ray structural analysis was not possible.

However, recently we have been successful in synthesizing the first organometallic compounds with lanthanide to silicon bonds, using the reaction



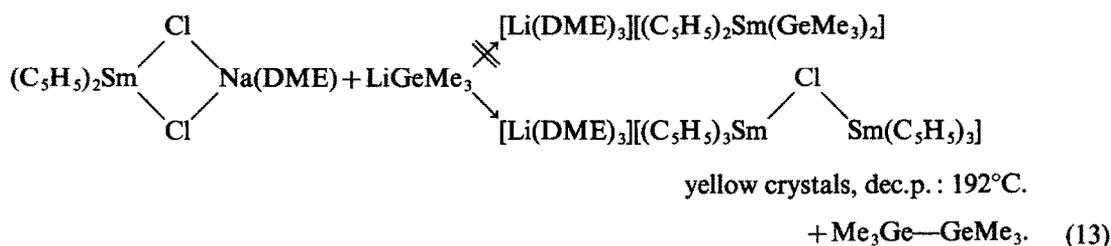
Structure 7.

between dicyclopentadienyllanthanide chlorides and lithiotrimethylsilane in DME at  $-78^{\circ}\text{C}$ :<sup>14</sup>



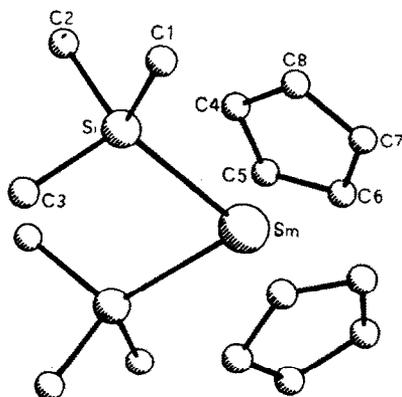
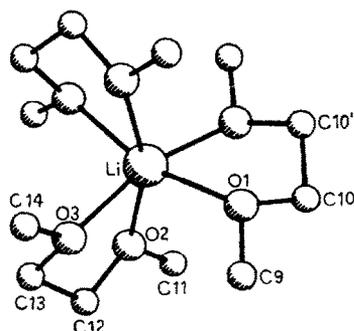
derivative shows a discrete cation–anion pair. At 80 K, the lithium cation is coordinated with three DME ligands resulting in coordination number six for Li. The anion is composed of two cyclopentadienyl and two trimethylsilyl ligands arranged in a distorted tetrahedral fashion around the samarium atom as shown in Structure 8. The Sm—Si distances are 2.88 Å, and the length of the Sm—C bonds varies between 2.582 and 2.637 Å, which is very short in comparison to the Sm—C bonds in other cyclopentadienylsamarium derivatives, indicating a partially covalent bonding in the bonds of the cyclopentadienyl rings to samarium.<sup>14</sup>

Lithiotrimethylgermane does not react with dicyclopentadienyllanthanide chlorides in the same way.  $(\text{C}_5\text{H}_5)_2\text{Sm}(\mu\text{-Cl})_2\text{Na}(\text{DME})$  and  $\text{LiGe}(\text{CH}_3)_3$  react in pentane first with the formation of hexamethyldigermene and ligand redistribution at the samarium atom yielding tricyclopentadienylsamarium, which on its turn reacts with chloride ions present in the reaction mixture, to give yellow  $[\text{Li}(\text{DME})_3][(\text{C}_5\text{H}_5)_3\text{Sm}-\text{Cl}-\text{Sm}(\text{C}_5\text{H}_5)_3]$ :

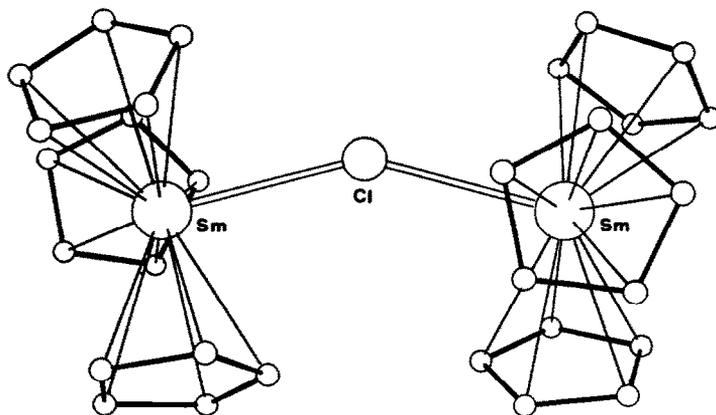


The coloured complexes are extremely sensitive toward moisture and air. They decompose slowly at room temperature, even when kept in an argon atmosphere. The molecular structure of the Sm

We could isolate the same complex, along with other unidentified products, from the reaction of  $(\text{C}_2\text{H}_5)_3\text{SiH}$  with  $(\text{C}_5\text{H}_5)_2\text{Sm}(\mu\text{-CH}_3)_2\text{Li}(\text{DME})$  which was contaminated with  $(\text{C}_5\text{H}_5)_2\text{Sm}(\mu\text{-}$



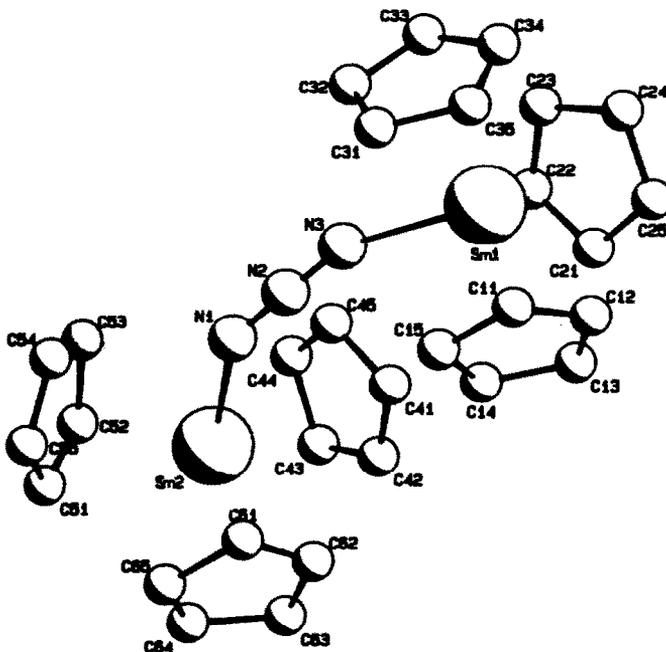
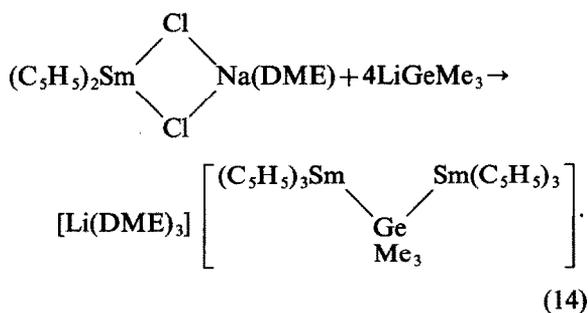
Structure 8.

Structure 9. The anion  $[(C_5H_5)_3Sm-Cl-Sm(C_5H_5)_3]^-$ .

$Cl)_2Li(DME)$ . X-ray structural analysis of both samples gave exactly the same result: a cation-anion pair, with the anion formed from two tricyclopentadienylsamarium units bridged by a chlorine atom, as shown in Structure 9. The  $Sm-Cl-Sm$  unit is angled by  $146.5^\circ$  and both  $Sm-Cl$  distances are  $2.82 \text{ \AA}$ . Some years ago, we found an analogous structural situation in  $[Na(THF)_6][[(C_5H_5)_3Lu-H-Lu(C_5H_5)_3]$ , where a hydrogen atom forms the bridge between two tricyclopentadienyllutetium units.<sup>15</sup>

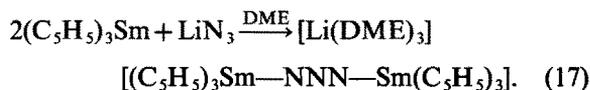
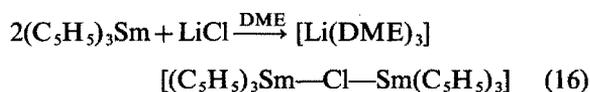
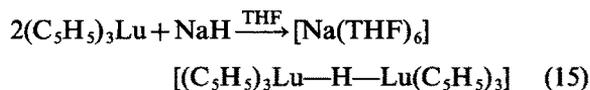
However, the reaction of  $(C_5H_5)_2Sm(\mu-Cl)_2Na(DME)$  with a four-fold excess of  $LiGe(CH_3)_3$  leads to the formation of an organometallic compound containing  $Ge-Sm$  bonds.

Elemental analyses and NMR spectra indicate a cation-anion pair with two tricyclopentadienylsamarium units now bridged by a trimethylgermanium ion:

Structure 10. The anion  $[(C_5H_5)_3Sm-NNN-Sm(C_5H_5)_3]^-$ .

The apparently high stability of the  $[(C_5H_5)_2Sm-Cl-Sm(C_5H_5)_3]^-$  anion, as well as that of the corresponding H bridged ion  $[(C_5H_5)_3Lu-H-Lu(C_5H_5)_3]^-$  focused our interest to the synthesis of anions built up from two other tricyclopentadienyllanthanide units bridged by different anions.

First we could demonstrate that both the known complexes of this type,  $[Na(THF)_6][(C_5H_5)_3Lu-H-Lu(C_5H_5)_3]$  and  $[Li(DME)_3][(C_5H_5)_3Sm-Cl-Sm(C_5H_5)_3]$ , can be prepared straight from tricyclopentadienyllutetium and sodium hydride or tricyclopentadienylsamarium and lithium chloride, respectively. Tricyclopentadienylsamarium also reacts with lithium azide in the same manner yielding the corresponding azide-bridged complex:



The X-ray structural analysis of the yellow crystals formed shows again an anion built up from two tricyclopentadienylsamarium units, bridged via a linear  $N_3^-$  anion (see Structure 10 for details). The following distances and bonding angles have been determined: Sm(1)—N(3): 2.47 and Sm(2)—N(1): 2.48 Å; N(1)—N(2): 1.13 Å; N(2)—N(3): 1.17 Å; Sm(1)—N(3)—N(2): 151°; Sm(2)—N(1)—N(2): 134°; N(1)—N(2)—N(3): 176°.

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