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Reactions of Phenylethynyl Cuprates of Lanthanides with Organyl Halides and Synthesis of the Related Polyfunctional Compounds

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Abstract—Phenylethynyl cuprate complexes of lanthanides react with organyl halides RX, Ph_3CX, R_3SiX, and RC(O)X (X = Cl, I; R = alkyl) in tetrahydrofuran to give polyfunctional organic and hetero-organic compounds with high yield. The reaction mechanism is discussed.

Keywords: phenylethynyl cuprates of ytterbium(II) and praseodymium(III), organyl halide, reaction mechanism, synthesis, polyfunctional compounds

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Procedures to prepare phenylethynyl cuprates of lanthanides were developed earlier [1, 2]. In particular, homoleptic phenylethynyl compounds of ytterbium(II), europium(II), praseodymium(III), and erbium(III) reacted with phenylethynylcopper at room temperature in tetrahydrofuran (THF) to yield the corresponding cuprates with high yields (80–97%).

$$2(\mathrm{PhC{\equiv}C})_2\mathrm{Yb} + 2\mathrm{PhC{\equiv}CCu} \xrightarrow{\mathrm{THF,\ 20^oC}} \underset{\mathbf{I}}{\{[(\mathrm{PhC{\equiv}C})_3\mathrm{Cu}][\mathrm{Yb(THF)}_2]\}_2}, \qquad (1)$$

$$2(\mathrm{PhC{\equiv}C})_3\mathrm{Pr} + 3\mathrm{PhC{\equiv}CCu} \xrightarrow{\mathrm{THF,\ 20^oC}} \underset{\mathbf{II}}{[(\mathrm{PhC{\equiv}C})_3\mathrm{Cu}]_3[\mathrm{Pr}_2(\mathrm{THF})_6]}. \qquad (2)$$

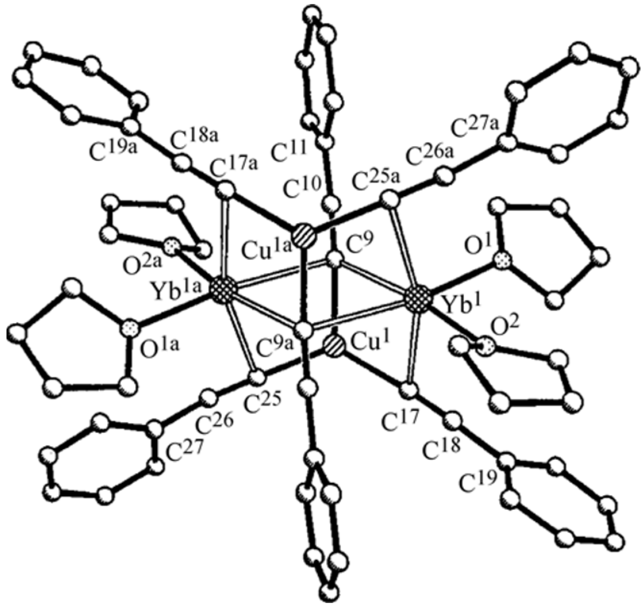
The cuprate complexes are fairly sensitive to oxygen and moisture. Their hydrolysis with excess of water in THF at room temperature gave phenylethynylcopper, phenylacetylene, and the lanthanide hydroxide with almost quantitative yields.

X-ray diffraction analysis showed that bis(tetrahydrofuran)ytterbium tris(phenylethynyl)cuprate (**I**) was a dimer (see figure).

Solution of complex **I** in THF behaved as weak electrolyte, as evidenced by measured conductivity (λ_∞ 1.2 cm^2 Ω^{-1} mol^{-1}, 20°C) and the dissociation constant (K_g 2.62 × 10^{-7}). Dissociation of complex **I** occurred according to Eq. (3).

$$\mathbf{I} \xrightleftharpoons[a]{\mathrm{THF}} 2[\mathrm{Yb(THF)}_2]^{2+} + 2[(\mathrm{PhC{\equiv}C})_3\mathrm{Cu}]^{2-} \xrightleftharpoons[b]{\mathrm{THF}} 2[\mathrm{Yb(THF)}_2]^{2+} + 4\mathrm{PhC{\equiv}C}^- + 2\mathrm{PhC{\equiv}CCu}$$
$$\xrightleftharpoons[c]{\mathrm{THF}} 2(\mathrm{PhC{\equiv}C})_2\mathrm{Yb(THF)}_2 + 2\mathrm{PhC{\equiv}CCu}. \qquad (3)$$

The reaction equilibrium was shifted towards formation of phenylethynylcopper insoluble in THF in the course of the ate-complex hydrolysis. Taking into account the ability of the parent cuprates to undergo dissociation [Eq. (3)], it was reasonable to suggest that reactions (1) and (2) were reversible; that was a factor



Molecular structure of the $\{[(PhC\equiv C)_3Cu][Yb(THF)_2]\}_2$ (**I**) complex.

explaining the instability of cuprate complexes **I** and **II** in the presence of oxygen and moisture.

In this work we studied reactions of phenylethynyl cuprates of praseodymium and ytterbium with various organyl halides (methyl iodide, benzyl chloride, triphenylmethyl chloride, trimethylsilicon iodide, and acetyl chloride) and revealed their applications to prepare polyfunctional compounds, combining various hydrocarbon fragments as well as various functional groups in the structure. Interaction of the halides with phenylethynyl cuprate of a lanthanide in THF was accompanied by change of the solution color and precipitation of phenylethynylcopper and the lanthanide halide.

The cuprate **I** reacted with methyl iodide (at the 20-fold excess of the latter) in THF at room temperature to form phenylethynylcopper, methylphenylacetylene, and ytterbium iodide (in the form of complex with THF) with high yields [Eq. (4)].

$$\mathbf{I} + CH_3I \xrightarrow{THF} \underset{96\%}{PhC\equiv CCu} + \underset{74\%}{PhC\equiv CCH_3} + \underset{86\%}{YbI_2(THF)_4}. \quad (4)$$

The almost quantitative yield of phenylethynylcopper pointed at its indifference towards methyl iodide.

Reaction (5) of the cuprate complex **I** with benzyl chloride (the molar ratio of 1 : 4 was taken according to the number of phenylethynyl groups capable of the substitution) occurred in THF at 50°C. After incubation of the reaction mixture at 90°C during 4 h, benzylphenylacetylene was isolated with yield of 83%.

$$\mathbf{I} + 4C_6H_5CH_2Cl \xrightarrow{THF} \underset{87\%}{2PhC\equiv CCu} + \underset{83\%}{4C_6H_5CH_2C\equiv CPh} + \underset{84\%}{2YbCl_2(THF)_4}. \quad (5)$$

Taking into account the ability of the parent cuprate complex towards ionization in THF and the high yield of cross-coupling products $PhC\equiv CR$ ($R = CH_3$, $C_6H_5CH_2$) in reactions (4) and (5), we concluded that the phenylethynyl carbanions formed as intermediates [Eq. (3), part *b*] could interact with the halide RX via nucleophilic substitution [Eq. (6)].

$$PhC\equiv C^- + \overset{\delta+}{R}\rightarrow\overset{\delta-}{X} \longrightarrow PhC\equiv CR + X^- \quad (6)$$

The halogenide ions X^- further recombined Eq. (7) with ytterbium cations formed according to Eq. (3).

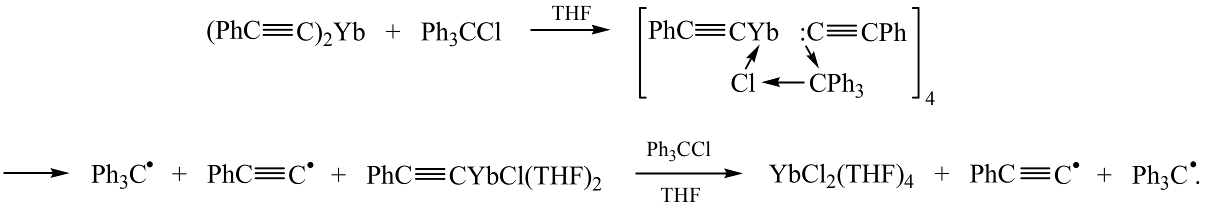
$$Yb(THF)_2^{2+} + 2X^- \xrightarrow{THF} YbX_2(THF)_4, \quad (7)$$

$$X = I, Cl.$$

Reaction of the ytterbium cuprate complex **I** with triphenylmethyl chloride occurred in a different way. The cross-coupling product triphenylmethylacetylene was not formed. ESR could detect the presence of triphenylmethyl radicals revealing the hyperfine interaction constant with protons of $a_{\mathrm{H}o}$ 0.255, $a_{\mathrm{H}m}$ 0.111, and $a_{\mathrm{H}p}$ 0.278 mT; g 2.0027. Formation of phenylacetylene was observed, further polymerizing into polyphenylacetylene.

The interaction of dimeric cuprate **I** with triphenylmethyl chloride at a molat ratio of 1 : 4 in THF at room temperature was accompanied by formation of phenylethynylcopper (91%), tetrahydrofuranates of phenylethynylytterbium chloride (71%), ytterbium chloride (18%), 1-(diphenylmethyliden)-4-(triphenylmethyl)-2,5-cyclohexadiene (63%), phenylacetylene and polyphenylacetylene (67%). Besides phenylethynylcopper, the products common with the similar reaction of bis(phenylethynyl)ytterbium with triphenylmethyl chloride [3] were formed. That suggested that the cuprate **I** acted as carrier of bis(phenylethynyl)-

ytterbium [Eq. (3), part *c*] that reacted with triphenylmethyl chloride via the radical-heterolytic mechanism to undergo stepwise dealkynylation including the stage of one-electron transfer [Eq. (8)].



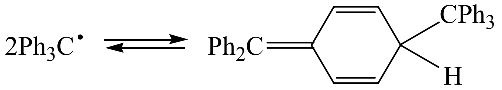
$$(PhC{\equiv}C)_2Yb + Ph_3CCl \xrightarrow{THF} \left[\begin{array}{c} PhC{\equiv}CYb\ \ :C{\equiv}CPh \\ Cl \leftarrow CPh_3 \end{array}\right]_4$$

$$\longrightarrow Ph_3C^\bullet + PhC{\equiv}C^\bullet + PhC{\equiv}CYbCl(THF)_2 \xrightarrow[THF]{Ph_3CCl} YbCl_2(THF)_4 + PhC{\equiv}C^\bullet + Ph_3C^\bullet. \quad (8)$$

Additionally, triphenylmethyl chloride could directly interact with phenylethynyl ions formed at the Eq. (3), *b* stage. However, taking into account that positive charge at methyl atom of triphenylmethyl chloride was more delocalized than that in benzyl chloride, that interaction did not lead to cross-coupling; instead, the process involving a one-electron transfer was more probable [Eq. (9)].

$$PhC{\equiv}\overset{-}{C}\!: \overset{-e^{-}}{\curvearrowright} + Cl \leftarrow \overset{\delta+}{C}Ph_3 \longrightarrow PhC{\equiv}C^\bullet + Ph_3C^\bullet + Cl^-. \quad (9)$$

Interaction of the counter-ions (chloride ions) and the ions generated via reaction (3), part *b* stipulated for formation of lanthanide compounds in the reaction. Triphenylmethyl radicals recombined to form equilibrium mixture with 1-(diphenylmethyliden)-4-(triphenylmethyl)-2,5-cyclohexadiene [Eq. (10)].



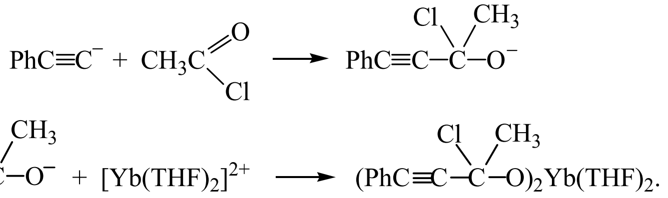
(10)

Phenylethynyl radicals could detahydrogen atoms from THF to form phenylacetylene; the latter was detected mainly in the form of polyphenylacetylene by IR spectroscopy [4].

Hetero-organic derivatives could be used as organyl halides as well [5]. In particular, interaction of trimethylsilicon iodide with phenylethynyl cuprates of ytterbium and praseodymium at the molar ratio of 4 : 1 and 6 : 1, respectively, in THF at room temperature led to separation of phenylethynylcopper [see reaction (3)]. Other products were similar to those of the reactions of phenylethynyl lanthanides $(PhC{\equiv}C)_nLn$ (Ln = Yb, Pr; $n = 2, 3$) with trimethylsilicon halogenide [6, 7]; those reactions were accompanied by formation of trimethylsilicon phenylacetylenide with yield of 91–95% (with respect to the substituted PhC≡C groups in the starting cuprate). The presence of phenylacetylene (5–10%) in the reaction mixtures was observed as well, being likely due to generation of phenylethynyl radicals as a result of the side process similar to the reactions (8) and (9).

Reactions of cuprate complexes of lanthanides with hetero-organic halides could serve as model process for production of asymmetric polyfunctional hetero-organic compounds.

Phenylethynyl cuprates of ytterbium and praseodymium reacted with acetyl and benzyl chlorides in THF at room temperature. In contrast to lithium organic cuprates $[R_2Cu]Li$ forming ketones in high yield when reacting with acyl halides [8], the interaction of lanthanides cuprate complexes with acetyl chloride resulted in formation of polyfunctional alkoxy derivatives of ytterbium and praseodymium, being the products of addition of the $(PhC{\equiv}C)_nLn$ (Ln = Yb, Pr; $n = 2, 3$ respectively) intermediates at carbonyl group of acetyl halide [9]. Further studies revealed the process mechanism in detail.



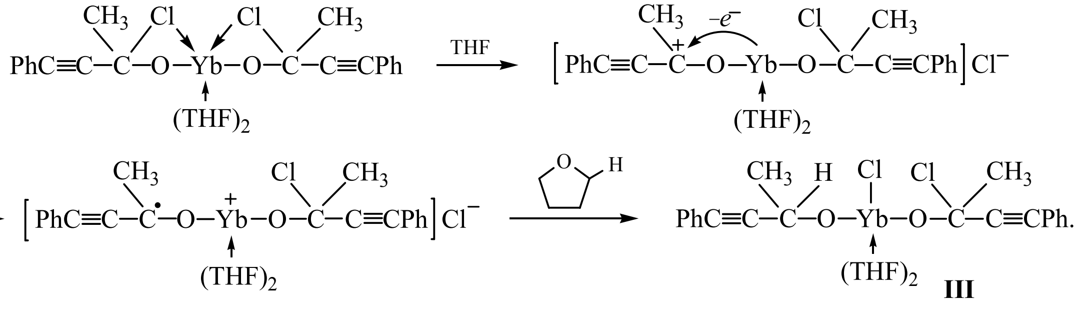
$$PhC{\equiv}C^- + CH_3C\begin{array}{l}{\nearrow}\!O\\ \searrow Cl\end{array} \longrightarrow PhC{\equiv}C{-}\overset{Cl\ \ CH_3}{C}{-}O^-$$

$$2\,PhC{\equiv}C{-}\overset{Cl\ \ CH_3}{C}{-}O^- + [Yb(THF)_2]^{2+} \longrightarrow (PhC{\equiv}C{-}\overset{Cl\ \ CH_3}{C}{-}O)_2Yb(THF)_2.$$

(11)

Reaction of the cuprate complex **I** with acetyl chloride at the molar ratio of 1 : 4 yielded phenylethynylcopper (96%) and the paramagnetic alkoxy derivative of ytterbium(III) (92%) having effective magnetic moment of 4 μ_B; according to the reference data that value was typical of Yb(III) compounds. Synthesis of the latter product is represented by scheme (11). Phenylethynyl carbanions formed in reaction (3) were added to acetyl chloride, and the so formed alkoxide ions reacted with ytterbium counter-ions.

Formation of the alkoxide was accompanied with its oxidation into the Yb(III) derivative, its molar mass being almost the same as in the previous case. Hence, we suggested that one of the chlorine atoms moved from the inner sphere of the complex into the outer sphere, according to the synchronous process (12).



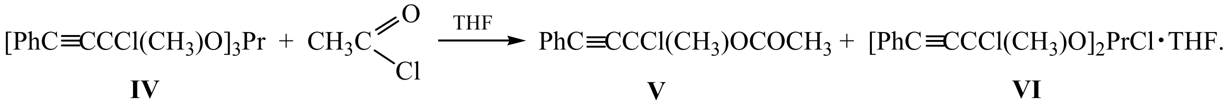
(12)

The substituent in the lanthanide alkoxide was at the same time a redox-active ligand capable of oxidation as well as of reduction. The isolated asymmetric ytterbium alkoxychloride **III**, [methyl(phenylethynyl)methyloxy][methyl(phenylethynyl)chloromethyloxy]ytterbium chloride was identified in the form of its bistetrahydrofuranate by elemental analysis and IR spectroscopy data as well as by products of its hydrolysis in THF [Eq. (13)].

$$\mathbf{III} + H_2O \xrightarrow{THF} PhC{\equiv}CCH(OH)CH_3 + PhC{\equiv}CC(O)CH_3 + Yb(OH)Cl_2. \qquad (13)$$

Methyl(phenylethynyl)carbinol and methyl(phenylethynyl)ketone were detected by IR spectroscopy using the characteristic absorption of O–H (3435 cm^{-1}, associated, broad band), C=O (1738 cm^{-1}), and C≡CPh (2204 cm^{-1}). Total yield of the products was of 1.8 mol per 1 mol of the starting complex **III**.

Samarium alkoxides react with acyl halides to form esters [10]. The corresponding ester was not observed among the products of reaction of phenylethynyl ytterbium cuprate with acetyl chloride at the molar ratio of 1 : 4. The initial acetyl chloride was exclusively consumed for the complex **III** formation. To investigate the ability of the formed complex **III** to react with acetyl halide, the reaction was run in the excess of the latter using hexa(tetrahydrofuranate)dipraseodymium tris(priphenylethynyl cuprate) **II**. Its interaction with acetyl chloride resulted in symmetric praseodymium alkoxide **IV**. At the molar ratio of the reactants of 1 : 8 the formed alkoxide reacted with excess of acetyl chloride to yield a polyfunctional ester, 1-(phenylethynyl)-1-chloroethyl ethanoate **V**, and bis[methyl(phenylethynyl)chloromethyloxy]praseodymium chloride tetrahydrofuranate **VI** with yields of 0.7 and 0.8 mol, respectively, per 1 mol of the alkoxide **IV** [Eq. (14)].



$$\underset{\mathbf{IV}}{[PhC{\equiv}CCCl(CH_3)O]_3Pr} + CH_3C\overset{\displaystyle{\nearrow}O}{\underset{\displaystyle{\searrow}Cl}{}} \xrightarrow{THF} \underset{\mathbf{V}}{PhC{\equiv}CCCl(CH_3)OCOCH_3} + \underset{\mathbf{VI}}{[PhC{\equiv}CCCl(CH_3)O]_2PrCl\cdot THF}. \qquad (14)$$

The ester **V** was identified by IR and NMR spectroscopy and elemental analysis, and structure of the alkoxide **VI** was confirmed by elemental analysis and by product of its hydrolysis [methyl(phenylethynyl)ketone PhC≡CC(O)CH_3], the composition and structure of the latter being in turn elucidated by elemental analysis and IR and NMR spectroscopy.

At the molar ratio of **II** to acetyl chloride of 1 : 12 the reaction gave phenylethynylcopper, praseodymium trichloride, and the ester **V**, yield of the latter being up to 1.85 mol per 1 mol of the starting complex **II**. A solid visually homogeneous substance soluble in THF and insoluble in hexane was isolated from the reaction mixture. Its IR spectrum contained the absorption bands characteristic of the ester **V** and the coordinated THF. Seemingly, praseodymium chloride and phenylethynylcopper formed the complex **VII**, similar to the cuprate **II** [Eq. (15)]. Unfortunately, complex **VII** could not be isolated in the crystalline state.

$$3PhC{\equiv}CCu + 2PrCl_3 \xrightarrow{THF,\ V} [(PhC{\equiv}C)Cl_2Cu]_3Pr_2{\cdot}4THF{\cdot}0.5PhC{\equiv}CCCl(CH_3)OCOCH_3. \qquad (15)$$

VII

Incubation of a mixture of complex **VII** in THF and water during 2 h at 50°C resulted in formation of the ester **V** and its partial hydrolysis into methyl(phenylethynyl)ketone.

Hence, reaction of phenylethynyl cuprates of ytterbium(II) and praseodymium(III) with acetyl chloride in THF could yield novel lanthanide alkoxides and ester **V**, depending on the reagents ratio.

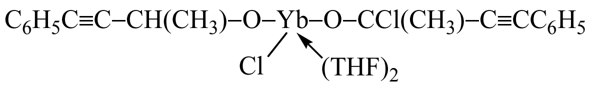
To conclude, we demonstrated that reactions of phenylethynyl cuprates of lanthanides with organyl halides could be used as potential procedures to prepare polyfunctional organic and hetero-organic compounds with high yields (see table).

EXPERIMENTAL

IR spectra were recorded using a FSM 1201 IR-Fourier spectrometer. The analyzed samples of the compounds instable in air were prepared under vacuum or under argon, the form of Vaseline oil suspension. Chromatographic analysis of the volatile compounds was performed using a Tsvet-100 chromatograph equipped with a katharometer detector (columns: 100 × 0.3 cm and 200 × 0.3 cm; filled with PEG-1500, 20% on Khezasorb AW-HMDS; carrier gas: helium). ESR spectrum of triphenylmethyl radical was recorded using a Bruker ER 2000-SRC instrument.

Preparation, purification, and isolation of all the compounds instable in air were carried out in the evacuated sealed ampoules using the Schlenk technique. Organic solvents were purified as described elsewhere [11]. THF and hexane were distilled from sodium–benzophenone solution, degassed, and put into an evacuated ampoule with sodium “mirror.” The required amount of the solvent was sampled via vacuum condensation.

Yield of polyfunctional reaction products

Compound	Yield, %
$C_6H_5CH_2C{\equiv}CC_6H_5$	84
$C_6H_5C{\equiv}C(CH_3)CClOCOCH_3$	71
$C_6H_5C{\equiv}CC(O)CH_3$	70
$(CH_3)_3SiC{\equiv}CC_6H_5$ [bp 82°C (6 mmHg)]	65
$[C_6H_5C{\equiv}C(CH_3)CClO]_2PrCl(THF)$ (decomp. 205–207°C)	80
 $C_6H_5C{\equiv}C{-}CH(CH_3){-}O{-}\underset{Cl\ \ \ \ \leftarrow (THF)_2}{Yb}{-}O{-}CCl(CH_3){-}C{\equiv}CC_6H_5$ (decomp. 140°C)	92

Reactions of complexes **I** and **II** with trimethylsilicon iodide were described elsewhere [5].

Reaction of complex I with methyl iodide. 2.1 g (14.8 mmol) of CH_3I was added to a solution of 1 g (0.73 mmol) of the ate-complex **I** in 20 mL of THF. The reaction mixture was stirred at room temperature during 3 h. Formation of yellow precipitate of $PhC{\equiv}CCu$ (mp 220°C) was observed, yield 0.23 g (1.4 mmol, 96%). After the precipitate separation off, the filtrate was condensed under vacuum into a liquid nitrogen-cooled trap. Hexane was added to the non-volatile residue, $YbI_2(THF)_4$ precipitated. Yield 0.9 g (1.26 mmol, 86.3%). Found, %: Yb 24.45; I 35.44. $C_{16}H_{32}I_2O_4Yb$. Calculated, %: Yb 24.19; I 35.52.

Methylphenylacetylene (about 70%) was detected in the hexane filtrate by GLC.

Reaction of complex I with benzyl chloride. 0.44 g (3.47 mmol) of benzyl chloride was added to a solution of 1.2 g (0.87 mmol) of **I** in 20 mL of THF. The reaction was monitored by the change of the reaction mixture color. At room temperature no visual changes occurred within 16 h. Upon heating to 50°C, the red solid complex **I** was dissolved within 2 h, and the solution turned green-yellow. The reaction mixture was incubated at 90°C during 4 h. The formed precipitate, a mixture of phenylethynylcopper and ytterbium chloride tetrahydrofuranate $YbCl_2(THF)_4$, was separated off, washed with THF, and dried. Yield 0.76 g. Part of the precipitate was mineralized, and further content of Cu^{2+}, Yb^{3+}, and Cl^- was quantified.

Another part of the precipitate was treated with hot benzene to separate phenylethynylcopper from ytterbium chloride. Cooling of the benzene solution gave yellow precipitate of phenylethynylcopper. Yield 0.25 g (1.52 mmol, 87.3%), mp 220°C. Found Cu, %: 38.98. C_8H_5Cu. Calculated Cu, %: 38.60.

THF was distilled off the filtrate, and hexane was added to the non-volatile residue to precipitate ytterbium chloride. The precipitate was separated off, washed with hexane, evaporated, and dried under vacuum. Yield 0.28 g $YbCl_2(THF)_4$. Total yield 0.78 g (1.46 mmol, 84%). Found, %: Yb 32.86; Cl 13.57. $C_{16}H_{32}Cl_2O_4Yb$. Calculated, %: Yb 32.52; Cl 13.34.

Slow evaporation of the hexane filtrate at ~5°C gave light-yellow crystals of 1,3-diphenylpropyne, molten at room temperature. Yield 0.56 g (83.9%). Found, %: C 92.39; H 6.29. $C_{15}H_{12}$. Calculated, %: C 93.75; H 6.25.

Reaction of complex I with triphenylmethyl chloride. 1.11 g (4.0 mmol) of triphenylmethyl chloride was added to a solution of 1.37 g (1.0 mmol) of complex **I** in 20 mL of THF. The reaction mixture was stirred at room temperature during 3 d. The precipitate was formed, containing phenylethynylcopper (0.3 g, 1.82 mmol, 91%) and ytterbium chloride $YbCl_2(THF)_4$ (0.2 g, 0.37 mmol, yield 18.5%). Phenylethynylcopper was recrystallized from benzene (mp 220°C). THF and the volatile reaction products were distilled off the filtrate. Phenylacetylene was detected in the distillate (yield ~7%, GLC).

Hexane was added to a residue after THF re-condensation. The formed precipitate of $PhC\equiv CYbCl\cdot ClCPh_3\cdot THF$ was washed with hexane and dried under vacuum. Yield 0.93 g (1.41 mmol, 70.5%). Found, %: Yb 24.81; Cl 11.23. $C_{31}H_{28}Cl_2OYb$. Calculated, %: Yb 26.91; Cl 10.76.

Hexane was further re-condensed in a trap cooled with liquid nitrogen, and ethanol was added to 1.0 g of the oily residue. Polyphenylacetylene precipitated (yield 0.25 g, 60%). IR spectrum, ν, cm^{-1}: 3070, 3040, 1600, 1500, 1450, 750, 700 [7].

Triphenylmethyl radicals were detected in the ethanolic solution by ESR, being in equilibrium with the Ph_6C_2 dimer. After removal of ethanol, light-yellow substance was isolated (yield 0.6 g, 2.5 mmol, 62.5%), mp 145°C.

Reaction of complex II with acetyl chloride. 1.07 g (13.6 mmol) of acetyl chloride was added to a solution of 3.08 g (1.7 mmol) of compound **II** in 15 mL of THF; the **II** : CH_3COCl molar ratio was of 1 : 8. The reagents mixing was accompanied by heating of the reaction mixture and precipitation of yellow phenylethynylcopper mixed with alkoxide **VI**. To ensure the complete reaction, the mixture was incubated at room temperature during 5 d. The precipitate insoluble in THF (1.1 g) was separated off, washed with THF, dried, and treated with nitric acid in the presence of H_2O_2. Concentrations of the formed Cu^{2+} ions (yield 0.32 g, 99%), Pr^{3+}, and Cl^- (the molar ratio of 1 : 3) were found by titration. Pr mass 0.05 g, ~10% with respect to the initial compound **II**.

The volatile reaction products were re-condensed from THF mother liquor into a trap cooled with liquid nitrogen. The distillate did not contain phenylacetylene and acetyl chloride. Hexane was added to the oily residue. The precipitated alkoxide **VI** was separated off, washed with hexane, and dried to constant mass of 1.67 g (2.7 mmol, yield ~80%). Brown solid, mp 205–207°C (decomp.). IR spectrum (Vaseline oil), ν, cm^{-1}: 3050, 2900–3000 s, 1677, 1598, 1489, 1251, 1029, 756, 697. Found, %: C 46.84; H 3.25; Cl 15.33; Pr 24.56. $C_{24}H_{24}Cl_3O_3Pr$. Calculated, %: C 47.41; H 3.95; Cl 17.53; Pr 23.21.

Removal of the solvent from the hexane extract gave 0.54 g (71 mol%) of methyl(phenylethynyl)-chloromethyl ethanoate **V**. IR spectrum (Vaseline oil), ν, cm^{-1}: 1734 s, 3458 w (C=O), 1238 s (C–O), 1030 s (C–O–C), 2204 m (C≡C). ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.58–7.38 m (2H), 7.24–7.05 d.d (1H, 76 Hz), 2.06 s (3H), 1.83 s (3H). Found, %: C 65.24; H 5.81. $C_{12}H_{11}ClO_2$. Calculated, %: C 64.72; H 4.91.

4-Phenylbut-3-yn-2-one. Suspension of 0.63 g (1.0 mmol) of alkoxide **VI**, 4 mL of hexane, and 1 mL of H_2O was stirred at 50°C during 1 h. 0.49 g of dark-brown compound was isolated, containing ~30% Pr, along with hexane extract of methyl(phenylethynyl) ketone. The ketone was purified via chromatography on a silica gel column (eluent: petroleum ether – dichloromethane, 1 : 1 v/v). ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.61–7.55 m (2H), 7.49–7.42 m (1H), 7.42–7.34 m (2H), 2.46 s (3H). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 184.75, 133.19, 130.87, 128.76, 120.06, 90.46, 88.41, 32.89.

Reaction of 1.35 mmol of compound **II** with 16.8 mmol of acetyl chloride (molar ratio of 1 : 12) was performed similarly in 15 mL of THF. The formed precipitate (0.41 g) mimeralized, and titration gave concentrations of the formed Pr^{3+}, Cu^{2+}, and Cl^{-} ions. Yields of Pr and Cu were of 0.6 and 0.8 mmol (22 amd 20% with respect to the initial cuprate **II**), respectively. Molar ratio of Cl^{-} to Pr^{3+} was above 3 : 1.

After washing out of THF and separation of the precipitate, volatile compounds were re-condensed into a trap cooled with liquid nitrogen. Hexane was added to the oily residue. Brown complex **VII** precipitated (yield 2.7 g, 1.95 mmol, 72.2%). Found, %: C 40.02; H 4.08; Cl 16.66; Cu 13.89; Pr 21.38. $C_{46}H_{52.5}\cdot Cl_{6.5}O_5Cu_3Pr_2$. Calculated, %: C 39.83; H 3.79; Cl 16.65; Cu 13.75; Pr 20.35.

Volatile compounds were re-condensed from the filtrate under vacuum at 30 °C into a trap cooled with liquid nitrogen, after washing with hexane and separation of the solid. The non-distilled liquid was ester **V** (1.15 g, 1.85 mol per 1 mol of the initial complex **II**).

A mixture of 0.55 g of compound **VII** in 7 mL of THF and 2 mL of water was heated during 2 h at 50°C. The volatile products were re-condensed into a trap cooled with liquid nitrogen. Hexane was added to the oily residue. Brown precipitate was isolated from the mixture (0.45 g), its composition being close to that of $PrCl_3\cdot 3THF$ and containing ~30% of Pr.

After removel of hexane, 0.10 g of a mixture of 4-phenylbut-3-yn-2-one and ester **V** was isolated from the filtrate, compound **V** was identified by IR and NMR spectroscopy. Formation of the ketone was due to partial hydrolysis of ester **V**.

Reaction of complex **I** with acetyl chloride was described elsewhere [9].

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REFERENCES

1. Bochkarev, L.N., Druzhkova, O.N., Zhiltsov, S.F., Zakharov, L.N., Fukin, G.K., Khorshev, S.Ya., Yanovsky, A.I., and Struchkov, Yu.T., *Organometallics*, 1997, vol. 16, no. 4, p. 500. DOI: 10.1021/om9603777.
2. Druzhkova, O.N., *Cand. Sci. (Chem.) Dissertation*, Nizhni Novgorod, 2000.
3. Zhyl'tsov, S.F., Pimanova, N.A., and Druzhkova, O.N., *Vestn. Nizhegorodsk. Univ. im. N.I. Lobachevskogo, Ser. Kimiya*, 2006, no. 1(5), p. 6.
4. Tkachenko, L.I., Lisitskaya, A.P., Roshchupkina, O.S., Smirnov, V.A., and Aldoshin, S.M., *Russ. Chem. Bull.*, 2004, vol. 53, no. 6, p. 1168. DOI: 10.1023/B:RUCB.0000042269. 52126.8d.
5. Pimanova, N.A., Dydykina, M.A., Druzhkova, O.N., and Zhyl'tsov, S.F., *Russ. J. Gen. Chem.*, 2012, vol. 82, no. 3, p. 504. DOI: 10.1134/S1070363212030231.
6. Pimanova, N.A., Zhyl'tsov, S.F., and Druzhkova, O.N., *Russ. J. Gen. Chem.*, 2003, vol. 73, no. 8, p. 1188. DOI: 10.1023/B:RUGC.0000007638.44196.89.
7. Zhyl'tsov, S.F. and Pimanova, N.A., *Vestn. Nizhegorodsk. Univ. im. N.I. Lobachevskogo, Ser. Kimiya*, 2004, no. 1(4), p. 13.
8. Posner, G.H. and Whitten, C.E., *Tetrahedron Lett.*, 1970, vol. 11, no. 53, p. 4647. DOI: 10.1016/S0040-4039(00)89398-3.
9. Zhyl'tsov, S.F., Dydykina, M.A., and Druzhkova, O.N., *Russ. J. Gen. Chem.*, 2010, vol. 80, no. 9, p. 1767. DOI: 10.1134/S1070363210090082.
10. Sankhla, B.S. and Kapoor, R.N., *Canad. J. Chem.*, 1966, vol. 44, no. 6, p. 1231. DOI: 10.1139/v66-322.
11. Weissberger, A., Proskauer, E., Riddic, J., and Toops, E., *Organic Solvents*, New York: Interscience Publishers, 1955.