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Organometallic Compounds of the Lanthanides with Ylide Ligands*

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$LuCl_3$ reacts with $Li(CH_2)_2P(t\text{-}C_4H_9)_2$ yielding a 1:3 complex which shows dynamic behaviour in solution. The addition of $(C_5H_5)_2LuCl$ to $Li(CH_2)_2P(t\text{-}C_4H_9)_2$ yields a 1:1 chelate complex with stable configuration. $(C_5H_5)_2Lu(t\text{-}C_4H_9)(THF)$ and $(C_5H_5)_2Lu(CH_2SiMe_3)(THF)$ react with $CH_2{=}P(C_6H_5)_3$ or $Me_3SiCH{=}P(CH_3)_3$ in toluene with exchange of the THF ligand for the ylides and formation of new dicyclopentadienyl(alkyl)lutetinyl methylene triorganophosphoranes. New zwitterionic complexes of the type $(C_5H_5)_2Lu(R)\ (CHR'{=}PR''_3)$ have been isolated and characterized by their nmr spectra. Other ylide complexes of organolanthanides are unstable at room temperature, decomposing with evolution of hydrocarbons and formation of metallacycles or polymeric organolanthanide derivatives.

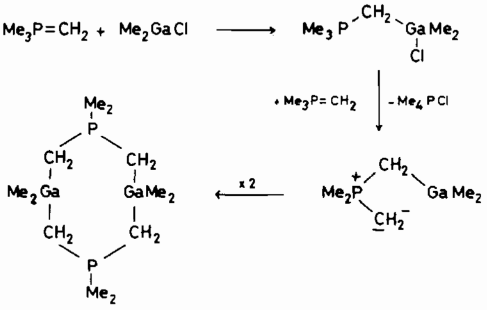
Introduction

Organometallic compounds of the early transition elements, especially of the lanthanides and actinides, are among the more recent organometallic compounds. The electronically unsaturated character of these elements made difficult the synthesis of satisfactorily stable compounds with metal to carbon bonds. New organic ligands with special properties – in steric and in an electronic manner – helped to solve this problem in the last 10 years. Our contribution to the solution of this problem included the use of phosphorus ylides as organic ligands bound to the rare earth metals.

Two formulae are of principal significance for the description of phosphorus ylides. The ylide formula $R_3\overset{+}{P}-\underset{-}{C}H_2$ emphasizes the dipolar zwitterionic nature of the compounds, involving an onium center at the phosphorus next to a carbanionic function, which can be at least partially delocalized into suitable substituents bound to this carbon atom. In the ylene formula $R_3P{=}CH_2$, a true double bond is postulated between the onium center and the ylide carbon, thus reducing or even eliminating the formal charges at these atoms.

Modern physical techniques and the results of theoretical calculations have made it increasingly clear that the ylide formula predominates in the ground state of these molecules. That is, ylides are stable molecules with a special type of carbanion. These carbanions are not associated with metallic cations, as in many organometallic reagents, but with an onium group fixed in a certain position of the system and giving rise to new specific features [1].

Phosphorus ylides react using their nucleophilic carbanionic center with organometallic compounds of the main group elements like trimethylaluminum complexes, with formation of classical adducts $Me_3\overset{+}{P}-CH_2-\overset{-}{A}lMe_3$, having also a zwitterionic nature [2] but in a more complicated way, as in the case of the reaction with dimethylgallium chloride [3]:



In the first step, a 1:1 adduct is formed, which reacts with an excess of ylide in a new transylidation process. The deprotonation occurs at one of the alkyl groups attached to phosphorus, followed by ring closure through intercomplexation. Thus the ylidic function is shifted away from the initial metal substituent. The resulting heterocyclic compound has alternating onium and metallate centers bridged by alkylene groups [3].

Transition metal compounds react in much the same way. Tetracarbonylnickel reacts with tricyclohexyl ethylenephosphorane to accommodate the ylide in its coordination sphere as a monodentate 2-electron ligand [4], and $(Me_3P)_2PtCl_2$ reacts with trimethyl methylenephosphorane yielding salt-like products in which two different modes of interaction

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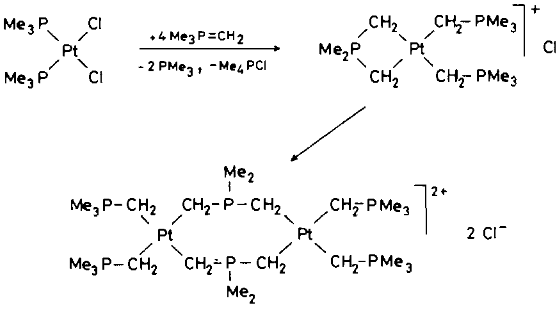
of ylidic carbanions with the metals are encountered [1]:



Because the ylides fully occupy the first coordination sphere of the metal, there is only partial transylidation possible by excess ylide. Two of the ligands are left as monodentate groups, and one is converted into a bidentate ligand [1].

To use phosphorus ylides as precursors for organometallic compounds of the lanthanides, another point is important. Phosphorus ylides $R_3\underset{+}{P}-\underline{C}H_2$ are isoelectronic to the trimethylsilylmethyl anion $R_3Si-\underline{C}H_2$. This ligand Me_3SiCH_2- was the first organic ligand used successfully to prepare and isolate the first stable, well-characterized homoleptic organometallic compounds of the rare earths, $Sc(CH_2SiMe_3)_3$ and $Y(CH_2SiMe_3)_3$ [5]. Therefore, using the isoelectronic principle, phosphorus ylides should give a good chance of preparing stable homoleptic organometallic compounds of the lanthanides.

Homoleptic Ylides of the Rare Earths

Trimethyl methylenephosphorane reacts with a suspension of several rare earth trichlorides in pentane or hexane with formation of pyrophoric phosphonium salts in quantitative yields [6]:

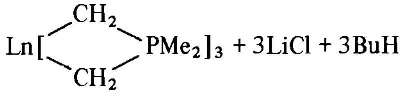
$$LnCl_3 + 3Me_3P{=}CH_2 \longrightarrow Ln[(CH_2-\overset{+}{P}Me_3)Cl^-]_3$$

Ln	dec. p.	Ln	dec. p.
La	155 °C	Gd	155 °C
Pr	140 °C	Ho	180 °C
Nd	160 °C	Er	166 °C
Sm	181 °C	Lu	140 °C

These insoluble products show no dehydrochlorination, as evidenced by the reaction with an excess of the ylide, which gave no formation of tetramethyl phosphonium chloride. But the complexes react with butyl lithium in ether–hexane with formation of lithium chloride, butane and a new class of uncharged homoleptic rare earth alkyl derivatives, corresponding to chromium(III)–tris[dimethylphosphonium bis(methylid)] prepared by Kurras *et al.* [7]:

$$Ln[(CH_2-\overset{+}{P}Me_3)Cl^-]_3 + 3Me_3P{=}CH_2 \not\longrightarrow Ln(CH{=}PMe_3)_3 + 3Me_4PCl$$

$$Ln[(CH_2-\overset{+}{P}Me_3)Cl^-]_3 + 3\ BuLi \longrightarrow$$



$$Ln[(CH_2)_2PMe_2]_3 + 3LiCl + 3BuH$$

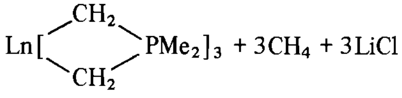
Ln	dec. p.	Ln	dec. p.
La	195–205 °C	Gd	180 °C
Pr	188–195 °C	Ho	190–200 °C
Nd	160–180 °C	Er	195–205 °C
Sm	179–186 °C	Lu	210 °C

The ^1H nmr spectrum of the diamagnetic lanthanum derivative shows two doublets for the CH_3 and the CH_2 protons with coupling constants $^2J(HP) = 12$ and 10 Hz, respectively, but also many such doublets with smaller intensities, some decreasing, some increasing after cooling to –30 °C. The lutetium derivative shows a similar spectrum, as do the spectra of the paramagnetic derivatives of the other lanthanide elements. Isolation of pure compounds which show simple nmr spectra was not possible.

A later re-investigation of the yttrium, lanthanum and lutetium complexes using the same procedure, but with methyl lithium as a base, or by another synthetic route using the lithiated trimethyl methylenephosphorane in tetrahydrofuran as a solvent, also yielded compounds having complicated nmr spectra. All three derivatives show 4 doublets and 2 singlets with intensities changing according to the recorded temperature [8]:

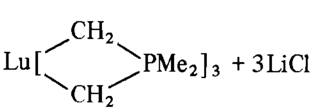
$$LnCl_3 + 3Me_3P{=}CH_2 \xrightarrow{Et_2O} Ln[(CH_2-PMe_3)Cl]_3$$

$$Ln[(CH_2-PMe_3)Cl]_3 + 3\ MeLi \xrightarrow{Et_2O}$$



$$Ln[(CH_2)_2PMe_2]_3 + 3CH_4 + 3LiCl$$

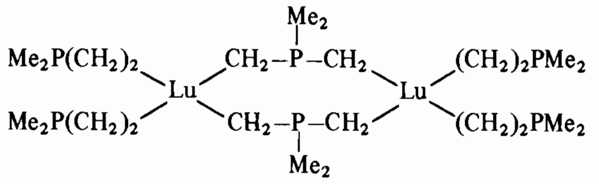
$$LuCl_3 + 3Li(CH_2)_2PMe_2 \xrightarrow{THF}$$



$$Lu[(CH_2)_2PMe_2]_3 + 3LiCl$$

	dec. p.	^{1}H nmr, δ
$\mathrm{Y[(CH_2)_2PMe_2]_3}$	178–190 °C	1.46d, 1.14d, 0.44s, 0.31s, 0.12d, –0.16d
$\mathrm{La[(CH_2)_2PMe_2]_3}$	195–205 °C	1.32d, 1.18d, 0.41s, 0.3s, –0.08d, –0.24d
$\mathrm{Lu[(CH_2)_2PMe_2]_3}$	202–208 °C	1.42d, 1.2d, 0.52s, 0.41s, 0.19d, –0.11d

$\mathrm{2Lu[(CH_2)_2PMe_2]_3} \rightleftharpoons$



The ^{31}P nmr spectrum of the lutetium derivative shows five different signals, indicating exchange equilibria between different complexes in solution, whereas a freshly prepared solution of the same complex shows immediately after formation of only two signals in benzene-d_6, which may be assigned to a dimer in equilibrium with the starting monomer.

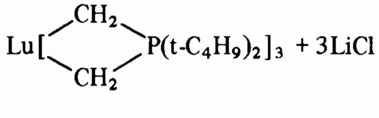
Attempts to isolate a rigid complex have not been successful using triphenyl methylenephosphorane as a phosphorus ylide. We found that lutetium trichloride and thulium trichloride react with this ylide in ether with formation of adducts which decompose without melting at 183 °C and 166 °C, respectively. A dehydrochlorination of both complexes was not possible, either with an excess of the ylide or with butyl lithium or methyl lithium [8]:

$$\mathrm{LuCl_3 + 3Ph_3P{=}CH_2 \longrightarrow Lu[(CH_2{-}PPh_3)Cl]_3}$$

$$\mathrm{TmCl_3 + 3Ph_3P{=}CH_2 \longrightarrow Tm[(CH_2{-}PPh_3)Cl]_3}$$

Lithium di-tert-butylphosphonium bis(methylid) reacts with lutetium trichloride in ether with formation of lithium chloride and a neutral complex, which can be isolated free of coordinating solvents. The colorless crystals decompose above 136 °C [9]:

$\mathrm{LuCl_3 + 3Li(CH_2)_2P(t\text{-}C_4H_9)_2 \longrightarrow}$



$$\mathrm{Lu[(CH_2)_2P(t\text{-}C_4H_9)_2]_3 + 3LiCl}$$

The ^{1}H nmr spectrum indicates a 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 undecoupled ^{13}C nmr 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 proton decoupled spectrum shows only a doublet, as expected. Passing from the lithium to the lutetium derivative, we notice a low field shift of 16.1 ppm and a decrease of the coupling constant ^{1}J(CP) from 35.7 to 28.1 Hz, as well as an increase of ^{1}J(HC) from 116.2 to 121.6 Hz. These nmr spectra argue for a dynamic behaviour in solution, in which monomeric symmetric lutetium ylide complexes are in a temperature dependent equilibrium with higher oligomers. Dominating species are the monomerics and dimerics, which can only be detected by nmr at low temperature. At elevated temperatures, higher oligomers are formed which decrease in amount with increasing molecular weight [9] (see next page).

Stabilization of such an ylide complex is possible using tetramethylethylenediamine (tmed) as a base. Lutetium trichloride reacts with lithium dimethylphosphonium bis(methylid) in tetrahydrofuran in the presence of tmed with formation of a pentane soluble colorless compound, which analyzed to be a complex of the homoleptic ylide with two tmed molecules. The ^{1}H nmr spectrum shortly after preparation shows only one broad signal for both the $\mathrm{CH_2}$ and $\mathrm{CH_3}$ groups of tmed, and two doublets at δ = 1.3 and 0.09 ppm for the ylidic methyl and methylene groups with coupling constants of 12.3 and 13 Hz [8]:

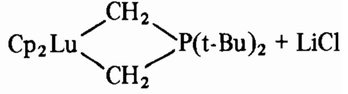
$$\mathrm{LuCl_3 + 3Li(CH_2)_2PMe_2 \xrightarrow[tmed]{THF}}$$

$$\mathrm{Lu[(CH_2)_2PMe_2]_3\cdot(tmed)_2 + 3LiCl}$$

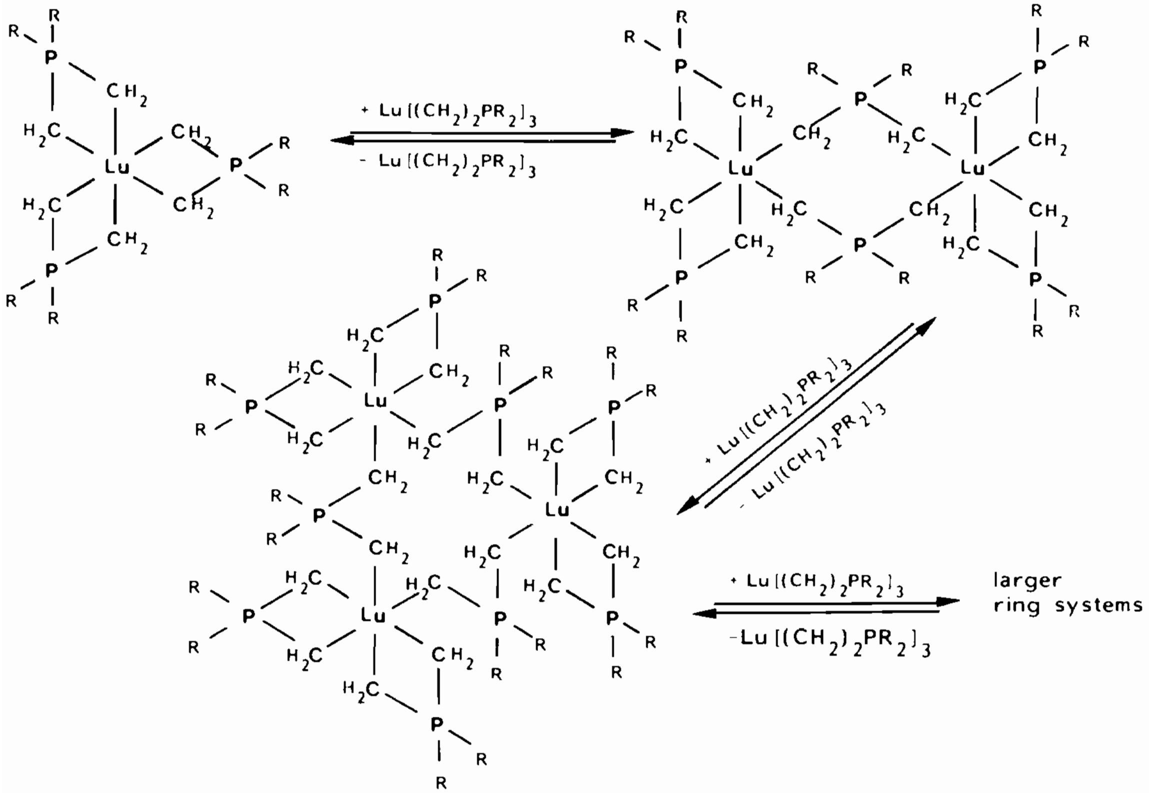
Dicyclopentadienyllutetium Ylide Complexes

A dynamic behaviour, as observed with the homoleptic rare earth ylide complexes, can be avoided by using blocking ligands such as penta*hapto*-bonded cyclopentadienyl groups. Dicyclopentadienyllutetium chloride reacts with the lithiated methylide of methyl di-tert-butylphosphine in tetrahydrofuran with formation of dicyclopentadienyl di-tert-butylphosphonium-bis(methylid), which is monomeric in solution. It crystallizes from toluene free of solvent. The nmr data confirm the proposed structure: ^{1}H: δCp 6.1 ppm (s), δ$\mathrm{CH_2}$ –0.3 (d), ^{2}J(HP) = 12 Hz, δ$\mathrm{CH_3}$ 1.02 (d), ^{3}J(HP) = 13.8; ^{31}P: δ 57 ppm; ^{13}C: δCp 110.2 ppm (s), δ$\mathrm{CH_2}$ 3.8 (d), ^{1}J(CP) = 17.6 Hz, δCP 33.8 (d), ^{1}J(CP) = 30.6, δ$\mathrm{CH_3}$ 28.9 (s) [9].

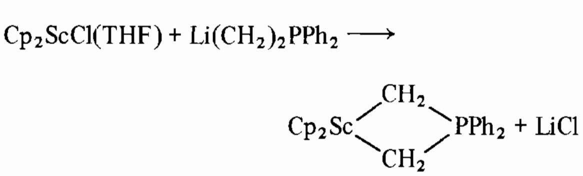
$\mathrm{Cp_2LuCl + Li(CH_2)_2P(t\text{-}Bu)_2 \xrightarrow{THF}}$



$$\mathrm{Cp_2Lu(CH_2)_2P(t\text{-}Bu)_2 + LiCl}$$

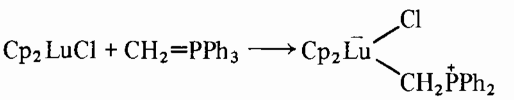


An analogous scandium derivative was prepared from dicyclopentadienylscandium chloride and the lithiated ylide of methyl diphenyl methylenephosphorane. It shows similar nmr parameters [10]:



$$Cp_2ScCl(THF) + Li(CH_2)_2PPh_2 \longrightarrow Cp_2Sc\begin{matrix}CH_2\\ \\CH_2\end{matrix}PPh_2 + LiCl$$

Dicyclopentadienyllutetium chloride reacts with triphenylmethylenephosphorane in toluene with formation of a 1:1 complex, which is zwitterionic containing a mono*hapto* lutetium–carbon σ-bond [11]:

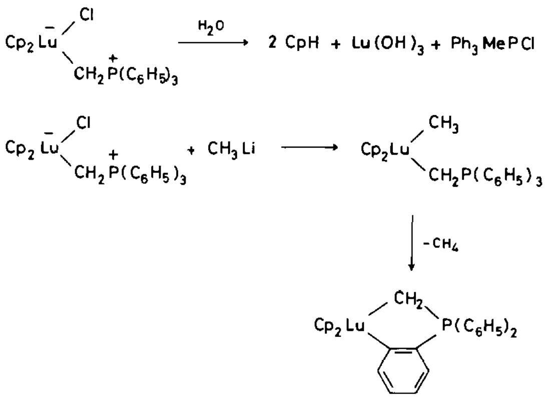


$$Cp_2LuCl + CH_2{=}PPh_3 \longrightarrow Cp_2\overset{-}{Lu}\begin{matrix}Cl\\ \\CH_2\overset{+}{P}Ph_2\end{matrix}$$

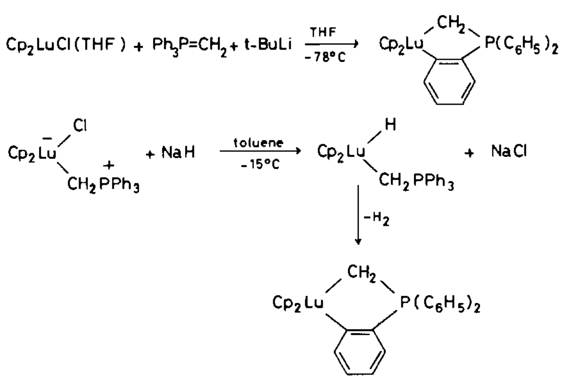
The colorless compound, which decomposes at 172 °C without melting, shows an nmr spectrum at room temperature with one sharp signal for the cyclopentadienyl protons at 6.1 ppm and the expected doublet for CH_2 at 0.92 with a large coupling constant $^2J(HP)$ of 17.5 Hz, in comparison to the 7.5 Hz for the starting ylide. The formation of the lutetium–carbon bond causes a decrease of electron density at the ylide carbon, shown by the low field shift in the ^{13}C nmr spectrum to δ −4.2 from 7.5 of the starting ylide and by the drastically reduced coupling constant $^1J(CP)$ of 28.8 Hz in comparison to 99.6 Hz in the ylide and 83.7 Hz for triphenylmethylphosphonium chloride. The undecoupled ^{13}C nmr spectrum confirms two protons at the ylide carbon, showing a coupling constant $^1J(CH)$ of 118 Hz.

$(C_5H_5)_2Lu(Cl)CH_2P(C_6H_5)_3$ hydrolyzes with fomation of cyclopentadiene, lutetium hydroxide and triphenylmethylphosphonium chloride. It reacts with methyl lithium in toluene at −78 °C with formation of the methylated derivative, which shows an additional nmr signal at δ −0.4 ppm for $LuCH_3$. It decomposes at room temperature with evolution of methane via a carbon–hydrogen activation at the δ position of the initial adduct and formation of a five-membered metallacycle [8]. The corresponding pentamethylcyclopentadienyl derivative shows the same behaviour [12].

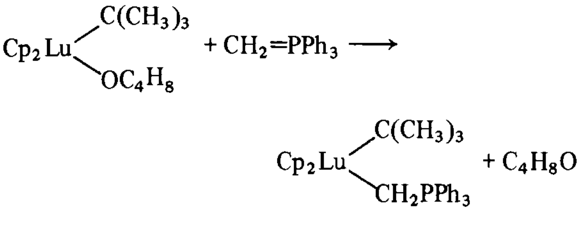
The same metallacycle is isolated as a product of the reaction of tert-butyl lithium with triphenylmethylenephosphorane and dicyclopentadienyllutetium chloride in tetrahydrofuran at −78 °C. Its nmr spectrum shows a doublet for the CH_2 protons at 0.38 ppm with a coupling constant $^2J(HP)$ of 14.6 Hz, a singlet for the cyclopentadienyl protons at 6.1 ppm and a multiplet for the phenyl and phenylene protons between 6.9 and 7.8 ppm. The ^{31}P nmr spectrum shows one peak at 25.6 ppm relative to 85% H_3PO_4. Dicyclopentadienyl chlorolutetinyl methylene triphenylphosphorane reacts with sodium



hydride in toluene at −15 °C with elimination of hydrogen from the intermediate hydride complex and formation of the metallacycle [8]:

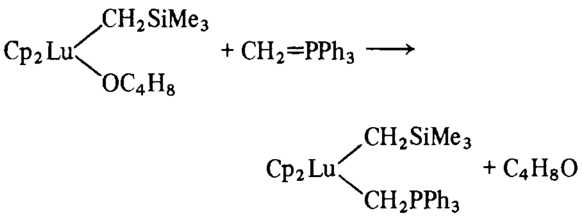


Organometallic compounds of the lanthanides such as dicyclopentadienyllanthanide chlorides or dicyclopentadienyl(alkyl) derivatives are stabilized by coordinating donor solvents like tetrahydrofuran, increasing the coordination number of the lanthanide metal. These donor solvents can be replaced by ylides, as shown with the formation of the zwitterionic complex $Cp_2Lu(Cl)CH_2PPh_3$ [11]:

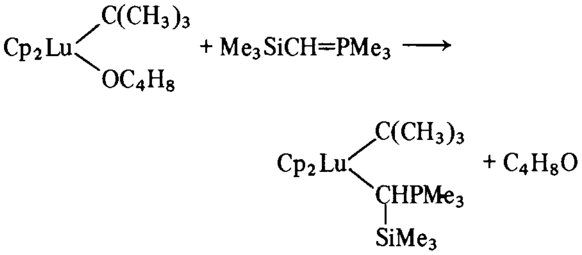


$$Cp_2Lu(C(CH_3)_3)(OC_4H_8) + CH_2{=}PPh_3 \longrightarrow Cp_2Lu(C(CH_3)_3)(CH_2PPh_3) + C_4H_8O$$

Dicyclopentadienyl(tert-butyl)lutetium tetrahydrofuranate also reacts at room temperature in toluene with triphenylmethylenephosphorane, yielding a colorless solid which decomposes above 122 °C with formation of isobutane. The same exchange reaction is found between dicyclopentadienyl(trimethylsilylmethyl)lutetium tetrahydrofuranate and triphenylmethylenephosphorane in toluene at −78 °C. Dicyclopentadienyl(tert-butyl)lutetium tetrahydrofuranate and trimethyl(trimethylsilyl)methylenephosphorane react in toluene at −15 °C, also with exchange of tetrahydrofuran against the ylide [13]:

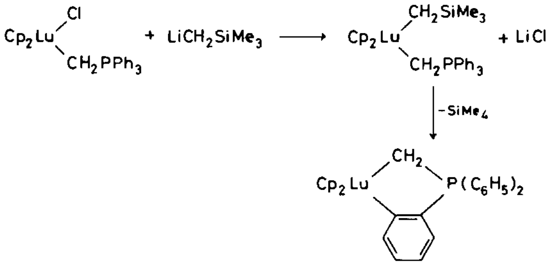


$$Cp_2Lu(CH_2SiMe_3)(OC_4H_8) + CH_2{=}PPh_3 \longrightarrow Cp_2Lu(CH_2SiMe_3)(CH_2PPh_3) + C_4H_8O$$



$$Cp_2Lu(C(CH_3)_3)(OC_4H_8) + Me_3SiCH{=}PMe_3 \longrightarrow Cp_2Lu(C(CH_3)_3)(CH(SiMe_3)PMe_3) + C_4H_8O$$

Dicyclopentadienyl(trimethylsilylmethyl)lutetinyl methylenetriphenylphosphorane is made in an alternative way from dicyclopentadienylchlorolutetinylmethylenetriphenylphosphorane and trimethylsilylmethyl lithium in ether. It decomposes slowly at room temperature with formation of tetramethylsilane and the mentioned lutetium containing heterocycle [13]:



Finally it could be shown that even compounds such as the tricyclopentadienyllutetium tetrahydrofuran complex react with ylides and triphenylmethylenephosphorane with elimination of tetrahydrofuran and formation of an ylide complex of tricyclopentadienyllutetium [8].

Acknowledgements

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