

PREPARATION OF ORGANOLANTHANIDE HALIDES BY OXIDATIVE ADDITION OF $RH\text{al}$ TO METALLIC LANTHANIDES

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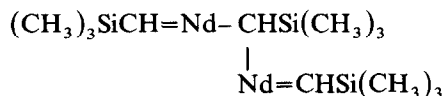
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(Received April 21st, 1983)

Summary

The possibility is demonstrated of obtaining organometallic compounds of trivalent lanthanides through oxidative addition of triphenylmethyl chloride, benzyl chloride and phenyl bromide to metallic lanthanides (Pr, Nd, Gd, Ho) in THF. The composition and stability of the organometallic compounds as functions of the reaction conditions and metal nature have been studied. The reaction mechanism is discussed.

Of the organolanthanide compounds, the cyclopentadienyl derivatives, first obtained by Wilkinson and Birmingham [1], have been studied most thoroughly. These compounds are very stable and may be sublimed by heating in vacuum. Alkyl compounds of lanthanides containing no other ligands were found to be unstable at normal temperatures. Thus tribenzylneodymium in THF, diethyl ether and toluene with small amounts of THF decomposes at 0–20°C to a carbene (carbene) complex of the general formula $(C_6H_5C\equiv Nd)_n$ and toluene [2]. Reaction of $NdCl_3$ with trimethylsilylmethyl lithium in an aromatic solvent [3] yields not NdR_3 but rather its decomposition product to which the structure:



has been attributed.

One of the ways of preparing alkyl(alkenyl)metal halides is the oxidative addition of $RH\text{al}$ to metals or metal(0) complexes e.e., metal carbonyls. Evans et al. [4] described the synthesis of organic derivatives of divalent samarium, europium and ytterbium by oxidative addition of alkyl(aryl) iodides (R is methyl, ethyl, phenyl etc.) to the above metals in THF. According to analytical data the compounds have the composition $RLnI$. No such organolanthanide halides are known for trivalent lanthanides.

In the present work it was found possible to produce aryl (arenyl, alkenyl)lanthanide halides of the general formula R_nLnHal_{3-n} (Hal is Cl, Br; $n = 1$ and 1.5) via oxidative addition of RHal to zerovalent metals ($Ln = Pr, Nd, Gd, Ho$). As RHal we used triphenylmethyl chloride, benzyl chloride and phenyl bromide which contained hydrocarbon groups not susceptible to β -, and in the case of triphenylmethyl chloride also to α -decomposition. We have found that oxidative addition of RHal to lanthanide takes place only in pure THF or its mixtures with toluene at 20–70°C. During the reaction, the metal is dissolved and a coloured organolanthanide compound is formed. For the organometallic products we determined the concentrations of the lanthanide and halide-ions as well as the number of metal–carbon bonds. The nature of RHal was found to exhibit a considerable influence on the course of the reaction and the composition of the organolanthanide products.

1. Reaction of trimethylphenyl chloride with lanthanides

The reaction between triphenylmethyl chloride and zerovalent lanthanides was carried out with Ph_3CCl/Ln ratios of 0.5 to 2. The reaction takes place at room temperature. The reddish-brown solution was separated from the residue and analyzed by the procedure described below. Table 1 presents data on the yield and composition of the triphenylmethyl-lanthanide chlorides. The number of carbon–lanthanide bonds per metal atom was obtained by acid titration. In runs 5 and 6 we also chromatographically identified triphenylmethane formed through hydrolysis of the C–Ln bonds. The results obtained by the two methods agree quite closely.

For the typical reaction between Ph_3CCl and metallic Nd it was found that when the initial molar RCl/Ln ratio is 1 the final reaction product is triphenylmethyl-neodymium sesquichloride, formed in yields of up to 95%. For $RCl/Ln = 1.5$ to 2

TABLE 1

REACTION OF TRIPHENYLMETHYL CHLORIDE WITH METALLIC LANTHANIDES Solvent THF; temperature 20°C

No	Ln	Added		Reaction time (h)	Found in solution				Yield of OL (%) ^b	Average product composition
		Ln (mmol)	RCl/Ln (mol)		Ln^{3+} (mmol)	C–Ln ^a / Ln^{3+} (mol)	Cl^-/Ln^{3+} (mol)	R–R (mmol)		
1	Nd	12.5	0.5	5.5	3.38	1.5	1.37	0.63	81	$R_3Nd_2Cl_3$
2	Nd	3.8	0.8	5.0	1.77	1.4	1.54	0.15	87	$R_3Nd_2Cl_3$
3	Nd	7.0	0.8	4.5	2.80	1.6	1.45	0.55	72	$R_3Nd_2Cl_3$
4	Nd	5.5	1.0	3.0	3.52	1.5	1.55	–	96	$R_3Nd_2Cl_3$
5	Nd	3.0	1.5	2.0	2.16	1.0	2.00	–	96	$RNdCl_2$
6	Nd	5.2	2.0	4.0	5.10	1.1	2.00	1.25	98	$RNdCl_2$
7	Pr	6.2	1.5	1.5	4.65	1.0	1.88	–	100	$RPrCl_2$
8	Gd	5.1	1.5	3.0	3.57	1.1	1.97	–	93	$RGdCl_2$
9	Ho	4.9	1.5	4.5	2.67	1.0	2.00	–	73	$RHoCl_2$

^a Data from acidimetric determination of the number of C–Ln bonds. ^b "Theoretical yield" refers to the amount of triphenylmethyl derivatives produced in accordance with the equation:

for $R_3Ln_2Cl_3$: $3 RCl + 2 Ln \rightarrow R_3Ln_2Cl_3$;

for $RLnCl_2$: $2 RCl + Ln \rightarrow RLnCl_2 + 0.5 R-R$.

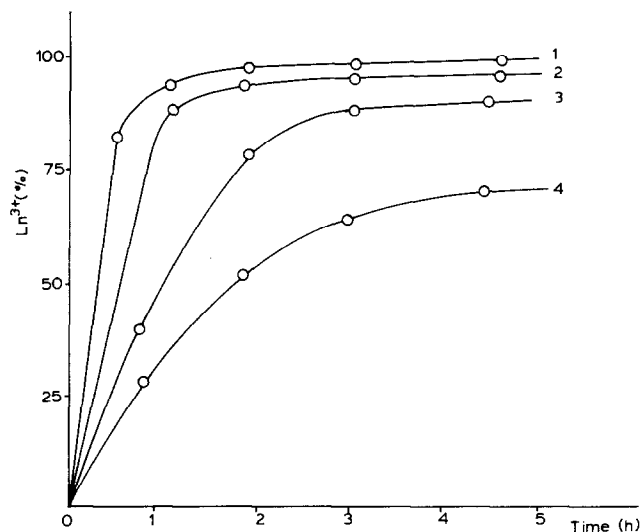


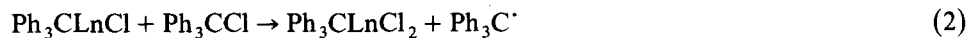
Fig. 1. Influence of the nature of the metal on the rate of formation of triphenylmethyllanthanide dichlorides; 1-Pr, 2-Nd, 3-Gd, 4-Ho; 23°C, THF, RCl/Ln = 1.5(mol)

the product is triphenylmethyln neodmium dichloride in nearly theoretical yield. Special experiments showed that if the reaction is first carried out with $\text{RCl}/\text{Nd} = 0.82$ and then some more Ph_3CCl is added until the final RCl/Nd ratio = 1.57, the sesquichloride is converted to the dichloride.

Reactions of triphenylmethyl chloride with praseodymium, gadolinium and holmium with $\text{RCl}/\text{Ln} = 1.5$ also yield triphenylmethyllanthanide dichloride.

Figure 1 illustrates the rate of formation of triphenylmethyllanthanide dichlorides of all of the above metals with $\text{RCl}/\text{Ln} = 1.5$ and the same concentration of Ph_3CCl . It is seen that the reaction is the fastest with praseodymium and neodmium: after two hours under the conditions used an almost theoretical yield of the organolanthanide compound is achieved. The reaction of Ph_3CCl with holmium is much slower than with praseodymium or neodmium.

On the basis of these results we propose the following route of formation of an organolanthanide compound by oxidative addition of triphenylmethyl chloride to zerovalent lanthanides:



The first step (eq. 1) leads to formation of an intermediate organolanthanide compound with a divalent metal. Reaction of this compound with the starting RCl (eq. 2) yields triphenylmethyllanthanide dichloride and triphenylmethyl radical which, by addition to the trithyl derivative of the divalent lanthanide produces R_2LnCl in an amount equimolecular to the amount of RLnCl_2 (eq. 3). That reaction 3 is possible is indicated by the increase of the rate of formation of the organoneo-

dymium compound after addition of hexaphenylethane (HFE) to the $\text{RCl} + \text{Nd}$ system. It should be noted that in the absence of Ph_3CCl hexaphenylethane does not react with metallic neodymium in THF. Acceleration of the reaction in the presence of HFE means that it is step 3 which is the limiting one. This may, apparently, be possible if the primary addition product containing divalent lanthanide exists in the dimer form. Reaction 2 involves intermediate free-radical reactions, as does the reaction of triphenylmethyl chloride with organotitanium compounds such as $(\text{C}_5\text{H}_5)_2\text{Ti}$, $(\text{C}_5\text{H}_5)_2\text{TiCl}$ [5,6].

In accordance with the above scheme the product with $\text{RCl}/\text{Nd} = 1.5$ must be triphenylmethylneodymium sesquichloride. However, as one can see from Table 1, it is RNdCl_2 which is formed under these conditions after consumption of all the RCl and in the presence of a certain amount of unreacted metal. These data suggest involvement R_2LnCl in a Wurtz reaction:



The presence in the reaction mixture of HFE after decomposition of triphenylmethylanthanide dichloride favors this assumption (the amount of HFE was determined according to the procedure described [7]). The contribution of this reaction increases with the RCl/Ln ratio. If the reaction is completed with the initial $\text{RCl}/\text{Nd} = 1.5$ ratio and then an additional amount of triphenylmethyl chloride is added to the system (final $\text{RCl}/\text{Nd} = 2$), one observes complete consumption of the metal and quantitative formation of RNdCl_2 .

During the synthesis and storage, the organoneodymium compound may metalate tetrahydrofuran producing triphenylmethane. To identify this compound we removed all the THF from the reaction mixture by evaporation and added hexane previously held over $\text{C}_4\text{H}_9\text{Li}$ to the residue. Only triphenylmethane (RH) can dissolve in hexane, since the organoneodymium compound is not soluble in hexane. The data on the content of RH in tetrahydrofuran solution of organoneodymium compounds after different storage periods are given in Table 2.

From this Table it follows that in solution stored at -78°C for 1 to 3 days the content of free triphenylmethane is only 10–20% of theory. When stored at 4°C the concentration of free RH markedly increases. However, the solution retains an intense brown colour typical of organoneodymium compounds and the neodymium

TABLE 2

CONTENT OF TRIPHENYLMETHANE IN THE TETRAHYDROFURAN SOLUTION OF TRIPHENYLMETHYL COMPOUNDS OF NEODYMIUM AS FUNCTION OF STORAGE TIME

Organoneodymium compound	Temperature ($^\circ\text{C}$)	Time (days)	RH Found (%)
RNdCl_2	4	2	40
	4	6	52
	4	3.5 months	78
	-78	1	20
	-78	3	20
	-78	9	33
	-78		
$\text{R}_3\text{Nd}_2\text{Cl}_3$	-78	1	10
	-78	5	28

TABLE 3

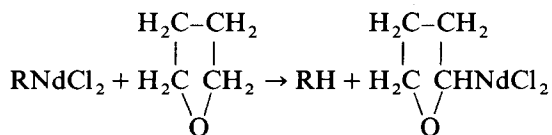
REACTION OF BENZYLCHLORIDE (RCl) WITH METALLIC LANTHANIDES (Ln). Solvent THF, 20°C

Ln	RCl consumed (mmol)	$\frac{\text{RCl}}{\text{Ln}}$ (mol)	Reaction time (h)	Found in solution								Total amount of R groups (% of RCl)
				Ln^{3+} (mmol)	Cl^- (mmol)	RH (mmol)	R-Ln bonds (mmol)	R-R (mmol)	$\frac{\text{Cl}^-}{\text{Ln}^{3+}}$ (mol)	$\frac{\text{R-Ln}}{\text{Ln}^{3+}}$ (mol)	Ln^{3+} (%) ^a	
Nd	6.90	1.0	4	3.18	6.2	0.69	1.27	1.64	1.96	0.40	92	76
	6.85	1.0	18	2.58	4.9	0.96	0.98	1.69	1.90	0.38	75	78
Pr	7.40	1.0	4	3.74	7.3	0.89	1.31	1.81	1.95	0.35	100	79
Ho	13.00	0.4	4	4.87	10.1	1.08	3.00	2.64	2.06	0.62	75	72

^a The "theoretical amount" is assumed to be the amount of Ln^{3+} that has passed into the solution via the reaction:



content in the solution remains practically unchanged. Hence, it may be just to assume that triphenylmethane is formed via metalation of THF:

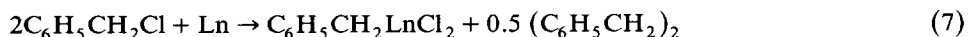


This reaction is quite similar to the known reaction of THF metalation with organolithium compounds. A similar reaction of pyridine metalation with an organolutecium compound ($(\text{C}_5\text{Me}_5)_2\text{LuCH}_3$) has been described [8].

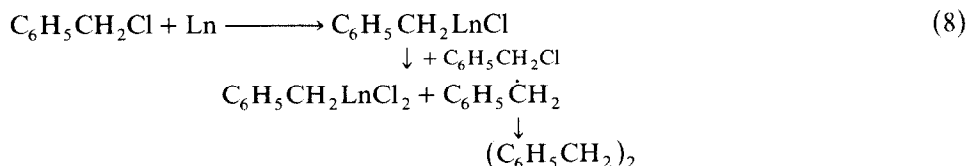
In the IR spectra of RPrCl_2 and RNdCl_2 one observes all the bands typical of a monosubstituted phenyl ring. In the longwave part of the spectrum there are bands at 450, 470, 535 cm^{-1} which can be attributed to vibration of the C-Ln bond since they rapidly disappear after exposure of sample to air. The 340 cm^{-1} band may be attributed to vibrations of the Ln-Cl bond.

2. Reaction of benzyl chloride with lanthanides

Reaction between benzyl chloride and lanthanides (Nd, Pr, Ho) was carried out in THF at 20°C and $\text{PhCH}_2\text{Cl}/\text{Ln} = 1$ for Nd and Pr and 0.4 for Ho. In all experiments benzyl chloride was consumed completely in the reaction. The analytical data given in Table 3 for the reaction mixture show that the reaction produces organolanthanide dichloride ($\text{Cl}^-/\text{Ln}^{3+} = 2$) with a yield of 75–100%. About half of all the benzyl groups are released as dibenzyl, the amount of which remains unchanged during storage. It follows hence that dibenzyl is the primary product of the reaction between benzyl chloride and lanthanides. These results suggest that the total equation for the oxidative addition of benzyl chloride to lanthanides is:



A reaction mechanism involving bimolecular steps may be represented by the following scheme:



The data of Table 3 show that on the average less than one group is bonded to the metal atom in solution but a considerable amount of toluene which is formed through decay of the benzyl derivatives of the lanthanides. Nevertheless, the total amount of benzyl groups found in the solution makes up only 72-79% of theory. Obviously, some of the benzyl groups are consumed in reactions of the organo-lanthanide compounds with THF accompanied by cleavage of the ring and formation of alkoxy compounds of lanthanides, in analogy with reactions of this type involving organolithium compounds.

As one can see from Table 4, as the exposure time of the reaction products is increased the amount of toluene in solution increases while the number of benzyl groups bonded to the metal drops. The fraction of dideuterotoluene in the toluene resulting from the hydrolysis by D_2O also rises with the time of exposure. Thus, the reaction products stored for a week produced more than 90% dideuterotoluene. Product that had been stored for 7 days contained more than 90% dideuterotoluene. It should be noted that the Ln^{3+} concentration in solution varies only insignificantly.

These results show that even after short exposure times the solution contains a considerable amount of organometallic compounds in which the metal is combined with benzyldiene groups into a carbene complex, $\text{C}_6\text{H}_5\text{CH}:\text{LnCl}_2$, or into compounds of formula $\text{C}_6\text{H}_5\text{CH}(\text{LnCl}_2)_2$ where one benzyldiene group is bonded to two Ln atoms. Such compounds may be obtained by disproportionation of the benzyl groups involving release of toluene:



TABLE 4

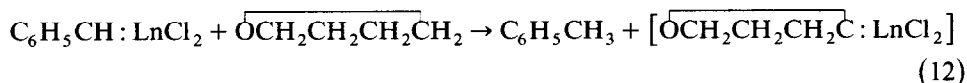
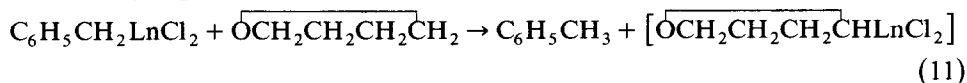
COMPOSITION OF PRODUCTS OF REACTION BETWEEN BENZYL CHLORIDE AND METALLIC LANTHANIDES AS FUNCTION OF THE EXPOSURE TIME. THF, 20°C

Ln	Exposure time ^a	Ln^{3+} concentration, (mol/l)	Found in solution, (% based on RCl)			$\frac{\text{R-Ln}}{\text{Ln}^{3+}}$ (mol)	Composition of deuterio toluenes after hydrolysis with D_2O (%)	
			RH	R-Ln bonds	R-R		$\text{C}_6\text{H}_5\text{CH}_2\text{D}$	$\text{C}_6\text{H}_5\text{CHD}_2$
Nd	4 h	0.210	10.0	18.4	47.5	0.40	57	43
	18 h	0.207	14.0	14.3	49.5	0.38	34	66
	1 day	0.207	16.8	11.3	47.5	0.23	28	72
	1 week	0.184	25.0	3.3	49.5	0.09	7	93
Pr	4 h	0.218	12.0	17.7	49.0	0.35	60	40
	1 day	0.218	14.0	15.6	49.2	0.31	44	56
	1 week	0.208	25.7	3.1	51.2	0.07	9	91
Ho	4 h	0.211	8.3	23.0	40.7	0.62	—	—
	2 months	0.194	15.4	15.5	41.0	0.46	100	0
	4 months	0.190	22.4	8.0	43.0	0.23	—	—

^a Including the time of reaction between RCl and Ln.

The formation of carbene complexes in the system is demonstrated by the fact that a small amount of stilbene (about 0.5% of all the benzyl groups) a recombination product of phenylcarbene species, was found in the reaction products.

The data of Table 4 also show that after a sufficiently long exposure of the product solutions almost all the benzyl and benzyldiene groups bonded to the metal undergo cleavage and are released as toluene. The following reactions with the solvent may explain this fact:



Reaction 11 is similar to that for triphenylmethyl compounds. Preference for Reaction 12 may arise when a carbene complex formed contain an oxygen atom in the α -position to the carbene centre. The organometallic compounds containing residues of THP apparently undergo further conversions, since in the products of hydrolysis of the resultant solutions with D_2O only traces of deuterated THF were found.

The increase of the dideuterated product in toluene released in hydrolysis of organoneodymium and organopraseodymium compounds with D_2O with time of exposure obviously means that the compounds containing benzyldiene groups decompose at a slower rate than benzyl compounds.

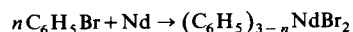
The stability of the organoholmium compound is much higher than that of neodymium and praseodymium compounds; after two months of storage in THF at room temperature the benzyl-Ho/ Ho^{3+} ratio decreased from 0.62 to 0.46 whereas in neodymium and praseodymium compounds the benzyl-Ln bonds practically disappear already after a week's storage (Table 4). It must be noted that only mono-deuterotoluene and virtually no dideuterotoluene were found in the products of hydrolysis of the organoholmium compound with heavy water. As a whole the experimental data (the decreased number of benzyl-Ho bonds in the organo-

TABLE 5

REACTION OF PHENYLBROMIDE WITH NEODYMIUM. Solvent THF, 70°C

No	Nd (mmol)	PhBr (mmol)	C_5H_8 (mmol)	Found in solution, (mmol)				Br^- Nd^{3+}	C-Nd Nd^{3+}	Yield of or- ganoneody- mium compound (%) ^b
				Nd^{3+}	Br^-	C_6H_6	PhBr	(mol)	(mol)	
1	5.17	10.34	—	1.02	1.90	1.02	3.15	1.86	1.20	36.5
2	1.71 ^a	7.16	—	0.36	0.68	0.27	—	1.85	1.30	39.0
3	12.00	12.00	5.6	7.40	11.70	1.40	0	1.58	1.21	98.0
4	13.00	13.00	10.0	7.75	12.70	1.49	0	1.65	1.50	98.0

^a 20°C, 15 h. ^b Theoretical yield is the amount of organometallic compound obtained according to the equation



where n = molar ratio of $\text{Br}^-/\text{Nd}^{3+}$ in the solution.

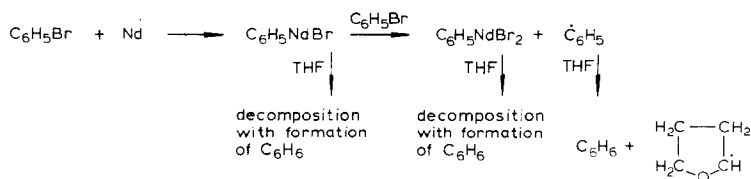
holmium compound, its rather high stability and presence of only monodeutero-toluene in the hydrolysis products) suggest that the organoholmium compound undergoes decay predominantly during the synthesis and specifically during the step at which the divalent metal compound is formed.

3. Reaction between phenyl bromide and neodymium

Reaction of phenyl bromide with neodymium requires a long induction period (5 to 7 hours at 70°C, 20 hours at 20°C). Only then does the reaction mixture begin to acquire an intense coloration. The reaction was carried out with $\text{C}_6\text{H}_5\text{Br}/\text{Nd} = 1$ to 4. In the organoneodymium compound obtained (c.f. Table 5, runs 1 and 2) the $\text{Br}^-/\text{Nd}^{3+}$ ratio is 1.85 and the number of phenyl groups associated with neodymium is 1.2–1.3. Obviously, the product is PhNdBr_2 with a minor amount of Ph_2NdBr . The solution of the organoneodymium compound contains much benzene and only traces of diphenyl.

At room temperature gradual cleavage of the phenyl groups in the form of benzene is observed, apparently, through THF metalation as it was in the case of the triphenylmethyl and benzyl derivatives.

On the basis of the above experimental data, the reaction between phenyl bromide and neodymium may be represented by the following scheme:



Formation of $(\text{C}_5\text{H}_6)\text{NdBr}$ may take place via the disproportionation reaction:



The data of Table 3 indicate that the yield of phenyl compounds of neodymium cannot be higher than 40%, the reaction mixture always containing unreacted phenylbromide.

The yield of organoneodymium compound increases to almost theoretical values if the reaction between phenyl bromide and neodymium is carried out in the presence of small quantities of isoprene (Table 5, Nos. 3,4). Under these conditions phenyl bromide is consumed totally and the relative concentration of benzene in the reaction mixture is considerably lower. The $\text{Br}^-/\text{Nd}^{3+}$ ratio in the product is about 1.6. No benzene is released on hydrolysis of this compound. However, iodometric and acidimetric techniques, the results of which were identical, showed that $\text{C}-\text{Nd}/\text{Nd}^{3+}$ is 1.2 to 1.5. Obviously, the product is a mixture of RNdBr_2 and R_2NdBr resembling the sesquibromide. As already noted, the relative yield of benzene sharply decreases when the reaction is carried out in the presence of isoprene, which is apparently due to the trapping of phenyl radicals by isoprene. The resultant allyl radicals are more stable than phenyl radicals and may react, like the triphenylmethyl radicals, with the intermediate Nd^{2+} compound via the reaction:



which considerably increases the yield of the organometallic compound. The in-

crease in yield may also be due to stabilization of the organometallic compound owing to addition of isoprene to the phenyl-Nd bond.

Under certain conditions the organolanthanide compounds produced may catalyze the stereo-specific polymerization of dienes.

Experimental

Reactions were carried out in a glass flask provided with a magnetic stirrer. To chips of metallic lanthanide activated by heating with a small quantity of iodine was added the RHal solution in THF and the reaction mixture was intensively agitated in argon atmosphere. After the reaction was complete, the solution was isolated from the unreacted metal by decantation or filtration through a glass filter. The solution which contained the organolanthanide compound was analyzed for the metal (by the trilonometric technique) and halide ions (using the Folhard method); also the number of the lanthanide-carbon bonds was determined (acidimetrically, iodometrically and by chromatographic analysis of the RH hydrocarbons produced in hydrolysis).

Triphenylmethane was determined by gas liquid and liquid absorption chromatography.

In the case of benzyl chloride, chromatography was also used for determining unreacted benzyl chloride, toluene and dibenzyl. The solvent was completely removed in vacuo at 20°C from an aliquot of the reaction solution and the amounts of benzyl chloride and toluene, formed by disproportionation of the benzyl groups of the organolanthanide compound, were determined in the condensate. Fresh THF was added to the dry residue and the solution was decomposed with H₂O or D₂O. The aqueous layer was separated from the organic layer and washed with hexane to completely remove the hydrocarbon products and then analyzed for lanthanide and chloride ions. The organic layer was mixed with hexane that had been used for elution of the aqueous layer, and the amounts of benzyl chloride, dibenzyl and toluene which correspond to the number of benzyl and benzyldiene groups bonded to the metal were determined chromatographically. Toluene produced in hydrolysis with D₂O was also analyzed by mass spectroscopy. Unreacted phenylbromide, diphenyl and benzyne formed by the phenyl groups cleaved from the lanthanide were determined chromatographically in the reaction products.

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