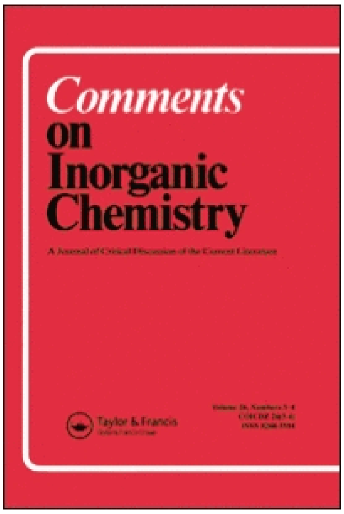

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Homoleptic Organometallic Compounds of the Rare Earths

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To cite this Article Schumann, Herbert(1983) 'Homoleptic Organometallic Compounds of the Rare Earths', Comments on Inorganic Chemistry, 2: 6, 247 — 259

To link to this Article: DOI: 10.1080/02603598308078122

URL: http://dx.doi.org/10.1080/02603598308078122

Homoleptic Organometallic Compounds of the Rare Earths

INTRODUCTION

Organometallic compounds of the transition metals containing metal-to-carbon σ bonds are in general extremely sensitive and unstable substances in contrast to the σ-bonded organometallic compounds of the main group elements. The reason for this is the electron deficiency in the outer orbitals of the metals, a factor that becomes much more important going from the transition elements to the lanthanides. The latter have 4*f* orbitals in their outer valence shells, creating 16 outer orbitals that have to be occupied by 32 electrons. Therefore, preparing organometallic compounds of the lanthanides should present a great problem for the synthetic organometallic chemist. In 1925 A. von Grosse postulated the nonexistence of alkyl and aryl derivatives of the lanthanides.[1]

The first description of such derivatives, the synthesis of $Sc(C_2H_5)_3$ and $Y(C_2H_5)_3$ in 1938, was in error[2] and the first attempts to prepare phenyl derivatives of lanthanum and some lanthanides by Gilman and co-workers failed. Biphenyl was the only reaction product isolated from the reactions of $LaCl_3$ with LiC_6H_5 in ether or from La with diphenylmercury at elevated temperatures in a sealed tube.[3]

The discovery of ferrocene and the other sandwich complexes initiated a new organometallic chemistry, the chemistry of the π complexes. Wilkinson and Birmingham prepared the first organometallic compounds of the rare earths, the tricyclopentadienyl complexes of Sc, Y,

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0260-3594/83/0206-0247/$18.50/0

La, Ce, Pr, Nd, Sm and Gd.[4] But another 14 years were required to demonstrate the synthesis of $Sc(C_6H_5)_3$, the first homoleptic, monophato σ-bonded organometallic compound of a rare earth.[5]

Organometallic chemistry of the rare earths entered a period of vigorous activity during the last decade, demonstrating that this long-neglected area of organometallic chemistry offers some very interesting aspects, ranging from theory to practical reagents and catalysts in synthetic chemistry.

SYNTHESIS OF HOMOLEPTIC ORGANOMETALLIC COMPOUNDS OF THE RARE EARTHS USING BULKY ALKYL AND ARYL LIGANDS

Scandium trichloride and yttrium trichloride react with methyllithium as well as with phenyllithium to yield air-sensitive products. But only the phenyl derivatives could be isolated and characterized as definite compounds[5,6]:

$$LnCl_3 + 3\ LiC_6H_5 \xrightarrow{THF} Ln(C_6H_5)_3 + 3\ LiCl,$$

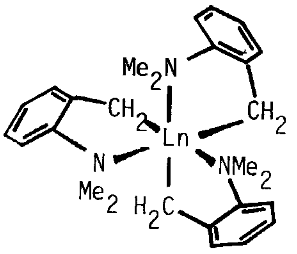
$$Ln = Sc, Y.$$

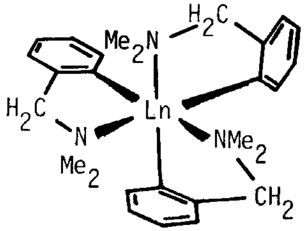
Their reactions with CO_2, benzophenone and $HgCl_2$, as well as their IR spectra, verify the given formula. The reaction of phenyllithium with $LaCl_3$ or the trichlorides of some lanthanides did not give analogous derivatives. In the cases of $LaCl_3$ and $PrCl_3$, compounds of the type $Li[Ln(C_6H_5)_4]$ formed; the other lanthanides did not give reproducible compounds.[6]

A considerable stabilization of homoleptic organometallic compounds of the rare earths can be achieved by the use of bulky alkyl or aryl groups such as neopentyl, CH_2SiMe_3, $CH(SiMe_3)_2$ or alkyl and aryl ligands containing built-in chelating groups, like *N,N*-dimethyl-amino-*o*-benzyl or *N,N*-dimethylaminomethylphenyl. The first compound of this class with a proven structure, tetrakis(tetrahydrofuran)lithium tetrakis(2,6-dimethylphenyl) lutetiate was prepared in the following way[7]:

$$LuCl_3 + 4\ LiC_6H_3Me_2 \xrightarrow{THF} [Li(THF)_4]\ [Lu(C_6H_3Me_2)_4] + 3\ LiCl.$$

Three-coordinate organolanthanide compounds can be considerably stabilized by the use of chelating ligands.[8–10] A benzylascandium complex can be prepared from $ScCl_3$ and $LiCH_2C_6H_4$-2-NMe_2 as an extremely air-sensitive compound, showing an octahedral arrangement formed by three covalent Sc–C σ bonds and three coordinative N–Sc bonds. The Y, La and Er derivatives could be prepared in the same way, as well as the compounds $Ln(C_6H_4$-2-$CH_2NMe_2)_3$ with Ln = Sc, Y, Nd, Er:





Other types of alkyl groups, bulky and with no possibility for a β-elimination reaction, have been used for the preparation of such organolanthanide complexes.[11–13] Sc and Y compounds with the ligands CH_2CMe_3, CH_2SiMe_3, $CH(SiMe_3)_2$ and $CH_2SiMe_2C_6H_4$-2-OCH_3 have been obtained from the reaction of the appropriate lithium reagent with $ScCl_3$ or YCl_3. The complexes were isolated from pentane as analytically pure, air-sensitive, colorless crystals containing two molecules of THF coordinated to the metal. The NMR data are consistent with a trigonal bipyramidal structure, the THF ligands occupying the axial sites. The coordinated THF could not be removed in vacuo, and only the compounds $Y[CH(SiMe_3)_2]_3$ and $Sc(CH_2SiMe_2C_6H_4OMe)_3$, with extremely bulky ligands, could be obtained free of solvent. The Tb, Er and Yb derivatives of the type $Ln(CH_2SiMe_3)_3 \cdot (THF)_2$ were obtained by a similar procedure and some ionic derivatives, $LiLnR_4$, $LiLnR_3Cl$ and $LiLnR_2Cl_2$, were also reported.[13] Their structures could be established by IR and NMR spectra as well as by a single-crystal x-ray analysis for $[Li(THF)_4]\{Yb[CH(SiMe_3)_2]_2Cl\}$.

We found that $ErCl_3$ and $TmCl_3$ give the pink or white air-sensitive complexes $Ln(CH_2SiMe_3)_3 \cdot (THF)_3$, which crystallize from pentane at low temperature.[14,15] Above −35 to −25°C one THF is lost irreversibly, precipitating the dissolved complexes on recrystallization. $YbCl_3$ and $LuCl_3$ form the corresponding complexes $Ln(CH_2SiMe_3)_3 \cdot (THF)_2$ in the first step.[13,15] The NMR of the lutetium compound is consistent with a trigonal bipyramidal structure with the THF ligands occupying axial sites.[15]

On keeping a pentane solution of $Ln(CH_2SiMe_3)_3 \cdot (THF)_2$ with Ln = Er or Lu at room temperature for several days, the complexes lose THF and tetramethylsilane. An extremely pyrophoric material precipitates. Quantitative experiments showed one $SiMe_4$ splits off from the complex, leaving polymeric complexes with the formula $[Ln(CH_2SiMe_3)(CHSiMe_3)]_x$ and having decomposition points between 380 and 390°C[15]:

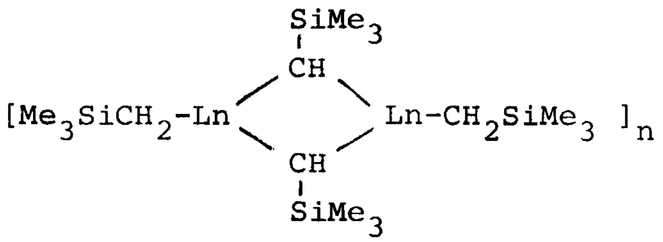
$$LnCl_3 + 3\ LiCH_2SiMe_3 \xrightarrow{THF} Ln(CH_2SiMe_3)_3 \cdot (THF)_3 + 3\ LiCl;$$

$$Ln(CH_2SiMe_3)_3 \cdot (THF)_3 \xrightarrow{-25^\circ C} Ln(CH_2SiMe_3)_3 \cdot (THF)_2 + THF;$$

$$Ln(CH_2SiMe_3)_3 \cdot (THF)_2 \xrightarrow{40^\circ C} [Ln(CH_2SiMe_3)(CHSiMe_3)] + SiMe_4 + 2\ THF;$$

Ln = Er, Tm, Yb, Lu.

We consider an α-elimination route reasonable. These polymeric complexes should have a structure involving CH_2SiMe_3 and bridging $CHSiMe_3$ groups:



A similar decomposition is reported for some related derivatives of yttrium and neodymium.[16–18] YCl_3 and $NdCl_3$ react with $LiCH_2SiMe_3$, $LiCH_2C_6H_5$ and $LiCH_2CMe_2C_6H_5$ to give unusual organometallic compounds. The first step is supposed to be the formation of the unstable compounds LnR_3, which decompose immediately in the reaction medium, yielding carbene-type complexes whose structure will have to be established in further investigations:

$$LnCl_3 + 3\ LiCH_2C_6H_5 \rightarrow Ln(CH_2C_6H_5)_3 + 3\ LiCl;$$

$$Ln(CH_2C_6H_5)_3 \rightarrow Ln(CH_2C_6H_5)(CHC_6H_5) + C_6H_5CH_3;$$

$$Ln = Y, Nd.$$

The "ate" complexes $[LiL_2]\ [Ln(CH_2SiMe_3)_4]$ with L = tetramethylethylenediamine (tmed) and $[LiL_4]\ [Ln(CH_2SiMe_3)_4]$ with L = THF and ether have been prepared by the reaction of the neutral homoleptic rare earth organyl $Ln(CH_2SiMe_3)_3 \cdot (THF)_2$ with $LiCH_2SiMe_3$, either in THF or tmed or from the rare earth trichlorides with excess of $LiCH_2SiMe_3$[11,15,19]:

$$Ln(CH_2SiMe_3)_3 \cdot (THF)_2 + LiCH_2SiMe_3 \xrightarrow{THF} [LiL_4][Ln(CH_2SiMe_3)_4];$$

$$Ln = Y, L = THF \qquad Ln = Y \text{ or } Er \qquad L_2 = \text{tmed}.$$

$$LuCl_3 + 4\ LiCH_2SiMe_3 \xrightarrow[-LiCl]{et_2O} [Li(et_2O)_2][Lu(CH_2SiMe_3)_4];$$

$$[Li(et_2O)_4][Lu(CH_2SiMe_3)_4] \xrightarrow[-4\ et_2O]{+2\ tmed} [Li(tmed)_2][Lu(CH_2SiMe_3)_4].$$

Proton and ^{13}C NMR spectra suggest a rapid dissociation-recombination equilibrium at room temperature for the yttrium derivative:

$$[Li(THF)_4][Y(CH_2SiMe_3)_4] \rightleftharpoons Y(CH_2SiMe_3)_3 \cdot (THF)_2 + LiCH_2SiMe_3 \cdot (THF).$$

The ether-stabilized lutetium complex[15] shows complex reactive behavior. The benzene soluble compound has a broadened CH_2 resonance in the ^1H NMR spectrum, which indicates a relatively slow dissociation with respect to the NMR time scale. In a subsequent reaction the complex loses $SiMe_4$ by an α-elimination route during a period of a week. At −10°C a white-green compound could be isolated:

$$[Li(et_2O)_4][Lu(CH_2SiMe_3)_4] \xrightarrow[-4\ et_2O]{-SiMe_4} Li[Lu(CH_2SiMe_3)_2(CHSiMe_3)].$$

Addition of a base such as tmed, THF or dme leads to stabilized but benzene insoluble compounds. The NMR spectrum of [Li(tmed)] [Lu($CH_2SiMe_3)_2$ ($CHSiMe_3$)] in THF-d_8 shows only some of the expected signals. At $\delta = 0.02$ and -0.05 ppm relative to TMS, two peaks appear for the Me_3Si groups, the one at -0.05 ppm having a half width of 5 cps. The CH_2 resonance at -1.06 ppm is also broadened to 5 cps; the CH signal cannot be located with certainty due to its low intensity. Cooling to -35°C produces two sharp signals for the trimethylsilyl protons with an approximate integrated ratio of 2:1, suggesting a definite kinetically stable compound.

Further splitting off of one $SiMe_4$ occurs for the solvent-free $Li[Lu(CH_2SiMe_3)_2(CHSiMe_3)]$ as revealed by NMR experiments. The spectrum collapses to a broad unresolved signal centered around 0.40 ppm. After three weeks the reaction is complete and the $SiMe_4$ concentration remains constant.

Careful investigations in the systems $LnCl_3$–$LiCH_2SiMe_3$ revealed the simultaneous formation of neutral and ionic species, even with an excess of $LnCl_3$. The ionic derivatives decompose by an α-elimination mechanism, finally resulting in an extremely pyrophoric compound with the unusual stoichiometry of Li:Ln = 1:2. All analytical results are best rationalized by the formulation $\{[Li(THF)_2][Ln_2(CH_2SiMe_3)_2(CHSiMe_3)(CSiMe_3)]\}_n$.[19,20]

tert-Butyl derivates of the rare earths are prepared by slow addition of a freshly prepared solution of tert-butyllithium to a suspension of anhydrous $SmCl_3$, $ErCl_3$, $YbCl_3$ or $LuCl_3$ in THF at -55°C. These are air-sensitive complexes which contain 4 THF for Sm, Er and Lu but only 3 for Yb[21,22]:

$$\mathrm{LnCl_3 + 4\ Li^{t}C_4H_9 \xrightarrow[-55^\circ C]{THF} Li[Ln(^{t}C_4H_9)_4]\cdot(THF)_{\mathit{x}} + LiCl;}$$

$$\mathrm{Ln} = \mathrm{Sm, Er, Lu},\ x = 4 \qquad \mathrm{Ln} = \mathrm{Yb},\ x = 3.$$

Variable temperature magnetic susceptibility measurements confirm the structure of the complexes with $\mu_{eff} = 9.7$ for the Er compound, 4.6 for the Yb compound and 2.1 for the Sm derivative, as well as a sharp singlet for the 36 tert-butyl protons at $\delta = -0.79$ ppm relative to TMS.

$TbCl_3$, $ErCl_3$ and $LuCl_3$ as well as the tert-butoxides of Er and Lu react in pentane in the presence of ether or tmed to form complexes of the same type, with ether or tmed as the stabilizing ligands[20]:

$$LnCl_3 + Li^tC_4H_9 \xrightarrow[et_2O]{pentane} [Li(et_2O)_4]\,[Ln(^tC_4H_9)_4] + 3\,LiCl;$$

$$Ln = Tb, Er, Lu;$$

$$Ln(O^tC_4H_9)_3 + 4\,Li^tC_4H_9 \xrightarrow[tmed]{pentane} [Li(tmed)_2][Ln(^tC_4H_9)_4]$$

$$+ 3\,LiO^tC_4H_9;$$

$$Ln = Er, Lu.$$

The ^1H NMR spectrum of $[Li(tmed)_2][Lu(^tC_4H_9)_4]$ in THF-d_8 gives the following chemical shifts: δ CCH_3 = 0.97 ppm, δ NCH_2 = 2.27 ppm and δ NCH_3 = 2.13 ppm relative to TMS.

The complexes $Li[Ln(^tC_4H_9)_4]$ are starting materials for the synthesis of homoleptic lanthanide alkynide compounds. They react with an excess of 3,3-dimethylbut-1-yne in tetrahydrofuran at room temperature with complete replacement of the tert-butyl ligands and formation of 2-methylpropane in addition to the new lanthanide alkynides[23]:

$$Li[Ln(^tC_4H_9)_4] \cdot (THF)_4 + 4\,HC\equiv CC\,(CH_3)_3 \rightarrow 4\,C_4H_{10}$$

$$+ Li\{Ln[C\equiv CC(CH_3)_3]_4\} \cdot (THF);$$

$$Ln = Sm, Er, Lu.$$

HOMOLEPTIC METHYL DERIVATIVES OF THE RARE EARTHS

The most exciting problem to be solved in organometallic chemistry of the lanthanides was the preparation of homoleptic permethylated derivatives. Erbium tribromide reacts with methyllithium in ether-tetrahydrofuran at 0°C with formation of a sensitive product, which seemed to be trimethylerbium coordinated with three tetrahydrofurans. The elemental analyses were reasonable for erbium and quite resonable for carbon and hydrogen, but they always showed some lithium which could not be removed. The ratio of erbium to lithium was 2:1 and the ratio of erbium to CH_3 was 1:3.

The problem was solved by using tetramethylethylenediamine as a stabilizing base.[24] Dropwise addition of an ether solution of methyllithium to a suspension of the rare earth trichloride in diethyl ether with a stoichiometric amount of tmed affords good yields of analytically pure reaction products, in some cases colored crystals, which were free of excess methyllithium after recrystallization[25,26]:

$$\mathrm{LnCl_3 + 6LiCH_3 + 3\ tmed \xrightarrow{et_2O} [Li(tmed)]_3[Ln(CH_3)_6] + 3\ LiCl.}$$

The scandium, cerium and europium compounds have not been isolated up until now for a number of reasons. All the other compounds are extremely sensitive to moisture and air. Hydrolysis and alcoholysis liberate six moles of methane per mole of lanthanide. The proton and ^{13}C NMR spectra of the diamagnetic Y, La and Lu compounds show singlets for the methyl groups bound to the rare earths and signals for the tmed ligands. The paramagnetic derivatives give broadened spectra which can be resolved in some cases.

The single-crystal x-ray structure analysis of the erbium[25] and the holmium derivatives[26] show the lanthanides surrounded by six methyl groups in a slightly distorted octahedral arrangement. Figure 1 shows the molecular structure of the Er derivative. All the Er–C bonds are of

TABLE I

Ln	Color	Dec.p. (°C)	δCH_3 (ppm)
Y	White	120–132	−0.52
La	White	79–82	
Pr	Green	59–62	−5.9
Nd	Blue	78–83	−6.2
Sm	Yellow	85–88	−2.8
Gd	Greenish	112	
Tb	White	115	−108
Dy	White	106	−74
Ho	Green	122	−60
Er	Pink	122–125	
Tm	Greenish	105–114	−92
Yb	Yellow	116–126	
Lu	White	141–142	−1.18

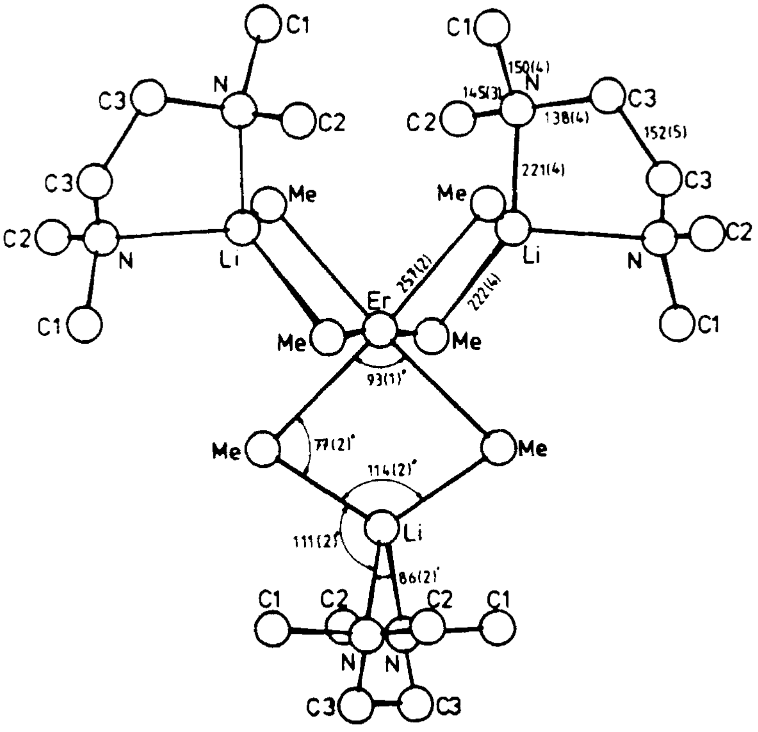


FIGURE 1 Molecular structure of [Li(tmed)]$_3$ [Er(CH$_3$)$_6$]. Rhombohedral, space group $R\bar{3}c, Z = 2$, $a = 130.9(2)$ pm, $\alpha = 79.39(10)^\circ$, $R = 0.085$.[25]

equal length and the methyl groups are bridged pairwise by lithium atoms, resulting in a slight widening of the corresponding CH$_3$–Er–CH$_3$ angles to 93°. The lithium atoms are each located in the centers of tetrahedra made up of two methyl groups and the two nitrogens of one tmed ligand. Thus, an octahedron results which is coupled via three corners to three tetrahedra not linked with each other.

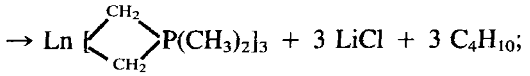
HOMOLEPTIC YLIDE COMPLEXES

Among the first isolated organometallic compounds of the lanthanides the trimethylsilylmethyl derivatives played an important role because they were more stable than the other derivatives. Trimethylmethylenephosphorane, the simplest phosphorus ylide, is isoelectronic to the $(CH_3)_3SiCH_2$ anion. Therefore, ylide complexes of the lanthanides should be as stable as the trimethylsilylmethyl derivatives.

The addition of $(CH_3)_3P{=}CH_2$ to a suspension of rare earth trichlorides in pentane or hexane results in the formation of pyrophoric phosphonium salts in quantitative yields. While no dehydrochlorination of these salts was observed by reaction with excess ylide to form tetramethylphosphonium chloride, the compounds react with butyllithium in ether-hexane with formation of LiCl, C_4H_{10} and a new class of uncharged homoleptic rare earth alkyls[27]:

$$\mathrm{LnCl_3 + 3\ (CH_3)_3P = CH_2 \rightarrow Ln[CH_2P(CH_3)_3Cl]_3;}$$

$$\mathrm{Ln[CH_2P(CH_3)_3Cl]_3 + 3\ LiC_4H_9}$$

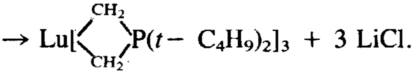


$$\rightarrow \mathrm{Ln}[\overset{\mathrm{CH_2}}{\underset{\mathrm{CH_2}}{\langle\quad\rangle}}\mathrm{P(CH_3)_2}]_3 + 3\ \mathrm{LiCl} + 3\ \mathrm{C_4H_{10}};$$

$$\mathrm{Ln = La, Pr, Nd, Sm, Gd, Ho, Er, Lu.}$$

These very air-sensitive complexes apparently owe their high stability to the incorporation of chelating phosphorus ylide ligands. The neutral complexes show dynamic behavior in solution, producing dimeric, trimeric and polymeric species in addition to the monomers, as could be shown with the di-tert-butyl phosphonium derivative of lutetium[28]:

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



$$\rightarrow \mathrm{Lu}[\overset{\mathrm{CH_2}}{\underset{\mathrm{CH_2}}{\langle\quad\rangle}}\mathrm{P(}t-\mathrm{C_4H_9)_2}]_3 + 3\ \mathrm{LiCl}.$$

The complex can be isolated free of coordinating solvents. The colorless crystals decompose above 136°C. The NMR spectra indicate dynamic behavior in solution. The complicated line-rich proton NMR spectrum at room temperature is reduced to two doublet signals at $-26°C$, which is assignable to an octahedral compound with six Lu–C–η^1 bonds. This spectrum, as well as the ^{13}C and ^{31}P NMR spectra which contain many signals of low intensity in addition to the main signals, argues for a dynamic oligomerization in solution as indicated in Figure 2.

This dynamic behavior can be frozen using blocking ligands like

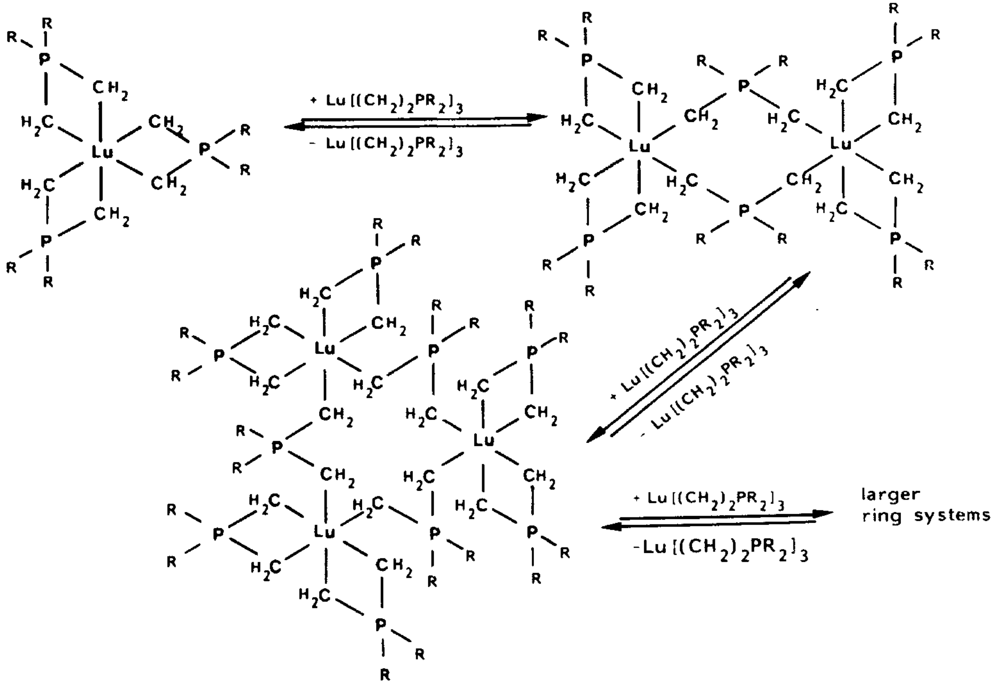
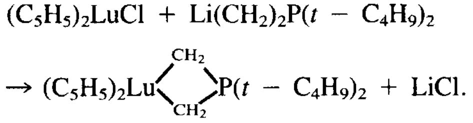


FIGURE 2 Oligomerization equilibria in the system $\{Lu[(CH_2)_2P(t\text{-}C_4H_9)_2]_3\}_n$ with n = 1,2,3, . . . , n.

cyclopentadienyl. $(C_5H_5)_2Lu(CH_2)_2P(t\text{-}C_4H_9)_2$ prepared in accordance with the following equation in tetrahydrofuran is a monomeric compound in solution, which crystallizes solvent-free from toluene[28]:



$$(C_5H_5)_2LuCl + Li(CH_2)_2P(t - C_4H_9)_2 \rightarrow (C_5H_5)_2Lu\overset{CH_2}{\underset{CH_2}{\langle\,\rangle}}P(t - C_4H_9)_2 + LiCl.$$

OUTLOOK

In the past ten years it has been possible to prepare not only homoleptic organometallic compounds with rare earth–carbon bonds but also homoleptic derivatives with bonds from the rare earths to phosphorus,[29] arsenic,[30] germanium,[31] tin[32] and even some transition metals.[33] The postulate of the nonexistence of organometallic compounds of the lanthanides that was made by von Grosse in 1925 has now been refuted. Organometallic compounds of the rare earths are preparable compounds. They are delicate but because of their coordinative unsaturation are highly reactive, offering new catalytic and synthetic possibilities on a large scale in organic chemistry.

Acknowledgment

I wish to thank my co-workers, whose names appear in the reference list, as well as the Fonds der Chemischen Industrie and the Senator für Wirtschaft und Verkehr des Landes Berlin, for supporting this work.

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