ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 8, pp. 1910–1919. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © S.F. Zhiltsov, O.N. Druzhkova, N.A. Pimanova, V.M. Makarov, 2015, published in Zhurnal Obshchei Khimii, 2015, Vol. 85, No. 8, pp. 1355–1364.

Chemistry of Homoleptic Phenylethynyl Complexes of Lanthanides

S. F. Zhiltsov, O. N. Druzhkova, N. A. Pimanova, and V. M. Makarov

Kozma Minin Nizhny Novgorod State Pedagogical University, ul. Ulyanova 1, Nizhny Novgorod, 603950 Russia
e-mail: chemical@mininuniver.ru

Received April 9, 2015

Abstract—Methods to prepare homoleptic phenylethynyl complexes of lanthanides, the products properties and possible applications in organoelement synthesis of polyfunctional compounds are discussed.

Keywords: homoleptic complex, phenylethynyl, lanthanide, complex, polyfunctional compound, synthesis, catalytic activity

DOI: 10.1134/S1070363215080198

Homoleptic phenylethynyl compounds of lanthanides $(PhC{\equiv}C)_2Ln$ and $(PhC{\equiv}C)_3Ln$ (Ln standing for a lanthanide) are notable for the presence of the reactive metal–carbon bond and the unsaturated ligand, the latter acting as the second active center of the molecule; hence, such compounds are bifunctional reagents suitable for various organoelement syntheses. Even though certain representatives of this class have been known for long [1], their wide application has been limited by the absence of the convenient preparation methods.

This work summarizes the preparation methods of the phenylethynyl compounds of lanthanides(II, III); their properties and application in the synthesis of polyfunctional organic and organoelement derivatives are discussed.

Phenylethynyl derivatives of lanthanides(II) have been described for samarium, europium, and ytterbium. They have been prepared for the first time via transmetalation of organomercury compounds [Eq. (1)] [2, 3] and the acid-base interaction of phenylacetylene with bis(pentafluorophenyl)- or bis(*tert*-butylethynyl)-ytterbium [Eq. (3)] [2].

$$(PhC{\equiv}C)_2Hg + Ln \rightarrow (PhC{\equiv}C)_2Ln + Hg\,, \quad Ln = Eu, Yb; \tag{1}$$

$$R_2Yb + PhC{\equiv}CH \rightarrow (PhC{\equiv}C)_2Yb + 2RH, \quad R = C_6F_5,\ t\text{-}C_4H_9C{\equiv}C. \tag{2}$$

We have developed a procedure to prepare phenylethynyl derivatives of lanthanides(III) via the interaction of tris[bis(trimethylsilyl)amides] of lanthanides with phenylacetylene at the molar ratio of 1 : 3 at room temperature in toluene or hexane [Eq. (3)] [4].

$$[(Me_3Si)_2N]_3Ln + 3PhC{\equiv}CH \rightarrow (PhC{\equiv}C)_3Ln + 3(Me_3Si)_2NH, \tag{3}$$
$$Ln = Pr, Sm, Eu, Gd, Tb, Er, Yb.$$

Phenylethynyl derivatives of lanthanides(III) were isolated with yields of 70–95% and identified by means of elemental analysis and IR spectroscopy. The products were dark-colored pyrophoric amorphous compounds decomposing upon heating above 200°C, soluble in 1,2-dimethoxyethane, tetrahydrofuran, and benzene, readily hydrolysable to give phenylacetylene and $Ln(OH)_3$. IR spectra of the prepared $(PhC{\equiv}C)_3Ln$ were similar to that of tri(phenylethynyl)scandium [5].

A drawback of the described synthesis of the homoleptic lanthanide compounds was a labor intensive stage of preparation of the starting silylamide derivatives. In detail, it consisted of four stages: preparation of butyllithium, its interaction with hexamethyldisilazane to form lithium bis(trimethylsilyl)amide, reaction of the latter with anhydrous lanthanide chloride, and the intermediate product reaction with phenylacetylene.

Reactions of lanthanides iodides LnI_2 and LnI_3 with phenylethynylsodium in THF [Eqs. (4), (5)] is a more convenient and universal method to prepare the phenylethynyl derivatives of lanthanides(II, III) [6].

Table 1. Yields and magnetic moments of phenylethynyl complexes of lanthanides prepared via reactions (3) and (4)

Compound	Yield, %	Color	μ_{eff}, μ_B
$(PhC{\equiv}C)_2Sm(THF)_2$[a]	88	Dark-brown	
$(PhC{\equiv}C)_2Yb(THF)$	85	Dark-violet	0
$(PhC{\equiv}C)_3Pr(THF)$	87	Dark-brown	3.52
$(PhC{\equiv}C)_3Nd(THF)$	89	Brown	3.67
$(PhC{\equiv}C)_3Dy(THF)$	91	Dark-brown	10.19
$(PhC{\equiv}C)_3Ho(THF)$[b]	90	Brown	10.28
$(PhC{\equiv}C)_3Er(THF)_2$[c]	92	Dark-brown	

[a] IR spectrum, ν, cm^{-1}: 3030 m, 2140 w, 2025 w, 1940 w, 1880 w, 1800 w, 1585 m, 1475 s, 1435 s, 1190 w, 1175 w, 1155 w, 1065 m, 1025 s, 915 m, 755 s, 690 s, 545 m, 490 m; 1040 m, 840 m (coordinated THF). [b] IR spectrum, ν, cm^{-1}: 3030 m, 2160 w, 2030 w, 1940 w, 1870 w, 1800 w, 1585 m, 1780 s, 1440 s, 1190 w, 1175 w, 1155 w, 1070 m, 1025 s, 960 w, 910 m, 755 s, 690 s, 535 m, 495 m; 1035 m, 870 m (coordinated THF). [c] IR spectrum, ν, cm^{-1}: 3050 m, 2170 w, 2115 w, 2045 m, 1945 w, 1880 w, 1800 w, 1590 m, 1480 s, 1195 w, 1175 w, 1155 w, 1070 m, 1035 m, 1026 s, 970 w, 910 m, 840 w, 755 s, 690 s, 610 w, 550 w, 516 m.

$$\mathrm{LnI_2(THF)_4 + 2PhC{\equiv}CNa} \xrightarrow[20°\mathrm{C}]{\mathrm{THF}} \mathrm{(PhC{\equiv}C)_2Ln(THF)}_x + 2\mathrm{NaI}, \tag{4}$$

$$\mathrm{Ln = Sm, Yb};\ x = 1, 2;$$

$$\mathrm{LnI_3(THF)_3 + 3PhC{\equiv}CNa} \xrightarrow[20°\mathrm{C}]{\mathrm{THF}} \mathrm{(PhC{\equiv}C)_3Ln(THF)}_x + 3\mathrm{NaI}, \tag{5}$$

$$\mathrm{Ln = Pr, Nd, Dy, Ho, Er};\ x = 1, 2.$$

Using of lanthanides iodides instead of the chlorides resulted in more complete substitution of the halogen with phenylethynyl moiety.

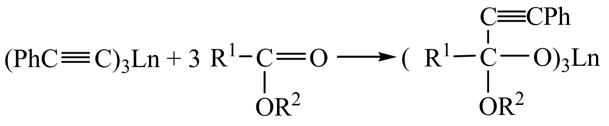
Table 1 lists the yields and compositions of the phenylethynyl derivatives of lanthanides in the form of the complexes with THF incubated in vacuum during 1.5–2 h at 40–50°C to constant mass. The products were characterized by means of elemental analysis, IR spectroscopy, and magnetochemistry.

The prepared phenylethynyl complexes were dark solids decomposing above 200°C, extremely sensitive to air moisture and oxygen, readily soluble in THF and benzene, and insoluble in hexane. The $(PhC{\equiv}C)_2Yb\cdot(THF)$ compound was diamagnetic, corresponding to the +2 oxidation state of ytterbium. UV spectrum of the $(PhC{\equiv}C)_2Sm(THF)_2$ complex solution in THF contained the absorption bands with maximums at 345 and 415 nm, typical of Sm^{2+} [7]. The μ_{eff} values for $(PhC{\equiv}C)_3Ln(THF)_x$ (Table 1) corresponded to the +3 oxidation state of the lanthanides. IR spectra of the phenylethynyl compounds of lanthanides(II, III) were practically identical and confirmed the presence of the PhC≡C groups and the coordinated THF molecules.

Hydrolysis of the phenylethynyl complexes in THF at room temperature resulted in hydrogen formation along with phenylacetylene, accompanied by the metal oxidation state to +3.

Organometallic compounds containing the polar metal–carbon bonds have been widely used in organic synthesis. They act as alkylating or arylating agents towards carbonyl compounds and organoelement halides. In order to prepare polyfunctional organic compounds, we performed the reactions of phenylethynyl derivatives of the lanthanides with esters and organoelement halides R_3EX and Ph_4SbX (E = C, Si, Ge, or Sn; R = CH_3 or C_6H_5; X = Cl, Br, or I).

Reactions (6) of tris(phenylethynyl)lanthanides with esters (ethyl acetate and methyl isobutyrate) occurred at room temperature via the nucleophilic addition of the ligand at the carbonyl group of the ester to form novel polyfunctional alkoxy derivatives of lanthanides (Table 2) [8]; the products were isolated with yields of 80–90%.



$$(\mathrm{PhC{\equiv}C})_3\mathrm{Ln} + 3\,\mathrm{R^1{-}\underset{OR^2}{C}{=}O} \longrightarrow (\mathrm{R^1{-}\overset{C\equiv CPh}{\underset{OR^2}{C}}{-}O})_3\mathrm{Ln} \tag{6}$$

Ln = Pr, Sm, Tb; $R^1 = CH_3, (CH_3)_2CH$; $R^2 = CH_3, C_2H_5$.

Alkoxy derivatives of the lanthanides were dark colored compounds decomposing at 220–230°C, unstable in air, soluble in THF, 1,2-dimethoxyethane, and toluene. Elemental analysis data for the prepared complexes are given in Table 2. Their IR spectra contained the absorption bands characteristic of the PhC≡C bonds (2140–2150 cm^{-1}), the absorption band of the carbonyl group (≈1720 cm^{-1}) being absent.

The reaction of aldehydes and ketones with phenylethynyl derivatives of lanthanides(II) [9] yielded the

Table 2. Yields and elemental analysis data for polyfunctional lanthanides alcoholates

Compound	Yield, %	Found, %			Formula	Calculated, %		
		C	H	Ln		C	H	Ln
$[CH_3(C_2H_5O)C(C{\equiv}CPh)O)]_3Pr$	89	61.54	5.67	20.08	$C_{36}H_{39}O_6Pr$	61.02	5.51	19.91
$[CH_3(C_2H_5O)C(C{\equiv}CPh)O)]_3Tb$	87	60.01	5.62	21.30	$C_{36}H_{39}O_6Tb$	59.50	5.37	21.90
$[(CH_3)_2CH(CH_3O)C(C{\equiv}CPh)O)]_3Pr$	81	62.75	6.12	19.10	$C_{39}H_{45}O_6Pr$	62.40	6.00	18.80
$[(CH_3)_2CH(CH_3O)C(C{\equiv}CPh)O)]_3Sm$	84	62.01	6.10	19.98	$C_{39}H_{45}O_6Sm$	61.63	5.93	19.80

Table 3. Products of reactions of bis(phenylethynyl)ytterbium $(PhC{\equiv}C)_2Yb(THF)$ with organoelement halides R_3ECl in the 1 : 2

Exp. no.	R_3ECl (mol)	Reaction products, mol per 1 mol of $(PhC{\equiv}C)_2Yb(THF)$				
		$PhC{\equiv}CER_3$	$PhC{\equiv}CYbCl(THF)_2$	$YbCl_2(THF)_4$	Ph_6C_2	$PhC{\equiv}CH$
1	Ph_3CCl (0.0042)	–	0.67	0.12	0.95	0.71
2	$(CH_3)_3SiCl$ (0.0036)	1.73	0.20	0.67	–	–
3	Ph_3GeCl (0.0029)	1.36	0.73	0.17	–	–
4	Ph_3SnCl (0.0020)	1.35	0.40	0.39	–	–

alkoxides, further hydrolyzed into the alcohols. The hydrolysis was accompanied by oxidation of the lanthanides atoms and formation of the $Ln(OH)_3$ hydroxide, and the evolving hydrogen favored the ketones transformation into the pinacones.

Bis(phenylethynyl)ytterbium(II) tetrahydrofuranate $(PhC{\equiv}C)_2Yb(THF)$ prepared via the reaction (4) reacted with triphenylmethyl, trimethylsilicon, triphenylgermanium, and triphenyltin chlorides at the molar ratio of 1 : 2 in THF at room temperature. The reagents mixing was accompanied by the solution discoloration and precipitate formation. Products of the reactions (7) and (8) are given in Table 3.

$$(PhC{\equiv}C)_2Yb(THF) + R_3ECl \xrightarrow{THF} R_3EC{\equiv}CPh + PhC{\equiv}CYbCl(THF)_2, \quad (7)$$

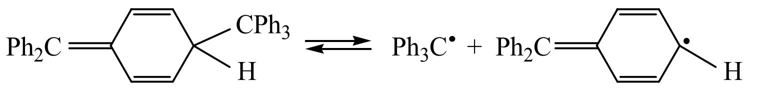
$$(PhC{\equiv}CYbCl(THF)_2 + R_3ECl \xrightarrow{THF} R_3EC{\equiv}CPh + YbCl_2(THF)_4, \quad (8)$$

$$E = Si, Ge, Sn;\ R = CH_3, C_6H_5.$$

The organolanthanide compound was capable of the sequential substitution of the phenylethynyl ligand with chlorine atoms. However, the nature of the interaction with triphenylmethyl chloride was substantially different from that of the similar reactions with R_3ECl (E = Si, Ge, or Sn), the latter yielding the non-symmetrical derivatives of silicon, germanium, or tin $R_3EC{\equiv}CPh$ as the major products (Table 3, exp. 2–4).

The $R_3EC{\equiv}CPh$ compounds were identified by means of elemental analysis and IR spectroscopy.

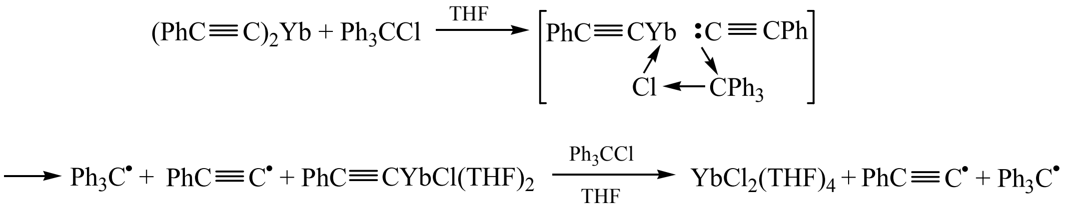
The interaction of bis(phenylethynyl)ytterbium with triphenylmethyl chloride occurred quantitatively to form phenylacetylene and 1-(diphenylmethylidene)-4-triphenylmethyl-2,5-cyclohexadiene (Ph_6C_2) being in the equilibrium (9) with triphenylmethyl radicals.



(9)

Triphenylmethyl radicals were identified by means of EPR with the hyperfine interaction constants with the protons of $a_{\mathrm{H}}^{o} = 0.255$, $a_{\mathrm{H}}^{м} = 0.111$, $a_{\mathrm{H}}^{n} = 0.278$ mT; $g = 2.0027$. Those parameters coincided with the reference data [11].

The experimental data suggested that the interaction of bis(phenylethynyl)ytterbium with triphenylmethyl chloride occurred via the radical-heterolytic mechanism [12]. The stepwise dealkynylation involved the one electron transfer stages [Eq. (10)].



$$(\mathrm{PhC{\equiv}C})_2\mathrm{Yb} + \mathrm{Ph_3CCl} \xrightarrow{\mathrm{THF}} \left[\mathrm{PhC{\equiv}CYb} \;\; \mathbf{:}\mathrm{C{\equiv}CPh} \;\; \mathrm{Cl} \leftarrow \mathrm{CPh_3}\right]$$

$$\longrightarrow \mathrm{Ph_3C^{\bullet}} + \mathrm{PhC{\equiv}C^{\bullet}} + \mathrm{PhC{\equiv}CYbCl(THF)_2} \xrightarrow[\mathrm{THF}]{\mathrm{Ph_3CCl}} \mathrm{YbCl_2(THF)_4} + \mathrm{PhC{\equiv}C^{\bullet}} + \mathrm{Ph_3C^{\bullet}} \qquad (10)$$

Phenylethynyl and triphenylmethyl radicals did not recombine to form phenyl(tripenylmethyl)acetylene. Phenylethynyl radicals interacted with THF to be converted into phenylacetylene, and the stable triphenylmethyl radicals gave the recombination product.

In contrast to bis(phenylethynyl)ytterbium, the similar compounds of lanthanides(III) prepared via the reaction (5) almost did not interact with triphenylmethyl chloride at room temperature. Tris(phenylethynyl)praseodymium and -dysprosium $(\mathrm{PhC{\equiv}C})_3\mathrm{Ln}\cdot(\mathrm{THF})$ interacted with $\mathrm{Ph_3CCl}$ (the molar ratio of 1 : 3) in THF at 50°C within 3.5 h to form (with respect to 1 mol of the starting lanthanide compound) 1.42 or 0.82 mol of 1-diphenylmethylidene-4-triphenylmethyl-2,5-cyclohexadiene along with 0.97 mol of phenylethynylpraseodymium dichloride or 0.98 mol of bis(phenylethynyl)dysprosium chloride, respectively. The reactions were accompanied by substitution of one or two of the phenylethynyl groups. Phenylacetylene was detected in the oligomer form rather than as monomer in the reaction products. IR spectrum of the compound isolated from the reaction mixture corresponded to that of poly(phenylacetylene) prepared via polymerization of phenylacetylene in toluene in the presence of $\mathrm{MoCl_5}$ as catalyst [13]; IR spectrum, ν, $\mathrm{cm^{-1}}$: 3040 m, 3070 m (CH); 1600 s ($\mathrm{C{=}C_{arom}}$); 1500 s, 1450 s (C=C); 750 s (CH); 700 s ($\mathrm{CH_{arom}}$).

Hence, phenylethynyl complexes of ytterbium, praseodymium, and dysprosium interacted with triphenylmethyl chloride via the same mechanism involving generation of the free radicals.

Reactions of the phenylethynyl derivatives of praseodymium(III) and dysprosium(III) with silicon, germanium, and tin alkyl(aryl)halides in THF at room temperature occurred slower than in the case of the similar ytterbium(II) compound. The major products of those reactions were phenylacetylenides $\mathrm{R_3EC{\equiv}CPh}$ (E = Si, Ge, or Sn; R = $\mathrm{CH_3}$ or $\mathrm{C_6H_5}$) and the hardly separable mixtures of lanthanide halides $(\mathrm{PhC{\equiv}C})_2\mathrm{LnX}\cdot(\mathrm{THF})_n$, $\mathrm{PhC{\equiv}CLnX_2(THF)}_n$, and $\mathrm{LnX_3(THF)_3}$ (Ln = Pr or Dy; X = Cl or I). They were isolated from the reaction mixtures after 3 days (room temperature) with high yields (Table 4). In the cases of the reactions with triphenylgermanium and triphenyltin chlorides, hexaphenyldigermanium and hexaphenylditin were formed in 5–10% yield. Likely, the heterolytic exchange via reactions (7) and (8) were accompanied by side generation of triphenylgermyl and triphenylstannyl radicals, similar to the reaction (10), followed by their recombination. The reaction products were identified using the elemental analysis (C, H, Hlg, and metal) and IR spectroscopy data.

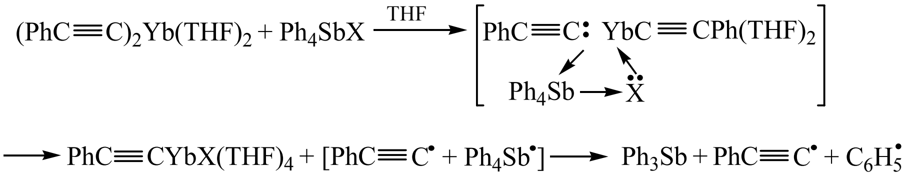
From the data in Table 4 it followed that the yield of the cross-coupling product $\mathrm{R_3EC{\equiv}CPh}$ depended on the nature of the heteroatom E. In the case of the organosilicon halides, the product yield was higher than that in the cases of germanium and tin compounds (cf. exp. 1, 4, 5 and 2, 3, 6, 7). The reaction occurred under mild conditions without any catalyst.

Bis(phenylethynyl)ytterbium $(\mathrm{PhC{\equiv}C})_2\mathrm{Yb(THF)_2}$ readily reacted with tetraphenylantimony halides (in the molar ratio of 1:2) in THF at room temperature to form triphenylantimony, benzene, phenylacetylene, phenylethynylytterbium halide $\mathrm{PhC{\equiv}CYbX(THF)_4}$, and $\mathrm{YbX_2(THF)_4}$ [14]. The high yields of benzene and phenylacetylene pointed at the participation of phenyl and phenylethynyl radicals in the reaction (11), occurring via the one electron transfer mechanism.

Table 4. Yields of major products of reactions of organic derivatives of praseodymium(III) and dysprosium(III) with organic halides of the IVA group elements

Exp. no.	Reaction (reactants ratio)	Yield, mol[a]	
		$R_3EC{\equiv}CPh$	mixture of lanthanide halides (yield with respect to Ln)
1	$(PhC{\equiv}C)_3Pr(THF) + (CH_3)_3SiI$ (1 : 3)	2.54	0.92
2	$(PhC{\equiv}C)_3Pr(THF) + Ph_3GeCl$ (1 : 3)	1.05	0.92
3	$(PhC{\equiv}C)_3Pr(THF) + Ph_3SnCl$ (1 : 3)	1.54	0.92
4	$(PhC{\equiv}C)_3Dy(THF) + (CH_3)_3SiCl$ (1 : 3)	2.43	0.85
5	$(PhC{\equiv}C)_3Dy(THF) + (CH_3)_3SiI$ (1 : 3)	2.41	0.84
6	$(PhC{\equiv}C)_3Dy(THF) + Ph_3GeCl$ (1 : 3)	1.45	0.84
7	$(PhC{\equiv}C)_3Dy(THF) + Ph_3SnCl$ (1 : 3)	1.93	0.80

[a] With respect to 1 mol of the lanthanide organic compound.



$$(PhC{\equiv}C)_2Yb(THF)_2 + Ph_4SbX \xrightarrow{THF} \left[PhC{\equiv}C\!:\ YbC{\equiv}CPh(THF)_2 \quad Ph_4Sb \rightarrow \ddot{X}\right]$$

$$\longrightarrow PhC{\equiv}CYbX(THF)_4 + [PhC{\equiv}C^{\bullet} + Ph_4Sb^{\bullet}] \longrightarrow Ph_3Sb + PhC{\equiv}C^{\bullet} + C_6H_5^{\bullet} \qquad (11)$$

X = Cl, Br, I.

Recombination of the radicals pair did not occur, since it gave the unstable compound. The metal-centered radical was stabilized via elimination of phenyl radical to form triphenylantimony. Phenylethynylytterbium halide was partially subject to further dealkynylation to form the ytterbium halide $YbX_2(THF)_4$.

The reactions of organic lanthanides compounds with organoelement halides R_3EX and Ph_4SbX (E = Si, Ge, or Sn; X = Cl, Br, or I) gave the non-symmetric organoelement compounds $R_3EC{\equiv}CPh$ and the mixed organolanthanide compounds $PhC{\equiv}CYbX(THF)_n$, $PhC{\equiv}CPrX_2(THF)_4$, and $(PhC{\equiv}C)_2DyX(THF)_4$ with high yields; the products properties are given in Table 5.

The organotin hydrides R_3SnH were readily added at the organoelement monoacetylenides $R'_3EC{\equiv}CH$ (E = Si, Ge, or Sn) to form the organobielement ethylene derivatives [Eq. (12)] at the equimolar ratio of the reagents [16]. Triphenyltin hydride reacting with phenylacetylene at the 2 : 1 ratio gave predominantly 2,2-bis(triphenylstannyl)-1-phenylethane [Eq. (13)] [17].

$$R_3SnH + R'_3EC{\equiv}CH \rightarrow R_3Sn{-}CH{=}CH{-}ER'_3, \qquad (12)$$

$$PhC{\equiv}CH + 2Ph_3SnH \rightarrow PhCH_2{-}CH(SnPh_3)_2. \qquad (13)$$

Phenylethynyllanthanides were subject to hydrostannylation upon the interaction with triphenyltin hydride in THF at 20–50°C in the absence of any catalyst. The reaction occurred in several stages depending on the molar ratio of the reactants. The vinyl tin-containing lanthanide derivative (mono adduct) was formed at the 1 : 3 ratio [Eq. (14)]. Further addition of 3 mol of Ph_3SnH to the mono adduct or the reaction with triphenyltin hydride at the 1 : 6 ratio gave rise to the products of complete addition (bis adducts **A**) [Eq. (15)].

$$(PhC{\equiv}C)_3Ln + 3Ph_3SnH \xrightarrow{THF} [PhCH{=}C(Ph_3Sn){-}]_3Ln, \qquad (14)$$

$$(PhC{\equiv}C)_3Ln + 6Ph_3SnH \rightarrow \underset{\mathbf{A}}{[PhCH_2{-}C(Ph_3Sn)_2{-}]_3Ln}, \qquad (15)$$

Ln = Pr, Tb.

The structure of the bis adduct could not be confirmed; the formation of the isomer $[Ph(Ph_3Sn)CHCH\cdot(SnPh_3)]_3Ln$ could not be excluded. The bis adduct **A** structure could not be determined via analysis of its hydrolysis products as well. Apparently, the organotin derivatives formed via the hydrolysis were subject to splitting in the alkaline medium [18] to yield hexaphenylditin and the non-identified compounds. The lanthanide hydroxide yield was quantitative.

The vinyl derivatives of the lanthanides were isolated with yield of 85–90%; they were dark-colored

Table 5. Melting points and elemental analysis data for polyfunctional organoelement compounds

Compound	Appearance	mp (decomp.), °C	Found, %				Formula	Calculated, %			
			C	H	Hlg	Ln		C	H	Hlg	Ln
$(CH_3)_3SiC{\equiv}CPh$	Yellow oily liquid	82[a] (6 mmHg)	75.36	7.90	–	–	$C_{11}H_{14}Si$	75.86	8.05	–	–
		[15]			–	–	$C_{26}H_{20}Ge$	74.13	4.94	–	–
$Ph_3GeC{\equiv}CPh$[b]	White crystals	84	74.10	5.04	–	–	$C_{26}H_{20}Sn$	69.23	4.44	–	–
$Ph_3SnC{\equiv}CPh$[c]	Colorless crystals	62	69.53	4.39							
$PhC{\equiv}CYbCl(THF)_2$[d]	Yellow amorphous compound	288	42.44	4.47	7.08	37.60	$C_{16}H_{21}ClO_2Yb$	42.34	4.63	7.83	38.15
$PhC{\equiv}CYbBr(THF)_4$	Light-brown compound	188			11.08	24.18	$C_{24}H_{37}BrO_4Yb$			12.46	26.95
$PhC{\equiv}CYbI(THF)_4$	Red-brown compound	250			18.25	24.23	$C_{24}H_{37}IO_4Yb$			18.43	25.11
$PhC{\equiv}CPrCl_2(THF)_4$	Light-brown compound	160			11.18	23.33	$C_{24}H_{37}Cl_2O_4Pr$			11.81	23.46
$(PhC{\equiv}C)_2DyCl(THF)_4$	Brown compound	240			4.93	23.10	$C_{32}H_{42}ClO_4Dy$			5.16	23.62

[a] Boiling point. [b] IR spectrum, ν, cm^{-1}: 3040 s, 2165 s (C≡C), 1480 s, 1425 m, 1085 s, 1065 w, 1020 w, 995 m, 730 s, 690 s, 460 s (Ph_3Ge). [c] IR spectrum, ν, cm^{-1}: 2125 s (C≡C), 1460 s, 1410 s, 1060 s, 1010 s, 985 s, 715 s, 685 s, 440 s (Ph_3Sn). [d] IR spectrum, ν, cm^{-1}: 2200 m (C≡C), 2050 m (C≡C), 1880 w, 1790 w, 1445 s, 1380 s, 1300 s, 1070 m, 1025 s, 995 s, 730 m, 670 s, 490 m; 1040 m, 840 m (coordinated THF).

powders, decomposing in the evacuated capillary without melting above 190°C, unstable in air, readily soluble in THF and 1,2-dimethoxyethane, and practically insoluble in hexane.

The bis adducts were isolated with yields of 86–90%; they were light-colored compounds, decomposing without melting above 215°C, readily soluble in THF and 1,2-dimethoxyethane and poorly soluble in hexane.

The products of the phenylethynyllanthanides hydrostannylation were identified by means of elemental analysis (Table 6) and IR spectroscopy. In particular, the IR spectra of the products contained the absorption bands typical of the Ph_3Sn group (3050, 1420, 1070, 730, 695, and 450 cm^{-1}). IR spectra of the mono adducts contained the absorption band assigned to the vinyl C=C bond at 1620 cm^{-1}. Formation of the bis adducts was confirmed by the absence of the bands of the C≡C, C=C (vinyl), and Sn–H (1800–1875 cm^{-1}) stretching in the IR spectra.

Hence, the phenylethynyl derivatives of the lanthanides were highly reactive in the interactions via the metal–carbon bond as well as at the ethynyl ligand, the latter being hydrostannilated to form the multinuclear organometallic compounds containing the lanthanide and tin atoms.

The multinuclear organometallic complexes were formed via the interaction of the phenylethynyl derivatives of the lanthanides with phenylethynylcopper in THF at room temperature [Eqs. (16), (17)] as well. Yield of the phenylethynyl cuprate complexes of lanthanides(II, III) was close to quantitative (81–97%).

$$(PhC{\equiv}C)_2Ln + PhC{\equiv}CCu \xrightarrow{THF} [(PhC{\equiv}C)_3Cu][Ln(THF)_2], \quad (16)$$

$$Ln = Yb, Sm.$$

$$2(PhC{\equiv}C)_3Ln + 3PhC{\equiv}CCu \xrightarrow{THF} [(PhC{\equiv}C)_3Cu]_3[Ln_2(THF)_6], \quad (17)$$

$$Ln = Pr, Er.$$

Chemistry of those complexes has been discussed in [12].

The phenylethynyl derivatives of praseodymium, samarium, europium, erbium, and ytterbium revealed the catalytic activity towards the low-temperature polymerization of methyl methacrylate. The monomer conversion was of 80% after 1 day incubation of the reaction mixture containing methyl methacrylate and 3.1 wt% of tris(phenylethynyl)praseodymium in a sealed ampoule at room temperature. The activity of

Table 6. Elemental analysis data for the products of hydrostannylation

Compound	Found, %			Formula	Calculated, %		
	C	H	Ln		C	H	Ln
$[PhCH{=}C(SnPh_3)]_3Pr$	62.10	4.38	9.05	$C_{78}H_{63}PrSn_3$	62.57	4.21	9.42
$[PhCH{=}C(SnPh_3)]_3Tb$	61.05	4.54	9.79	$C_{78}H_{63}Sn_3Tb$	61.82	4.16	10.50
$[PhCH_2C(SnPh_3)_2]_3Pr$	63.10	4.60	4.93	$C_{132}H_{111}PrSn_6$	62.17	4.36	5.53
$[PhCH_2C(SnPh_3)_2]_3Tb$	62.03	4.73	5.69	$C_{132}H_{111}Sn_6Tb$	61.73	4.36	6.20

the lanthanide derivatives towards polymerization was revealed for the monomers prone of the radical and the anionic initiation (methyl methacrylate and acrylonitrile). The co-polymerization of acrylonitrile and methyl methacrylate in the presence of $(PhC{\equiv}C)_3Pr$ as catalyst yielded the polymer enriched by acrylonitrile, pointing at the anionic mechanism of initiation. The lanthanides derivatives acted as both a catalyst and a co-monomer (owing to the presence of the phenylethynyl group), leading to formation of a cross-linked polymer enriched with lanthanide; the so formed polymer was insoluble in acetone. Incorporation of the lanthanide in the polymer resulted in its biological activity and the X-ray protective properties (Table 7).

The 150×150 mm specimens of the polymeric glass were tested for the X-ray [$\lambda(CuK_\alpha)$ 0.154 nm] absorption using a Dron-2 diffractometer in the BSV-10S50kV-20 mA tube operation mode. The mass absorption coefficient μ/ρ revealed the relative reduction of the radiation intensity after passing through a layer of the material containing 1 g of the substance per 1 cm^2. The half-absorption thickness $d_{0.5}$ was equal to the thickness of the substance layer reducing the radiation intensity by one half.

As seen from Table 7, the polymer prepared in the presence of the phenylethynyl lanthanides derivatives (exp. 1–4) revealed the X-ray protective properties as compared to the reference sample prepared with benzoyl peroxide as catalyst (exp. 5).

EXPERIMENTAL

Phenylethynyl derivatives of lanthanides were prepared as described in [4, 6]. All the experiments were carried out in evacuated sealed ampoules using the thoroughly dried and degassed solvents. The reagents used were purified via the standard procedures.

IR spectra were recorded using Perkin-Elmer-577 and FSM 1201 instruments; the samples were prepared under argon atmosphere in the form of Vaseline oil suspension. Magnetochemical tests were performed as described in [19]. EPR spectrum of paramagnetic triphenylmethyl radical was detected using a Bruker ER-2000-SRC instrument.

Content of the lanthanide in the organolanthanide compounds was determined prior to the experiments. Since the reactions were performed in THF, its elimination from the coordination sphere of the used derivatives was not necessary.

Praseodymium tris[2-methoxy-4-phenylbut-3-yn-2-olate]. 0.80 g of $(PhC{\equiv}C)_3Pr$ was dissolved in 15 mL of degassed anhydrous ethyl acetate, and the formed bright orange-brown solution was incubated during 2 h at room temperature. The excess of the ester was removed via re-condensation in vacuum, and the reaction product was extracted with toluene to remove the unreacted $(PhC{\equiv}C)_3Pr$. Toluene was removed via re-condensation, the residue was washed three times with hot hexane and dried in vacuum. Yield 1.08 g (89%), decomp. > 230°C. Other alkoxides of praseodymium, terbium, and samarium were prepared similarly (Table 2).

Trimethylsilicon phenylacetylenide. *a.* 0.40 g (0.0036 mol) of $(CH_3)_3SiCl$ was added to a solution of 0.67 g (0.0015 mol) of $(PhC{\equiv}C)_2Yb(THF)$ in 30 mL of THF; the solution color was changed, and precipitate was formed. The reaction mixture was incubated during 1 day at room temperature. The precipitate was filtered off and washed with THF. The precipitate was $YbCl_2(THF)_4$; yield 0.54 g (0.0010 mol, 67.7%), the Yb^{2+}-to-Cl^- ratio of 1 : 2. The tetrahydrofuran extracts were combined, the volatile components were re-condensed under vacuum in a trap cooled with liquid nitrogen, and hexane was added to the residue. The substance insoluble in hexane was majorly $PhC{\equiv}CYbCl(THF)_2$; Yield 20% (0.1 g, 0.0003 mol). Content of ytterbium 51.23%, that of chlorine 10.84%; the Yb^{2+} : Cl^- molar ratio of 1 : 1.

Table 7. Resistance to bacteria[a] and X-ray protective properties of poly(methyl methacrylate)

Exp. no.	Catalyst	c, wt %	X-ray protection		Resistance to bacteria,[b] points
			μ/ρ, cm^2/g	$d_{0.5}$, mm	
1	$(PhC{\equiv}C)_3Eu$	2.1	8.73	0.70	1 (resistant)
2	$(PhC{\equiv}C)_3Er$	1.5	9.14	0.70	0 (resistant)
3	$(PhC{\equiv}C)_3Yb$	1.5	15.71	0.40	0 (resistant)
4	$(PhC{\equiv}C)_3Yb$	0.9	9.38	0.70	–
5	Benzoyl peroxide	0.8	2.01	3.44	4 (non-resistant)

[a] *Aspergillus oryzae*, *Aspergillus flavus*, *Aspergillus niger*, *Aspergillus terreus*, *Penicillium funiculosum*, *Penicillium chrysogenium*, *Penicillium cyclopium*, *Chaetomium globosum*, *Trichoderma viride*, *Paecilomyces varioti*. [b] The mark of a resistant specimen is 0–2 points.

Slow evaporation of the solvent from the hexane extract gave 0.46 g of $Me_3SiC{\equiv}CPh$. Yield 1.73 mol per 1 mol of the starting lanthanide derivative (Table 3, exp. 2).

b. 0.76 g (0.0038 mol) of $(CH_3)_3SiI$ was added to a solution of 0.67 g (0.0013 mol) of $(PhC{\equiv}C)_3Pr(THF)$ in 20 mL of THF. The reaction mixture was incubated during 3 days at room temperature. THF and other volatile components were re-condensed in vacuum. Hexane was added to the residue. The hexane-insoluble praseodymium iodine derivatives $(PhC{\equiv}C)_2PrI$, $(PhC{\equiv}C)PrI_2$, and PrI_3 were separated off, washed with hexane, and dried. Yield 0.95 g, praseodymium content 17.9% (total yield with respect to the lanthanide 0.0012 mol, 92.3%).

The hexane extract was evaporated in vacuum to isolate 0.57 g (0.0033 mol) of $Me_3SiC{\equiv}CPh$, identical to that prepared via procedure *a*. Yield 2.54 mol per 1 mol of the starting lanthanide (Table 4, exp. 1; Table 5, exp. 1).

The yield of $(CH_3)_3SiC{\equiv}CPh$ in the similar reactions of $(PhC{\equiv}C)_3Dy$(ТГФ) with trimethylsilicon chloride and iodide in THF was of 2.43 mol and 2.41 mol, respectively, per 1 mol of the starting compound (Table 4, exp. 4, 5).

Triphenylgermanium phenylacetylenide. *a*. 1.0 g (0.0029 mol) of Ph_3GeCl was added to a solution of 0.64 g (0.0014 mol) of $(PhC{\equiv}C)_2Yb(THF)$ in 30 mL of THF. The reaction mixture was incubated during 1 day at room temperature. The precipitate insoluble in THF was separated off, washed with THF, and dried to constant mass (0.16 g). The product composition was close to that of ytterbium(II) chloride tetrahydrofuranate. Found, %: Cl 20.09; Yb 42.62. $C_8H_{16}Cl_2O_2Yb$. Calculated, %: Cl 18.30; Yb 44.59.

The filtrate was evaporated in vacuum, and hexane was added to the residue. The products mixture insoluble in hexane was separated off, washed, and dried. Yield 0.41 g. Part of the mixture was used for determination of ytterbium and chlorine content. $PhC{\equiv}CYbCl(THF)_2$ was isolated from the rest of the specimen (Table 5, exp 4).

The hexane extract was evaporated to get 0.77 g (0.0019 mol) of $Ph_3GeC{\equiv}CPh$, mp 84°C (Table 3, exp. 3; Table 5, exp. 2).

b. 1.80 g (0.0053 mol) of Ph_3GeCl was added to a solution of 0.92 g (0.0018 mol) of $(PhC{\equiv}C)_3Pr(THF)$ in 20 mL of THF. The reaction mixture was incubated during 3 days at room temperature. THF was distilled off in vacuum, and benzene was added to the residue. Hexaphenyldigermanium was filtered off and dried. Yield 0.13 g (12%), mp 331°C. Found, %: C 69.80; H 5.34. $C_{36}H_{30}Ge_2$. Calculated, %: C 71.17; H 4.94.

The benzene filtrate was evaporated in vacuum, and the residue was extracted with hexane. The substance insoluble in hexane was filtered off and dried in vacuum at room temperature during 1 h. Yield 1.74 g (92% with respect to praseodymium, Table 4, exp. 2) of a mixture of organic derivatives of praseodymium (13.5% of Pr and 8.05% of Cl). IR spectrum, ν, cm^{-1}: (PhC≡C) 2125 w (PhC≡C), 2025 m (C≡C), 1880 w, 1790 w, 1450 s, 1350 s, 1070 m, 1060 m, 1025 s, 995 s, 750 s, 730 s, 690 s, 490 m; 1040 m, 800 m (coordinated THF).

The hexane filtrate was evaporated. 0.77 g (0.0019 mol) of $Ph_3GeC{\equiv}CPh$ was isolated; yield 1.05 mol per 1 mol of the starting lanthanide (Table 4, exp. 2; Table 5, exp. 2).

A similar reaction of $(PhC{\equiv}C)_3Dy(THF)$ with Ph_3GeCl yielded 1.45 mol of triphenylgermanium phenylacetylenide per 1 mol of the starting lanthanide (Table 4, exp. 6).

Triphenyltin phenylacetylenide. 1.55 g (0.0040 mol) of Ph_3SnCl was added to a solution of 0.68 g (0.0013 mol) of $(PhC{\equiv}C)_3Pr(THF)$ in 20 mL of THF. The reaction mixture was incubated during 3 days at room temperature. THF was re-condensed in vacuum, and hexane was added to the residue. The insoluble products mixture was separated off, washed with hexane, and dried in vacuum during 1 h. Yield 0.84 g (0.0012 mol, 92% with respect to praseodymium). The product contained 20.4% of Pr.

The hexane extract was evaporated. Yield 0.91 g (0.0020 mol) of $Ph_3SnC{\equiv}CPh$; 1.54 mol per 1 mol of the starting lanthanide. Colorless crystalline solid, mp 62°C (Table 4, exp. 3; Table 5, exp. 3), stable in air, well soluble in THF, benzene, and hexane.

In a similar reaction of $(PhC{\equiv}C)_3Dy(THF)$ (0.0014 mol) with Ph_3SnCl (0.0041 mol), benzene was added to the reaction mixture after THF revomal. Hexaphenylditin was isolated; yield 0.04 g (4 mol %), mp 237°C. Phenylethynyltriphenyltin was isolated from the solution; yield 1.93 mol per 1 mol of the starting lanthanide (Table 4, exp. 7).

Reaction of $(PhC{\equiv}C)_3Tb$ with triphenyltin hydride. *a.* A solution of 1.52 g of Ph_3SnH in 10 mL of THF was added in vacuum to a solution of 0.68 g of $(PhC{\equiv}C)_3Tb$ in 10 mL of THF (the reactants molar ratio 1 : 3). The ampoule with the reaction mixture was sealed, heated on a water bath (45–50°C) during 8 h, and then incubated during 12 h at room temperature. The solvent was removed, and the residue was washed three times with hot hexane and then dried. Yield 1.92 g (85%) of $[PhCH{=}C(SnPh_3)]_3Tb$, brown fine powder, decomp. > 190°C.

Tris[1-triphenylstannyl)-2-enylvinyl]praseodymium was prepared similarly (Table 6, exp 1).

b. A solution of 1.60 g of Ph_3SnH in 10 mL of THF was added in vacuum to a solution of 0.31 g of $(PhC{\equiv}C)_3Tb$ in 10 mL of THF (the reactants molar ratio 1:6). The ampoule with the reaction mixture was sealed, heated on a water bath (45–50°C) during 10 h, and then incubated during 12 h at room temperature. The solvent was removed, and the residue was washed three times with hot hexane and then dried. Yield 1.50 g (86%) of $[PhCH_2C(SnPh_3)_2]_3Tb$ (Table 6, exp. 4), decomp. > 215°C.

Reaction of $(PhC{\equiv}C)_3Pr$ with Ph_3SnH was performed similarly (Table 6, exp. 3).

Methyl methacrylate polymerization. 0.20 g (1.5 wt %) of $(PhC{\equiv}C)_3Eu$ was added portionwise to 13.2 mL of dry degassed methyl methacrylate in the evacuated ampoule cooled with liquid nitrogen. The catalyst was completely dissolved upon defrosting the mixture to 20–25°C. A brown-red non-transparent polymer insoluble in acetone was formed within 50 h at room temperature with conversion of 78%.

Polymerization of methyl methacrylate in the presence of other lanthanide-containing catalysts were performed similarly.

ACKNOWLEDGMENTS

This work was financially supported by Ministry of Education and Science of Russian Federation (governmental task no. 4.70.2014/K).

REFERENCES

1. Bochkarev, M.N., Zakharov, L.N., and Kalinina, G.S., *Organo-Derivatives of Rare Earth Elements*, Dordrecht: Kluwer Acad. Publ., 1995, p. 1.
2. Deacon, G.B. and Koplick, A.J., *J. Organometal. Chem.,* 1978, vol. 146, no. 3, p. C43. DOI: 10.1016/S0022-328X(00)88767-7.
3. Deacon, G.B., Koplick, A.J., and Tuong, T.D., *Austral. J. Chem.,* 1982, vol. 35, no. 5, p. 941. DOI: 10.1071/CH9820941.
4. Shustov, S.B., Bochkarev, L.N., and Zhil'tsov, S.F., *Metalloorg. Khim*., 1990, vol. 3, no. 3, p. 6248.
5. Hart, F.A., Massey, A.G., and Saran, M.S., *J. Organomet. Chem.,* 1970, vol. 21, no. 1, p. 147. DOI: 10.1016/S0022328X(00)90605-3.
6. Druzhkova, O.N., Pimanova, N.A., and Bochkarev, L.N., *Russ. J. Gen. Chem.,* 1999, vol. 69, no. 11, p. 1724.
7. Okaue, Y. and Isobe, T., *Inorg. Chim. Acta*, 1988, vol. 144, no. 1, p. 143. DOI: 10.1016/S0020-1693(00)80978-0.
8. Shustov, S.B., Zhil'tsov, S.F., Bochkarev, L.N., and Makarov, V.M., *Metalloorg. Khim*., 1991, vol. 4, no. 2, p. 407.
9. Deacon, G.B. and Tuong, T.D., *J. Organomet. Chem*., 1981, vol. 205, no. 1, p. C4. DOI: 10.1016/S0022-328X(00)82946-0.
10. Pimanova, N.A., Zhil'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.
11. Higasi, K., Baba, H., and Rembaum, A., *Quantum Organic Chemistry*, New York: Interscience, 1965.

12. Zhyl’tsov, S.F., Druzhkova, O.N., Dydykina, M.A., and Makarov, V.M., *Russ. J. Gen. Chem.,* 2014, vol. 84, no. 11, p. 2167. DOI: 10.1134/S1070363214110206.
13. 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.
14. Zhil’tsov, S.F., Pimenova, N.A., Gushchin, A.V., and Morgunova, V.A., *Russ. J. Gen. Chem.,* 2006, vol. 76, no. 5, p. 705. DOI: 10.1134/S1070363206050070.
15. Gailyunas, G.A., Biktimirov, R.Kh., Nurtdinova, G.V., Monakov, Yu.B., and Tolstikov, G.A., *Russ. Chem. Bull.,* 1984, vol. 33, no. 6, p. 1322. DOI: 10.1007/BF00949015.
16. Nesmeyanov, A.N. and Borisov, A.E., *Dokl. Akad. Nauk SSSR*, 1967, vol. 174, no. 1, p. 96.
17. Delmas, M., Maire, J.C., and Pinselli, R., *J. Organomet. Chem*., 1969, vol. 16, no. 1, p. 83. DOI: 10.1016/S0022328X(00)81638-1.
18. Mal’tseva, E.N., Zavgorodnii, V.S., and Petrov, A.A., *Zh. Obshch. Khim*., 1969, vol. 39, no. 1, p. 152.
19. Protchenko, A.V. and Bochkarev, M.N., *Pribory i tekhnika eksperimenta* (Instruments and Experimental Techniques), Moscow: Nauka, 1990, no. 1, p. 194.