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Advances in the Chemistry of Organolanthanides

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The results of studies on the synthesis, structure, and reactivity of organometallic derivatives of the lanthanide elements are surveyed. Data concerning their practical applications are presented.
The bibliography includes 235 references.

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I. INTRODUCTION

The chemistry of organometallic derivatives of the lanthanides began to develop vigorously after the characteristics of the formation of organic derivatives of d elements had been elucidated in broad outline. In the last decade an increasing number of investigators have turned their attention to this little studied field in the search for new highly effective stereospecific and regioselective catalysts. Since 1975, Soviet chemists have taken an active part in the development of methods of synthesis of new types of organometallic derivatives of the lanthanides[1,2] although physicochemical studies on the known cyclopentadienyl complexes had been made earlier in our country.[3,4]

The first organometallic lanthanide compounds isolated and reliably characterised were the cyclopentadienyl complexes obtained in the middle of the 1950's.[5,6] Compounds of this type remained for a long time the only ones known for the lanthanides. However, at the present time virtually all classes of organic derivatives of the lanthanides (Ln), also known for transition metals, have been synthesised, including the hydrides, the carbonyls, the σ-alkyl and σ-aryl compounds, the carbonyl derivatives, and the dienyl, allyl, indenyl, cyclo-octatetraenyl, and other complexes. Organometallic derivatives containing an Ln–E bond, where E = nitrogen, phosphorus, oxygen, sulphur, selenium, mercury, boron, germanium, or tin, as well as complexes in which the lanthanide is present in combination with molybdenum tungsten, cobalt, manganese, and rhenium have been synthesised. Carbon-containing clusters with an Ln–Ln bond have been obtained. Only the arene complexes of the lanthanides apparently remain unknown.

In the study of the properties of organometallic derivatives of the lanthanides, their high catalytic activity in the polymerisation of olefins and especially dienes was discovered. In recent years processes have been discovered in which organolanthanides play the role of activators of hydrogen and carbon monoxide and dioxide. All these facts indicate great potential possibilities of the derivatives of *f* elements in catalysis.

The main distinctive factor determining the catalytic activity and specific properties of the compounds considered is the presence of a completely or partly filled 4*f* sublevel in the lanthanide atoms. A detailed discussion of the characteristics of the electronic structure of the lanthanide complexes is found in another review[7] and the literature quoted therein. Here we shall only note the principal characteristics which determine the behaviour of the free lanthanides and their organic derivatives in chemical reactions.

All the 15 elements which follow barium in Mendeleev's Table are electropositive metals. Their normal electrode potentials (+2.522–2.255 V) are close to those of the alkali metals. Accordingly, the organic complexes of the lanthanides are as a rule ionic and exhibit clearly the properties of Lewis acids. The most characteristic oxidation state is Ln^{3+}. Only three elements, namely samarium, europium, and ytterbium, form stable bivalent derivatives, although the Ln^{2+} state is known for all the lanthanides.[7,8] Organometallic compounds with the quadrivalent metal (Ln^{4+}) are known only for cerium. The high ionic radius (0.848–1.061 Å) characteristic of the lanthanides is responsible for their high coordination numbers (up to 12). Compounds with an octacoordinate lanthanide atom are the most common.

A series of reviews,[7,9–17] a collection of articles,[8] and a chapter in one of the books of the "Methods of Organoelemental Chemistry" series[18] have been devoted to organometallic derivatives of the lanthanides. However, the available information in this field has been increasing so rapidly that at the present time it is already felt that a systematic survey of the accumulated data is necessary. In the present review we attempted to examine as fully as possible advances in the chemisty of the organic derivatives of the lanthanides in the field of synthesis and reactivity, including catalytic processes, during the last 5–7 years (up to 1984 together with a few later studies). In addition, data are presented on the synthesis and properties of the phthalocyanide complexes and alkoxides of the lanthanides. In order to create an integral picture of the modern organometallic chemisty of the lanthanides, the review includes a series of earlier studies as well as data for scandium and yttrium compounds.

II. HYDRIDES

The lanthanide hydrides LnH_2 and LnH_3 are readily formed when the free metals are saturated with hydrogen at room temperature.[19] They are usually isolated in the form of powders but, at an elevated temperature, it is possible to obtain crystalline specimens. Heating the hydrides decomposes them into the initial elements. The decomposition temperature depends strongly on the metal: CeH_3 is the least stable (decomposition temperature 157 °C) and LuH_3 is the most stable (decomposition temperature 416 °C). All the

hydrides, with the exception of ScH_2, are rapidly oxidised in air. Water decomposes the trihydrides, LnH_3, at an appreciable rate; the dihydrides LnH_2 are hydrolytically more stable.

Unstable variable-composition hydrides LnM_xH_y are formed when lanthanide melts containing various metals (Mg, Al, Mn, Fe, Co, Ni, etc.) are saturated with hydrogen.[19] The tetrahydroborates $Ln(BH_4)_3$ and the extremely unstable tetrahydroaluminates $Ln(AlH_4)_3$ are obtained in the reactions of the salts LnX_3 with $MM'H_4$ (M = Li or Na; M' = B or Al).[20,21]

The first communication about the synthesis of organometallic complexes containing an Ln–H bond appeared in 1974.[22] It stated that Cp_3CeCl and Cp_2CeCl_2 (Cp = η^5-C_5H_5) afford respectively Cp_3CeH and Cp_2CeH_2 on interaction with sodium hydride in boiling tetrahydrofuran (THF). The structure of these products was confirmed by elemental analysis and infrared spectroscopy (the bands in the region of 2040 cm^{-1} were assigned to the Ce–H bond vibrations).

The lutetium hydride $Cp_2LuH.THF$ was obtained in two ways:[23]

$$Cp_2Lu{-}R\cdot THF + H_2 \xrightarrow[50\ bar]{} Cp_2Lu{-}H\cdot THF + RH,$$
$$R = CH_2Ph,\ CH_2SiMe_3;$$
$$Cp_2LuCl\cdot THF + NaH \xrightarrow[20^\circ]{} Cp_2Lu{-}H\cdot THF + NaCl.$$

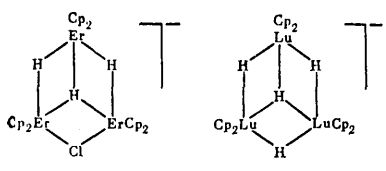
It has been stated[23] that the frequencies ν(Lu–H) and ν(Lu–D) in the infrared spectra of the product and its deuterio-analogue are 770 and 720 cm^{-1} and 540 and 510 cm^{-1} respectively. Apart from elemental analysis, the structure of the hydride has been confirmed by its reaction with Me_3SiCl, which gave rise to trimethylsilane and Cp_2LuCl.

The use of t-butyl derivatives in the synthesis of the hydrides by the hydrogenolysis of the Ln–R σ-bond made it possible to carry out the reaction at atmospheric pressure:[24,25]

$$2(RC_5H_4)_2Ln\text{-}Bu\text{-}t.\cdot THF + 2H_2 \rightarrow [(RC_5H_4)_2Ln{-}H\cdot THF]_2 + 2t\text{-}BuH;$$
$$Ln = Y,\ Er,\ Lu.$$

The deuterio-derivatives have been synthesised analogously. Bands in the ranges 1350–1240 and 975–900 cm^{-1} respectively have been assigned to the Ln–H and Ln–D vibrations in the compounds obtained. X-Ray diffraction analysis of the yttrium dimer $[(MeC_5H_4)_2YH.THF]_2$ and the samarium dimer $[(Me_5C_5)_2SmH]_2$ dimer confirmed the presence of bridging hydrogen atoms, although their coordinates were not accurately established. The differences between the properties (infrared and ^1H NMR spectra and solubility) of the lutetium complex synthesised by Evans and co-workers and the hydride described by Schumann and Genthe[23] led Evans and co-workers[24,25] to the conclusion that the hydride has a different structure.

The dimeric hydrides $(Cp_2LnH.THF)_2$ are also formed on thermal decomposition of the same t-butyl complexes at 20–75 °C via the mechanism of the β-hydride decomposition.[24] It is of interest that thermolysis in the presence of a small amount of LiCl leads to the formation of other products. The erbium complex afforded a product having the composition $\{[Cp_2ErH]_3Cl\}[Li.(THF)_4]$ containing the trinuclear anion (A) according to X-ray diffraction (XRD) data:



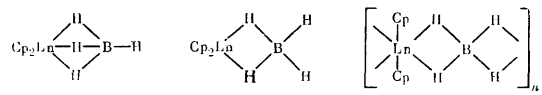
(A) (B)

The analogous anion (B), free of chlorine, has been obtained in the thermolysis of Cp_2Lu–Bu-t.THF.[24] The hydride band in the infrared spectra of the anions (A) and (B) is observed in the region of 1200 cm^{-1}.

The formation of the bivalent ytterbium hydride BuC ≡ CYbH is postulated in the initial stage of the reaction of atomic ytterbium cocondensed with hex-1-yne at 77 K.[26] This complex multistage process leads ultimately to the oligomer $[(BuC \equiv C)_3Yb_2H]_n$. Under the same conditions, samarium gives rise to a product for which the formula $[(C_6H_9)_2SmH]_n$ has been suggested.

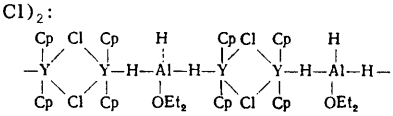
The chemical properties of the lanthanide hydrides are similar to those of the organohydrides of electropositive transition metals. They are hydrolysed by water and D_2O to H_2 or HD respectively and readily exchange hydrogen for a halogen on interaction with RX (R = CCl, Me, or Me_3Si). The yttrium hydrides $[(RC_5H_4)_2YH.THF]_2$ combine with two equivalents of t-butyl isocyanide, giving (according to XRD data) the dimers $\{(RC_5H_4)_2Y[C(H) = N\text{-}Bu\text{-}t]\}_2$ with bridging formimidoyl groups.[27]

The vibrational spectra methods of the complexes Cp_2LnBH_4. .THF (Ln = Sm, Er, or Yb), synthesised by the interaction of Cp_2LnCl with sodium tetrahydroborate, suggested[28] that, for Ln = Sm the anion is a tridentate ligand (C). When the Ln^{3+} cation is smaller (for example, when Ln = Yb) a complex with a bidentate tetrahydroborate group (D) is formed and the removal of coordinated THF by heating *in vacuo* gives polymeric structures, (E):



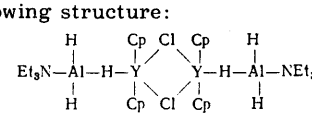
(C) (D) (E)

The complex $(Cp_2YCl)_2AlH_3.Et_2O$ has been obtained by the reaction of AlH_3 with dicyclopentadienylyttrium chloride.[29] Its investigation by X-ray diffraction showed that two of the three hydrogen atoms in the AlH_3 group are involved in the formation of the intermolecular Y–H–Al bridges, which leads to the formation of oligomeric chains containing the dimeric units $(Cp_2YCl)_2$:



The secondary Cl...Al bonds formed evidently make a significant contribution to the stability of the complex.

The same workers showed[30] that, when the ether in this complex is replaced by the more basic triethylamine, only one of the three hydrogen atoms in AlH_3 assumes the bridging position. As a result, the product of the reaction of $[Cp_2YCl]_2$ with $AlH_3.NEt_3$ is no longer a polymer but a dimer having the following structure:



The interaction of lithium tetrahydroaluminate with Cp_2YCl gives rise to the hydrides $(Cp_2YH)_2(AlH_3)_2$ containing bridging hydrogen atoms.[31]

III. COMPOUNDS WITH A LANTHANIDE–CARBON σ-BOND

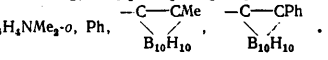
The following main types of lanthanide compounds containing σ-linked organic ligands are known:

$$R_3Ln,\ R_2LnX,\ RLnX_2,\ Li_x[LnR_{3+x}],\ Cp_2LnR,$$
$$Cp_2Ln(\mu\text{-}R)_2AlR_2,\ Cp_2Ln\langle^{CH_2}_{CH_2}\rangle PR_2,\ Cp_2Ln\langle^{R}_{CH_2-PR'_2}$$

A general and most convenient method of synthesis of complexes of the R_3Ln series involves reactions of alkyl- or aryl-lithium with the lanthanide trichlorides:[32–39]

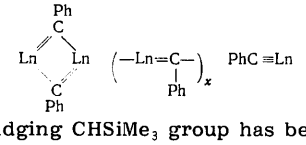
$$3RLi + LnCl_3 \xrightarrow{THF} R_3Ln + 3LiCl\ ;$$

Ln = Sc, Y, La, Tb, Er, Tm, Yb, Lu; R = CH_2—Bu-t, CH_2SiMe_3, $CH_2(SiMe_3)_2$, $CH_2SiMe_2C_6H_4OMe$-*o*, $CH_2C_6H_4NMe_2$-*o*, Ph,

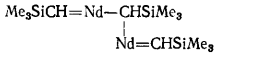


In most cases the products contain the coordinated solvent ($R_3Ln.2THF$). The formation of $Me_3La.THF$ has been noted,[32] but this compound has not been isolated in a pure state.

All the complexes R_3Ln decompose rapidly on contact with oxygen and moisture. Their thermal stability is determined by the nature of the substituent R. Alkyl derivatives decompose in the temperature range 50–100 °C. The compounds with R = CH_2SiMe are still less stable, decomposing slowly at room temperature.[37] Decomposition of the compound $(Me_3SiCH_2)_3Er.(THF)_2$ leads to the evolution of Me_4Si and the formation of the polymeric complex $[(Me_3SiCH)(Me_3SiCH_2)Er]_x$. Analogous results were obtained in a study of the reactions of YCl_3 and $NdCl_3$ with the alkyl-lithium reagents $LiCH_2Ph$, $LiCH_2C(Me)_2Ph$, and $LiCH_2SiMe_3$.[40–43] In the reaction with benzyl-lithium the formation of $(PhCH_2)_3Ln$ complexes in the initial stages has been postulated. These then decompose rapidly with evolution of toluene and the formation of compounds having the composition PhCLn. According to the authors of the above studies, the products can have the structures of carbene- or carbyne-metal complexes:



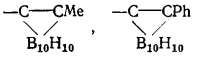
A dimer with a bridging $CHSiMe_3$ group has been proposed for the structure of the product of the reaction of $NdCl_3$ with $LiCH_2SiMe_3$.[42]



Derivatives of bivalent lanthanides of the type R_2Ln are known for europium and ytterbium. Most of them have been obtained by the oxidation reduction transmetallation reaction between R_2Hg and the metallic lanthanide:[44–49]

$$R_2Hg + Ln \rightarrow R_2Ln + Hg$$

Ln = Eu, Yb; R = C≡C—Bu-t, C≡CPh, C_6F_5, HC_6F_4-*p*,



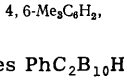
The acetylides $(RC \equiv C)_2Ln$ can be synthesised in addition by the direct interaction of the substituted acetylene RC ≡ CH with the metallic lanthanide in liquid ammonia[50] or by the reaction of phenylacetylene with R_2Yb (R = C_6F_5 or C ≡ C–Bu-t).[49]

The phenylethynyl and carbaboranyl complexes decompose on heating above 200 °C. The polyfluorophenyl derivatives are less stable and decompose at an appreciable rate even at room temperature. Judging from the conditions and products of the reactions of R_2Yb (R = C_6F_5, *p*-HC_6F_4, or C ≡ CPh) with aldehydes, ketones,[51] Ph_3SnCl, $HgCl_2$, I_2, C_6F_5COOH, and certain nickel, rhodium, and platinum complexes,[52] the reactivity of R_2Ln is similar to that of the organolithium and organomagnesium compounds.

The ease of their reactions with alkyl or aryl-iodides is extremely characteristic of the lanthanides. In most cases this results in the formation of a mixture of R_3Ln, R_2LnI, $RLnI_2$, and LnI_3, which are difficult to separate. However, under these conditions, samarium, europium, and ytterbium give rise to the compounds RLnI, whose properties are close to those of Grignard reagents:[53,54]

$$RI + Ln \xrightarrow{THF} RLnI$$

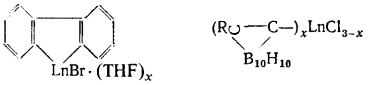
Ln = Sm, Eu, Yb; R = Me, Et, Ph, *o*-MeC_6H_4, 2.6-$Me_2C_6H_3$, 2, 4, 6-$Me_3C_6H_2$,



The carbaboranyl derivatives $PhC_2B_{10}H_{10}LnI$ (where Ln = Sm, Eu, or Yb) have been obtained in addition by the reaction of phenylcarbaboranyl-lithium with LnI_2.[54]

The compounds RLnI are in many respects similar to organomagnesium derivatives, but significant differences have been observed in their reactivities, particularly in the interaction with carbonyl compounds[55–58] and unsaturated hydrocarbons.[59,60]

It has been noted[57] that praeseodymium, neodymium, gadolinium, and dysprosium react with iodoethane to form coloured solutions containing EtLnI complexes but evidence for their structure is not quoted. On the other hand, a study of the reactions of Ph_3CCl, $PhCH_2Cl$, and PhBr with metallic praeseodymium, neodymium, gadolinium, and holmium established[61–63] that these reactions lead to the formation of compounds of tervalent lanthanides $RLnX_2$. The latter decompose slowly at room temperature, producing more complex organolanthanides and products of the reactions of the radicals R. The lanthanum complex $Ph_3CLaCl_2.N(CH_2CH_2OCH_2.CH_2OCH_2CH_2)_3N$ has been obtained by the reaction of triphenylmethyl-lithium with $LaCl_3.L$.[64] The interaction of 2,2′-dilithiobiphenyl and carbaboranyl-lithium with $Ln(Hal)_3$ also leads to the formation of the corresponding derivative of a mixed type:



Ln = Pr, Sm, Ho, Yb (Ref.65) Ln = La, Tm; R = Me, Ph
x = 1, 2 (Ref.39)

In those cases where the molar ratio of the reactants in the reactions of RLi with $Ln(Hal)_3$ described above exceeds 3, the products are bimetallic complexes of the *ate*-type:

$$LnCl_3 + (3 + x)\,RLi \rightarrow Li_x[LnR_{3+x}] + 3LiCl\ .$$

The phenyl derivatives $Li[LnPh_4]$ (Ln = La or Pr) have been isolated in a form free from the solvent.[32] All the remaining complexes contain electron-donating ligands [THF, tetramethylethylenediamine (TMED), and ether]: $[Li(THF)_4].[LnR_4]$ (Ln = Y, Sm, Er, Tb, Yb, or Lu; R = 2,6-$Me_2C_6H_3$, t-Bu, or CH_2SiMe_3,[38,66,67] $[Li(THF)_4][LnClR_3]$ [Ln = Er or Yb; R = $CH(SiMe_3)_2$,[38] $[Li(TMED)_2][LnR_4]$ (Ln = Y, Er, Yb, or Lu; R = t-Bu or CH_2SiMe_3),[36,68] $[Li(TMED)_3][LnMe_6]$ (Ln = Y or La–Lu).[68,69]

Bimetallic compounds with bulky carbaboranyl substituents $(MeC_2B_{10}H_{10})_3Yb.THF.MeC_2B_{10}H_{10}Li.(THF)_2$ and $Me_2C_2B_{10}H_{10}YbCl_2.MeC_2B_{10}H_{10}Li.2THF$[39] apparently also have the structure of *ate*-complexes.

The alkynyl complexes $[Li(THF)_4][Ln(C \equiv C\text{-Bu-t})_4]$ (Ln = Sm, Er, or Lu) are formed when isobutane is displaced from $[Li(THF)_4][Ln(t\text{-Bu})_4]$ by t-butylacetylene.[70] X-Ray diffraction study of $[Li(THF)_4][Lu(2,6\text{-}Me_2C_6H_3)_4]$ [66] and $[Li(THF)_4]\{Yb[CH(SiMe_3)_2]_3Cl\}$ [38] showed that the lanthanide atoms in these compounds are tetrahedrally coordinated, while those in $[Li(TMED)_3][LnMe_6]$ (Ln = Ho or Er)[68] are octahedrally coordinated.

All the bimetallic complexes rapidly decompose in air but are fairly stable, with the exception of the etherate $[Li(Et_2O)_4][Lu(CH_2SiMe_3)_4]$, in an inert atmosphere or *in vacuo*.

A large group of compounds containing a wide variety of σ-linked ligands is formed by cyclopentadienyl derivatives of the type Cp_2LnR. They are usually synthesised by the reaction of RLi with the corresponding chloride:

$$Cp_2LnCl + RLi \xrightarrow{THF} Cp_2LnR\cdot THF + LiCl\ ;$$

Ln = Y, Dy, Ho, Er, Yb; R = Me [71—73]; Ln = Gd, Er, Yb, Lu; R = Me, Et, iso-Pr, Bu, t-Bu, t-C_6H_{11}, CH_2SiMe_3, CH_2Ph, Ph_3C, 4-ClC_6H_4, 4-MeC_6H_4 (Refs.74, 75); Ln = Gd, Yb; R = (Ref.71); Ln = Sc, Gd, Ho, Er, Yb; R = C ≡ CPh (Refs.71, 76).

The ethynyl derivatives are also obtained by substituting the methyl group in Cp_2LnMe [70] or one Cp group in Cp_3Ln [77] by acetylenes:

$$Cp_2LnR + HC{\equiv}CR' \rightarrow Cp_2LnC{\equiv}CR' + RH\ ;$$

Ln = Nd, Er, Yb; R = Me, η⁵-Cp, R'=Bu, C_6H_{11}, Ph, ferrocenyl.

Using the same reactions, complexes with methylcyclopentadienyl rings have been synthesised:

$(Me_5C_5)_2LnMe\cdot Et_2O$ (Ln=Yb, Lu) (Ref.78),

$(Me_5C_5)_2YbMe\cdot THF$, $[(Me_5C_5)_2YbMe_2]Lu\times$ $\times(Et_2O)_2$, $[(Me_5C_5)_2YbClMe]Li\cdot(Et_2O)_2$ (Ref.79),

$(MeC_6H_4)_2SmC{\equiv}C-Bu\text{-}t$ (Ref.80),

[1, 1'—$(CH_2)_3(C_5H_4)_2$] $LnC{\equiv}CPh$ (Ln=La, Ce) (Ref.81).

Depending on the nature of R and the isolation method, the complexes can contain solvent or can be non-solvated. In the majority of the complexes the substituents R are of the bridging type, which is the reason for the dimeric form of these compounds. X-Ray diffraction of the complexes $Cp_2LnBu\text{-}t.THF$,[82] $Cp_2LuCH_2SiMe_3.THF$, and $Cp_2LuC_6H_4Me\text{-}4$ [74] has shown that in the presence of bulky substituents the compounds are monomeric.

The study of the reactivity of these complexes in relation to $(Me_5C_5)_2LnMe$ (Ln = Y or Lu) has shown recently[83,84] that a methyl group linked to the metal is readily displaced not only by acetylenes but also by hydrocarbons without activated C—H bonds:

$$(Me_5C_5)_2LnMe + RH \rightarrow (Me_5C_5)_2LnR + MeH\ ;$$

R = Me, Et, Pr, Ph, CH_2SiMe_3, C_5H_4N.

On interaction with diphenylacetylene, the bivalent lanthanide derivative $(Me_5C_5)_2Sm$ gives rise to the adduct $(Me_5C_5)_2Sm(Ph)C \equiv C(Ph)Sm(C_5Me_5)_2$.[25]

σ-Complexes with Ln^{4+} are known for cerium: Cp_3CeR, $(Ind)_2CeR_2$ (Ind = indenyl; R = Me, Et, Ph, CH_2Ph or COPh).[85]

The first cyclo-octetetraenyl complexes with σ-linked ligands, namely $(C_8H_8)Lu(CH_2SiMe_3).(THF)_2$ and $(C_8H_8)Lu.(C_6H_4CH_2NMe_2\text{-}o).THF$ have been obtained recently by the reaction of RLi with the chloride $(C_8H_8)LuCl.THF$.[86]

The bimetallic lanthanide derivatives $Cp_2Ln(R)_2AlR_2$ with bridging alkyl groups are formed in the reaction of cyclopentadienyl-lanthanide chlorides with lithium tetra-alkylaluminates:[72,87,88]

$$Cp_2LnCl + LiAlR_4 \rightarrow Cp_2Ln(R)_2AlR_2 + LiCl\ ;$$

R = Me, Et.

The presence of bridging alkyl groups has been confirmed by X-ray diffraction of the ytterbium compound $Cp_2Yb(\mu\text{-}Me_2).AlMe_2$.[88]

The zwitter-ionic lanthanide complexes $Ln[(CH_2)_2PR_2]_3$ (Ln = La, Pr, Nd, Sm, Gd, Ho, Er, or Lu; R = Me or t-Bu),[89,90] $Cp_2Lu(Cl)CH_2PPh_3$,[90] $Cp_2Lu(R)CH_2PPh_3$ (R = t-Bu or CH_2SiMe_3), and $Cp_2Lu(Bu\text{-}t)CH(SiMe_3)PMe_3$ [91] have been obtained by the reactions of the ylides CH_2PR_3 with the lanthanide chloride derivatives $LnCl_3$ and Cp_2LnCl.

IV. π-COMPLEXES OF ORGANOLANTHANIDES

1. Complexes with Alkenes and Alkynes

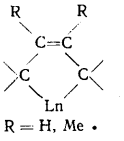
Like the compounds of *d*-metals, the lanthanide derivatives are capable of forming stable π-complexes with alkenes and alkynes. Allyl derivatives of samarium, holmium, and erbium have been obtained by the Girgnard reaction:[92]

$$Cp_2LnCl + C_3H_5MgBr \xrightarrow[-78^\circ]{} Cp_2LnC_3H_5 + MgBrCl\ .$$

The scandium complex $Cp_2ScC_3H_5$ had been synthesised earlier by the same method.[76]

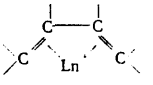
The allyl complexes are readily oxidisable and hydrolysable. Their infrared spectra contain an absorption band at 1533 cm^{-1}, which is characteristic of the delocalised C—C bonds in the allyl fragment.

The cocondensation of the lanthanide and buta-1,3-diene of 2,3-dimethylbuta-1,3-diene at −196 °C yielded the solids $Ln(C_4H_6)_3$ and $Ln(Me_2C_2H_4)_2$ (Ln = La, Sm, or Er),[93] which decompose in air. Their structure has not been accurately established. Judging from the hydrolysis products, among which the main one is but-2-ene, the compounds contain dialkyl groups:



R = H, Me.

However, in this case one can assume that the metal in the complexes is in the +4 oxidation state for LnR_2 and +6 for LnR_3, which appears unlikely. As an alternative, the authors propose a π-dienyl group with a formally zerovalent metal:



Apparently complexes of an analogous kind are formed in the cocondensation of the lanthanide metal vapours with disubstituted acetylenes RC ≡ CR.[94] The high molecular weights of the complexes indicate their oligomeric structure.

More definite structural data have been obtained for the 2,4-dimethylpentadienylneodymium complex $(C_7H_{11})_3Nd$, synthesised by the reaction of $NdCl_3$ with the 2,4-dimethylpentadienyl anion.[95] According to XRD data, the neodymium atom is surrounded by three dienyl groups. The atoms of the pentadienyl chain have a nearly planar disposition. The lengths of the Nd—C[1(5)] [2.801(9)Å] and Nd—C(3) [2.749(10) Å] bonds are reduced compared with those of the Nd—C[2(4)] [2.855(8) Å] bonds, which reflects the difference between the charge densities on the carbon atoms in the different positions and indicates a significantly ionic nature of the metal—carbon bond.

2. Cyclopentadienyl Derivatives

Compounds with cyclopentadienyl substituents are the most thoroughly investigated organic derivatives of the lanthanides. The following main groups of complexes are known at the present time: Cp_2Ln (Ln = Sm, Eu, or Yb); Cp_3Ln (Ln = La—Lu); Cp_4Ce, Cp_3CeX, and Cp_2CeX_2; Cp_2LnX, $CpLnX_2$,

$(Cp_2LnX_2)M$, Cp_2LnR, and $(Cp_2LnR_2)M$ (Ln = La–Lu; M = Li or Al). The last two groups contain an Ln–C σ-bond and were examined above in Section III.

The most general method of synthesis of the cyclopentadienyl compounds, including Cp_4Ce, involves the interaction of alkali metal or magnesium cyclopentadienides with the salts LnX_3:[96–98]

$$LnX_3 + 3CpM \rightarrow Cp_3Ln + 3MX;$$
$$(PyH)_2[CeCl_6] + 4CpNa \rightarrow Cp_4Ce + 4NaCl + 2(PyH)Cl.$$

However, one should note that the possibility of synthesising Cp_4Ce by the above reaction has been denied by Deacon et al.[99] and it has been shown that this pathway leads to Cp_3Ce. Doubt has also been cast on studies on the synthesis of Cp_3CeX and fluorenyl and cycloheptatrienyl derivatives of cerium(IV).[99]

Tricyclopentadienylpromethium has been obtained using Cp_2Be as the donor of Cp groups.[100]

The products contain as a rule molecules of the electron-donating solvent, in which these reactions are carried out, coordinated to the lanthanide atom. Complexes free from the solvents are obtained when the products are sublimed or heated cautiously *in vacuo* (Ln = Eu)[101] and also when the syntheses are carried out in benzene or ether.

Complexes with a bivalent Ln atom have been obtained in the case of europium and ytterbium by the reaction of cyclopentadiene with the corresponding metal in liquid ammonia[102] and by the reduction of Cp_2LnCl to Cp_2Ln with sodium or ytterbium in THF.[103]

A method has been proposed for the synthesis of the cyclopentadienyl complexes of the lanthanides based on the oxidation-reduction transmetallation reaction between Cp_2Hg and the lanthanides.[104–106] Depending on the reactant ratio and the nature of the lanthanide, Ln^{2+} and Ln^{3+} derivatives can be obtained in 30–60% yield:

$$Cp_2Hg + mLn \xrightarrow{THF} (m-1)\,Ln/Hg + Cp_2Ln\cdot(THF)_x;$$
$$Ln = Sm,\ Eu,\ Yb;\ m = 4,\ 5;\ x = 2–4;$$
$$3Cp_2Hg + 2Ln \rightarrow 3Hg + 2Cp_3Ln\cdot(THF)_x.$$

The reaction of metallic lanthanides with cyclopentadienylthallium is more convenient from the preparative standpoint:[107]

$$x\,CpTl + Ln \rightarrow Cp_xLn + x\,Tl;$$
$$Ln = Nd,\ Sm\ (x = 3);\ Ln = Yb\ (x = 2,\ 3).$$

The authors of the same study showed that the synthesis of Cp_2Yb involved the initial formation of Cp_3Yb, but Yb^{3+} is rapidly reduced further to Yb^{2+}.

The first soluble bivalent samarium complex $(Me_5C_5)_2Sm.(THF)_2$ has been obtained by the cocondensation of the metal and ligand vapours at −120 °C.[108]

All the cyclopentadienyl derivatives of lanthanides, including halogenoderivatives and bimetallic complexes, are solids (m.p. 250–400 °C) and are extremely sensitive to moisture and oxygen (only the Ce^{4+} complexes are stable). On heating *in vacuo*, they sublime (with the exception of Cp_3Eu, which decomposes, and the involatile bimetallic compounds) in the temperature range 150–250 °C and at a pressure of 10^{-3} mmHg. The unsubstituted Cp_3Ln are sparingly soluble in alkanes and aromatic hydrocarbons but are readily soluble in THF, pyridine, and other electron-donating solvents. The introduction of alkyl groups into the Cp rings increases the volatility and solubility of the complexes. The structures of more than 20 compounds of this series have now been investigated: $(Cp_3Pr)_n$,[109] $(Cp_3Sm)_n$,[110] $(Cp_3Sc)_2$,[111] $[(MeC_5H_4)_3Nd]_4$,[112] $Cp_3Pr.CNC_6H_{11}$,[113] $Cp_3Gd.THF$,[96] $(Cp_3Yb)_2.NC_4H_4N$,[114] $(Me_3C_5)_2Sm.(THF)_2$,[108] $(Me_5C_5)_2Yb.(C_5H_5N)_2$,[115] $(MeC_5H_4)_2Yb.THF$,[116] $(Me_5C_5)_2Yb.THF.(PhMe)_{1/2}$,[117] $(Me_3SiC_5H_4)_2Yb.(THF)_2$,[118] and $Cp_2Yb.DME$[119] [the complexes Cp_2LnCl and $(Cp_2LnCl_2)M$, whose structures have been investigated are considered below].

X-Ray diffraction, vibrational, electronic spectroscopic data, and measurements of magnetic susceptibility have shown that the bond between the cyclopentadienyl rings and the lanthanide atom is ionic.[7,120,121] The most characteristic chemical property of the compounds Cp_xLn (x = 2 or 3), apart from their hydrolytic and oxidative instability, is a very marked tendency towards the formation of complexes of the type $Cp_3Ln.L$ with Lewis acids, for example, with NH_3, THF, DME, R_3P, etc.[7,115,122,123] Less basic ligands are then displaced by more basic ones.

It is of interest that $Me_2PCH_2PMe_2$ is a monodentate ligand in the complex $(MeC_5H_4)_2YbCl.Me_2PCH_2PME_2$, in contrast to the bidentate ligand $Me_2PCH_2CH_2PMe_2$ in the coordination polymer $[(MeC_6H_4)_2Yb.Me_2PCH_2CH_2PMe_2]_n$.[124] The CO and NO groups of the nitrosyl carbonyl complexes of transition metal derivatives of the type $[(MeC_5H_4)Mn(CO)NO]_2$ and $Me_2Sn[Mn(CO)_5]_2$ can also play the role of electron donors.[125–127] The adducts formed under these conditions have been investigated by infrared spectroscopy and NMR.

The cyclopentadienyl rings in Cp_3Ln are readily split off in reactions with proton-containing reagents (HCl, HCN)[16,123] and metal salts ($FeCl_3$, $LnCl_3$),[7,16] which leads to derivatives of the type Cp_2LnX. Fragmentation of the Cp derivatives of the lanthanides under electron impact begins with the elimination of the Cp ring.[3,128] The energy of the bond between the Ln^{3+} cation and the cyclopentadienyl rings is in the range 45–78 kcal mol^{-1}.[128,129]

Complexes of the type Cp_2LnX are readily obtained also in the reactions of $LnCl_3$ with alkali metal[16] or thallium[28] cyclopentadienides (in proportions of 1 : 2). Among them lanthanum, cerium, and praseodymium derivatives were missing for a long time. However, the use of trimethylene-1,1-bis-cyclopentadienyl or Me_3Si-substituted Cp rings as ligands made it possible to obtain halogen-containing complexes of these metals as well.[81,97] The same methods, i.e. the reactions of Cp_3Ln with LnCl and HCl or $LnCl_3$ with CpNa, are used to synthesise the monocyclopentadienyl compounds $CpLnCl_2$.[130] Dicyclopentadienylmercury can also serve as a donor of Cp groups.[106]

In terms of their physical properties, the halogeno-derivatives are close to the compounds of the Cp_3Ln series. Their reactivity is determined by the presence of a mobile anion X, which can be readily replaced by another functional group by reaction with the corresponding alkali metal derivative:

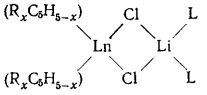
$$Cp_2LnX + M\text{-}Z \rightarrow Cp_2Ln\text{-}Z + MX;$$
$$M = Li,\ Na;\ Z = Alk,\ OR,\ OCOR,\ NH_2,\ PR_2.$$

These reactions are examined in detail in other Sections of this review. The complexes Cp_3CeCl and Cp_2CeCl_2 [synthesised by the reactions of $(PyH)_2CeCl_6$ with CpNa][7] and their derivatives Cp_3CeZ,[131,132] obtained like the complexes Cp_2LnZ, are known for cerium.

In recent years attention has been concentrated in the study of derivatives of Cp_2LnX series (as well as other cyclopentadienyl complexes of the lanthanides) on the determination of their structure by X-ray diffraction. It was found that the metal atoms in the $CpErCl_2.(THF)_2$,[133] $(Me_5C_5)_2.YbSCSNEt_2$,[134] $(MeC_5H_4)_2YbCl.Me_2PCH_2PMe_2$,[124] and $\{[(Me_3Si)_2C_5H_3]_2LnCl\}_2$ (Ln = Sc, Pr, or Yb)[97] have distorted tetrahedral coordination, as in the dimers $[(MeC_5H_4)_2YbCl]_2$[135] and $(Cp_2ScCl)_2$[136] investigated previously.

A distinctive feature of the cyclopentadienyl complexes of the lanthanides is their tendency to form bimetallic complexes of the type $[Cp_2LnCl_2]Li.(THF)_2$.[16,97,137–139] These compounds are apparently formed in the intermediate stages of all the reactions of $LnCl_3$ with alkali metal cyclopentadienides.

For the 1 : 2 reactant ratio, they become the final products and can be isolated in high yields. X-Ray diffraction studies of the complexes $\{[(Me_3Si)_2C_5H_3]_2NdCl_2\}Li.(THF)_2$,[122] $[(Me_5C_5)_2YbCl_2]Li.(Et_2O)_2$,[139] and $[(Ph_2MeSiC_5H_4)_2.YbCl_2]Li.(Et_2O)_2$ [139] showed that the Ln and Li atoms in them are linked by bridging Cl atoms:



The iodine analogue $[(Me_5C_5)_2YbI_2]Li.(Et_2O)_2$ and the aluminium-containing complex $[(Me_5C_5)_2YbCl_2]AlCl_2$ have the same structure.[139] The solvents L in these complexes are usually THF or Et_2O, in which the syntheses were carried out. These solvent molecules can also be readily substituted by other stronger bases, for example DME [dimethoxyethane (Editor of Translation)] and tetramethylethylenediamine.

A different structure, characterised by the presence of the anion $[(Me_3SiC_5H_4)_2NdCl_2]^-$, has been proposed for the complex $[(Me_3SiC_5H_4)_2NdCl_2][Li(THF)_4]$ formed when $[(Me_3SiC_5H_4)_2NdCl]_2$ reacts with $LiCl.(THF)_4$ or when $Me_3SiC_5H_4Li$ reacts with $NdCl_3$.[140] The authors found evidence supporting this structure, namely the fact that the Cl–Nd–Cl angle (99.3°), the Nd–Cl distance [2.668(4) Å], and the average Nd–C_{ring} distance (2.78 Å) in the complex $[(Me_3SiC_5H_4)_2][AsPh_4]$ differ appreciably from the corresponding values (81.1°, 2.744 Å, and 2.76 Å) in the bridged compound $[(Me_3Si)_2C_5H_3]_2Nd(\mu\text{-}Cl)_2Li.(THF)_2$.

The reaction of equimolar amounts of $YbCl_3$ and Me_5C_5Li yielded the monocyclopentadienyl complex $[Me_5C_5YbCl_3]Li.THF$.[139] The analogous iodine derivative $(Me_5C_5YbI_3)Li.(Et_2O)_2$ has been obtained by the reaction of metallic ytterbium with Me_5C_5I in the presence of LiI.[79]

3. Indenyl, Fluorenyl, and Cycloheptatrienyl Complexes

A study of the idenyl complexes of the lanthanides was first undertaken by Tsutsui and Gyfling in their search for evidence that *f* electrons are involved in the formation of chemical bonds.[141,142] The compounds $(C_9H_7)_3Ln.THF$ (Ln = La, Sm, Gd, Tb, Dy, or Yb) were obtained by the reaction of C_9H_7Na with $LnCl_3$ in THF. On the basis of NMR data, it was postulated that the samarium complex is covalent. However, subsequent X-ray diffraction study of a non-solvated $(C_9H_7)_3Sm$ specimen demonstrated the η^5-coordination of the indenyl ligands.[143]

The cerium derivatives $(C_9H_7)_xCeCl_{4-x}$ (x = 2, 4)[22,98] and the tetrahydroindenyl complexes $(C_9H_{11})_xLnCl_{3-x}$ (Ln = La, Nd, or Er; x = 1, 2)[144] were synthesised analogously.

The properties of the indenyl complexes are similar to those of the cyclopentadienyl compounds, but, in contrast to the latter, they do not sublime and are soluble in hydrocarbons.

Among the series of fluorenyl derivatives, tri- and tetrafluorenylcerium, synthesised by the reaction of fluorenylsodium with $(PyH)_2CeCl_6$,[145] and the bimetallic complexes $(C_{13}H_9)_2LnCl_2Li.(THF)_2$ (Ln = La, Nd, Sm, Ho, or Lu) are known.[146,147] The latter are formed by the reaction of $C_{13}H_9Li$ with the chlorides $LnCl_3$. Analysis of the infrared and ^1H NMR spectra of these complexes indicated that the fluorenyl residues are linked via σ-bonds to the Ln atom, while the chlorine atoms are bridging; the THF molecules are coordinated to the lithium atom.

It has been shown[148] that the addition of UCl_4 to lithium R-cycloheptadienide induces the rapid formation of an unstable organouranium compound containing the cycloheptatrienyl anion $C_7H_6R^-$ (R = H, Me, or Bu) as the ligand.

Analogous complexes have been obtained with gadolinium and erbium chlorides. It has been suggested that the ions of the *f* elements attract to themselves the electron density of the cycloheptadienyl ligands, increasing thereby the polarisation of the C–H bonds of the methylene groups and hence facilitating the elimination of the proton and the formation of trienyl ligands.

The cerium complex $(C_7H_7)_2CeCl_2$ has been obtained in the form of brown crystals by the reaction[149]

$$(PyH)_2CeCl_6 + 2C_7H_8 \rightarrow (C_7H_7)_2CeCl_2 + 2C_5H_5N\cdot HCl + 2HCl\,.$$

Its structure has been confirmed by elemental analysis and infrared spectroscopic data.

4. Cyclo-octatetraenyl Complexes

During the last five years, these compounds have not been investigated; after the establishment of their similarity to the thoroughly investigated "uranocene", the interest in them decreased appreciably. The lanthanide compounds containing the $C_8H_8^{2-}$ dianion can be obtained by the reaction of the metal with cyclo-octatetraene in liquid ammonia:[150]

$$Ln + C_8H_8 \rightarrow LnC_8H_8\,;$$
$$Ln = Eu,\ Yb\,.$$

In a more universal method, $K_2C_8H_8$ is used:[151,152]

$$LnCl_3 + xK_2C_8H_8 \xrightarrow{THF} \begin{cases} \rightarrow [(C_8H_8)_2Ln]K + 3KCl\,; \\ \quad Ln = Sc,\ Y,\ La,\ Ce,\ Pr,\ Nd,\ Sm,\ Gd,\ Tb\,. \\ \rightarrow [C_8H_8LnCl\cdot(THF)_2]_2 + 2KCl\,; \\ \quad Ln = Sc,\ Ce,\ Pr,\ Nd,\ Sm\,. \end{cases}$$

In the latter case, bimetallic or chlorine-containing complexes are formed, depending on the ratio of the initial reactants. It has been shown by X-ray diffraction[153] that the cerium and bridging chlorine atoms in the cerium dimer $[C_8H_8CeCl.(THF)_2]_2$ form a planar four-membered ring with Ce–Cl distances of 2.855(2) and 2.935(2) Å. The cerium atom is located symmetrically relative to the C_8H_8 planar ring. The anion $(C_8H_8)_2Ce^-$ in the complex $[(C_8H_8)_2Ce][K(MeOCH_2CH_2)_2O]$ has the characteristic "metallocene" structure with an average Ce–C distance of 2.742(8) Å.[154]

The complex $(C_8H_8)_2Ce$ has been isolated in the form of a black crystalline substance on reduction of tetraisopropoxycerium with triethylaluminium in the presence of cyclo-octatetraene.[155] A decrease of the excess of C_8H_8 leads to the formation of the complex $(C_8H_8)_3Ce_2$, in which there are two different types of C_8H_8 ligands according to infrared spectroscopic data. Products with the same stoichiometry have been obtained by the cocondensation of the lanthanide (Ln = La, Ce, Nd, or Er) and cyclo-octatetraene vapours at −196 °C.[156,157] It has been shown by X-ray diffraction of the neodymium derivative $[(C_8H_8Nd.(THF)_2][(C_8H_8)_2Nd]$ [157] that the C_8H_8 rings in the anion $(C_8H_8)_2Nd^-$ are not parallel and are separated by different distances from the Nd atom. The cation $[C_8H_8Nd.(THF)_2]^+$ is located asymmetrically relative to the anionic group and two carbon atoms of one of the C_8H_8 rings of the anion are in the coordination sphere of the cationic Nd atom (see Figure). The corresponding lanthanum, cerium, and erbium complexes are isostructural with the neodymium complex.

Quantum-chemical calculation for the anion $(C_8H_8)_2Ce^-$ showed[158] that the interaction of the 5*d* orbitals of the metal with the ligands makes a decisive energy contribution, while the *f* electron is localised at the metal.

The cyclopentadienyl-cyclo-octatetraenyl complexes C_8H_8LnCp are known for Sc, Y, Nd, Sm, Ho, and Er.[151,159] A "sandwich" structure has been proposed for these compounds.

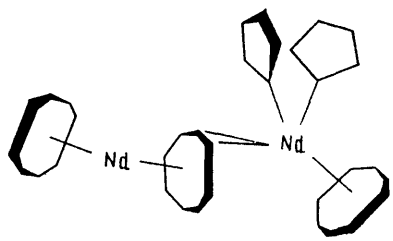
V. COMPOUNDS WITH AN Ln–E BOND

1. Compounds with an Ln–N Bond

The amido-derivatives $Ln(NR_2)_x$ (x = 2, 3), $Cl_2Ln\,NR_2$, and Cp_2LnNR_2, the phthalocyanines Pc_2Ln and PcLnH, and porphyrins are known among complexes of this class. In all cases R in the NR_2 fragment is the trimethylsilyl group. Only a mention has been made of the isopropylamides $Ln[N(Pr\text{-}iso)_2]_3$ (Ln = Y, Yb, or Nd)[160] without any description of the methods of synthesis and properties of these compounds. The amidolanthanides, obtained for the first time in 1972[161] by the reaction

$$LnCl_3 + 3LiN(SiMe_3)_2 \rightarrow Ln[N(SiMe_3)_2]_3 + 3LiCl$$

have been most thoroughly investigated.



The structure of the complex $[C_8H_8Nd(THF)_2][(C_8H_8)_2Nd]$.

Derivatives of bivalent ytterbium and europium are formed when EuI_2 and YbI_2 are used in this process[162] and also when the chloride $ClEu(NR_2)_2$ is reduced with sodionaphthalene.[163]

The disproportionation reaction[164]

$$2\,PrCl_3 + Pr[N(SiMe_3)_2]_3 \rightarrow 3Cl_2PrN(SiMe_3)_2$$

which is extremely characteristic of lanthanide compounds, has been used to synthesise mixed chloroamide complexes. The same product and its neodymium analogue have been obtained by the hydrochlorination of $Ln[N(SiMe_3)_2]_3$.[164]

An X-ray diffraction study has been made of the complexes $Ln[N(SiMe_3)_2]_3$ (Ln = Nd,[165] Sc, Eu, or Yb[166]), $Eu[N(SiMe_3)_2]_2(DME)_2$,[163] and $Yb[N(SiMe_3)_2]_2[Me_2PCH_2CH_2.PMe_2]$[162] and showed that, in the absence of a coordinating ligand, the group $Ln(N\langle)_3$ has a pyramidal configuration (the Ln atom is displaced from the N_3 plane by approximately 0.4 Å). The addition of the ligand (DME) increases the polarity of the $Ln(N\langle)_3$ fragment.

In the last of the complexes enumerated above interaction between the Yb atom and the carbon atoms of the $SiMe_3$ groups, which is unusual for a compound of this kind, was observed. (The Yb...C distance is 3.4 Å, which is less than the sum of the covalent radius of Yb^{2+} and the van der Waals radius of the methyl group.)

Compounds with the NH_2 group at the lanthanide atom, namely $CpLnNH_2$ (Ln = Er or Yb) have been synthesised in the course of a study of the reactivity of the cyclopentadienyl derivatives. They are formed when Cp_2LnCl interacts with sodium amide[167] and in the thermolysis of the ammine complexes Cp_3LnNH_3.[168] The last reaction has also been used to synthesise the cyclopentadienylbis(trimethylsily)amide complexes $(Me_5C_5)_2LnN(SiMe_3)_2$ and $Me_5C_5Ln[N(SiMe_3)_2]_2$ (Ln = Nd or Yb).[137]

The lanthanide amides $Ln(NR_2)_3$ are crystalline substances, which are extremely sensitive to moisture and which sublime *in vacuo* at 80–100 °C. The cyclopentadienyl derivatives Cp_2LnNR_2 are less volatile. Their high reactivity and relative availability makes these compounds convenient starting materials for the synthesis of organolanthanides of other classes. Thus it has been found that $Ln[N(SiMe_3)_2]_3$ (Ln = Pr or Nd) react exothermically with carbon dioxide in DME at 20 °C and 1 atm, forming the complexes $Ln[N(SiMe_3)_2]_3.2CO_2$.[169] Their structure has not been accurately established, but, on the basis of infrared spectroscopic data, one may conclude that it differs from that of the erbium and ytterbium carbamate complexes $Ln(OCONR_2)$, obtained by the reaction of LnX_3 with carbon dioxide and amines R_2NH.[170]

The phthalocyanine and porphyrin complexes of metals constitute a specific group of coordination compounds and are usually not dealt with in reviews and monographs devoted to the chemistry of organometallic compounds. We thought it useful to consider these compounds briefly, because they possess a number of interesting properties and information about them significantly completes our ideas about the possibilities of organolanthanides.

The complexes Pc_2LnH ($Pc = C_{32}H_{16}N_8^{2-}$), obtained by the reaction of lanthanide acetates with *o*-phthalonitrile at 280–290 °C, should probably be regarded as the first reliably characterised lanthanide-phthalocyanines.[171,172] This method is virtually the only convenient procedure for the synthesis of phthalocyanine compounds, which can have the compositions Pc_2LnX, Pc_2Ln, and Pc_3Ln_2. They are all intensely coloured crystalline substances which are stable in air. The interest in them has increased particularly after the discovery of the electrochemical properties of lanthanide-diphthalocyanines.[173] It has been established[174] that their colour is determined by the oxidation state of the lanthanide in the complex: violet for Pc_2Lu^{2-}, blue for $PcLu^-$, green for Pc_2Lu, and red-brown for Pc_2Lu^+.

An X-ray diffraction study of Pc_2NdH[175] showed that the neodymium atom in this complex occupies the central position between two parallel phthalocyanine ligands, one of which has the form of a saucer extended towards the Nd atom. One ligand has been rotated relative to the other by 45° around the normal to their planes. The Nd–N distance varies from 2.39 to 2.49 Å. The photoelectron spectrum of this complex[175] indicates the chemical equivalence of all eight central nitrogen atoms, whence it follows that the mobile hydrogen atom does not form a strong bond with any of them, although a weak interaction is not excluded.

A porphyrin complex, tetraphenylporphyrinacetylacetonato-europium, has been obtained (for use as a shift reagent) by heating $(C_5H_7O_2)_3Eu$ with tetraphenylporphyrin.[176] The compound is readily soluble in organic solvents and is stable in relation to oxygen and water. The samarium, gadolinium, erbium, and ytterbium complexes as well as the octaethylporphyrin complexes of europium, gadolinium, ytterbium, and lutetium have been obtained analogously.[177] The single band in the photoelectron spectra of the nitrogen atoms in these compounds indicates their equivalence. The relatively high energy of this band (398 eV) indicates a significantly covalent character of the Ln–N bond, according to the authors.[177]

2. Compounds with an Ln–P Bond

Apart from the complexes containing a P–Ln coordinate bond (which are considered among cyclopentadienyl derivatives), only a few compounds with the Ln–P group are known. They include the trisphosphine compounds

$Ln[P(Bu\text{-}t)_2]_3.(THF)_2$ (Ln = Y, Ho, Er, Tm, Yb, or Lu)[178] and derivatives of the Cp_2LnPR_2 series (Ln = Tb, Ho, or Er and R = t-Bu;[179] Ln = Yb and R = cyclo-C_6H_{11} [180]). Compounds of both types have been obtained by the reaction of $LiPR_2$ with the corresponding lanthanide chloride:

$$LnCl_3 + 3LiP(Bu\text{-}t)_2 \xrightarrow{THF} Ln[P(Bu\text{-}t)_2]_3.(THF)_2 + 3LiCl;$$
$$Cp_2LnCl + LiPR_2 \rightarrow Cp_2LnPR_2 + LiCl .$$

The exchange reaction between Cp_2ErCl and $Me_3SiP(Bu\text{-}t)_2$ has been used to obtain $Cp_2ErP(Bu\text{-}t)_2$.[175] When the tris-phosphine complexes are heated *in vacuo*, they lose the solvate THF and are converted into the coordination polymer $\{Ln[P(Bu\text{-}t)_2]_3\}_x$.

Bis(methylcyclopentadienyl)(diphenylphosphine)samarium was synthesised recently by the hydride method:[80]

$$[(MeC_5H_4)_2SmC{\equiv}CPh]_2 + 2HPPh_2 \rightarrow 2(MeC_5H_4)_2SmPPh_2 + 2PhCCH .$$

This reaction is particularly convenient for the formation of the metal–heteroelement bond.

All the phosphine derivatives of lanthanides are yellow or orange substances which are stable in an inert atmosphere, but, like the majority of the organolanthanides, hydrolyse extremely readily in moist air.

3. Compounds with Ln–O, Ln–S, and Ln–Se Bonds

The greatest number of publications on derivatives of the Ln–O group referred to β-diketonates and similar chelate complexes. They have been surveyed in a recent review[15] devoted to the Ln–O–C derivatives and will not be considered here. The compounds discussed below include the alkoxides $Ln(OR)_3$, $Cl_xLn(OR)_{3-x}$, and $R'_xLn(OR)_{3-x}$, complexes of the $Ln[M(OR)_4]_3$ series, the mercaptides $Ln(SR)_3$, and thier Se analogues.

The alkoxides $Ln(OR)_3$ are comparatively readily available, are appreciably volatile and soluble, and exhibit a high reactivity, as a result of which they are convenient starting materials for the synthesis of other derivatives. The lanthanide isopropoxides are used particularly frequently. The alkoxides can be obtained by the reaction of the alcohols with the metal, $LnCl_3$, or another alkoxide $Ln(OR')_3$:[181]

$$Ln + 3ROH \rightarrow Ln(OR)_3 + {}^3/_2H_2 ;$$
$$LnCl_3 + 3ROH \xrightarrow{NH_3} Ln(OR)_3 + 3NH_4Cl ;$$
$$Ln(OR')_3 + 3ROH \rightarrow Ln(OR)_3 + 3R'OH .$$

The OR/OR′ exchange is also observed in the reaction of $Ln(OR)_3$ with the esters CH_3COOR' (R′ = alkyl or $SiMe_3$).[182] The reaction of $LnCl_3$ with alkali metal (Li, Na) alkoxides is more convenient for the synthesis of trialkoxides:

$$LnCl_3 + 3MOR \rightarrow Ln(OR)_3 + 3MCl_3 .$$

It is preferable to use NaOR, since LiCl dissolves in the solvents employed more readily than NaCl, which hinders the isolation of the pure $Ln(OR)_3$.

In a recent study[183] it has been shown that scandium, yttrium, and lanthanum tri-isopropoxides can be fairly readily obtained by a direct electrochemical method. The anodic dissolution of the metal is achieved by means of diaphragm-free electrolysis in absolute alcohol with Bu_4NBr as the electrically conducting additive; best results have been obtained using an alternating current.

The alkoxides $Ln(OR)_3$ can exist in the form of monomers and associated coordination species,[183] the degree of association (and hence the volatility and solubility of the alkoxide) being determined by the nature of Ln, the bulk of R, the method of synthesis, and the technique used to isolate the product. With increase of the degree of branching of R, the degree of association diminishes sharply.

The monomeric phenoxides $Ln(OAr)_3$ [Ar = hindered 2,6-di(t-butyl)-4-methylphenyl, Ln = Sc, Y, La, Pr, Nd, Dy, Ho, or Yb] have been synthesised by the usual method, i.e. by the reaction of NaOAr with $LnCl_3$.[184] X-Ray diffraction of the scandium derivative of this series showed that the Sc and O atoms form a planar group; the average O–Sc–O angle is 119.5°.

The use of LiOAr in reactions with lanthanide chlorides with a specific stoichiometry leads to bimetallic complexes with bridging chlorine atoms, namely $[Ln(OAr)_2(\mu\text{-}Cl)_2Li.(THF)_2]$ and $[LnCl(OAr)(\mu\text{-}Cl)_2Li.(THF)_2]$.[122]

The asymmetric cerium(IV) complex $Cp_3CeOPr\text{-}iso$ has been obtained in a low yield by the reaction of cerium tetraisopropoxide with Cp_2Mg.[155]

A characteristic feature of lanthanide alkoxides is their ability to form bimetallic complexes of the type $Ln[M(OR)_4]_3$ (R = iso-Pr; M = Al, Ga, In, or Zr).[15,185] These products are readily soluble and are appreciably volatile (they distil or sublime at 180–200 °C and 0.1 mmHg). They are readily formed on interaction of $LnCl_3$ with $KM(OR)_4$ or with potassium alkoxide in the presence of the salt MCl_3 as well as on simple mixing of the alkoxides $Ln(OR)_3$ and $M(OR)_x$ in alcoholic or tetrahydrofuran solution. The latter reaction was subjected to a detailed investigation,[185] which showed that the complexes can contain solvating alcohol molecules and can have a variable composition with respect to the metals; their solubility changes significantly under these conditions.

The study of the interaction of PhLnI (Ln = Ce, Sm, Eu, or Yb) with the ketones RCOR′ showed[58] that under mild conditions the products are the alkoxides RR′PhCOLnI, which afford the corresponding alcohols after hydrolysis. In the presence of an excess of PhLnI the alkoxide formed is deoxygenated; the hydrolysis product is in this case an olefin. It is noteworthy that in the reaction with a chalcone the PhLnI adds exclusively in the 1,2-positions, while PhLi and PhMgI give rise to both 1,2- and 1,4-adducts.[58]

The first compounds containing an Ln–S bond (thioacetonate, thiocarbamate, and phosphinothioate complexes and thiophenoxides) were obtained at the end of the 1960's.[15,186] The methods of their synthesis do not differ fundamentally from those for the oxygen analogues.

A series of compounds with substituted thiophenyl groups, having the general formula $(iso\text{-}PrO)_{3-x}Ln(SAr)_x$ (Ln = Pr, Nd, or Sm; Ar = 4-ClC_6H_4, 4-t-BuC_6H_4, or 4-t-Bu-2-Me-C_6H_3; x = 1, 2, 3), have been obtained in the reactions of lanthanide tri-isopropoxides with the corresponding phenols for different reactant ratios.[187] The mercaptides derived from the cyclopentadienyl and indenyl complexes Cp_3CeSr and $(C_9H_7)_2Ce(SR)_2$ are known for cerium(IV).[132]

Lanthanide alkylmercaptides were obtained recently[188] via the amido-derivatives:

$$[(Me_3Si)_2N]_3Ln + x\,n\text{-}BuSH \rightarrow [(Me_3Si)_2N]_{3-x}Ln(SBu\text{-}n)_x;$$
$$Ln = Pr, Nd, Sm, Gd;\ x = 1{-}3 .$$

The asymmetric derivatives (x = 1, 2) are readily formed also in the disproportionation reaction between $(R_2N)_3Ln$ and $(n\text{-}BuS)_3Ln$.

The lanthanide organoselenides of the type $(n\text{-}BuSe)_3Ln$ (Ln = Pr, Nd, or Sm) have been synthesised very recently[189] by analogy with the thio-derivatives. Ytterbium(II) butylselenide has been obtained by the reaction of n-BuSeH with $[(Me_3Si)_2N]_2Yb$.

All the symmetrical mercaptides and selenoxides are very sensitive to the action of moisture, are almost insoluble in organic solvents, and, in contrast to the alkoxides, are involatile. On the other hand, the monomercaptides $[(Me_3Se)_2N]_2LnSBu\text{-}n$ sublime *in vacuo* at 140–160 °C and are readily soluble in toluene, THF, and hexane.

In the study of the reactivity of lanthanide compounds relative to small molecules, it was found that the tervalent lanthanide alkoxides, mercaptides, and selenides readily combine with three equivalents of carbon dioxide under normal conditions.[189,190] The addition is accompanied in all cases by the insertion of CO_2 in the Ln–X bond with formation of carbonate, thiocarbonate, and selenocarbonate structures, which is indicated by the appearance of intense absorption bands in the ranges 1530–1580 and 1330–1350 cm^{-1} in the infrared spectra of the products:

$$(t\text{-}BuO)_3Ln + 3CO_2 \rightarrow \quad (t\text{-}BuOCO_2)_3Ln \ ;$$
$$Ln = Pr,\ Nd,\ Sm \ .$$

A difference is observed in the reaction of CO_2 with the mercaptides $(n\text{-}BuS)_3Ln$. The addition of the third carbon dioxide molecule is accompanied in this case by the appearance of a band at 2380 cm^{-1} in the infrared spectrum. The high value of this frequency suggests that the third CO_2 molecule adds as a coordinated species. The thiocarbonates readily undergo decarboxylation:[190]

$$(RS)_3Pr \underset{-CO_2;\ 200°}{\overset{+CO_2;\ 20°}{\rightleftarrows}} RSCO_2Pr(SR)_2 \underset{-CO_2;\ 130°}{\overset{+CO_2;\ 20°}{\rightleftarrows}} (RSCO_2)_3PrSR \rightleftarrows$$
$$\underset{-CO_2;\ 90°}{\overset{+CO_2;\ 20°}{\rightleftarrows}} (RSCO_2)_2PrR\cdot CO_2 \ ;$$
$$R = n\text{-}Bu.$$

The decarboxylation of the carbonates $(t\text{-}BuOCO_2)_3Ln$ is accompanied by the side reactions, which render the process irreversible.[190]

4. Compounds with an Ln–M Bond

A report was published in 1971[191] stating that the reaction of metallic erbium with $Hg[Co(CO)_4]_2$ in THF leads to the formation of the product $Er[Co(CO)_4]_3.(THF)_4$. On the basis of infrared spectroscopic data, the authors suggested that the compound contains the Er–Co bond. The same method was used to synthesise the cobalt carbonyl complexes $Ln[Co(CO)_4]_x.(THF)_y$ (Ln = Sm, Eu, Tm, or Yb; $x = 2, 3$; $y = 3, 4$).[192,193] Analogous products containing a variable amount of THF are formed when the free lanthanides react with dinuclear carbonyls[194] or when lanthanide halides react with the anion $Co(CO)_4^-$:[195]

$$Co_2(CO)_8 + Ln \xrightarrow{THF} Ln[Co(CO)_4]_3\cdot(THF)_x;$$
$$M_2(CO)_{10} + Ln \xrightarrow{THF} Ln[M(CO)_5]_3\cdot(THF)_x;$$
$$Ln = Sm,\ Tm,\ Yb; \quad M = Mn,\ Re \ .$$
$$LnCl_3 + 3\,NaCo(CO)_4 \xrightarrow{THF} Ln[Co(CO)_4]_3\cdot(THF)_x;$$
$$Ln = Er,\ Yb; \quad x = 1-4 \ .$$

In the presence of an equimolar reactant ratio, the last reaction gives rise to the formation of the unstable dinuclear compounds $Cl_2LnCo(CO)_4$ (Ln = La, Sm, Dy, Ho, or Yb)[196] and $Cl_2SmM(CO)_5$ (M = Mn or Re).[197]

The easy cleavage of the metal–metal and metal–halogen bonds by metallic lanthanides had also been noted earlier.[198] However, in characterising the lanthanide complexes formed in these reactions, the authors[198] confined themselves to indicating their similarity to Grignard reagents without specifying their structure.

The presence of a direct Ln–M bond has been postulated in all the lanthanide complexes with metal carbonyls indicated above on the basis of the method of their preparation, their reactivity, and their infrared spectra. The exact structure of one of these products, namely $[CpMo(CO)_3]_3La.(THF)_6$, has been recently established by X-ray diffraction.[199] It was found that the La atom is surrounded by three equivalent $CpMo(CO)_3$ fragments and that the bond between the La and Mo atoms is formed via the carbonyl group: Mo–C–O–La. It is natural to suppose that in the erbium analogue $[CpMo(CO)_3]_3Er.(H_2O)_7$ obtained earlier[124] and in the majority of other metal carbonyl complexes of the lanthanides, there is no direct bond between the metal and the lanthanide either. This has been confirmed by structural studies of the cyclopentadienylytterbium complexes $(Me_5C_5)_2YbCo(CO)_4.THF$ and $[(Me_5C_5)_2Yb]_2.[Fe_3(CO)_7(\mu\text{-}CO)_4]$[200,201]), where the presence of a carbonyl bridge has also been established.

One can speak with much confidence about the presence of an Ln–M bond in non-transition metal derivatives. Three main methods for the synthesis of such compounds are known:[2,44,164,202–205]

$$(A)\ Ln[N(SiMe_3)_2]_3 + 3R_3SnH \xrightarrow{DME} Ln(SnR_3)_3\cdot DME + 3(Me_3Si)_2NH \ ;$$
$$Cl_2LnN(SiMe_3)_2 + R_3SnH \xrightarrow{DME} Cl_2LnSnR_3\cdot DME + (Me_3Si)_2NH \ ;$$
$$Ln = Pr,\ Nd;\ R = CH_2SiMe_3 \ .$$
$$(B)\ LnCl_3 + 3LiMPh_3 \rightarrow Ln(MPh_3)_3 + 3LiCl \ ;$$
$$Cp_2LnCl + LiMPh_3 \rightarrow Cp_2LnMPh_3 + LiCl \ ;$$
$$Ln = Pr,\ Nd,\ Gd,\ Er,\ Yb; \quad M = Ge,\ Sn \ .$$
$$(C)\ 7[(C_6F_5)_3M]_2Hg + 2Ln \xrightarrow{DME} 2Ln\{Hg_2[M(C_6F_5)_3]_7\}\cdot(DME)_3 + 3Hg \ ;$$
$$Ln = Pr,\ Nd,\ Ho;\ M = Ge,\ Sn \ .$$

All three methods, (A), (B), and (C), are general and are widely used to synthesise polynuclear compounds, but there are many limitations as regards lanthanide derivatives. Thus, if the germanium hydride Ph_3GeH or triethyltin hydride is used in the Razuvaev–Vyazankin reaction [method (A)], the ether linkage in the solvent (DME) is cleaved and the alkoxides $(R_3M)_xPr(OCH_2CH_2OMe)_{3-x}.DME$ are formed.[202] Compounds obtained by method (B) contain admixtures of side products too difficult to separate (the dicyclopentadienyl complexes, which have been obtained in an analytically pure state, are an exception).[203] The transmetallation reaction [method (C)] requires the presence of electron-accepting substituents at the mercury atom. The complexes obtained by this method are ionic {they comprise the Ln^{3+} cation and anionic species of the type $[(C_6F_5)_3Ge]_3Hg^-$ and $[(C_6F_5)_3Ge]_4Hg^{2-}$} and do not contain, as suggested initially,[204] a direct Ln–Ge bond. Praseodymium does not interact (at 100°, 10 h) with compounds which do not contain electron-accepting substituents, namely $(Et_3Ge)_2Hg$, $(Ph_3Ge)_2Hg$, and $[(Me_3SiCH_2)_3Sn]_2Hg$.[205]

Analogous ionic complexes have been obtained by method (A).[206,207] This is the first example of the synthesis of ionic compounds by the hydride method. The reaction between the lanthanide alkoxide and the hydrogermane is carried out in the presence of acceptors of the germyl anions $(C_6F_4)_3Ge^-$ formed in the first stage of the process. Trinuclear compounds with pentafluorophenyl substituents are used as such acceptors:

$$3(C_6F_5)_3GeH + \quad (t\text{-}BuO)_3Pr + 2[(C_6F_5)_3M]_2M' \xrightarrow{DME}$$
$$\rightarrow\{[(C_6F_5)_3Ge]_3[(C_6F_5)_3M]_4M'_2\}Pr\cdot(DME)_3 + 3\ t\text{-}BuOH;$$
$$M = Si,\ Ge,\ Sn; \quad M' = Cd,\ Hg \ .$$

$(C_6F_5)_3SnH$ reacts analogously. The bifunctional hydrides $(C_6F_5)_2GeH_2$ and $(C_6F_5)_2Ge(H)Ge(C_6F_5)_2H$ produces, in such processes, more involved complexes with anions incorporating up to 10 germanium and mercury atoms.[208]

The disproportionation reaction, which is characteristic of lanthanide derivatives, makes it possible to convert the trisubstituted complexes into asymmetric products:[164]

$$2[(Me_3Si)_2N]_3Pr + [(Me_3SiCH_2)_3Sn]_3Pr\cdot DME \xrightarrow{DME}$$
$$\rightarrow 3[(Me_3Si)_2N]_3PrSn(CH_2SiMe_3)_3\cdot{}^1/_2\ DME \ .$$

All the compounds with the Ln–M group are solids, which are unstable in air and are sparingly soluble in aliphatic and aromatic hydrocarbons; they melt with decomposition on heating to temperatures above 150–200 °C. Their reactivity

has been investigated mainly in relation to $[(Me_3SiCH_2)_3Sn]_3Pr.DME$[202] and $\{[(C_6F_5)_3Ge]_7Hg_2\}Pr.(DME)_3$:[205]

$$(R_3Sn)_3Pr\cdot DME \begin{cases} \xrightarrow[50^\circ]{H_2O} R_3SnMe + (R_3Sn)_2O + Pr(OH)_3 ; \\ \xrightarrow[20^\circ]{HCl} R_3SnMe + R_3SnCl + PrCl_3 + H_2 ; \\ \xrightarrow[120^\circ]{BrCH_2CH_2Br} R_3SnSnR_3 + PrBr_3 + H_2C{=}CH_2 ; \\ \xrightarrow[50^\circ]{(PhCOO)_2} R_3SnOCOPh + R_3SnPr(OCOPh)_2 ; \\ \xrightarrow{CF_3COOAg} R_3SnOCOCF_3 + (CF_3COO)_3Pr + Ag . \end{cases}$$

When the hydrolysis is carried out under milder conditions (20 °C, 30 min), one Sn–Pr bond is retained. The complex $R_3SnPr(OH)_2$ formed is stable in air like the benzoyloxy-derivative $R_3SnPr(OCOPh)_2$, in contrast to the majority of organometallic lanthanide derivatives.

It has been found recently[169] that stannyl-lanthanide complexes combine with carbon dioxide at 20 °C under normal pressure:

$$(R_3Sn)_xPr[N(SiMe_3)_2]_{3-x}\cdot DME + 2CO_2 \rightarrow (R_3Sn)_xPr[N(SiMe_3)_2]_{3-x}\cdot 2CO_2\cdot DME$$
$$x = 1, 3;\ R = CH_2SiMe_3 .$$

The infrared spectra of the adducts contain absorption bands characteristic of coordinated CO_2 (at 2180, 1620, and 1520 cm^{-1}). It is of interest to note that, depending on the conditions, the hydrolysis of these complexes may be accompanied by carbon dioxide evolution or can give rise to a new CO_2-containing product: $R_3SnPr(OH)_2.2CO_2$.

Lanthanide germylmercurates do not combine with carbon dioxide under comparable conditions. Their reactions with hydrogen chloride have been used to determined their structures:[205]

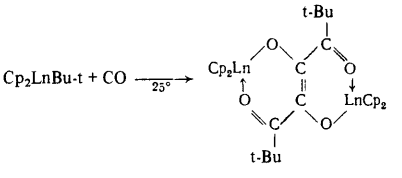
$$\left\{\begin{matrix}[(C_6F_5)_3Ge]_8Hg^- \\ [(C_6F_5)_3Ge]_4Hg^{2-}\end{matrix}\right\} Pr^{3+}\cdot(DME)_3 \begin{cases} \xrightarrow{HCl} (C_6F_5)_3GeH + \{[(C_6F_5)_3Ge]_4Hg\}PrCl \times \\ \times(DME)_3 + [(C_6F_5)_3Ge]_2Hg \\ \xrightarrow{3HCl} 3(C_6F_5)_3GeH + PrCl_3 + \\ + 2[(C_6F_5)_3Ge]_2Hg ; \\ \xrightarrow{\text{(excess) HCl}} 5(C_6F_5)_3GeH + 2(C_6F_5)_3GeCl + \\ + 2Hg + PrCl_3 . \end{cases}$$

It is seen from the equations presented above that the ionic groups are the first to decompose.

VI. OTHER COMPOUNDS

The cocodensation of lanthanide vapour with CO in an argon matrix at 4 K leads to the formation of extremely unstable metal carbonyls of the type $Ln(CO)_x$ ($x = 1–6$).[209,210] Analysis of the infrared spectra of these complexes showed that they resemble transition metal carbonyls.

An interesting dionediolate complex has been obtained by the reaction of $Cp_2LnBu\text{-}t$ with an excess of carbon monoxide.[211] The structure of the product has been postulated on the basis of X-ray diffraction data:



Use of 1-pyrazolyl borate ligands frequently makes it possible to obtain unusually high coordination numbers of the metal atoms, for example, six in the case of tin.[212] The interaction of $KHB(C_3H_3N_2)_2$ with $LnCl_3(H_2O)_x$ in water leads to crystalline anhydrous complexes $Ln[HB(C_3H_3N_2)_3]_3$ (Ln = Y, La, Ce, Pr, Sm, Gd, or Er).[213] The asymmetric complexes $Cl_2Er[HB(C_3H_3N_2)_3]$ and $ClEr[HB(C_3H_3N_2)_3]_2$ have been synthesised from anhydrous erbium chloride in THF.

Until recently, only halide clusters of the type Er_7I_{10} were known in the series of lanthanides.[214] However, the first carbon-containing lanthanide clusters, namely $Gd_{10}C_4Cl_{18}$ and $Gd_{10}C_4Cl_{17}$, were obtained in 1982 and their structures were characterised.[215] They are formed in an overall yield of 90% on heating stoichiometric amounts of $GdCl_3$, Gd, and graphite to 800–850 °C. The metallic skeleton of these clusters is made up to two Gd_6 octahedra having a common edge. All the accessible faces of the octahedra are centred on binary carbon groups C_2 with a C–C distance of 1.47 Å and have bridging chlorine atoms. The Gd–Gd bond length is in the range 3.212–4.086 Å for $Gd_{10}C_4Cl_{18}$ and 3.121–4.014 Å for $Gd_{10}C_4Cl_{17}$ (the atomic radius of gadolinium is 1.79 Å).

VII. APPLICATIONS OF ORGANOLANTHANIDES

The principal field in which organic derivatives of the lanthanides are used is catalytic reactions. The catalytic properties of inorganic lanthanide compounds have been known for a long time and have been used in a wide variety of processes, such as the cracking of petroleum, the hydrogenation and dehydrogenation of hydrocarbons, the isomerisation of olefins, the dehydration of alcohols, the synthesis of ketones from alcohols and acids, the cracking of alkanes, the emulsion of polymerisation of acrylonitrile, the manufacture of nylon, etc.[8] The olefin and diolefin polymerisation processes in which catalysts based on the lanthanides as a rule exhibit a higher activity and stereospecificity than other catalytic systems, are the most important.

In the middle 1960's it was observed that a mixture of $LnCl_3$ (Ln = Y, La, Ce, Pr, Nd, Sm, Gd, Er, or Yb) and trialkylaluminium induces the polymerisation of butadiene under mild conditions with the preferenital (>95%) formation of 1,4-*cis*-polybutadiene.[216] Studies on these lines have developed greatly and have now reached the level of industrial application. It has been established that, apart from the mixture inidcated above, stereospecific polymerisation and copolymerisation of diolefins are catalysed by the $LnCl_3.xL/R_3Al$[217–219] and cerium octanoate/R_3Al/halogen[220] systems and by lanthanide phosphates, naphthenates, and carboxylates mixed with R_3Al and a halogen.[219]

Systems based on the "light" lanthanides (Ce, Pr, and Nd) show the highest activity. Catalysts with bivalent lanthanides are inactive. The addition of a small amount of alcohol to the $LnCl_3/R_3Al$ binary system appreciably increases its activity without altering its stereospecificity.[221] It has been found that a new effective catalyst, namely $LnCl_3.3ROH/R_3Al$, is formed under these conditions. Allyl complexes of the type $LiLn(C_3H_7)_4.$dioxan (Ln = Ce, Nd, Sn, Gd, or Dy) induce the rapid and far-reaching polymerisation of butadiene.[8] A stereoregular 1,4-polymer is also formed in this instance, but (in contrast to the catalyst quoted above) it has the *trans*-structure to the extent of 80–90%. The 1,4-*trans*-polymer is also obtained in the presence of tribenzylneodymium etherate $(PhCH_2)_3Nd.(Et_2O)_3$.[40] It has been suggested that all three Nd–C bonds participate in the polymerisation with formation of tricrotyl- (or tri-isopropenyl)-neodymium complexes in the intermediate stages.

The LnX_3/R_3Al, $LnX_3(LnO)/RLi(RMgX)$, $Ln/Mo_2O_3/Al_2O_3$, $Ln(acac)_3/R_3\text{-}_mAlX_mPPh_3$, LnO/MH,[8] $(Me_5C_5)_2Ln.L$, and $(Me_5C_5)_2LnMe$ (Ln = Sm, Eu, Yb, or Lu; L = Et_2O, THF, or R_3Al) systems are used for the polymerisation of ethylene and its derivatives.[222] Weak catalytic properties have been

observed also in catalysts of the Ziegler–Natta type containing the cyclo-octatetraenylcerium complexes $Ce(C_8H_8)_2$, $Ce_2(C_8H_8)_3$, and $C_8H_8Ce(O\text{-}Pr\text{-}iso)_2AlEt_2$. The dimeric complexes $[(RC_5H_4)_2LnMe]_2$ and $(RC_5H_4)_2LnMe_2AlMe_2$ (Ln = Y, Ho, Er, or Yb; R = H, Me, or $SiMe_3$) are effective homogeneous catalysts of the polymerisation of ethylene.[87] The processes take place at 75 °C and 5 atm in the presence of the lanthanide complex and at 95° and 33 atm in the presence of an aluminium-containing catalyst.

The stereospecific polymerisation of phenylacetylene with formation of the *cis*-polymer (80–100%) in the presence of systems comprising lanthanide naphthenate or phosphonate complexes and R_3Al, sometimes with the addition of a third component, has been mentioned.[223]

Thus, in all the catalytic lanthanide systems active in the polymerisation reactions of unsaturated hydrocarbons, an Ln–C bond is present or is formed in the initial stages of the process. A study of the mechanism of these processes in relation to the model reaction of $(Me_5C_5)_2LuMe.Et_2O$ with propene[78] and of the thermal decomposition of the butyl derivative $(Me_5C_5)_2LuBu$ [224] enabled the authors of these investigations to propose a general mechanism of polymerisation in the presence of organolanthanide catalysts. Three main reaction pathways involving the Ln–R groups have been suggested: (a) the insertion of the olefin with formation of Ln–C–C–R; (b) the β-hydride decomposition of Ln–R and the subsequent insertion of the olefin in the Ln–H bond with formation of Ln–C–C–H; (c) the β-alkyl decomposition of Ln–R and the subsequent insertion of the olefin in the Ln–R′ bond. One should note that, in the presence of coordinated ligands in the catalyst molecule, the above stages are preceded by the dissociation of the Ln ← L bond.[78,222] This mechanism of the polymerisation of olefins in the presence of organic derivatives of the lanthanides is consistent with other data, for example, the incorporation of CO_2 in the oligomeric complex $Ln–(CH_2)_x–Me$, which leads to the corresponding acids $Me–(CH_2)_x–COOH$ after hydrolysis.[219]

The complexes formed on cocodensation of the vapours of the lanthanide (Nd, Sm, Er, and Yb) and acetylene derivatives RC ≡ CR′ catalyse the hydrogenation of alkenes and alkynes by hydrogen under normal conditions.[26,95,108,225] The mechanism of these reactions, proposed by Evans et al,[26] involves the formation of the lanthanide hydride in the initial stage:

$$Ln–R + H_2 \rightarrow Ln–H + RH \quad ;$$

$$Ln–H + RC{\equiv}CR \rightarrow \underset{R}{\overset{Ln}{\diagdown}}C{=}C\underset{R}{\overset{H}{\diagup}} \quad ;$$

$$\underset{R}{\overset{Ln}{\diagdown}}C{=}C\underset{R}{\overset{H}{\diagup}} + H_2 \rightarrow \underset{R}{\overset{H}{\diagdown}}C{=}C\underset{R}{\overset{H}{\diagup}} \quad .$$

The complexes formed when the SmMg alloy is treated with anthracene in THF[226] and the alloy $LaNi_5$ [227] are also capable of activating molecular hydrogen. Both compounds readily absorb hydrogen to form hydrides and the latter reduce olefins to alkanes under mild conditions.

The lanthanide salts have marked catalytic properties. For example, SmI_2 and YbI_2 catalyse the deoxygenation of epoxides and sulphoxides, the reduction of aldehydes, the conversion of alkyl halides into alkanes, and the synthesis of tertiary alcohols from ketones and RX.[228,229] The salts of tervalent lanthanides promote or catalyse the oxidation of benzoins to benzils,[230] the formation of pyrimidine,[231] and the selective 1,2-reduction of conjugated ketones by sodium tetrahydroborate.[232] It has been found that lanthanum, cerium, praseodymium, neodymium, and samarium β-nitroso-α-naphthoxides, deposited on alumina, catalyse the dehydrohalogenation of 3,4-dichlorobut-1-ene to give chloroprene.[233]

In the above processes the initial catalysts are inorganic derivatives, but organolanthanides are apparently formed in all cases as intermediates.

Cerium amalgam readily reacts with alkyl and benzyl iodides in a ketone to form the tertiary alcohol $H_2C = CHCH_2C(R).(R')OH$ or $PhCH_2C(R)(R')OH$.[234] These reactions demonstrate the preparative possibilities of the lanthanides.

The use of organic derivatives of lanthanides as antiknocking agents in motor fuels is promising.[8] Particularly satisfactory results have been obtained for cerium, praseodymium, neodymium, and ytterbium, 2,2,6,6-tetramethylhepta-3,5-dionates whose antiknocking properties are superior to those of tetraethyl-lead.

The β-diketonates and similar chelate complexes of the lanthanides have also found extensive applications as shift reagents in NMR spectroscopy.[235]

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