Reaction of Lanthanide(II) and Lanthanide(III) Phenylethynyl Cuprates with Acetyl Chloride

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Abstract—Praseodymium and ytterbium phenylethynyl cuprates $[(PhC\equiv C)_3Cu]_3Pr_2(THF)_6$ and $\{[(PhC\equiv C)_3Cu]_Yb(THF)_2\}_2$ react with acetyl chloride in tetrahydrofuran with elimination of phenylethynylcopper and formation of alkoxides $[PhC\equiv C-CCl(CH_3)O]_nLn$ (n = 3, Ln = Pr; n = 2, Ln = Yb). Then praseodymium alkoxide forms ester [methyl (phenylethynyl)chloromethylethanoate] and praseodymium chloride, alkoxy derivative. Itterbium alkoxide is oxidized to unsymmetrical dialkoxyitterbium chloride PhC=C-CH(CH_3)-O-Yb(Cl)-O-CCl(CH_3)C=CPh·2THF.

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Earlier [1], we reported on the methods for the preparation of cationic lanthanide complexes of new type by an example of phenylethynyl cuprates. It was of interest to compare their reactivity with the wellstudied lithium organocuprates, which found application as highly selective alkylarylating and arylating agents in organic and organometallic synthesis.

This work is devoted to the reaction of praseodymium(III) and ytterbium(II) phenylethynyl cuprates $[(PhC\equiv C)_3Cu]_3Pr_2(THF)_6$ (I) and $\{[(PhC\equiv C)_3Cu] \cdot Yb(THF)_2\}_2$ (II) with acetyl chloride in a THF

solution. As known [2], lithium organocuprates [R₂Cu]Li react with acyl halides to form ketones in high yields. In contrast, lanthanide phenylethynyl cuprates show special features in the reactions with acetyl chloride. We found that compounds I and II react with AcCl at room temperature in THF affording copper phenyl-ethynyl. As is well known [3, 4], the latter reacts with acyl halides only at heating. The lanthanide phenylethynyl derivatives formed at decomposition of the complexes I and II add at the carbonyl group of acetyl chloride, like in the case of reactions with esters [5]:

$$(PhC \equiv C)_{3}Pr + 3 CH_{3}C \xrightarrow{O}_{Cl} (PhC \equiv C - C - O)_{3}Pr$$

The resulting praseodymium alkoxy derivative shows high activity toward the acid chloride, typical for the compounds of this type [6]:

In the reaction of acetyl chloride with compound I at the molar ratio 4:1 calculated on triphenylethynylprazeodimium (III), ester IV and bis[methyl(phenyl-



Comp.	Yield,	mp, °C	Found, %					Calculated, %			
no.	%		С	Н	Cl	Ln	Formula	С	Н	Cl	Ln
IV	71–185	-	65.24	5.81	_	_	$C_{12}H_{11}ClO_2$	64.72	4.91	-	_
	mol										
V	80	205-207 (decomp.)	46.84	3.25	15.33	24.56	$C_{24}H_{24}Cl_3O_2Pr$	47.41	3.95	17.53	23.21
VI	92.8	~200 (decomp.)	40.80	4.83	17.66	26.85	$C_{18}H_{24}Cl_3O_3Pr$	40.34	4.48	19.89	26.33
VIII	92.3	140 (decomp.)	50.07	4.96	10.44	25.06	$C_{28}H_{33}Cl_2O_4Yb$	49.63	4.87	10.49	25.55

Yields and data of elemental analysis of compounds IV-VIII

ethynyl)chloromethyloxy]prazeodimiumfuranate chloride (**V**) were isolated from the reaction mixture with the yields, respectively, 0.7 and 0.8 mol per 1 mol of **III**. They were identified by elemental analysis (see the table) and by infrared spectroscopy. Methyl (phenylethynyl)chloromethylethanoate **IV** is a slightly colored liquid. IR spectrum (mineral oil), v, cm⁻¹: 1734 s, 3458 w (C=O), 1238 s (C–O), 1030 s (C–O–C), 2204 m (C≡C). The absorption bands 3458, 1238 and 1030 cm⁻¹ indicate the presence of the ester acetate group. The formed ester **IV** together with THF can

form a complex of type V with organolantanide compound [7]. Compound V is dark brown substance, moderately soluble in THF and insoluble in hexane. We failed to isolate it in crystalline state.

At the increased molar ratio of acetyl chloride to compound III of 6:1 the yield of ester IV grows to 1.85 mol per 1 mol of III. At the same time from the reaction mixture was separated methyl(phenylethynyl)chloromethyloxyprazeodimiumdifuranate dichloride VI, a brown substance insoluble in hexane.

$$(PhC \equiv C - C - O)_{3}Pr + 2 CH_{3}C \bigcirc \xrightarrow{C_{1}} PhC \equiv C - C - OCOCH_{3} + PhC \equiv C - C - O - PrCl_{2} \cdot 2THF$$

Compound **VI** was identified by elemental analysis (see the table) and the products of its hydrolysis. At the

hydrolysis of 1 mol of complex **VI** in hexane or dimetoxyetane about 0.7 mol of ketone **VII** was isolated.

$$PhC \equiv C - C - OPrCl_2(THF)_2 + H_2O \longrightarrow PhC \equiv C - C - CH_3 + PrCl_3(THF)_x$$

$$O$$

$$VII$$

Methyl phenylethynyl ketone **VII** was identified by elemental analysis and by infrared spectroscopy. IR spectrum (mineral oil), v, cm⁻¹: 1738 s (C=O), 2204 m (PhC=C).

Hydrolysis of alkoxy derivative V in hexane also led to the formation of ketone VII. Reaction of complex **II** with acetyl chloride in a molar ratio 1:4 is also accompanied by elimination of phenylethynylcopper and addition of ytterbium phenylethynyl fragment to the acyl halide carbonyl group with subsequent oxidation of the adduct to [methyl(phenylethynyl)methyloxy][methyl(phenylethynyl)chloromethyloxy]ytterbiumdifuranate chloride (**VIII**):



One of the chlorine atoms from the inner sphere of the substituent is passed to the outer sphere, obviously, with the participation of THF. The parent complex II is diamagnetic. The effective magnetic moment of the reaction product VIII is 4.3μ B, which corresponds to the state of ytterbium(III). The complex VIII was isolated from the reaction mixture in 85–90% yield and identified by elemental analysis (see the table) and the hydrolysis products. We failed to get it in the crystalline state. Hydrolysis of the complex VIII in hexane in contrast to compounds V and VI proceeds with the formation of not only the ketone VII, but also of alcohol IX:

VIII + H₂O

$$\downarrow$$
 hexane
C₆H₅C=C-CH(OH)CH₃
IX
+ C₆H₅=C-C-CH₃ + Yb(OH)Cl₂
VII

Methyl(phenylethynyl)carbinol (IX) and methyl phenylethynyl ketone were identified using IR spectroscopy by the characteristic absorption frequency O–H (3435 cm⁻¹, broad, intensive), C=O (1738 cm⁻¹, s) and PhC=C (2204 cm⁻¹, m). Phenylacetylene was not detected in the products of hydrolysis.

EXPERIMENTAL

The IR spectra were taken on spectrophotometers Perkin-Elmer-577 and SPECORD 75 IR. The samples of the compounds instable in air were prepared in a vacuum or in an argon atmosphere as suspensions in mineral oil. The melting and decomposition temperatures of the substances were determined in sealed evacuated capillaries. The values of melting and decomposition temperature are given without correction. Magnetochemical measurements were carried out by method [8].

The preparation, separation, and purification of the compounds unstable in air were carried out in evacuated sealed ampoules using the Schlenk technique. Organic solvents were purified by known methods [9]. THF and hexane were additionally distilled from sodium–benzophenone solution, degassed and placed into evacuated ampule with pre-prepared

sodium mirror. The necessary amount of solvent was collected by condensation in a vacuum.

Reaction of [(PhC=C)₃Cu]₃Pr₂(THF)₆ (I) with acetyl chloride. To a solution of 3.08 g of compound I in 15 ml of THF was added 1.07 g of acetyl chloride (molar ratio I : CH₃CClO = 1:8). At mixing the reagents the reaction mixture warmed spontaneously, and yellow precipitate of copper phenylethynyl with admixture of alkoxide V formed. For completeness of the reaction the ampule with the mixture was kept at room temperature for 5 days. The solid insoluble in THF, weighing 1.1 g, after separation, washing with THF, and drying was mineralized with nitric acid in the presence of H₂O₂. The resulting concentrations of the Cu²⁺ ions (0.32 g, yield 99%), Pr³⁺ and Cl⁻ (in molar ratio 1:3) were determined by titration. Weight of praseodymium 0.05 g (10% of the initial compound I).

THF and possible volatile components of the reaction were recondensed from the mother liquor in a vacuum into a trap cooled with liquid nitrogen. In the distillate were not detected phenylacetylene or acetyl chloride. To the oily residue in the reaction ampule hexane was condensed for precipitation of alkoxide **V**, the latter was isolated, washed with hexane, and dried to constant weight (1.67 g, yield ~80%). Brown substance, mp 205–207°C (decomp.). IR spectrum (mineral oil), v, cm⁻¹: 3050, 2900–3000 (s), 1677, 1598, 1489, 1251, 756, 697; coordinated THF 1029.

From the hexane extract obtained after removal of the solvent was isolated 0.54 g (yield 71 mol %) of methyl(phenylethynyl)chloromethylethanoate **IV**.

A suspension prepared from 0.63 g (0.001 mol) of alkoxide V, 4 ml of hexane and 1 ml of H₂O, was subjected to hydrolysis at 50°C for 1 h. As a result, 0.49 g of dark brown substance was isolated containing \sim 30% of Pr, and hexane extract of ketone VII.

Similarly the reaction of compound I (2.54 g) was carried out with acetyl chloride (1.32 g) at a molar ratio 1:12, in 15 ml of THF. Yield of ester IV was 1.15 g (1.85 mol per 1 mol of the organopraseodymium compound III). From the reaction mixture methyl-(phenylethynyl)chloromethyloxyprazeodimiumdifuranate dichloride VI was separated, yield 1.4 g (92.8%). The IR spectrum (mineral oil), v, cm⁻¹: 2900–3000 s, 1634, 1546, 1261, 1080, 803, 700, 611; coordinationally bound THF 1026.

A solution of 0.55 g of compound VI in 7 ml of THF and 2 ml of water was warmed for 2 h at 50° C.

Then the volatile products from the reaction mixture were recondenced into a trap cooled with liquid nitrogen. To the oily residue hexane was condensed. From the resulting mixture a brown precipitate (0.45 g) was isolated with the composition close to $Pr(OH)Cl_2$. 3THF. Found, %: C 33.54, H 4.32, Cl 14.82, Pr 32.15. $C_{12}H_{25}Cl_2O_4Pr$. Calculated, %: C 32.36, H 5.62, Cl 15.95, Pr 31.69.

After removal of hexane, from the filtrate 0.1 g (70%) of ketone **VII** was isolated. Found, %: C 82.62, H 6.05. $C_{10}H_8O$. Calculated, %: C 83.33, H 5.56.

Reaction of {[(PhC=C)₃Cu]Yb(THF)₂}₂ (II) with acetyl chloride. To a solution of 1.78 g of compound II in 15 ml of THF was added 0.41 g of acetyl chloride. The reaction mixture was kept at room temperature for 5 days. The change in color of the solution and precipitation of phenylethynylcopper contaminated with alkoxide VIII were observed. The precipitate was separated, washed with THF, and dried in a vacuum, weight 0.59 g. Then it was subjected to mineralization with subsequent determination of Cu²⁺, Yb³⁺, and Cl⁻ by titration method. The weight of copper was 0.16 g (yield 96.1%), and ytterbium, 0.02 g, 3.8% of its weight in the starting compound II. Molar ratio of Yb³⁺ and Cl⁻ is ~1:2.

The THF from the filtrate was recondesed into a trap cooled with liquid nitrogen. To the residue in the ampule hexane was condensed. The ytterbium chloride alkoxy derivative **VIII** precipitated. A paramagnetic shiny brown substance (4.3 μ B), mp 140°C (decomp.). After washing with hexane and drying in a vacuum it weighed 1.63 g (yield 92.3%). IR spectrum (mineral oil), v, cm⁻¹: 3050, 2900–3000 (s), 1679, 1565, 1488, 1258, 756, 690; coordinated THF 1023, 865.

To a solution of 0.68 g of the compound **VIII** in 8 ml of THF was added 2 ml of water, and the mixture was hydrolyzed at 50°C for 1 h. The formation of a yellowish-white precipitate was observed, which was separated, washed with water first, and then with THF, and dried in a vacuum; it weighed 0.4 g. Water filtrate contained about 2% of chloride ions. The composition of the precipitate corresponds to Yb(OH)Cl₂·3THF. Found, %: C 31.58, H 4.96, Cl 12.79, Yb 37.01. $C_{12}H_{25}O_4Yb$. Calculated, %: C 30.19, H 5.24, Cl 14.88, Yb 36.27.

Volatile liquid substances from the tetrahydrofuran filtrate were recondensed in a vacuum into a trap cooled with liquid nitrogen. To the oily residue hexane was condensed. The solution formed was slightly turbid. By centrifugation, the solution was separated from the solid, and hexane was recondensed from it. In the ampule remained slightly colored oil consisting of a mixture of ketone **VII** and alcohol **IX**, weight 0.27 g, which corresponds to the yield of a mixture 1.8 mol per 1 mol of initial **VIII**. Compounds **VII** and **IX** differ little in quantitative composition, the average formula of the mixture is $C_{10}H_9O$. Found, %: C 82.26, H 6.64. $C_{10}H_9O$. Calculated, %: C 82, 76, N 6,21.

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