The reactions of phenylacetylene with naphthalene complexes of europium and ytterbium. Molecular structure of [IYbC=CPh(DME)₂]₂

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Reactions of naphthaleneeuropium and naphthaleneytterbium, $C_{10}H_8Ln(DME)$ (Ln = Eu or Yb), with phenylacetylene are accompanied by the formation of the C-C bond and yield the complexes of composition $Ph_2C_4H_2Ln(DME)_2$. Hydrolysis of the $Ph_2C_4H_2Ln(DME)_2$ complexes affords a mixture of isomers of 1,4-diphenyl-1,3-butadiene. Reactions of $C_{10}H_8[Ln1(DME)_2]_2$ with PhC=CH yield mixed iodine-ethynyl complexes [ILn(μ -C=CPh)(DME)_2]_2. According to the data of X-ray diffraction analysis, the ytterbium complex consists of two Yb1(DME)_2 units bonded through two bridging C=CPh groups. The crystals of this complex belong to the space group $P2_1/c$. The central cyclic Yb-C-Yb-C fragment is planar; the C(1)-Yb(1)-C(1') angle is 86.4(3)°. The Yb-C bond lengths are 2.584(8) and 2.603(9) Å.

Key words: naphthaleneytterbium, naphthaleneeuropium, phenylacetylene, ethynyl ligand, hydrolysis, europium and ytterbium acetylides.

Alkynyl derivatives of rare-earth elements are among the best studied organolanthanide complexes with σ -bonded ligands.¹ The majority of these compounds were obtained by reactions of phenylacetylene with compounds containing the Ln-R group $(R = alkyl,^2 aryl,^3)$ $Cp,^4$ or $(Me_3Si)_2N^5$) or with complexes of divalent metals of the $(C_5Me_5)_2Sm(THF)_2$ type.⁶⁻⁹ X-ray structural analysis was carried out only for the complexes with substituted cyclopentadienyl ligands: $(C_5Me_5)_4Yb_3(\mu-C=CPh)_4, 6 [(C_5Me_5)Eu(\mu-C=CPh)_4] = (C_5Me_5)Eu(\mu-C=CPh)_4$ $C=CPh)(THF)_{2}]_{2},^{6} (C_{5}Me_{5})_{2}SmC=CPh(THF),^{7} [(Bu^{t}C_{5}H_{4})_{2}Sm(\mu-C=CPh)]_{2},^{8} [Cp_{2}Er(\mu-C=CBu^{t})]_{2},^{9} and [(MeC_{5}H_{4})_{2}Sm(\mu-C=CBu^{t})]_{2}.^{10} It was demon$ strated¹¹ that the reaction of phenylacetylene with $(C_5Me_5)_2SmR$ (R = H or CH(SiMe_3)_2) is accompanied by dimerization of $(C_5Me_5)_2SmR$ and yields the butadienyl complex $[(C_5Me_5)_2Sm]_2(\mu-\eta^2:\eta^2-PhC_4Ph).$ In this work, we report on the reactions of PhC=CH with naphthalene and iodine-naphthalene complexes of europium and ytterbium and on the structural characteristics of one of the resulting products, $[IYb(\mu-C=CPh)(DME)_2]_2.$

Results and Discussion

When phenylacetylene is added to a suspension of $C_{10}H_8Yb(THF)_3$ in 1,2-dimethoxyethane (DME), naph-

thaleneytterbium dissolves completely, and the solution turns violet. Addition of hexane to the reaction mixture precipitates product la as thin shiny black-violet plates. The ytterbium content in **1a** corresponds to the $(PhCH_2)_2Yb(DME)_2$ formula. The IR spectrum of 1a shows the bands attributable to the coordinated DME fragment, phenyl groups, and the PhC=C fragment (1605 cm⁻¹). Hydrolysis of **1a** affords a mixture of isomers of 1,4-diphenyl-1,3-butadiene as viscous pale-yellow liquid along with DME and ytterbium hydroxide. The structure of the hydrolysis product was confirmed by the data of elemental analysis, liquid chromatography, and IR spectroscopy (1735 cm⁻¹ (C=C); 1455, 1605 cm^{-1} (PhC=C); 3080, 3040, 2980, 2940, 2860 cm⁻¹ (Ph)). Because hydrogen is not evolved and the products of hydrogenation of naphthalene do not form, it can be suggested that the reaction of phenylacetylene with naphthaleneytterbium involves the stages of formation of intermediates containing metallacyclopropene and metallacyclopentadiene fragments.

The europium complex $C_{10}H_8Eu(THF)_3$ reacts similarly. Product (1b) is isolated as red-orange thin plates, which decompose at 138–140 °C. Hydrolysis of 1b affords (based on the data of liquid chromatography) a mixture of four isomers of diphenylbutadiene with *trans*-1,4-diphenyl-1,3-butadiene predominating (more than 60 %). The magnetic moments (1a is diamagnetic; for

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1b, $\mu = 9.6 \mu_B$) indicate that the metal atom in the complexes is in the oxidation state 2+.

In the case of mixed iodine—naphthalene complexes $C_{10}H_8[LnI(DME)_2]_2$, the reaction proceeds as metallation of C-H-acids with the liberation of hydrogen. Like most of cyclopentadienyl—ethynyl complexes, the resulting products are dimers.

$$C_{10}H_{8}[LnI(DME)_{2}]_{2} + PhC=CH \longrightarrow$$

$$(PhC=CLnI(DME)_{2}]_{2} + C_{10}H_{8} + H_{2}$$

$$2a,b$$

Ln = Yb (2a), Eu (2b)

Complexes **2a,b** were obtained as red crystals unstable in air; their decomposition temperature is > 140 °C. Oxidation of the metal atom to the trivalent state (**2a** is diamagnetic; for **2b**, $\mu_{eff} = 8.9 \ \mu_B$) does not occur in the course of these reactions. Hydrolysis of **2a,b** affords phenylacetylene along with metal salts and DME. Previously, ^{12,13} it was suggested that compounds analogous to **2a,b** were formed in reactions of PhC=CH with MeYbI.

X-ray structural analysis demonstrated that molecule 2a contains two $(DME)_2IYb$ fragments linked through two PhC=C bridges (Fig. 1). The crystals of 2a belong to the space group $P2_1/c$. The Yb(1)--C(1,1') bond lengths are 2.584(8) and 2.603(9) Å, respectively, which exceed somewhat the distance between the bridging C atoms and the divalent ytterbium atoms (2.52(1) Å) in the (C₅Me₅)₄Yb₃(µ-C≡CPh)₄ complex⁶ containing Yb^{II} and Yb^{III} atoms. The Yb-I bond length (3.1183(9) Å) is somewhat smaller than the La-I bond lengths (3.218(1) and 3.222(1) Å), but is close to the Eu-I bond length (3.237(1) Å) in the $[(THF)_3I_2La]_2C_{10}H_8$ and [(DME)₂IEu]₂C₁₀H₈ complexes¹⁴ taking into account the difference in the ionic radii of Yb^{II}, La^{III}, and Eu^{II}, which are 1.02, 1.17, and 1.032 Å,¹ respectively. The C(1)-Yb(1)-C(1') and Yb(1)-C(1)-Yb(1') angles in the central Yb(1)-C(1)-Yb(1')-C(1') fragment are 86.4(3) and 93.6(3)°, respectively; these values are close to those of the corresponding angles in other dimeric alkynyl complexes: $[(C_5Me_5)Eu(\mu-C=CPh)(THF)_2]_2$ (84.6(2) and 95.4(2)°)⁶, $[(MeC_5H_4)_2Sm(\mu-C\equiv CBu^t)]_2^{10}$ (83.6(5) and 96.2(5)°), and $[Cp_2Er(\mu-C\equiv CBu^t)]_2^{9}$ (83.4(7) and 96.6(7)°). Each Yb atom is coordinated also by four O atoms of two DME molecules. The Yb-O distances are in the range of 2.520(7) - 2.554(7) Å, which is close to the lengths of the corresponding bonds in Cp₂Yb(DME).¹⁶

Experimental

All reactions were carried out using the standard Schlenk vacuum technique. The solvents were distilled from benzophenone ketyl immediately before use. Concentrations of Eu and



Fig. 1. Structure of complex 2a.

Table 1. Atomic coordinates $(\times 10^4)$ and equivalent isotropic

temperature parameters* for molecule 2a

 $U_{\rm eq} \cdot 10^3/{\rm \AA}^2$ Atom x У Ζ Yb 5253(1) 1164(1) 721(1) 37(1) I 7241(1) 3233(1) 1322(1) 52(1) C(1) 3605(11) -712(9) 469(4) 50(2) C(2) 2810(10) -1473(10)687(5) 49(2) C(3) 1847(8) -2322(9)1003(5) 41(2) C(4) 1066(9) -3205(9)614(5) 49(2) C(5) -4016(9)925(6) 148(10) 54(2) C(6) -3963(10)1631(6) -47(11)60(3) C(7) -3137(12)2010(6) 682(11) 64(3) C(8) 1621(10) -2307(11)1705(5) 54(2) C(9) 8618(12) -238(17)813(9) 100(5) O(1) 7235(9) -321(7)1070(5) 73(2) C(10) 7198(21) -737(15)1804(9) 118(7) -790(13)1995(8) C(11) 5739(24) 109(6) 1064(13) 2565(6) C(12) 5156(24) 118(7) 1939(4) O(2) 5130(11) 365(7) 84(3) C(13) 2026(19) 1385(22) 1606(13) 175(13) O(3) 3054(10) 2046(11) 1296(5) 100(3) C(14) 2556(36) 3160(31) 926(15) 290(27) C(15) 3045(26) 3614(17) 432(12)130(8) O(4) 4012(9) 2944(8) 82(4) 73(2)

* U_{eq} was determined as 1/3 of the trace of the ortogonalized U_{ij} tensor.

3356(20)

C(16)

4378(27)

198(15)

-556(12)

Yb were determined by complexonometry. Volatile organic products were analyzed by GLC on a Tsvet-104 chromatograph (a 3-m-long column, 10 % PEG-20M on Chromaton N-AW); nonvolatile products were analyzed on a Milikhrom 1A liquid chromatograph (a 64×2 mm steel column, Separon SGX (5 μ m) was used as an adsorbent, and hexane was used as an eluent).

The IR spectra were recorded on a Perkin-Elmer 577 instrument.

The initial compounds $C_{10}H_8Ln(DME)$ (Ln = Eu or Yb) were prepared using a procedure similar to that for the synthesis of the tetrahydrofuran analogs¹⁵ with the use of 1,2-dimethoxyethane instead of THF as the solvent. The $C_{10}H_8[Eu1(DME)_2]_2$ complex was synthesized as described previously.¹⁴

Reaction of naphthaleneytterbium with PhC=CH. Phenylacetylene (0.23 g, 2.2 mmol) was added to a suspension of $C_{10}H_8$ Yb(DME) (0.5 g, 1.1 mmol) in DME. After 10 min, the precipitate of naphthaleneytterbium dissolved almost completely, and the mixture turned violet. The solution was centrifuged and decanted from the precipitate. DME was removed *in vacuo*. The resulting dark-red finely crystalline precipitate was washed with hexane (3×5 mL) and dried *in vacuo*. The yield of **1a** was 0.47 g (79 %); decomp. temp. > 140 °C. Found (%): Yb, 32.5. $C_{24}H_{32}O_4$ Yb. Calculated (%): Yb, 31.1. IR (Nujol mull), v/cm⁻¹: 690, 760, 1030, 1490, 1600, 2060, 3040.

Naphthalene (0.16 g, 100 %) was determined in the mother liquor by GLC.

Compound **1a** was hydrolyzed in an ether—water mixture; after the removal of the solvent and other volatile products from the organic layer, a mixture of isomers of 1,4-diphenyl-1,3-butadiene was isolated as a viscous pale yellow liquid; according to the data of liquid chromatography, the major

Table 2. Bond lengths (d) in molecule 2a

Bond	d/Å	Bond	d/Å
Yb(1)-O(2)	2.520(7)	O(4)-C(16)	1.36(2)
Yb(1) - O(1)	2.536(7)	Yb(1) - O(3)	2.537(8)
Yb(1) - C(1)	2.584(8)	Yb(1) - O(4)	2.554(7)
Yb(1)—I	3.1183(9)	Yb(1)-C(1')*	2.603(9)
C(1) - C(2)	1.187(13)	Yb(1)Yb(1')	3.7820(9)
C(2)-C(3)	1.426(13)	C(1)-Yb(1')*	2.603(9)
C(3)-C(4)	1.413(13)	C(3) - C(8)	1.382(13)
C(5)-C(6)	1.39(2)	C(4) - C(5)	1.369(14)
C(7) - C(8)	1.390(14)	C(6) - C(7)	1.34(2)
O(1) - C(10)	1.49(2)	C(9) - O(1)	1.396(14)
C(11)-O(2)	1.37(2)	C(10)-C(11)	1.42(2)
C(13)-O(3)	1.34(2)	C(12) - O(2)	1.430(14)
C(14)-C(15)	1.17(3)	O(3)-C(14)	1.47(3)
		C(15)-O(4)	1.35(2)

* Symmetrically equivalent atoms were generated by the symmetry transformation -x + 1, -y, -z.

product is *trans*, *trans*-1,4-diphenyl-1,3-butadiene. Found (%): C, 92.30; H, 7.59. C₁₆H₁₄. Calculated (%): C, 93.16; H, 6.84. IR, ν/cm^{-1} : 700, 760, 800, 840, 1260, 1455, 1605, 1680, 1735, 2860, 2940, 2980, 3040, 3080.

The reaction of PhC=CH with $C_{10}H_8Eu(DME)$ was carried out in a similar manner. The yield of **1b** was 77.0 %; decomp. temp. > 140 °C, μ_{eff} 9.6 = μ_B .

Synthesis of $[IYb(\mu-C=CPh)(DME)_2]_2$ (2a). Phenylacetylene (0.16 g, 1.5 mmol) was added to a suspension of $C_{10}H_8[YbI(DME)_2]$ (0.69 g, 0.6 mmol) in DME. The reaction mixture turned red-brown, and red crystals precipitated. The solution was centrifuged and decanted from the precipitate. Crystals were washed with hexane (3×5 mL) and dried *in vacuo*. Complex 2a was obtained as red diamagnetic crystals in a yield of 0.48 g (65 %), decomp. temp. >140 °C. Found (%): Yb, 29.0. $C_{16}H_{25}IO_4Yb$. Calculated (%): Yb, 29.7. IR (Nujol mulls), v/cm⁻¹: 690, 760, 1030, 1490, 1605, 2060, 3040. Naphthalene (0.1 g, 100 %) was determined in the mother liquor by GLC. Compound 2a was hydrolyzed in an ether—water mixture, and after the removal of the solvent, phenylacetylene (0.06 g, 89.5 %) was isolated from the organic layer.

The $[IEu(\mu-C=CPh)(DME)_2]_2$ complex (2b) was obtained in a similar manner. The yield was 62 %, decomp. temp. >140 °C, $\mu_{eff} = 8.9 \mu_B$.

X-ray structural analysis of 2a. The single crystal of 2a of dimensions of 0.1×0.2×0.2 mm suitable for X-ray diffraction study was obtained by slow diffusion of hexane into a saturated solution of 2a in DME. The unit cell parameters and intensities of 3407 independent reflections were measured on a fourcircle Enraf-Nonius CAD 4 diffractometer at 163(2) K (Mo-Ka radiation, $\lambda = 0.71069$ Å, the scanning range was $2.10^{\circ} \leq$ $2\theta \le 25.01^\circ$). Crystals of **2a** are monoclinic, a = 9.370(4), b =10.742(2), c = 19.426(4) Å, $\beta = 90.58^{\circ}$, V = 1955.3(10) Å³; $d_{calc} = 1.975 \text{ g cm}^{-3}$; Z = 4; the space group $P2_1/c$. Absorption correction ($\mu_{calc} = 6.374 \text{ mm}^{-1}$) was applied using the DIFABS program. The structure was solved by direct methods in combination with difference syntheses (the SHELX-86 and SHELX-76 programs) and refined by the full-matrix leastsquares method with anisotropic thermal parameters for nonhydrogen atoms. Hydrogen atoms were placed in calculated positions and refined isotropically. The maximum and minimum densities of free electrons in the final F-map were 1.206 and

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
O(2) - Yb(1) - O(3)	70.7(3)	C(4)-C(3)-C(2)	121.7(8)	C(1)-Yb(1)-I	168.7(2)
O(3) - Yb(1) - O(1)	135.5(3)	C(4) - C(5) - C(6)	120.0(10)	$O(2) - Yb(1) - Yb(1')^*$	117.6(2)
O(3) - Yb(1) - O(4)	64.3(3)	C(6) - C(7) - C(8)	120.9(10)	$O(1) - Yb(1) - Yb(1')^*$	82.4(2)
O(2) - Yb(1) - C(1)	83.0(3)	C(9)-O(1)-C(10)	113.0(11)	$C(1) - Yb(1) - Yb(1')^*$	43.4(2)
O(1) - Yb(1) - C(1)	89.7(3)	C(10) - O(1) - Yb(1)	114.8(9)	$1 - Yb(1) - Yb(1')^*$	144.94(2)
$O(2) - Yb(1) - C(1')^*$	42.5(3)	O(2) - C(11) - C(10)	110.1(14)	$C(2)-C(1)-Yo(1')^*$	117.0(7)
$O(1) - Yb(1) - C(1')^*$	79.2(3)	C(11) - O(2) - Yb(1)	111.2(8)	C(1)-C(2)-C(3)	174.9(10)
$C(1) - Yb(1) - C(1')^*$	86.4(3)	C(13)-O(3)-C(14)	115(2)	C(8) - C(3) - C(2)	121.4(8)
O(3) - Yb(1) - I	93.1(3)	O(2) - Yb(1) - O(1)	64.8(3)	C(5) - C(4) - C(3)	121.1(9)
O(4)—Yb(1)—I	85.2(2)	O(2) - Yb(1) - O(4)	133.4(3)	C(7) - C(6) - C(5)	120.1(9)
C(1')-Yb(1)-I	102.5(2)	O(1) - Yb(1) - O(4)	158.4(3)	C(3) - C(8) - C(7)	121.1(10)
$O(3) - Yb(1) - Yb(1')^*$	118.5(3)	O(3) - Yb(1) - C(1)	83.6(4)	C(9) - O(1) - Yb(1)	122.9(8)
O(4) - Yb(1) - Yb(1')*	94.7(2)	O(4) - Yb(1) - C(1)	102.9(3)	C(11) - C(10) - O(1)	107.1(11)
$C(1') - Yb(1) - Yb(1')^*$	43.0(2)	$O(3) - Yb(1) - C(1')^*$	143.5(4)	C(11) - O(2) - C(12)	113.8(12)
C(2) - C(1) - Yb(1)	147.8(7)	$O(4) - Yb(1) - C(1')^*$	84.1(3)	C(12) - O(2) - Yb(1)	128.3(7)
Yb(1)-C(1)-Yb(1')*	93.6(3)	O(2) - Yb(1) - I	85.7(2)	C(13) - O(3) - Yb(1)	126.1(12)
C(8) - C(3) - C(4)	116.9(8)	O(1) - Yb(1) - I	85.1(2)		• •

Table 3. Bond angles (ω) in molecule 2a

* Symmetrically equivalent atoms were generated by the symmetry transformation -x + 1, -y, -z.

 $-0.909 \ \tilde{c} \cdot A^{-3}$, respectively. The final refinement with the use of 3210 independent reflections with $I > 2\sigma(I)$ converged to R = 0.0397, $R_w = 0.0994$, and S = 0.832.

The final atomic coordinates, bond lengths, and bond angles are given in Tables 1-3, respectively.

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