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Review

ORGANOMETALLIC COMPOUNDS OF THE RARE EARTHS *

HERBERT SCHUMANN

Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, Strasse des 17.Juni 135, D-1000 Berlin 12 (West Germany)

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Introduction and history

A malodorous spontaneously inflammable liquid, later referred to as "Cadet's Fuming Liquid", formed by heating arsenous oxide with potassium acetate, was described in 1760 [1]. This marks the starting point of organometallic chemistry although it was not until 100 years later that Cahours and Rieche established that this first compound had a covalent σ-bond between carbon and a metalloid, arsenic [2]. The first genuine organometallic compound with a metal–carbon σ-bond, ethyl zinc iodide, was prepared by Frankland in 1849 [3]. Publication of this work initiated the development of organometallic chemistry between 1850 and 1950. However, the only compounds which were characterized during this period were those having σ-bonds between carbon and metals with completely empty or completely filled *d*-orbitals (the main group elements) or metals of the zinc group. The first example of a fully characterized organotransition metal compound, with a covalent transition metal–carbon σ-bond, was phenyltitanium tri-isopropylate, which was prepared by Herman and Nelson in 1952 [4], although Zeise's salt was noted in the 19th century [5].

In contrast to the σ-bonded organometallic compounds of the main group elements, organometallic compounds containing transition metal to carbon σ-bonds are mostly thermally unstable and moisture sensitive. The high reactivity of these compounds is due to the incompletely filled *d*-orbitals. The main group metals form stable metal to carbon σ-bonds if the element has sufficient electrons available for it to have 8 valence electrons after bond formation, and the transition metals need to achieve a total of 18 valence electrons. This situation becomes much more complicated when going from the transition metals to the lanthanides, which include 4*f*-orbitals in their valence shells, making 16 orbitals which have to be occupied by 32 electrons. Therefore problems in preparing organometallic compounds of the lanthanides are to be expected.

In 1925 Aristid von Grosse postulated that alkyl or aryl derivatives of the lanthanides could not exist [6], but 10 years later Rice and Rice found that free

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radicals react with a variety of metals including lanthanum [7]. Three years later Plets described $Sc(C_2H_5)_3$ and $Y(C_2H_5)_3$, the first organometallic compounds of the rare earths [8], although this work could not be repeated by others. Gilman and Jones described, in connection with the Manhattan-project, the next attempts to prepare organometallic compounds of the lanthanides. They found that biphenyl was produced in the reactions of $LaCl_3$ with phenyllithium in ether, and of lanthanum metal with diphenylmercury at 135°C in a sealed tube for 100 days [9].

The discovery of ferrocene and of the other sandwich complexes initiated a new era in organometallic chemistry, that of the chemistry of the π-complexes. Wilkinson and Birmingham prepared the first organometallic π-complexes of the rare earths in 1954 [10]:

$$LnCl_3 + 3\ NaC_5H_5 \rightarrow Ln(C_5H_5)_3 + 3\ NaCl$$

(Ln = Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb)

Trisindenyl complexes of some rare earths were prepared by Tsutsui and Gysling in 1968 by the reaction of the metal trichlorides with the sodium salt of indene [11], and cyclooctatetraenyl derivatives of the rare earth species europium(II) and ytterbium(II) were synthesized by Hayes and Thomas 1969, shortly after the characterization of uranocene [12].

$$LnCl_3 + 3\ NaC_9H_7 \rightarrow Ln(C_9H_7)_3 + 3\ NaCl$$

(Ln = La, Sm, Gd, Tb, Dy, Yb)

$$Ln + C_8H_8 \xrightarrow{NH_{3(l)}} Ln(C_8H_8)$$

(Ln = Eu, Yb)

The first homoleptic organometallic compounds of the rare earths were prepared by Hart and his coworkers in 1968. The reaction of phenyllithium with $ScCl_3$ gave $Sc(C_6H_5)_3$, a pyrophoric compound, but the analogous derivatives were not obtained from $LaCl_3$ or $PrCl_3$, which gave the homoleptic tetraphenyl rare earth compounds [13,14]:

$$ScCl_3 + 3\ LiC_6H_5 \rightarrow Sc(C_6H_5)_3 + 3\ LiCl$$

$$LnCl_3 + 4\ LiC_6H_5 \rightarrow Li[Ln(C_6H_5)_4] + 3\ LiCl$$

(Ln = La, Pr)

The first biscyclopentadienyl rare earth alkyl and aryl derivatives were described 1975 by Tsutsui and Ely [15]. The methyl and phenyl derivatives of bis(cyclopentadienyl)-gadolinium, -erbium and -ytterbium were prepared, but no structural information was obtained. The dimeric nature of the solvent-free derivatives was demonstrated in 1976 by the structural investigations of Atwood and Lappert and their coworkers [16].

$$(C_5H_5)_2LnCl + LiC_6H_5 \rightarrow (C_5H_5)_2LnC_6H_5 + LiCl$$

$$(C_5H_5)_2LnCl + LiCH_3 \rightarrow (C_5H_5)_2LnCH_3$$

Although the organometallic chemistry of the rare earths is one of the most recent areas of organometallic chemistry, it has developed rapidly at many research groups around the world. Our own research on the synthesis and structural characterization of homoleptic methyl derivatives of the rare earths, and in the field of ylide complexes of lutetium are reviewed in the following sections.

Homoleptic methyl derivatives of the rare earths

Erbium tribromide reacts with methyllithium in a mixture of tetrahydrofuran and ether at 0°C with the formation of an air-sensitive product, which seems to be erbium trimethyl coordinated to three tetrahydrofuran molecules. Complete elemental analyses, although quite reasonable for carbon, hydrogen and erbium, always showed the presence of some lithium, which could not be removed. Ratios of Er : Li of 1 : 0.43 and of Er : CH_3 of 1 : 3 were found [17]:

$$ErBr_3 + 3\ LiCH_3 \xrightarrow[0°C]{THF/Et_2O} Er(CH_3)_3 \cdot (THF)_3 + 3\ LiBr$$

As a more bulky ligand has a better stabilizing effect on such compounds, the trimethylsilylmethyl group was used. $ErCl_3$ and $TmCl_3$ react in tetrahydrofuran with trimethylsilylmethyllithium with formation of the homoleptic triorgano lanthanides which are coordinated to three tetrahydrofuran ligands, but which do not contain any lithium. Both compounds decompose below 0°C with the formation of complexes containing only two tetrahydrofuran ligands; such bis(THF) complexes are formed directly in the reaction of $YbCl_3$ or of $LuCl_3$ with trimethylsilylmethyllithium in the same solvent [18]:

$$LnCl_3 + 3\ LiCH_2SiMe_3 \xrightarrow{THF} Ln(CH_2SiMe_3)_3 \cdot (THF)_3 + 3\ LiCl$$

(Ln = Er, Tm)

$$LnCl_3 + 3\ LiCH_2SiMe_3 \xrightarrow{THF} Ln(CH_2SiMe_3)_3 \cdot (THF)_2 + 3\ LiCl$$

(Ln = Yb, Lu)

The chlorides $TbCl_3$, $ErCl_3$ and $LuCl_3$ react with t-butyllithium in pentane in the presence of diethyl ether below 0°C to form unstable complexes with ether as the stabilizing ligand and which contain lithium, regardless of the mol ratio of the starting materials. The use of tetramethylethylenediamine (tmed) as a stabilizing base gives the more stable homoleptic tetraorgano derivatives of the same lanthanides, with a tmed-coordinated lithium cation, and which may be isolated. The reaction of erbiumtri(t-butoxide) with t-butyllithium gives 1 : 3 complex and the reaction of lutetiumtri(t-butoxide) with t-butyllithium in pentane in the presence of tmed gives, at room temperature, the stable, colorless, bis(*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)lithium tetra(t-butyl)lutetate(III); a complex which contains a homoleptic tetraorgano lanthanide anion [19]:

$$LnCl_3 + 4\ LiC(CH_3)_3 \xrightarrow[-30°C]{pentane,\ Et_2O} [Li(Et_2O)_4][Ln\{C(CH_3)_3\}_4] + 3\ LiCl$$

(Ln = Tb, Er, Lu)

$$LnCl_3 + 4\ LiC(CH_3)_3 \xrightarrow{pentane,\ tmed} [Li(tmed)_2][Ln\{C(CH_3)_3\}_4] + 3\ LiCl$$

(Ln = Tb, Er, Lu)

$$Er[OC(CH_3)_3]_3 + 3\ LiC(CH_3)_3 \rightarrow Er[C(CH_3)_3]_3 \cdot [LiOC(CH_3)_3]_3$$

$$Lu[OC(CH_3)_3]_3 + 4\ LiC(CH_3)_3 \xrightarrow{pentane,\ tmed} 3\ LiOC(CH_3)_3 + [Li(tmed)_2][Lu\{C(CH_3)_3\}_4]$$

Dropwise addition of an etheral solution of methyllithium to a suspension of $ErCl_3$ in diethyl ether containing an excess of tmed, affords good yields of a pink product, which analyzed for $Li_3Er(CH_3)_6$ coordinated by 3 molecules of tmed as stabilizing ligands [20]:

$$ErCl_3 + 6\,CH_3Li \xrightarrow[-20°C]{Et_2O/tmed} [Li(tmed)]_3[Er(CH_3)_6] + 3\,LiCl$$

This method can be used for the preparation of a series of homoleptic methyl derivatives of the rare earths. By starting the reaction at −78°C and stirring at room temperature for 2 h after completion of the addition of methyllithium, yields of between 22 and 65% have been obtained. The air-sensitive complexes are obtained as crystalline powders after precipitation with pentane and subsequent recrystallization from ether-pentane (see Table 1). Their thermal stability varies with the rare earth. All of the compounds decompose without melting or at their melting point. The methyl derivatives of yttrium and of the heavier lanthanides are more stable than those of the lighter ones, in line with the crystal radii of the Ln^{3+} ions. The smallest ions, Lu^{3+}, Yb^{3+}, Tm^{3+}, Er^{3+}, Ho^{3+}, and Y^{3+} give complexes which decompose above 120°C. The europium derivative could not been made because of the immediate reduction of $EuCl_3$ to Eu^{2+} by the methyllithium. No attempt was made to prepare the radioactive promethium derivative. All of the compounds except those of Sc, Y, La, and Lu are paramagnetic. The diamagnetic scandium, yttrium, lanthanum, and lutetium derivatives show (in benzene-d_6-diethyl ether solution) the expected ^1H and ^{13}C NMR signals for the CH_3 groups and the tmed ligands. The spectra of the weakly paramagnetic compounds of praseodymium, neodymium, and samarium show broadened signals with half-widths of the methyl peaks of between 15 and 48 Hz [21].

TABLE 1

HOMOLEPTIC HEXAMETHYL DERIVATIVES OF THE RARE EARTHS

$LnCl_3 + 6\,LiCH_3 + 3\,tmed \rightarrow [Li(tmed)]_3[Ln(CH_3)_6] + 3\,LiCl$

Ln	Color	Dec.p. (°C)	δ CH_3 (ppm)	δ $^{13}CH_3$ (ppm)	δ ^{13}C(tmed) (ppm)
Sc	colorless	94–98	−0.3		
Y	colorless	120–132	0.52	5.9	57.3/46.3
La	colorless	79–82	0.33	17.8	57.1/46.2
Ce	yellow	86–89	−6.4		
Pr	green	59–62	5.9		61/49.3
Nd	violet	78–83	−6.2		60/49.0
Pm					
Sm	yellow	85–88	2.8		58/46.3
Eu					
Gd	light green	112			
Tb	colorless	115	−108		
Dy	colorless	106	−74		58.1/46.8
Ho	yellowish	122	60		
Er	pink	122–125			
Tm	greenish	109–114	92		
Yb	yellow	116–126			55.1/44.1
Lu	colorless	142	−1.18	4.5	58.2/45.9

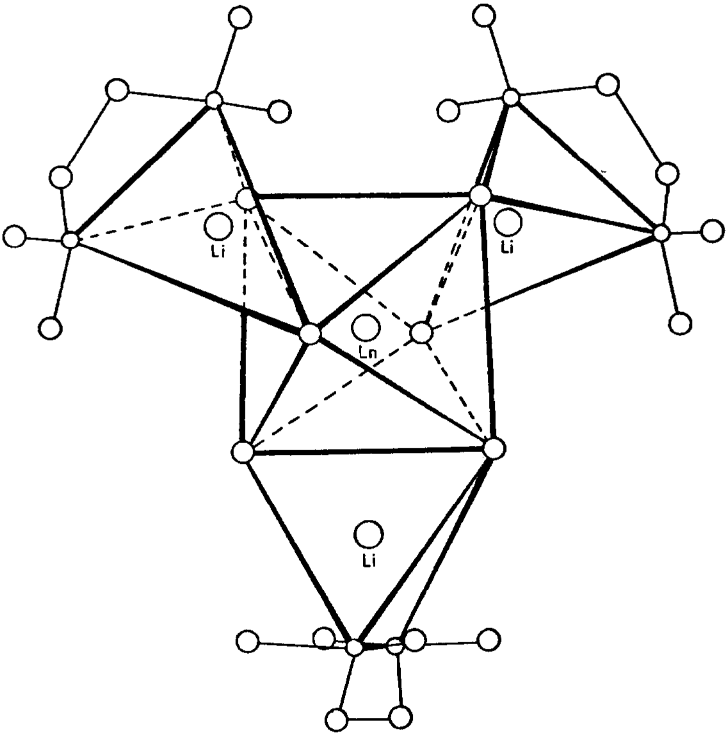


Fig. 1. Molecular structure of the compounds $[Li(tmed)]_3[Ln(CH_3)_6]$.

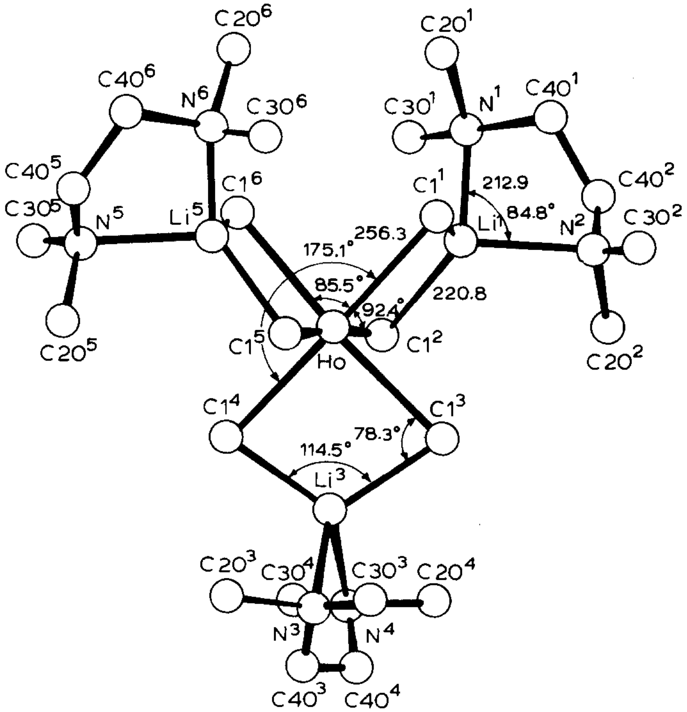


Fig. 2. Bond distances and angles in $[Li(tmed)]_3[Ho(CH_3)_6]$.

The molecular structure of these compounds was found by X-ray structural analysis of the holmium and the erbium derivatives. Both compounds consist of monomeric units in which the lanthanide metals are surrounded by 6 CH_3 groups in a slightly distorted octahedral arrangement. The lithium atoms are located at the centers of tetrahedra which are each made up of two of the lanthanide CH_3 groups and the two nitrogen atoms of one tmed ligand. Thus the octahedron is connected to three tetrahedra in such a way that each tetrahedron shares one common edge with the octahedron (Fig. 1) [22]. As an example, the structure of the holmium complex (Fig. 2) shows all the Ho–C bond lengths to be equal (256.3 pm) and the methyl groups bridged in pairs by lithium atoms, resulting in a slight increase of the corresponding Me–Ho–Me angles to 92.4°. The CH_3–Li distances are normal for such compounds (220.8 pm). The structure shows a distorted tetrahedron around each lithium, with bond angles of 114.5° and 84.8°, and an Ho–CH_3–Li angle of 78.3°. The distances and the angles in the tmed group are normal [21].

The lithium-centered tetrahedra can be arranged around the central octahedron in two ways. Thus the monomeric molecules there exist in two enantiomeric forms, which are both present, as optical antipodes, in each unit cell. In Fig. 3 the relative positions of the tmed ligands are indicated by black dashes, in order to illustrate the left-hand helix of one and the right-hand helix of the other formula unit.

The structure of the holmium complex shows disorder in the tmed ligands. The nitrogen atoms accupy fixed positions but the carbons rotate around the Li–N axes. Figure 4 shows both arrangements. The rotation angle C(20)–N–C(21) is 19° [21].

The reaction of the lanthanide trichlorides with an excess of methyllithium in

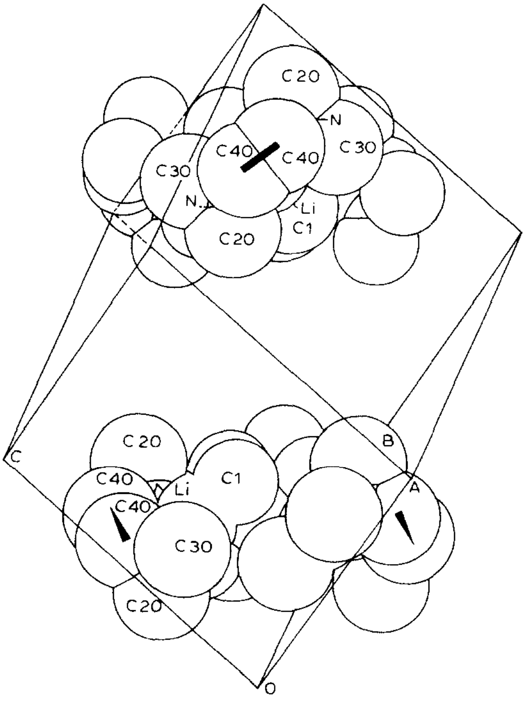


Fig. 3. Arrangement of the optical antipodes in the unit cell of $[Li(tmed)]_3[Ho(CH_3)_6]$.

diethyl ether in the presence of only two equivalents of tetraethylethylenediamine (teed) gives complexes which have bridging methyl ligands between both the two lanthanide metals and the lanthanide metal and lithium. We have isolated such dinuclear lanthanide complexes with praseodymium, neodymium, samarium, and lutetium [23]:

$$2\,\mathrm{LnCl_3} + 10\,\mathrm{LiCH_3} \xrightarrow[-78^\circ\mathrm{C}]{\mathrm{teed(Et_2O)}} [\mathrm{Li_2(teed)(Et_2O)_2}]_2[\mathrm{Ln(CH_3)_5}]_2 + 6\,\mathrm{LiCl}$$

(Ln = Pr, Nd, Sm, Lu)

The first permethylated organometallic compounds of the lanthanides, stabilized only by oxygen donors, were synthesized by using 1,2-dimethoxyethane (dme). The trichlorides of holmium, erbium, thulium, ytterbium and lutetium react with CH_3Li in diethyl ether in the presence of a stoichiometric amount of dme, to give the tris[(1,2-dimethoxyethane)lithium]hexamethylmetallates. The colorless, yellow or pink compounds are sensitive to moisture and air [23]:

$$\mathrm{LnCl_3} + 6\,\mathrm{LiCH_3} + 3\,\mathrm{dme} \xrightarrow[-78^\circ\mathrm{C}]{\mathrm{Et_2O}} [\mathrm{Li(dme)}]_3[\mathrm{Ln(CH_3)_6}] + 3\,\mathrm{LiCl}$$

(Ln = Ho, Er, Tm, Yb, Lu)

Single crystals of the lutetium compound could be obtained, and an X-ray diffraction study of them shows an arrangement similar to that of the tmed-stabilized complexes; an octahedron of 6 methyl groups around each lutetium atom, and lithium atoms in the centers of three tetrahedra, each tetrahedron being made up of two lutetium methyl groups and the two oxygen atoms of one dme ligand (Fig. 5) [23].

The mean Lu–C distance of 253.3 pm in $[\mathrm{Li(dme)}]_3[\mathrm{Lu(CH_3)_6}]$ is slightly shorter than the metal–carbon distances of 256.3 pm in $[\mathrm{Li(tmed)}]_3[\mathrm{Ho(CH_3)_6}]$ and 257 pm in $[\mathrm{Li(tmed)}]_3[\mathrm{Er(CH_3)_6}]$. It is in the same range as the Yb–C distance in the $(C_5H_5)_2Yb(\mu\text{-}CH_3)_2Yb(C_5H_5)_2$ and $(C_5H_5)_2Yb(\mu\text{-}CH_3)_2Al(CH_3)_2$ complexes

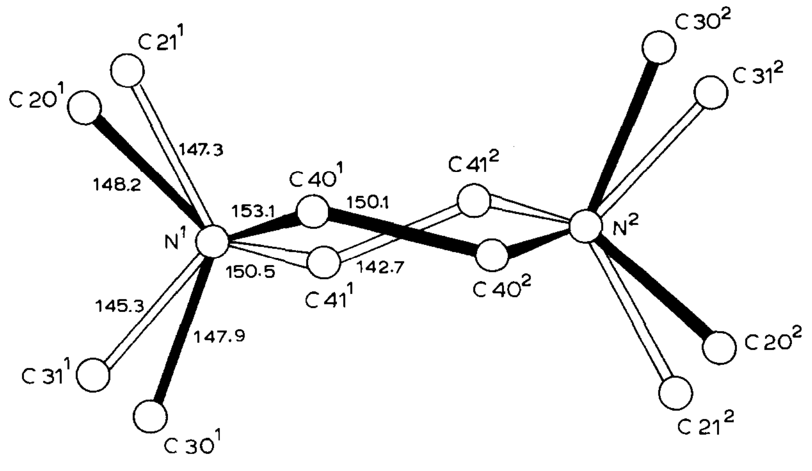


Fig. 4. PLUTO-drawing of the tmed ligands in $[\mathrm{Li(tmed)}]_3[\mathrm{Ho(CH_3)_6}]$ showing the two different arrangements of the tmed ligand in relation to the Li–N axis.

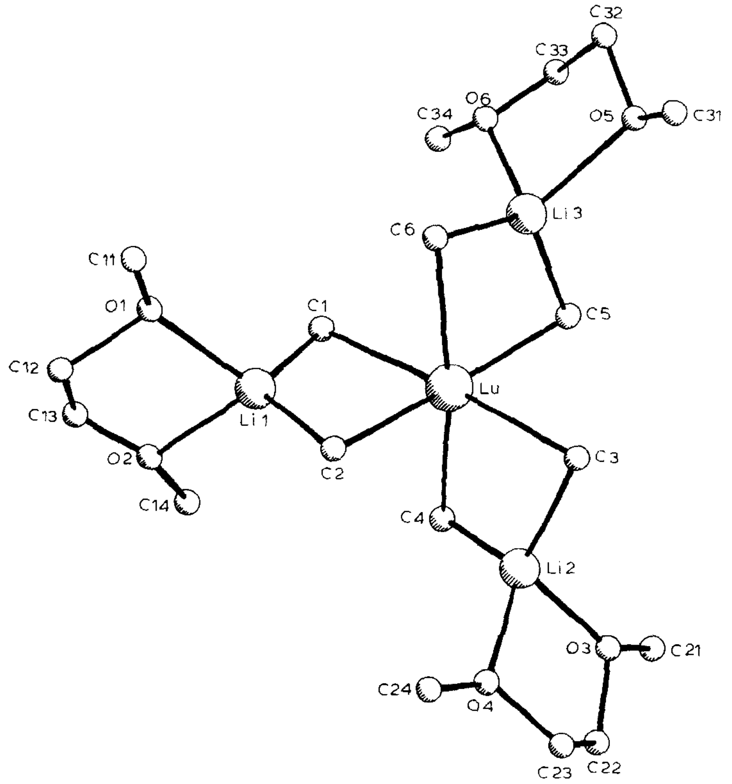


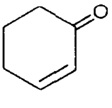
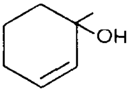
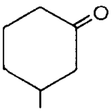
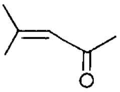
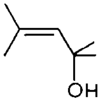
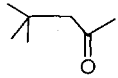
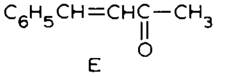
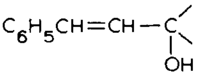
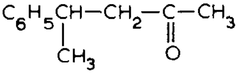
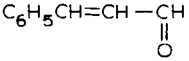
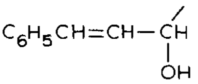
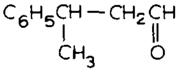
Fig. 5. PLUTO-drawing of [Li(dme)]$_3$[Lu(CH$_3$)$_6$].

[16,24], but it is significantly longer than the observed Lu–C distance in compounds which do not contain electron-deficient methyl bridges, such as (C$_5$H$_5$)$_2$-LuCH$_2$SiMe$_3$ · (THF) (238 pm) [25].

The homoleptic tris(tetramethylethylenediamine lithium) hexamethyl derivatives of the rare earths are potential reagents for use in organic synthesis. To explore the reactivity of the complexes in the methylation of α,β-unsaturated aldehydes and ketones, some preliminary experiments were carried out with the praseodymium and the samarium derivatives. 2-Cyclohexen-1-one reacts in ether at −78°C with both the praseodymium and the samarium complex to form 1-methyl-2-cyclohexen-1-ol and 3-methylcyclohexanone in a ratio of 4 : 1. 4-Methyl-3-penten-2-one, benzalacetone, and cinnamic aldehyde are methylated in the same way, but the yields of the 1,2-adducts are more than 9 times those of the 1,4-addition products. The overall yields are more than 89%, but we have not as yet optimized the reaction conditions (Table 2). To test the chemoselectivity of the rare earth complexes we treated a 1 : 1 mixture of benzalacetone and cinnamic aldehyde with the praseodymium complex and found that addition to the aldehyde is favored over the ketone in a ratio of approximately 1.5 to 2.0 : 1 [21].

TABLE 2

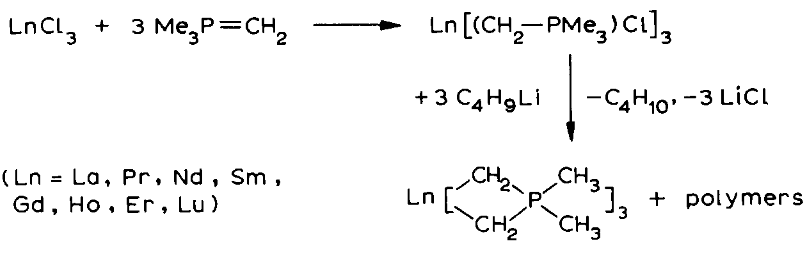
METHYLATION OF α,β-UNSATURATED ALDEHYDES AND KETONES BY [Li(temd)]$_3$-[Pr(CH$_3$)]$_6$ AND [Li(tmed)]$_3$[Sm(CH$_3$)$_6$]

Precursor	Product distribution (%)			
		>80		<20
		>95		<5
 $C_6H_5CH{=}CH\underset{O}{\underset{\Vert}{C}}-CH_3$ E		>90	 $C_6H_5\underset{CH_3}{\underset{\vert}{C}}H-CH_2-\underset{O}{\underset{\Vert}{C}}-CH_3$	<10
 $C_6H_5CH{=}CH-\underset{O}{\underset{\Vert}{C}}H$ E		>90	 $C_6H_5\underset{CH_3}{\underset{\vert}{C}}H-CH_2\underset{O}{\underset{\Vert}{C}}H$	<10

Ylide complexes of lutetium

The first reported examples of alkyl compounds of the lanthanides were the trimethylsilylmethyl derivatives, such as Sc(CH$_2$SiMe$_3$)$_3$ [26] and Er(CH$_2$SiMe$_3$)$_3$ · (THF)$_3$ [18]. The bulky trimethylsilylmethyl ligand stabilizes the organometallic compound. Schmidbaur has shown that the isoelectronic phosphorus ylid, trimethylmethylenephosphorane Me$_3$P=CH$_2$, which is isoelectronic with the trimethylsilylmethyl anion, Me$_3$Si–CH$_2$$^-$, is a valuable precurser for stable organometallic compounds of the transition metals [27]. Therefore, on the basis of the isoelectronic principle, the use of phosphorus ylides should lead to stable homoleptic organometallic compounds of the rare earths.

Trimethylmethylenephosphorane reacts with suspensions of several rare earth trichlorides in pentane-hexane, with the formation of pyrophoric phosphonium salts. These salts react with butyllithium to give lithium chloride, butane and a new class of uncharged, homoleptic rare earth alkyl derivatives. These pyrophoric compounds exist in solution in an equilibrium between oligomers and polymers [28]:

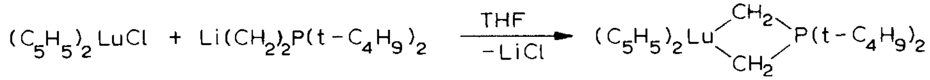


(Ln = La, Pr, Nd, Sm, Gd, Ho, Er, Lu)

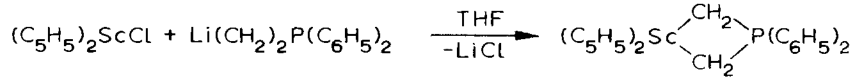
To avoid this flexible behaviour, we used an ylide with two bulky alkyl groups, di(t-butyl)methyl methylenephosphorane. The reaction with $LuCl_3$ of the lithium derivative of this ylide in ether gives a neutral complex which can be isolated free of coordinating solvent. The colorless crystals decompose above 130°C.

The ^1H NMR spectrum indicates dynamic behaviour of the compound in solution. The complicated line-rich spectrum at room temperature is reduced to two doublet signals at −26°C, which are assigned to an octahedral compound with six lutetium–carbon σ-bonds. The methylene part of the spectrum shows a triplet of doublets because of the coupling of the carbon atom with the directly bonded phosphorus and the two directly bonded hydrogens. The ^1H decoupled ^{13}C NMR spectrum shows only a doublet, as expected. In going from the lithium to the lutetium derivatives, there is a low field shift of 16.1 ppm and a decrease of $^1J(PC)$ from 35.7 to 28.1 Hz, as well as an increase of $^1J(CH)$ from 116.2 to 121.6 Hz. These NMR spectra indicate a dynamic behaviour in solution, in which symmetrical monomeric lutetium ylide complexes are in a temperature-dependent equilibrium with higher oligomers. Only the dominant monomeric and dimeric species can be detected by NMR spectroscopy at low temperature. At elevated temperatures, higher oligomers are formed in amounts which decrease with increasing molecular weight (Fig. 6) [29].

Dynamic behaviour, as observed with the homoleptic rare earth ylide complexes, can be avoided by using blocking ligands such as pentahapto-bonded cyclopentadienyl groups. Bis(cyclopentadienyl)lutetium chloride reacts with the lithiated methylide of methyl-di-t-butylphosphine in tetrahydrofuran to give bis(cyclopentadienyl)di-t-butylphosphonium bis(methylide), which is completely monomeric in solution. It crystallizes from toluene free of solvent. Its NMR spectrum confirms the structure, with the cyclopentadienyl protons giving a singlet at 6.1 ppm, the ylidic protons one at −0.3 ppm (d, $^2J(PH)$ 12 Hz), and the t-butyl protons one at 1.2 ppm (d, $^3J(PH)$ 13.8 Hz) [29].



The analogous scandium derivative was prepared from bis(cyclopentadienyl)scandium chloride and the lithiated ylide of methyldiphenylmethylenephosphorane. It has similar NMR parameters [30].



Even better stabilization is possible when pentamethylcyclopentadienyl groups are bonded to lutetium. The complex $(C_5Me_5)_2Lu(\mu\text{-}Cl)_2Na \cdot (Et_2O)_2$ reacts with $Li(CH_2)_2P(CH_3)_2$ in tetrahydrofuran with the formation of a bis(pentamethylcyclopentadienyl)lutetinyl ylide complex, which crystallizes as a colorless solid, melts without decomposition at 205–208°C, and ignites spontaneously in air.

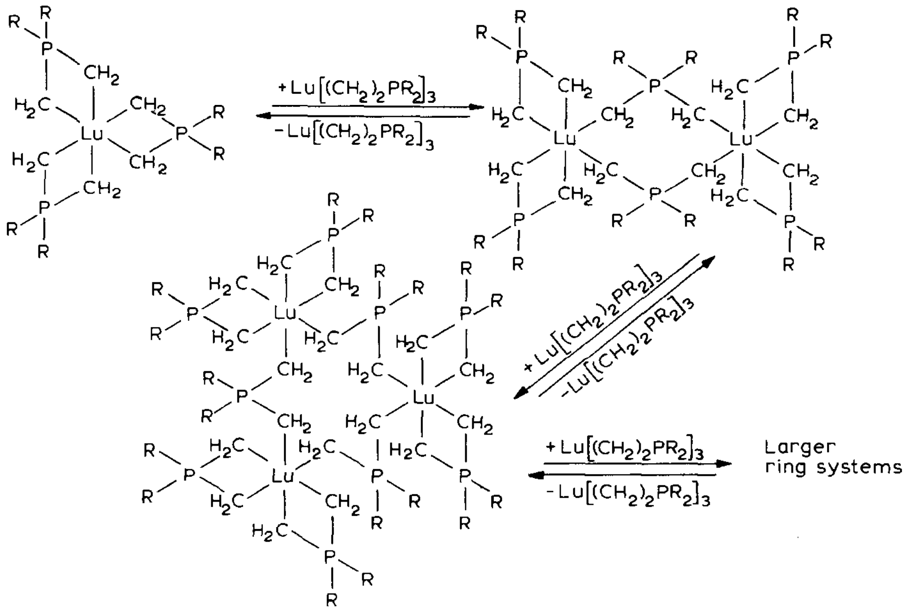


Fig. 6. Oligomerization equilibria in the system $\{Lu[(CH_2)_2P(t\text{-}C_4H_9)_2]_3\}_n$ with $n = 1, 2, 3, \ldots$.

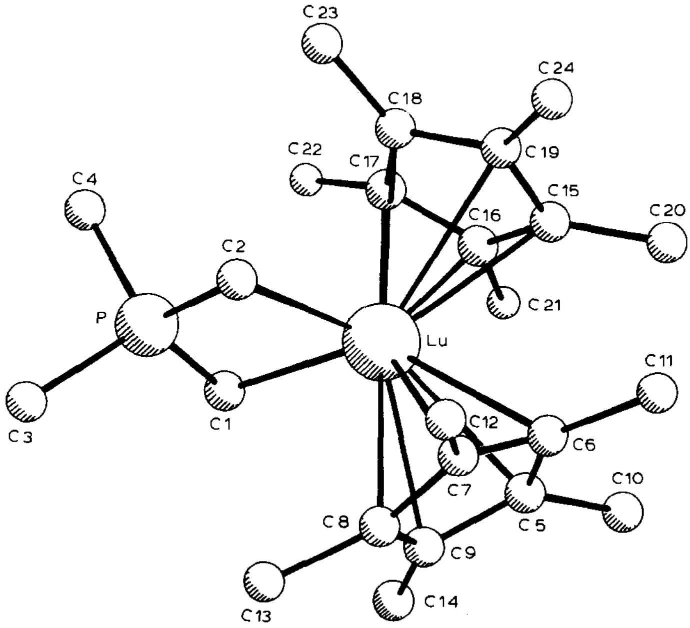
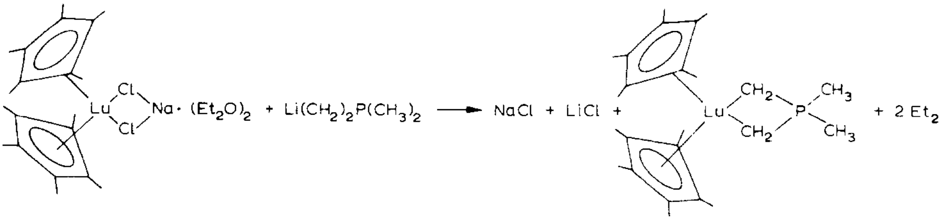
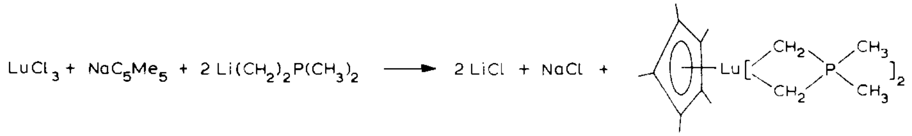


Fig. 7. PLUTO-drawing of $(C_5Me_5)_2Lu(CH_2)_2P(CH_3)_2$.



The compound crystallizes in the monoclinic space group $P2_1$ with the lutetium atom in the center of a tetrahedron which is very highly distorted because of the bulky pentamethylcyclopentadienyl groups. The angle at lutetium between the cyclopentadienyl groups has widened to 140° (Fig. 7). The ylide has tetrahedral coordination around the phosphorus, with nearly equal bond distances of 181 pm to the terminal carbon atoms and 178 pm to the ylidic carbons. The angles at phosphorus are approximately tetrahedral, at 112°; however, the C–Lu–C bond angle has widened to 120° [31].

A bis(ylid) complex of lutetium was prepared via pentamethylcyclopentadienyllutetium dichloride, by the reaction of $LuCl_3$ with one equivalent of C_5Me_5Na in tetrahydrofuran, followed immediately by the addition of two equivalents of the lithium derivative of trimethylmethylenephosphorane. The colorless complex, which crystallizes from pentane, is less stable than the bis(pentamethylcyclopentadienyl) compound, and decomposes at 152°C. Its NMR spectra confirm the proposed structure: ^1H: δ C_5Me_5 2.32, δ CH_2 0.06 (d, $^2J(PH)$ 10.8 Hz), δ CH_3 1.17 (d, $^2J(PH)$ 11.7 Hz); ^{13}C: δ C_5Me_5 12.04 and 114.8, δ CH_2 19.9 (d, $^1J(PC)$ 34.8 Hz), δ CH_3 21.5 (d, $^1J(PC)$ 38.1 Hz); ^{31}P: δ 4.9 ppm [31].

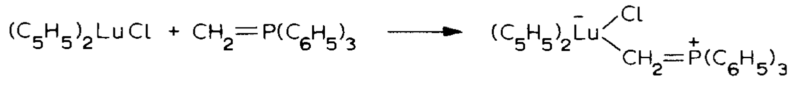


Solid triscyclopentadienyl rare earth complexes are Lewis acids, which polymerize in the solid state via bridging cyclopentadienyl ligands which increase the coordination number at the rare earth element. They also coordinate Lewis basic solvent molecules such as tetrahydrofuran, forming 1 : 1 complexes such as $(C_5H_5)_3Lu\cdot$(THF). The THF molecule coordinated to tris(cyclopentadienyl)lutetium can be exchanged for an ylide, such as triphenylmethylenephosphorane:

$$(C_5H_5)_3Lu\cdot(THF) + CH_2{=}P(C_6H_5)_3 \xrightarrow[-THF]{} (C_5H_5)_3Lu\cdot CH_2{=}P(C_6H_5)_3$$

The complex crystallizes from solution after the two components are mixed at room temperature, and it decomposes at 108°C [32].

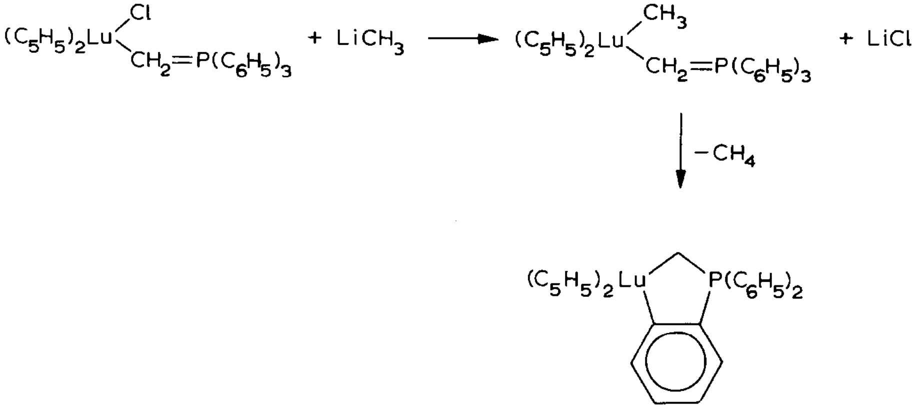
Bis(cyclopentadienyl)lutetium chloride reacts with triphenylmethylenephosphorane in toluene to form a 1 : 1 complex, which is a zwitterion containing a monohapto lutetium–carbon σ-bond:



$$(C_5H_5)_2LuCl + CH_2{=}P(C_6H_5)_3 \longrightarrow (C_5H_5)_2\overset{-}{Lu}(Cl)-CH_2{=}\overset{+}{P}(C_6H_5)_3$$

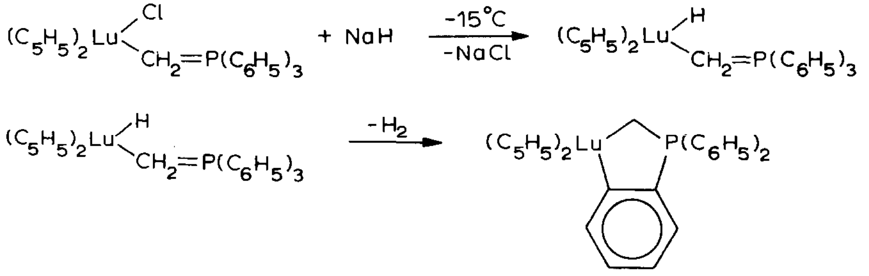
The colorless compound, which decomposes at 172°C without melting, gives an NMR spectrum at room temperature which contains one sharp signal at 6.1 ppm for the cyclopentadienyl protons and the expected doublet at 0.92 ppm for CH_2 with a large $^2J(PH)$ of 17.5 Hz compared with 7.5 Hz for the starting ylide. The formation of the lutetium–carbon bond causes a decrease in the electron density at the ylide carbon; this is shown by the low field shift in the ^{13}C NMR spectrum to δ -4.2 from 7.5 ppm for the starting ylide and by the drastically reduced $^1J(PC)$ of 28.8 Hz, in comparison to 99.6 Hz for the ylide and 83.7 Hz for triphenylmethylphosphonium chloride. The coupled ^{13}C NMR spectrum confirms that two protons are bonded to the ylide carbon, with a $^1J(CH)$ of 118 Hz [33].

The complex $(C_5H_5)_2Lu(Cl)CH_2P(C_6H_5)_3$ hydrolyzes with the formation of C_5H_6, $Lu(OH)_3$ and $(C_6H_5)_3PCH_3^+Cl^-$. The complex reacts with methyllithium in toluene at -78°C to give the methylated derivative, which shows the additional NMR signal at -0.4 ppm for the CH_3 group. This compound decomposes at room temperature with evolution of CH_4 and formation of a five-membered metallacycle involving one of the activated carbon–hydrogen bonds at the *ortho* positions of the phenyl rings of the initial adduct [32]:



The corresponding pentamethylcyclopentadienyl derivative $(C_5Me_5)_2Lu(CH_3)$-$CH_2{=}P(C_6H_5)_3$ has the same reactivity and forms an analogous metallacycle [34].

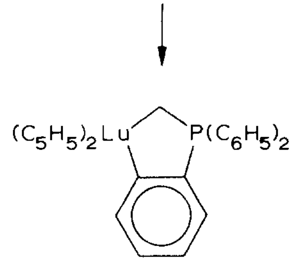
The same metallacycle is also obtained by the reduction with sodium hydride of the ylide complex of bis(cyclopentadienyl)lutetium chloride. The ylide complex of bis(cyclopentadienyl)lutetium hydride is formed as an intermediate, and this decomposes, with the evolution of H_2, via attack at the activated C–H bond [32]:



This 1-phospha-3-luteta-indane is also isolated as the main product from the reaction of t-butyllithum with trimethylmethylenephosphorane and bis(cyclopentadienyl)lutetium chloride in tetrahydrofuran at −78°C. The reaction proceeds through the formation of a lithiated ylide, which has a red color in the reaction vessel, followed by the elimination of LiCl to give the bis(cyclopentadienyl)lutetium-substituted ylide. This ylide complex is also red, but rearrangement to the metallacycle leads to decolorization of the reaction mixture:

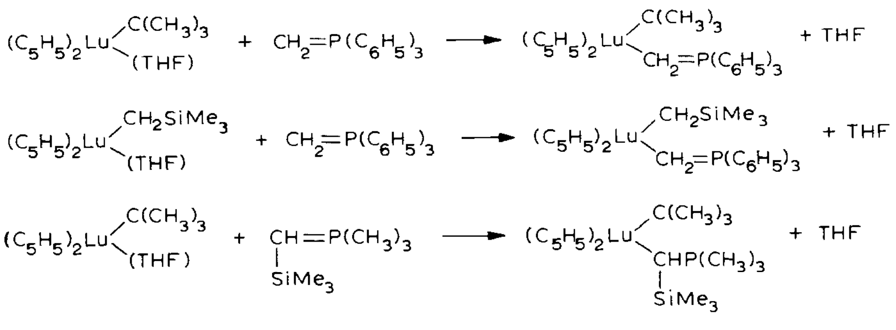
$$CH_2{=}P(C_6H_5)_3 + LiC(CH_3)_3 \longrightarrow LiCH{=}P(C_6H_5)_3 + C_4H_{10}$$

$$LiCH{=}P(C_6H_5)_3 + (C_5H_5)_2LuCl \longrightarrow (C_5H_5)_2Lu{-}CH{=}P(C_6H_5)_3 + LiCl$$



The ${}^1H$ NMR spectrum of this metallacycle shows a doublet for the CH_2 group, a singlet for the cyclopentadienyl protons and a multiplet for the phenyl and the phenylene protons. The ${}^{13}C$ NMR spectrum shows (Fig. 8) a number of doublets in the phenyl region which can be assigned to different carbon atoms of the phenyl and phenylene groups, since the phosphorus–carbon coupling constants increase with increasing distance from the phosphorus atom [32].

Organometallic compounds of the lanthanides, such as bis(cyclopentadienyl)-lanthanide chlorides and bis(cyclopentadienyl)(alkyl)-derivatives, are stabilized by the coordination of donor solvents, such as tetrahydrofuran, increasing the coordination number of the lanthanide metal. These donor solvents can be replaced by ylides, as shown by the formation of the zwitterionic complex $(C_5H_5)_2Lu(Cl)CH_2P(C_6H_5)_3$ [33]. Bis(cyclopentadienyl)(t-butyl)lutetium tetrahydrofuranate also reacts at room temperature in toluene with triphenylmethylenephosphorane, to give a colorless solid which decomposes above 122°C with the evolution of isobutane. The same exchange reaction occurs between bis(cyclopentadienyl)(trimethylsilylmethyl)lutetium tetrahydrofuranate and triphenylmethylenephosphorane in toluene at −78°C. Bis(cyclopentadienyl)(t-butyl)lutetium tetrahydrofuranate and trimethyl(trimethylsilyl)methylenephosphorane also react in toluene at −15°C, with replacement of the tetrahydrofuran by the ylide [35]:



$$(C_5H_5)_2Lu\begin{matrix}C(CH_3)_3\\(THF)\end{matrix} + CH_2{=}P(C_6H_5)_3 \longrightarrow (C_5H_5)_2Lu\begin{matrix}C(CH_3)_3\\CH_2{=}P(C_6H_5)_3\end{matrix} + THF$$

$$(C_5H_5)_2Lu\begin{matrix}CH_2SiMe_3\\(THF)\end{matrix} + CH_2{=}P(C_6H_5)_3 \longrightarrow (C_5H_5)_2Lu\begin{matrix}CH_2SiMe_3\\CH_2{=}P(C_6H_5)_3\end{matrix} + THF$$

$$(C_5H_5)_2Lu\begin{matrix}C(CH_3)_3\\(THF)\end{matrix} + \begin{matrix}CH{=}P(CH_3)_3\\|\\SiMe_3\end{matrix} \longrightarrow (C_5H_5)_2Lu\begin{matrix}C(CH_3)_3\\CHP(CH_3)_3\\|\\SiMe_3\end{matrix} + THF$$

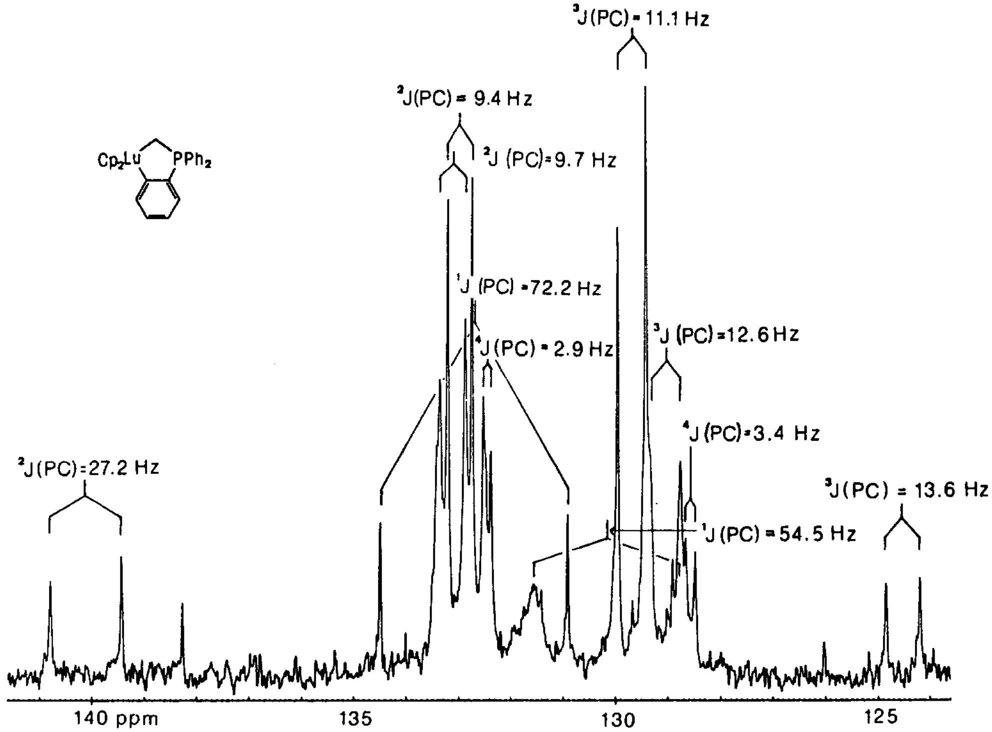
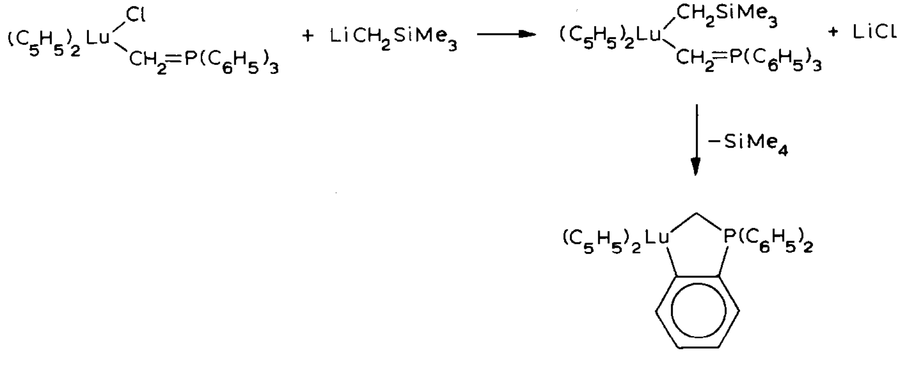


Fig. 8. ^{13}C NMR spectrum of $(C_5H_5)_2LuCH_2P(C_6H_5)_2C_6H_4$ (^{1}H-decoupled) in the range between 124 and 141 ppm.

Bis(cyclopentadienyl)(trimethylsilylmethyl)lutetinyl methylenetriphenylphosphorane can also be made from bis(cyclopentadienyl)chlorolutetinyl methylenetriphenylphosphorane and trimethylsilylmethyllithium in ether. It decomposes slowly at room temperature with the formation of tetramethylsilane and 1,1-bis(cyclopentadienyl)-3,3-diphenyl-1-luteta-3-phospha-indane [35]:



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