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Review

# Organolanthanides RLnX (R is alkyl, aryl, X is halogen) and lanthanide complexes with aromatic hydrocarbon dianions: synthesis, structure, and reactivity

Eduard S. Petrov *, Dmitrii M. Roitershtein, Ludmila F. Rybakova

*'Karpov Institute of Physical Chemistry', State Scientific Centre of Russian Federation, Vorontsovo Pole Street 10, Moscow 103064, Russia*

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## Abstract

A short review of authors' papers on synthesis, structure, and reactivity of RLnX organolanthanides (R = alkyl, aryl; Ln = Yb, Sm, Eu; X = I, Br, Cl) as well as Yb(III), Lu(III), and Y(III) complexes with organic dianionic ligands is presented. The results of study of reactions of RLnX with CH- and NH-acids, alkyl, aryl, and acyl halides, carbonyl compounds, and a variety of organic derivatives of Group 14 elements are discussed. Synthesis and structure of the lanthanide complexes with anthracene and tetraphenylethylene dianions are described. © 2002 Published by Elsevier Science B.V.

*Keywords:* Organolanthanides; Ytterbium; Lutetium; Yttrium; Deoxygenation; Dianionic ligands

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## 1. Introduction

Organolanthanide compounds RLnX with $\eta^1$-bounded ligands R (R = alkyl, aryl; X = halogen) can be used successfully in organic syntheses instead of Grignard reagents and organolithium compounds [1–4]. Therefore the study of their reactivity is of great interest. Another interesting type of organolanthanides includes complexes with dianions of aromatic hydrocarbons, which may formally be considered as $\eta^2$-dialkyl chelating ligands. Their relatively high polarisability favours the increasing covalence degree of the Ln–C bond [5], affecting the reactivity of these complexes. Basic results of our study of these two organolanthanide types are submitted herein. All the syntheses of RLnX compounds and their reactions were carried out under dry argon atmosphere, all experiments with dianionic lanthanide complexes were carried out in sealed glass vessels under vacuum.

## 2. Compounds RLnX

It has been known that RLnX reagents can be obtained by an exchange reaction of organolithium compounds RLi and $LnX_2$ salts [6] or by an oxidative addition of Ln(0) to organic iodides RI [7]. In the latter case, lanthanide is introduced in reaction as metal filing activated by the addition of $CH_2I_2$. For instance, the first heteroaromatic lanthanide derivatives (R = 2-thienyl, Ln = Yb, Sm, Eu, Ce) were prepared by this procedure [8].

We found that finely dispersed Ln(0) suspensions obtained by the reduction of $LnX_3$ salts (Ln = Sm, Yb, Eu) with sodium naphthalenide provide much more possibilities for the synthesis of RLnX [9]. The suspensions are likely similar to those obtained by reaction of the same reducing agent with transition metal halides [10]. On the other hand, such suspensions prepared by reaction of lithium naphthalenide with $LnI_2$ (Ln = Yb, Sm, Eu) were considered as lanthanide–naphthalene complexes, $C_{10}H_8Ln(thf)_3$ [11]. However, this viewpoint was under serious criticism [12].

The above-mentioned Ln(0) suspensions allowed RLnBr from 2-bromothiophene and bromobenzene to be synthesised [13]. Oxidative addition of Ln(0) activated with $CH_2I_2$ to arylbromides was found previously

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* Corresponding author. Fax: + 7-95-975-2450.
*E-mail address:* petrov@cc.nifhi.ac.ru (E.S. Petrov).

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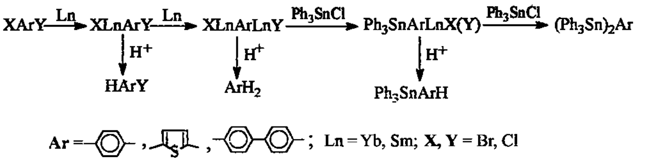
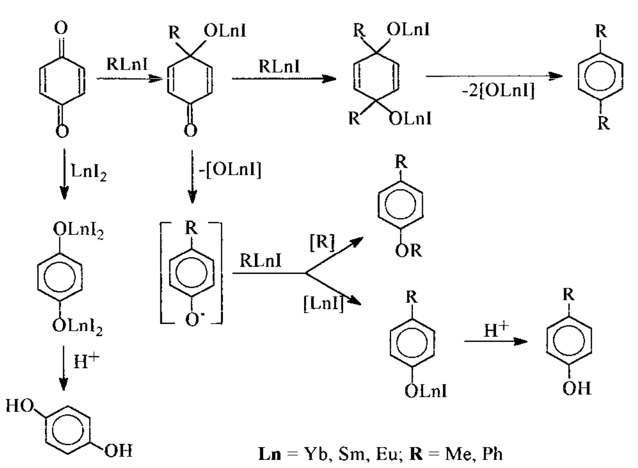
only in the case of $C_6F_5Br$ (Ln = Yb, Sm, Eu) [8]. Moreover, finely dispersed samarium and ytterbium quantitatively react with arylene dihalides (1,4-dibromobenzene, 1-bromo-4-chlorobenzene, etc.) at both carbon–halogen bonds in THF or in DME [14]. Organolanthanides obtained by reaction (1) were not isolated and identified from analysis of the products of their hydrolysis and reaction with $Ph_3SnCl$ (the main products were $ArH_2$ and $Ph_3SnArH$, respectively).



(1)

The use of the Ln(0) suspensions allowed us to realise the first preparation of organolanthanides from higher alkyl halides. Thus, the reaction of Yb, Sm, and Ce with $C_8H_{17}X$ (X = Cl, Br, I) in THF (20–35 °C) gives corresponding $C_8H_{17}LnX$ with high yields (up to 100% in the case of bromides) [15]. It has to be noted that only formation of $C_8H_{17}LnI$ is complicated by the Wurtz–Grignard homocoupling to yield hexadecane, but this by-process can be suppressed by decreasing the reaction temperature to − 15 °C. Transmetallation reaction between Ln(0) and organomercury compounds can also be used in syntheses of organolanthanides [16]. In particular, the reaction of Yb(0) with $Ph_2Hg$ was shown to give diphenylytterbium with high yield [17]. Later this method was used successfully for the syntheses of a variety of homoleptic organolanthanides $R_nLn$ (R = Me, Ph; $n = 2, 3$) [18].

Organolanthanides RLnX are comparable in reactivity with organomagnesium analogues. The compounds RLnI derived from organic iodides similar to Grignard reagents react with organo halides in the presence of transition metal complexes [19,20]. We showed that bromine- and chlorine-containing RLnX compounds also enter in cross-coupling reaction (2) catalysed by the $NiCl_2L_2$ or $PdL_4$ ($L = Ph_3P$) complexes [21,22]. It is interesting that ArLnX compounds unlike magnesium analogues react with alkyl halides. The coupling with dihalides, for example, $BrC_6H_4Br$, is also possible to give disubstituted benzene.



Scheme 1. Routes of the RLnI reaction with 1,4-benzoquinone.

$$\mathrm{RLnX} + \mathrm{R'Y} \xrightarrow{\mathrm{Cat/THF}} \mathrm{R{-}R'} + \mathrm{LnXY}$$

$$\mathrm{R,R'} = \mathrm{Me, Ar;\ Ln = Yb, Sm, Eu;\ X = Cl, Br;\ Y} = \mathrm{Br, I;\ Cat} = \mathrm{NiCl_2(Ph_3P)_2, Pd(Ph_3P)_4} \qquad (2)$$

Lanthanide(II) derivatives prepared in situ by the oxidative addition of Ln(0) to benzoyl chloride or bromide in THF vigorously react with the starting substrate [23]. The major product is 1,2-diketone (benzil) that cannot be obtained by a similar reaction with sodium or magnesium. The equimolar amount of $LnX_2$ salt is produced simultaneously. This salt being the reducing agent [24] induces conversion of diketone to keto-alcohol (benzoin) and then to benzyl phenyl ketone (reaction (3)). The degree of acyl halide conversion and the ratio of products obtained depend on Ln, the way of its activation, reaction temperature, and utilised solvent.

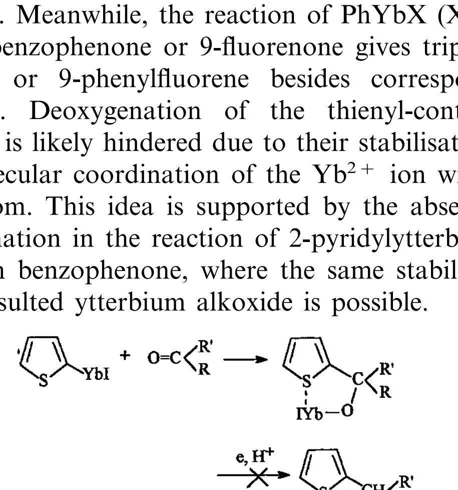
$$\mathrm{PhC(O)X} \overset{\mathrm{Ln}}{\rightarrow} \mathrm{PhC(O)C(O)Ph} + \mathrm{PhC(O)CH(OH)Ph} + \mathrm{PhC(O)CH_2Ph} \quad \mathrm{Ln = Yb, Sm, Eu;\ X = Cl, Br} \qquad (3)$$

Organic derivatives of Ln(II) are strong bases able to deprotometallate relatively weak CH- and NH-acids (p*K* 18–31) [25–27]. For example, replacement of NH-bond hydrogen by LnI occurs almost quantitatively under PhLnI action on arylamines and azoles in THF [27]. Similar reactions can be used in the syntheses of organolanthanides, when other synthetic ways are not effective or corresponding initial reagents are hardly available. Thus, some phenylethynyl derivatives of Ln(III) were obtained by metallation of phenylacetylene with lanthanide-containing amides [28].

Reactions of lanthanide(II) derivatives with arylsubstituted ketones and aldehydes are quite specific. Enolates resulted from the addition of RLnI to C=O group are able to abstract a fragment OLnI (to be deoxygenated) under the action of reducing agents (e.g. biphenyllithium) [29,30]. However, reaction of RLnI with quinones leads to the products whose deoxygenation occurs without assistance of a reducing agent. Thus, the reaction of RLnI with 1,4-benzoquinone in THF is followed by the reconstruction of diene structure into aromatic and gives mono- and disubstituted benzenes: $RC_6H5$, $p$-$RC_6H_4R$, $p$-$RC_6H_4OH$, and $p$-$RC_6H_4OR$ [31,32] (Scheme 1).

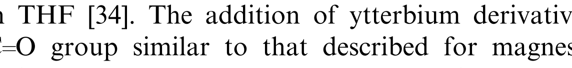
The mechanism of formation of $RC_6H_5$ is not clear yet. We only may suppose that $RC_6H_4O^{\bullet}$ radical is the precursor. The ratio of the final products depends on several factors including the reducing ability of Ln(II), the energy gain on transformation of electron structure of six-membered ring, and the contribution of R group to the stabilisation of aromatic structure [32]. Note that $LnI_2$ salt arising in the syntheses of RLnI from RI and Ln(0) also reacts with 1,4-benzoquinone, and subsequent hydrolysis of the reaction mixture gives a small amount (about 10%) of hydroquinone.

Reactions of 2-thienylytterbiumbromide and iodide with benzaldehyde, benzophenone, and 9-fluorene in THF proceed to a high degree of conversion of carbonyl compound (70–80%). However, they are not followed by deoxygenation of the resulted Yb(II) alcoholates (reaction (4)) [33]. A small amount of 9-(2-thienyl)fluorene can be obtained only under action of biphenyllithium on the product of reaction (4c) (yield is 10–15%). Meanwhile, the reaction of PhYbX (X = Br, I) with benzophenone or 9-fluorenone gives triphenylmethane or 9-phenylfluorene besides corresponding carbinols. Deoxygenation of the thienyl-containing products is likely hindered due to their stabilisation by intramolecular coordination of the $Yb^{2+}$ ion with the heteroatom. This idea is supported by the absence of deoxygenation in the reaction of 2-pyridylytterbiumiodide with benzophenone, where the same stabilisation of the resulted ytterbium alkoxide is possible.



(4)

An unusual result was obtained while studying the reaction of $Ph_2NYbI$ with aromatic aldehydes and ketones (benzaldehyde, benzophenone, and 9-fluorenone) in THF [34]. The addition of ytterbium derivative to C=O group similar to that described for magnesium amides does not occur [35]. The reaction results in tetraphenylhydrazine and carbinol corresponding to the initial carbonyl substrate. The latter likely induces homolytic cleavage of the ytterbium-containing amide, which is followed by the formation of ketyl and recombination of radical $Ph_2N^{\bullet}$ (reaction (5)).



$$Ph_2NYbI + Ph_2CO \longrightarrow \underset{\downarrow H^+ \atop Ph_2CHOH}{Ph_2COYbI} + [Ph_2N^{\bullet}] \longrightarrow Ph_2N\text{-}NPh_2 \qquad (5)$$

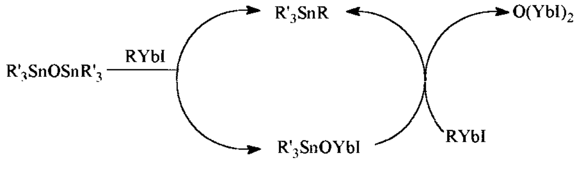
Study of reactions of RYbI (R = Me, Ph) with acyl bromides PhC(O)Br and MeC(O)Br, respectively, showed that R substitutes for bromine on the initial stage. Then the second RYbI molecule adds to carbonyl group of the resulted acetophenone to give carbinolates $Me_2PhCOYbI$ and $Ph_2MeCOYbI$, respectively [36]. These two compounds are not deoxygenated even under the action of biphenylpotassium probably because of a low thermodynamic stability of the corresponding carbanions ($Me_2PhC^-$ and $Ph_2MeC^-$). Both acyl bromides also react with Yb(0) remaining intact during preparation of RYbI. As it is shown above (see reaction (3)), the reaction results in the formation of benzil in the case of benzoyl bromide, whereas in the case of acetyl bromide further conversion occurs likely with participation of $YbI_2$ to give 3-acetoxy-2-butanone.

Reactions of RLnX with organic derivatives of Group 14 elements, proceeding with cleavage of element–carbon or element–element bonds open up new synthetic opportunities [37–39]. Thus, organolanthanides can be prepared by transmetallation reaction of mixed alkylaryl(vinyl)tin compounds [37]. The procedure is highly suitable for the synthesis of unsaturated organolanthanide derivatives that are not easily accessible by oxidative addition or by deprotonation of CH-acids. For example, the reaction of PhYbI with $R_3SnCX{=}CX_2$ (R = alkyl, X = H, F) in THF at −20 °C gives $CX_2{=}CXYbI$, and fluorine atoms of trifluorovinyl group are untouched.

We found that compounds RLnI (Ln = Yb, Sm, Eu; R = alkyl, phenyl) are able to cleave easily a Sn–Sn bond of distannanes $R'_3Sn–SnR'_3$ (R′ = *n*-Bu, Ph) in THF at room temperature to give asymmetrical tetrasubstituted stannanes $R'_3SnR$ and heterobimetallic derivatives $R'_3SnLnI$ [38,39]. The action of $YbI_2$ salt on a distannane is also efficient, but $R'_3SnI$ arises instead of $R'_3SnR$. As it was shown compounds RLnI also cleave a Sn–Si bond of trimethylsilyltriphenyltin to yield $Me_3SiLnI$ [39]. It follows from the results obtained that lanthanide-substituted stannanes are quite reactive and may be used in situ for syntheses of various organotin compounds.

Like organolithium [40] or organomagnesium [41] compounds, RYbI (R = Me, Ph) react with organotin oxides breaking Sn–O bonds [42]. The reaction with distannoxanes $(R'_3Sn)_2O$ readily proceeds at room temperature. Judging from quantitative composition of the final mixture (more than 90% of $R'_3SnR$, 5–7% of $R'_3SnOH$ after hydrolysis), the major product is formed in two ways (Scheme 2).

In the reaction of RYbI (R = Et, Ph) with oxide $Ph_2SnO$, tetrastannanes ($Ph_2SnR_2$) are major products, whereas the reaction with oxide $Bu_2SnO$ mainly leads



Scheme 2. Formation of tetrastannanes in reactions of RYbI with organotin oxides.

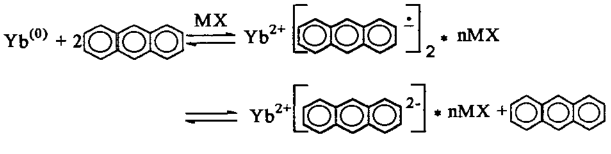
to the formation of triorganohydroxystannanes $Bu_2RSnOH$ (66–75% after hydrolysis) [42]. Compounds RLnI (R = Alk, Ar; Ln = Yb, Eu, Sm) also easily rupture Si–O, Pb–O, and Sb–O bonds to give tetraorganosubstituted derivatives of lead and silicon or triorganosubstituted derivatives of antimony [39].

The above results show that the organic derivatives of divalent lanthanides can be prepared in a comparatively easy manner; they are rather reactive and favourably differ from organolithium and organomagnesium analogues by difference in their chemical behaviour. These observations confirm that organolanthanides RLnX are the promising reagents in the organic synthesis.

## 3. Lanthanide complexes with organic dianions

The initial stage of our studies was the synthesis of organolanthanide complexes containing the anthracene dianion. Two approaches seemed to be fruitful in solving the problem. The first one is the generation of the dianion (or/and anion radical) by the reaction of zerovalent lanthanide metals with anthracene. The second one considers the use of exchange reaction between sodium adduct of anthracene and complexes of lanthanide halides. Another approach to the synthesis of complexes with dianionic ligands was developed by Evans et al., who used redox reaction between Ln(II) derivatives and aromatic hydrocarbons [43].

Zerovalent ytterbium was found to react with anthracene in THF or DME solution to give complexes with anion radical and dianion of anthracene [44]. This reaction (6) was studied in detail using different kinds of Yb(0) as a starting material (metal filing, activated by $CH_2I_2$; the ytterbium suspension prepared by reduction of $YbBr_3$ with sodium naphthalenide [7]; and the fine ytterbium powder obtained by the dissolution of metal filing in liquid ammonia at −40 °C followed by rapid evaporation of the solution).

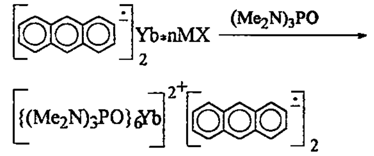


MX = LiI. NaI, KI, NaBr, LiCl, (n.Bu)$_4$NI

(6)

It was found that the reaction does not proceed if a halide salt is absent or the salt (KCl, NaCl) is completely insoluble in the organic solvent used as well as if MX is $Na[BPh_4]$ [45]. Therefore, halide anion plays the crucial role for this reaction. Apparently it serves as an electron-transfer species, as it was postulated earlier for redox reactions between transition metal complexes [46]. In this context, it should be mentioned that the most of the well-known reactions of zerovalent lanthanides with different substrates include activation of metal filing with organic iodides, i.e. iodide anion is always present in reaction mixture.

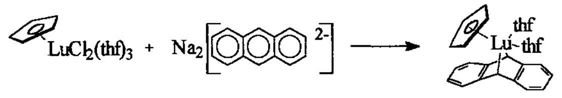
The ytterbium complex with anthracene anion radical registered by UV and ESR spectroscopy could not be isolated from the solution because a removal of the solvent shifted equilibrium towards the formation of the dianionic complex. Nevertheless, treatment of the reaction mixture with a polar solvent (HMPA) allowed us to stabilise the anion radical intermediate (reaction (7)), whose structure was determined by the X-ray technique.



(7)

The complex consists of an isolated cation $[(Me_2N)_3PO)_6Yb]^{2+}$ and two planar anthracene radical-anions non-coordinated with the ytterbium atom. The latter coordinates six HMPA molecules, in which oxygen atoms form an octahedron with Yb–O spacing ranging from 2.37(1) to 2.42(1) (Å) [47]. A similar reaction of Yb(0) with benzophenone resulting in dianionic complex was described in Ref. [48].

Since the use of anthracene dianion ligand without auxiliary ligands caused serious difficulties in isolation and crystallisation of the reaction products, we decided to study heteroleptic complexes containing cyclopentadienyl and anthracenediide ligands. The reactions of cyclopentadienyllutetium chlorides $Cp_2LuCl{\cdot}(thf)$ and $CpLuCl_2{\cdot}(thf)_3$ with equimolar amounts of disodium anthracene resulted in the formation of mono- and biscyclopentadienyllutetium-anthracenediide derivatives (reactions (8) and (9)); their structures were determined by the X-ray method [49–51].



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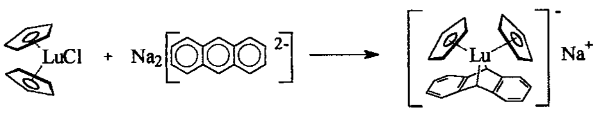


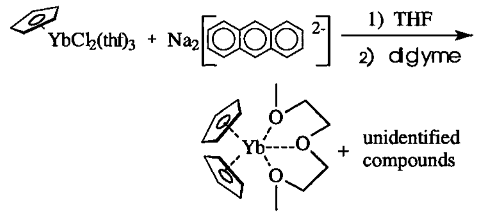
(9)

In both the complexes obtained lutetium atom is bound to the anthracene dianion by carbon atoms in 9, 10 positions. The dianionic ligands are bent along the C(9)–C(10) line, the bond lengths between C(9) or C(10) carbon atoms and adjacent carbon atoms are longer than C–C bonds of the side rings (Fig. 1) [51].

Comparison of these complexes with other anthracenediide derivatives containing a similar structure motif $[M(C_{14}H_{10})^{2-}]$ demonstrates covalent character of lutetium–anthracene dianion bond. The essentially covalent nature of this bond causes a significant decrease in reductive ability of the coordinated anthracene dianion compared to alkali metals anthracenediide [51]. The interaction between the sodium cation and the complex anion $[Cp_2Lu(C_{14}H_{10})]-$ may be described as ionic one; this complex exists in THF solution as an ionic pair separated by solvent [50]. Another evidence of an effective binding of the anthracene dianion with $Lu^{3+}$ cation is based on the fact that reactions of $Cp_2LuCl$ and $CpLuCl_2$ with the ion radical adduct $Na[C_{14}H_{10}]$ also lead to the formation of the aforementioned lutetium complexes with the dianion ligand rather than complexes with the anthracene anion radical.

Later a similar reaction was carried out by Thiele et al. using $Cp_2^*LaCl$ as an initial compound [52]. However, this reaction led to the binuclear complex $(Cp_2^*La)_2[C_{14}H_{10}]$ containing planar anthracene dianion. A similar binuclear complex $(Cp_2^*Sm)_2[\mu\text{-}C_{14}H_{10}]$ was obtained by Evans et al. by the reduction of anthracene with decamethylsamarocene [43a]. Unsubstituted Cp ligand allows the mononuclear complex with a chelating anthracene dianion ligand to be obtained, whereas the use of bulky Cp* environment leads to the structure with a bridging dianion.

In contrast to the results of the reactions of lutetium derivatives with the disodium anthracenide, our attempts to obtain a mixed cyclopentadienyl anthracenediide complex of $Yb^{2+}$ failed. The reaction of $CpYbCl_2{\cdot}(thf)_3$ with the disodium anthracene resulted in the reduction of $Yb^{3+}$ to $Yb^{2+}$ and ligand redistribution giving a mixture of organoytterbium derivatives and sodium anthracenide. The complex $Cp_2Yb{\cdot}$(diglyme) was the single organolanthanide compound obtained by reaction (10). This complex was identified by the X-ray technique [53].



(10)

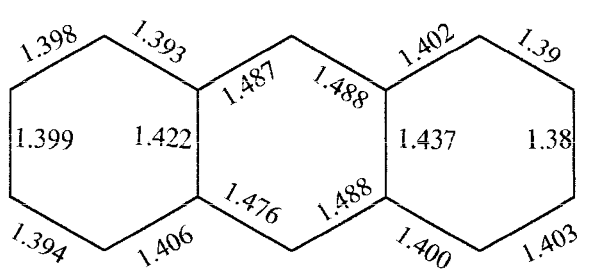
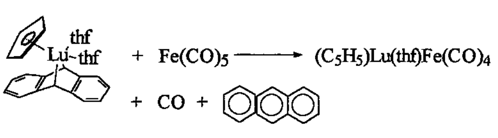


Fig. 1. C–C bond lengths in the anthracene dianion ligand in $Na(diglyme)_2[Cp_2Lu(C_{14}H_{10})]$.

A number of lanthanide complexes with the naphthalene dianion was described by Bochkarev and co-workers [54]. In some cases, these complexes demonstrate a $\eta^2$-coordination mode of the dianion to $Ln^{3+}$ cation, which is more or less similar to that found by us for the anthracenediide complexes.

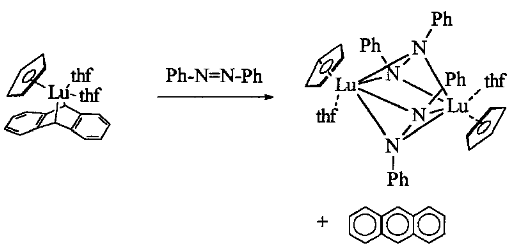
The anthracene dianion used as a ligand in organometallic complexes of 4f metals can evidently act as a reducing agent and allows the redox reactions in organolanthanide chemistry to be carried out so that (+2) oxidation state does not arise. This suggestion has been discussed in the recent review [55] in detail.

The reaction of iron pentacarbonyl with the cyclopentadienylanthracendiide complex of lutetium led to the oxidation of the coordinated anthracene dianion, and lutetium cyclopentadienyl tetracarbonylferrate and CO were formed (reaction (11)) [56]. Because of the insolubility of this heterometallic complex in organic solvents its detailed investigation was impossible, and it was identified only by chemical analysis, IR spectroscopy, and X-ray fluorescent spectroscopy; the 1:1 Fe–Lu ratio was found by the latter method.



(11)

The reaction with azobenzene can serve as an another example for the redox reactivity of such complexes. The lutetium cyclopentadienylanthracenediide reacts with azobenzene to form a binuclear organolutetium compound containing bridging azobenzene dianions (reaction (12)) [57].



(12)

Structure of the reaction product was confirmed by the X-ray method. The structure of the lutetium complex appeared to be quite similar to that of $CpYb(thf)[\mu\text{-}PhN{-}NPh]$ obtained by the reduction of azobenzene with $Cp_2Yb(thf)_2$ [58]. Hence the anthracene dianion ligand in 4f metal series allows to realise the redox reactions using organolanthanides that have a single stable oxidation state. The product of reaction (12), lutetium complex, illustrates dynamic processes caused by rotation of phenyl rings of the bridging azobenzene ligand. The rotation is slow on the NMR time scale [57]. Due to the strong conjugation between the central fragment of the dianion and phenyl rings, the energy of the rotation barrier, found from the

NMR data, is rather high and equal to 67.2 kJ mol$^{-1}$ [59].

Electronic structure of anthracene is rather specific; namely, the LUMO and HOMO are localised on two carbon atoms (C-9 and C-10). As a result, an excessive electron density of the dianion is also localised to significant degree on these two atoms. In this respect the anthracene dianion is similar to vinylarene dianion. Considering this similarity, we attempted to obtain complexes of lanthanides with tetraphenylethylene dianion. The first yttrium complex with this dianion (reaction (13)) was obtained by one of the authors in collaboration with Professor W.J. Evans in his laboratory at the UCI. Reaction of yttrium trichloride with disodium or dipotassium adducts of tetraphenylethylene led to the formation of ate-complexes $[M(thf)_n]Y[Ph_2CCPh_2]_2$ [60].

$$YCl_3(thf)_3 + 2M_2[Ph_2C{=}CPh_2] \rightarrow [M(thf)_n][Y(Ph_2CCPh_2)_2]^- + 3MCl \quad M = Na, K;\ n = 4\text{–}6 \qquad (13)$$

Two tetraphenylethylene dianions of the complex anion $[Y(Ph_2CCPh_2)_2]^{3-}$ form a $S_4$ symmetrical sandwich-like structure. One of the most interesting features of this structure is the existence of six short intramolecular Y–C contacts for each of the coordinated tetraphenylethylene dianions (Fig. 2).

It was found that the unusual $\eta^6$-coordination of the tetraphenylethylene dianion with yttrium cation is kept unchanged in the THF solution, and strong interaction between yttrium and carbon atom in *ortho*-position of the phenyl ring in solution was confirmed by $^1H\{^{89}Y\}$-NMR decoupling experiment [60]. In order to study the generality of application of the tetraphenylethylene dianion as a ligand in the organolanthanide chemistry and to elucidate the details of the $\eta^6$-coordination mode, we synthesised homo- and heteroleptic complexes of lutetium with the tetraphenylethylene dianion. The reaction of the lutetium trichloride with the dipotassium or disodium adducts of tetraphenylethylene led to the homoleptic ate-complexes, which are similar to the mentioned yttrium complex (reaction (14)) [61]. The structure of the sodium derivative $[Na(diglyme)_2][Lu(Ph_2CCPh_2)_2]\cdot(thf)_{0.5}$ was determined by the X-ray method.

$$LuCl_3(thf)_3 + 2M_2[Ph_2C{=}CPh_2] \rightarrow [M(thf)_5][Lu(Ph_2CCPh_2)_2] + 3MCl \quad M = Na, K \qquad (14)$$

The reaction of $CpLuCl_2\cdot(thf)_3$ with disodium adduct of tetraphenylethylene led to the heteroleptic lutetium complex $CpLu(Ph_2CCPh_2)\cdot(thf)_2$ (reaction (15)); its structure was also determined by the X-ray method.

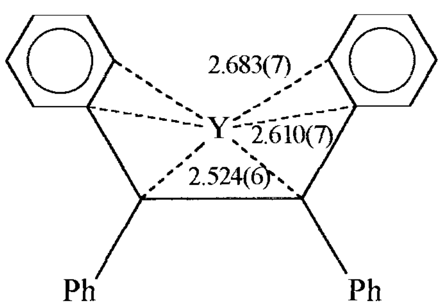


Fig. 2. Y–C bond lengths (Å) in $[Na(thf)_6][Y(Ph_2CCPh_2)_2]$, one of the tetraphenylethylene dianions omitted for clarity.

$$CpLuCl_2(thf)_3 + Na_2[Ph_2C{=}CPh_2] \rightarrow CpLu(Ph_2CCPh_2)(thf)_2 + 2NaCl \qquad (15)$$

The tetraphenylethylene dianion is $\eta^6$-coordinated to lutetium in both homo- and heteroleptic complexes. Detailed investigation of the structural parameters both by X-ray technique in solid state and NMR spectroscopy in solution showed that the $\eta^6$-coordination mode resulted from bis-$\eta^3$-allyl binding rather than from the agostic interaction with C–H bonds in the *ortho*-positions of the phenyl ring. All lanthanide complexes with the tetraphenylethylene dianion ligand demonstrate a temperature-dependent dynamic behaviour in the THF solution caused by the rotation of phenyl rings around Ph–C bond [60,61].

Thus, it follows from the results discussed above that the use of dianions of aromatic or vinylaromatic hydrocarbons as ligands in organolanthanide chemistry provides the new type of complexes, which may be applied in redox reactions even for metals with a single stable oxidation state.

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