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FORMATION OF ORGANOMETALLIC COMPOUNDS OF CARBENE AND CARBINE TYPES BY THE INTERACTION OF RLi WITH NEODYMIUM AND YTTRIUM CHLORIDES IN VARIOUS MEDIA *

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Summary

It has been established that in the interaction of $NdCl_3$ and YCl_3 with RLi, where R = $CH_2C_6H_5$, $CH_2C(CH_3)_2C_6H_5$, $CH_2Si(CH_3)_3$, unusual organometallic compounds are formed. They are stable in hydrocarbon solutions. The benzyl and neophyl derivatives are carbene type complexes containing one R group at a trivalent metal atom. In all cases the reaction is accompanied by the evolution of RH as the main product and some stilbene and tolan when R = $CH_2C_6H_5$. The mechanism of this reaction is discussed.

The decomposition of alkyl derivatives of transition metals is known to be accompanied by the formation of products of disproportionation of the alkyl groups (equimolar amounts of R — H and R + H) and recombination (R—R) with the metal reduction. The major reaction product is usually R—R, provided that R is CH_3, C_6H_5, $CH_2C_6H_5$. A specific characteristic of the decomposition of organometallic compounds of W, Mo, Nb and Ta (resulting from the interaction of chlorides of the corresponding metals with organolithium compounds containing functions incapable of β-elimination (R = $CH_2C(CH_3)_3$, $CH_2Si(CH_3)_3$, $C_6H_5CH_2$, CD_3)) has been recently established [1—5]. Such decomposition is accompanied by the evolution of considerable amounts of the hydrocarbon RH and the formation of carbene, carbine and carbide complexes of the transition metals.

The present paper deals with the study of the interaction of neodymium and yttrium chlorides with RLi (R = $CH_2C_6H_5$, $CH_2C(CH_3)_2C_6H_5$, $CH_2Si(CH_3)_3$); the formation of unusual organometallic compounds is demonstrated.

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* Dedicated to Prof. G.A. Razuvaev on the occasion of his 85th birthday on August 23rd, 1980.

TABLE 1

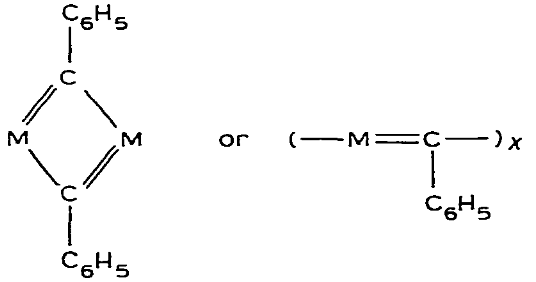
STUDY OF INTERACTION OF YTTRIUM AND NEODYMIUM CHLORIDES WITH BENZYLLITHIUM (LiR) IN TETRAHYDROFURAN (Reaction time 3–4 hours, Temperature 23°C)

MCl_3	Reactants			Products after hydrolysis of benzene solution of organometallic compound							Yield[a] of organometallic compound (% of RLi)
	MCl_3 (mmol)	RLi (mmol)	$\frac{RLi}{MCl_3}$	M^{3+} (mmol)	RH (mmol)	$\frac{RH}{M^{3+}}$	tolan (mmol)	stilbene (mmol)	dibenzyl- (mmol)	diphenylmethane (mmol)	
YCl_3	2.15	6.45	3 : 1	1.62	1,62	1 : 1	0,24	0.16	0.13	0.13	75
YCl_3	4.80	14.4	3 : 1	3.84	3.84	1 : 1	—	—	—	—	80
YCl_3	5.10	15.0	2.95 : 1	3.58	3.50	0.98 : 1	—	—	—	—	72
$NdCl_3$	9.40	18.8	2 : 1	3.60	3.95	1.1 : 1	0.008	0.17	0.40	0.17	57.5
$NdCl_3$	5.80	17.4	3 : 1	3.80	4.00	1.05 : 1	—	—	—	—	65
$NdCl_3$	3.03	6.06	2 : 1	2.05	2.04	0.99 : 1	—	—	—	—	100.0

[a] The yield of the compound R_3M formed according to the scheme: $3\ LiR + MCl_3 \rightarrow R_3M + 3\ LiCl$ is taken as 100%.

The reaction of neodynium and yttrium compounds with benzyllithium was conducted at a RLi/MCl_3 ratio of 2—3 in tetrahydrofuran at room temperature. On completion of the reaction the liquid phase was distilled off under vacuum and the content of toluene was then determined, while the residue was extracted with benzene. The yield of the resulting organometallic compound was 60—100% (Table 1). In the resulting solution lithium and chlorine were absent. The organometallic compounds have a high stability in solution: the ratio of $C_6H_5CH_3/M^{3+}$ after hydrolysis of a sample remained unchanged and equal to 1 over several months at room temperature.

It was found quite unexpectedly that only one mole of toluene per one g-ion of metal was formed upon hydrolysis of the synthesized compounds. It should be noted that 3 g-equiv. of protons are consumed per 1 g-ion of a metal. The absence of molecular hydrogen indicates that the metal retains the oxidation state of +3 in the benzyl derivatives under consideration. These data, as well as the fact that about 1.6—1.7 moles of toluene per mole of the resulting organometallic compound are evolved in the synthesis, point to an unusual structure of the synthesized benzyl derivatives of yttrium and neodymium. The presence of stilbene and tolan in the reaction products (Table 1) indicates the formation of compounds of carbene and carbine complexe type. In the IR spectrum of the toluene formed upon the decomposition of the organoneodymium compound with D_2O only one unsplit band was observed in the 2220 cm^{-1} region which may be attributed to the absorption of valent oscillations of C—D in the CD_3 group. The absence of splitting of this band shows that the system contain no $C_6H_5CHD_2$ and $C_6H_5CH_2D$. It follows that the formation of 1.6—1.7 moles of toluene during the reaction of benzyllithium with MCl_3 in solvating media occurs by disproportionation of benzyl groups similar to that previously described [4,5] in the case of the decomposition of $(CD_3)_nWX_m$. The data obtained indicate that in the synthesized compounds the benzyl function is bonded to the metal by means of three carbon—metal bonds. This is shown by the following schematic structures:



$(—M{=}\underset{\displaystyle C_6H_5}{\underset{|}{C}}—)_x$

(I)

and

$C_6H_5C{\equiv}M$

(II)

Using IR spectroscopy it was shown that after the interaction of the organoneodymium compound with oxygen an intensive absorption band appeared in the 1740 cm^{-1} region which is characteristic for the C=O group. As a result of hydrolysis of the oxidized benzyl derivative of neodymium, benzoic acid was formed which was identified by thin-layer chromatography.

Summarizing, the interaction of benzyllithium with yttrium and neodymium

TABLE 2

STUDY OF THE INTERACTION OF YCl_3 WITH NEOPHYLLITHIUM (RLi) IN DIETHYL ETHER

Reactants			Reaction conditions	Products after hydrolysis of ethereal solution of organometallic compound				RH in the condensate after the synthesis (mmol)	RH (in the condensate)	Yield of organometallic compound (% of RLi)
YCl_3 (mmol)	RLi (mmol)	$\frac{RLi}{YCl_3}$		Y^{3+} (mmol)	RH (mmol)	$\frac{RH}{Y^{3+}}$	$\frac{H^+}{Y^{3+}}$		Y^{3+}	
8.7	21.3	2.45 : 1	22°C, 3 h	6.72	7.36	1.1 : 1	2.9 : 1	—	—	94
15.2	45.6	3 : 1	35°C, 1 h	12	12	1 : 1	2.96 : 1	24	2 : 1	79

TABLE 3

INTERACTION OF $(CH_3)_3SiCH_2Li$ WITH $NdCl_3$ IN HYDROCARBON SOLVENT ($RLi/NdCl_3 = 1$, temperature 20°C)

Starting amount of $NdCl_3$ (mmol)	Solvent	Reaction time (h)	Amount of $(CH_3)_4Si$ evolved		Products after hydrolysis of solution of organometallic compound				Yield of organoneodymium compound (%) [a]
			(mmol)	(% of $(CH_3)_3Si$-CH_2Li)	Nd^{3+} (mmoles)	Li^+ (% of Nd^{3+})	$(CH_3)_4Si$ (mmol)	$\frac{(CH_3)_4Si}{Nd^{3+}}$	
8	Benzene	30	4.8	60	1.36	—	2.05	1.5	51
13	Benzene	30	7.8	60	3.12	15	4.10	1.3	72
2	Toluene	20	—	—	0.37	20	0.52	1.4	55
2.2	Toluene	20	—	—	0.38	7	0.50	1.3	52

[a] The theoretical yield was assumed to be the yield of the organoneodymium compound obtained in the reaction: $3(CH_3)_3SiCH_2Li + NdCl_3 \rightarrow [(CH_3)_3SiCH_2]_3Nd$

trichlorides may be represented by the following general scheme:

$$\begin{array}{ll} 3\ C_6H_5CH_2Li + MCl_3 \rightarrow & [(C_6H_5CH_2)_3M] + 3\ LiCl \\ & \quad\downarrow \\ & [C_6H_5CH{=}M\text{-}CH_2C_6H_5] + C_6H_5CH_3 \\ & \quad\downarrow \\ & \begin{array}{l}\text{the above mentioned}\\ \text{reaction products}\end{array} + C_6H_5CH_3 \end{array}$$

Similar results were obtained in the investigation of the interaction of yttrium trichloride with neophyllithium in diethyl ether (Table 2).

As it follows from the data given in the Table 2, in the synthesized neophyl derivative of yttrium one hydrocarbon grouping is bonded with the metal atom; during the synthesis, 2 moles of tert.butylbenzene were evolved per g-ion of yttrium:

$$3\ C_6H_5C(CH_3)_2CH_2Li + YCl_3 \rightarrow C_6H_5C(CH_3)_2C{\equiv}Y + 2\ C_6H_5C(CH_3)_3{}^+ + 3\ LiCl$$

The resulting organoyttrium compound, formed in 80—90% yield, was only soluble in solvating solvents. A certain amount of LiCl passed into the ethereal solution.

The reaction of trimethylsilylmethyllithium with $NdCl_3$ was conducted in benzene or toluene with equimolar proportions of the components and at a temperature of 20°C (the reaction does not proceed significantly at a lower temperature). On completion of the reaction the hydrocarbon solution of the organoneodymium compounds was separated from the unreacted $NdCl_3$ and the resulting LiCl. The product yield was 50—70% (Table 3). In all cases the hydrocarbon solution contained the starting organolithium compound in up to 20% of the neodymium content in the solution *, but no chlorine was present.

As it follows from Table 3, during the reaction of $NdCl_3$with Me_3SiCH_2Li, $(CH_3)_4Si$ was evolved in, up to 60% of the amount of introduced RLi. By the hydrolysis of a solution of the organoneodymium compound after removal of $(CH_3)_4Si$ the molar ratio $(CH_3)_4Si/Nd$ was determined as 1.3—1.5. No hydrogen was evolved on hydrolysis of the reaction solution which indicates the absence of reduced forms of neodymium in this compound. Tetramethylsilane containing two deuterium atoms in one methyl group and only traces of monodeuterized product were formed on hydrolysis of the resulting compound with D_2O.

These data demonstrate that in the resulting organoneodymium compound neodymium remains in its trivalent state and contains 1.3 to 1.5 trimethylsilylmethyl groups. The formation of a large amount of tetramethylsilane during the reaction points to the occurrence of disproportionation of the trimethylsilylmethyl groups, resulting in a decrease in the number of groups attached to the

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* It was not possible to completely remove the organolithium compound, even by the addition of extra $NdCl_3$.

neodymium atom. In the compound obtained the alkylsilyl groups are either bonded to one neodymium atom by a double bond (i.e. neodymium carbene complex) or by single bonds to two neodymium atoms. In both cases tetramethylsilane containing two deuterium atoms in one methyl group must be evolved upon hydrolysis by D_2O.

The resulting organoneodymium compound is rather stable in hydrocarbon solution. Keeping a solution of the organoneodymium compound in benzene or toluene for 12 hours at 50°C or for several days at 20°C did not result in a change in the concentration of neodymium and no evolution of tetramethylsilane was observed.

Experimental

Anhydrous chlorides of rare-earth metals were obtained from oxides of these metals and ammonium chloride following the procedure described in ref. 6. The resulting anhydrous trichlorides of neodymium and yttrium were stored in an apparatus which enabled sampling of the required amount of a salt under an atmosphere of argon. Benzyllithium was synthesized in two ways. In the first method benzylethyl ether was treated with metallic lithium in tetrahydrofuran to give a mixture of benzyllithium and lithium ethylate [7]. The yield of benzyllithium determined from the amount of toluene evolved upon hydrolysis, under an atmosphere of argon, of a sample with a 0.1 *M* solution of H_2SO_4 was 80—90% of the theoretical. In the second method benzyllithium free from lithium alkoxide was produced by the reaction of tribenzylantimony with ethyllithium in a benzene-pentane mixture at a temperature of 0°C [8]. The benzyllithium precipitated was dissolved in ether or tetrahydrofuran and recondensed under a vacuum from RLi. Solutions of benzyllithium were stored at below —10°C. Neophyllithium was prepared from neophylchloride (obtained according to ref. 9) and a 5-fold excess of finely cut lithium in toluene at 40°C (80—85% yield). The toluene solution of neophyllithium separated by filtration was slowly cooled to —15°C. The resulting colourless transparent crystals of neophyllithium were separated from the liquid phase and dissolved in diethyl ether; the solution was used immediately. Trimethylsilylmethyllithium was synthesized by a reported method [10].

The method for carrying out the interaction of MCl_3 with RLi is illustrated by the reaction between neodymium or yttrium trichloride and benzyllithium. Into a reactor provided with a magnetic stirrer a portion of MCl_3 and tetrahydrofuran were charged and then a solution of $LiCH_2C_6H_5$ in the same solvent was added under stirring at room temperature. After 3—4 hours, the liquid phase is removed under vacuum at room temperature and the residue was evacuated at 40°C to 10^{-2} mmHg. The amount of toluene formed during the synthesis was determined by GLC of the collected condensate. The dry residue was extracted with benzene and the solution of the organometal compound was separated by filtration through a No. 4 filter under an atmosphere of argon. After hydrolysis of the product with an oxygen-free H_2SO_4 (0.1 *M*), the content of the rare-earth metal was determined trilonometrically in the aqueous phase; the lithium content was determined using atomic absorption. The chlorine content was determined argentometrically and the amount of acid consumed during the decomposition of the organometal compound was determined alkalimetrically using methyl red as indicator. The amount of toluene formed in the hydrolysis was chromatographically determined in the hydrocarbon phase.

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