

Synthesis and crystal structure of cationic complex of ytterbium with organogermanium cuprate anions $\{[\text{Yb}(\text{THF})_6]^{2+}[(\text{Ph}_3\text{Ge})_2\text{Cu}]_2^-\} \cdot 2\text{THF}$

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Abstract

The cationic complex of ytterbium $\{[\text{Yb}(\text{THF})_6]^{2+}[(\text{Ph}_3\text{Ge})_2\text{Cu}]_2^-\} \cdot 2\text{THF}$ (**1**) was synthesized by redox transmetallation reaction of Yb with $\text{Ph}_3\text{GeCu}(\text{PPh}_3)_3$ in the presence of a catalytic amount of $\text{YbI}_2(\text{THF})_4$ and by the exchange reactions of $(\text{Ph}_3\text{Ge})_2\text{Yb}(\text{THF})_4$ with $\text{Ph}_3\text{GeCu}(\text{PPh}_3)_3$ or $\text{PhC}\equiv\text{CCu}$. X-ray diffraction study has shown that crystals of **1** have an ionic structure composed of isolated $[\text{Yb}(\text{THF})_6]^{2+}$ cations (Yb–O 2.350(5), 2.369(4), 2.383(5) Å) and $[(\text{Ph}_3\text{Ge})_2\text{Cu}]_2^-$ anions (Cu–Ge 2.335(1), 2.339(1) Å; GeCuGe 175.96(5)°). The Yb and Cu atoms in **1** have distorted octahedral and linear coordinations respectively. © 1997 Elsevier Science S.A.

Keywords: Ytterbium; Germanium; Copper; Lanthanide complexes; Cuprate anion; X-ray diffraction

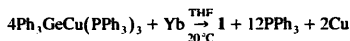
1. Introduction

Cationic complexes of lanthanoids represent only a small group of compounds [1–3] among organoderivatives of rare earth elements [4]. Similar cationic complexes of alkali metals are well known [5] and organocuprates of lithium were found to be unique reagents in organic synthesis [6]. In the previous researches we found that lanthanoids easily form organocuprates with phenylethynyl and organogermanium substituents of the types $\{[(\text{PhC}\equiv\text{C})_3\text{Cu}][\text{Eu}(\text{Py})(\text{THF})_2]\}_2$, $\{[(\text{PhC}\equiv\text{C})_3\text{Cu}][\text{Yb}(\text{THF})_2]\}_2$ [7], $\{[(\text{C}_6\text{F}_5)_3\text{Ge}]_2\text{Cu}\}_3[\text{Ln}(\text{DME})_3]$ (Ln = Sm, Yb) [8]. Now we report the synthesis and crystal structure of the novel organogermanium cuprate of ytterbium **1**.

2. Results and discussion

For preparation of the titled compound we used the redox transmetallation reaction which is widely used as

a synthetic route to organolanthanoids [4] and the exchange reactions of gemylytterbium complex $(\text{Ph}_3\text{Ge})_2\text{Yb}(\text{THF})_4$ ¹ with organocopper derivatives $\text{Ph}_3\text{GeCu}(\text{PPh}_3)_3$ ² and $\text{PhC}\equiv\text{CCu}$ ³. Yb was found to react with $\text{Ph}_3\text{GeCu}(\text{PPh}_3)_3$ in THF only in the presence of ytterbium diiodide as catalyst⁴. The interaction for ca. 60 h leads to the formation of metallic copper, triphenylphosphine and complex **1**.



The complete transmetallation does not occur even at prolonged reaction time (120 h). The complex **1** was isolated in 72.3% yield as unstable in air diamagnetic

¹ $(\text{Ph}_3\text{Ge})_2\text{Yb}(\text{THF})_4$ was prepared by the method which we described in Ref. [9].

² For the preparation of the known gemylcopper compound $\text{Ph}_3\text{GeCu}(\text{PPh}_3)_3$ [10] we used another method—the reaction of Ph_3GeH with $t\text{-BuOCu}$ in the presence of PPh_3 . The details of the synthetic procedure are now being prepared for publication.

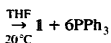
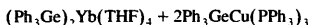
³ $\text{PhC}\equiv\text{CCu}$ was prepared by the reported method, see Ref. [11].

⁴ A catalytic activation of lanthanoid metals with lanthanoid halides we used earlier in the reactions of the metals with R_2EER_3 (E = Si, Ge, Sn) [2,9,12], dimer of triphenylmethyl radicals [3], Ph₂Hg, and Ph₂Bi [13].

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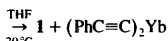
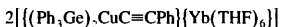
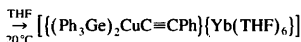
pale-brown crystals, soluble in THF, DME and insoluble in hexane. It melts with decomposition at 155–160 °C. The IR spectrum confirms the presence of Ph_3Ge fragments, coordinated and solvated THF. In THF solution the complex **1** was found to be a weak electrolyte (conductivity (THF, 20 °C): $\lambda_{\infty} = 49.0 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$, $K_D = 1.20 \times 10^{-7} \text{ mol}^{-1}$).

The exchange reaction between $(\text{Ph}_3\text{Ge})_2\text{Yb}(\text{THF})_4$ and $\text{Ph}_3\text{GeCu}(\text{PPh}_3)_3$ proceeds smoothly at room temperature and leads to complex **1** in 85.1% yield.



The reaction of $(\text{Ph}_3\text{Ge})_2\text{Yb}(\text{THF})_4$ with $\text{PhC}\equiv\text{CCu}$, instead of the expected ytterbium cuprate with mixed organocuprate anions of the type $(\text{Ph}_3\text{Ge})_2\text{CuC}\equiv\text{CPh}^{2-}$, gave known bis(phenylethynyl)ytterbium [14] and complex **1** in high yields. It can be suggested that mixed organocuprate of Yb is formed at the initial steps of the reaction, but the following disproportionation of the

intermediate leads to symmetrical ytterbium compounds.



Complex **1**, isolated in 62.1% yield from the reaction of the digermlytterbium compound with phenylethynylcupper, according to elemental analysis, m.p. and IR data is identical to the organogermanium cuprate obtained by the transmetallation reaction and by the exchange reaction of $(\text{Ph}_3\text{Ge})_2\text{Yb}(\text{THF})_4$ with $\text{Ph}_3\text{GeCu}(\text{PPh}_3)_3$.

An X-ray diffraction study has shown that crystals of **1** have an ionic structure composed of $[\text{Yb}(\text{THF})_6]^{2+}$ cations and $[(\text{Ph}_3\text{Ge})_2\text{Cu}]^-$ anions. Besides these ions the crystal structure of **1** contains solvating THF

Table 1
Selected bond lengths (Å) and angles (deg) for **1**

Yb(1)–O(1)	2.350(5)	Yb(1)–O(2)	2.369(4)
Yb(1)–O(3)	2.383(5)	Cu(1)–Ge(1)	2.3351(12)
Cu(1)–Ge(2)	2.3390(13)	Ge(1)–C(13)	1.975(7)
Ge(1)–C(25)	1.981(7)	Ge(1)–C(19)	1.996(7)
Ge(2)–C(43)	1.979(7)	Ge(2)–C(37)	1.985(7)
Ge(2)–C(31)	1.998(7)	C(13)–C(14)	1.379(10)
C(13)–C(18)	1.396(10)	C(14)–C(15)	1.401(10)
C(15)–C(16)	1.380(11)	C(16)–C(17)	1.356(11)
C(17)–C(18)	1.395(10)	C(19)–C(20)	1.384(10)
C(19)–C(24)	1.385(9)	C(20)–C(21)	1.393(11)
C(21)–C(22)	1.353(12)	C(22)–C(23)	1.379(12)
C(23)–C(24)	1.399(11)	C(25)–C(26)	1.375(10)
C(25)–C(30)	1.399(11)	C(26)–C(27)	1.381(11)
C(27)–C(28)	1.363(12)	C(28)–C(29)	1.376(13)
C(29)–C(30)	1.373(13)	C(31)–C(36)	1.375(10)
C(31)–C(32)	1.374(10)	C(32)–C(33)	1.402(12)
C(33)–C(34)	1.355(12)	C(34)–C(35)	1.355(12)
C(35)–C(36)	1.382(10)	C(37)–C(38)	1.378(10)
C(37)–C(42)	1.384(10)	C(38)–C(39)	1.399(13)
C(39)–C(40)	1.36(2)	C(40)–C(41)	1.368(14)
C(41)–C(42)	1.387(11)	C(43)–C(44)	1.392(10)
C(43)–C(48)	1.400(9)	C(44)–C(45)	1.383(10)
C(45)–C(46)	1.378(10)	C(46)–C(47)	1.373(10)
C(47)–C(48)	1.372(9)		
O(1)–Yb(1)–O(2)	88.5(2)	O(1)–Yb(1)–O(2) ^a	91.5(2)
O(1)–Yb(1)–O(3) ^a	90.1(2)	O(2)–Yb(1)–O(3) ^a	88.5(2)
O(1)–Yb(1)–O(3)	89.9(2)	O(2)–Yb(1)–O(3)	91.5(2)
Ge(1)–Cu(1)–Ge(2)	175.96(5)	C(13)–Ge(1)–C(25)	101.3(3)
C(13)–Ge(1)–C(19)	98.0(3)	C(25)–Ge(1)–C(19)	105.4(3)
C(13)–Ge(1)–Cu(1)	118.3(2)	C(25)–Ge(1)–Cu(1)	116.9(2)
C(19)–Ge(1)–Cu(1)	114.5(2)	C(43)–Ge(2)–C(37)	103.4(3)
C(43)–Ge(2)–C(31)	101.1(3)	C(37)–Ge(2)–C(31)	102.2(3)
C(43)–Ge(2)–Cu(1)	120.7(2)	C(37)–Ge(2)–Cu(1)	114.5(2)
C(31)–Ge(2)–Cu(1)	112.6(2)		

^a Symmetry transformations used to generate equivalent atoms: $-x + 1, -y + 1, -z + 2$.

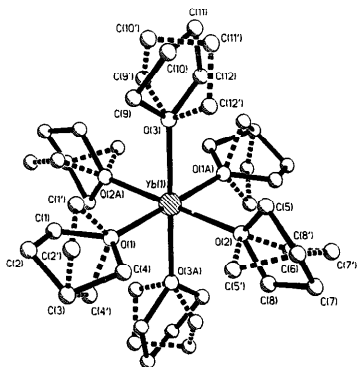


Fig. 1. The general view of the cation $[\text{Yb}(\text{THF})_6]^{2+}$ in **1** and atom labeling. All THF molecules in the $[\text{Yb}(\text{THF})_6]^{2+}$ cation are disordered on two positions. One of these positions is denoted by the dashed lines.

molecules. The ions and solvating THF molecules are isolated in the crystal structure. The minimum $\text{Yb} \dots \text{Cu}$ distance in **1** is 7.62 Å.

The $[\text{Yb}(\text{THF})_6]^{2+}$ cation in **1** has a slightly distorted octahedral coordination (Fig. 1): the OYbO angles are in the range $88.5(2)$ – $91.5(2)^\circ$ (Table 1). The Yb atom of the cation in the crystal structure is on a center of symmetry. All THF molecules in the $[\text{Yb}(\text{THF})_6]^{2+}$ cation are disordered on two positions (see Section 3). One of these positions is denoted by the dashed lines in Fig. 1. The $\text{Yb}(1)\text{--O}(1)$, $\text{Yb}(1)\text{--O}(2)$ and $\text{Yb}(1)\text{--O}(3)$ distances are 2.350(5) Å, 2.369(4) Å and 2.383(5) Å respectively. The geometry of the $[\text{Yb}(\text{THF})_6]^{2+}$ cation in

1 is close to that for a similar cation with an ideal octahedral structure (Yb--O 2.390 Å) in $[\text{Yb}(\text{THF})_6]^{2+}[\text{Ph}_3\text{C}]_2^-$ [3].

The general view of the $[(\text{Ph}_3\text{Ge})_2\text{Cu}]^-$ anion is shown in Fig. 2. The environment of the $\text{Cu}(1)$ atom is somewhat distorted from linear: the $\text{Ge}(1)\text{Cu}(1)\text{Ge}(2)$ angle is $175.96(5)^\circ$. The $\text{Cu}(1)\text{--Ge}(1)$ and $\text{Cu}(1)\text{--Ge}(2)$ distances are 2.339(1) Å and 2.335(1) Å respectively. As we know, these are the first values of the Cu--Ge distances found in organo-element compounds. The Ge atoms have a distorted tetrahedral coordination. The CuGeC angles ($114.5(2)$ – $118.2(2)^\circ$ at the $\text{Ge}(1)$ atom and $112.6(3)$ – $120.7(2)^\circ$ at the $\text{Ge}(2)$ atom) are slightly larger than the ideal tetrahedral angle. The Ge--C distances range from 1.975(7) to 1.998(7) Å (average: 1.986(9) Å) (Table 1).

3. Experimental section

The synthesis and isolation of **1** were performed under vacuum in sealed ampoules using thoroughly dried solvents. The IR spectra were recorded on a Perkin-Elmer-577 spectrometer. $\text{YbI}_2(\text{THF})_3$ used as a catalyst was synthesized by reaction of Yb with I_2 in THF.

3.1. X-ray diffraction studies

X-ray data for **1** was collected on a Siemens P3/PC diffractometer at 153 K (Mo $K\alpha$ radiation, graphite monochromator, θ – 2θ scan mode, $2 \leq \theta \leq 25^\circ$, 5545 independent reflections measured ($R_{\text{int}} = 0.044$), 3981 reflections observed ($I > 2\sigma(I)$). Crystal data for **1** at 153 K: $\text{C}_{104}\text{Cu}_2\text{Ge}_2\text{H}_{124}\text{O}_8\text{Yb}_1$, f.w. 2092.5, mono-

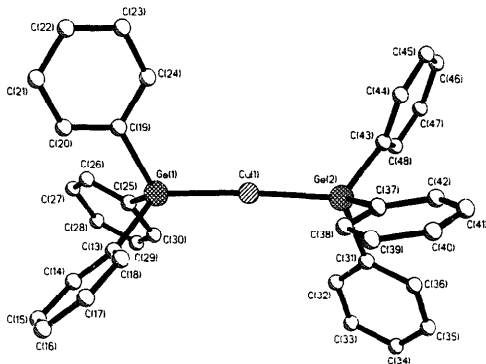


Fig. 2. The general view of the anion $[(\text{Ph}_3\text{Ge})_2\text{Cu}]^-$ in **1** and atom labeling.

Table 2
Atomic coordinates ($\times 10^3$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**

	x	y	z	U_{eq}^a
Yb(1)	5000	5000	10000	38(1)
O(1)	4970(2)	3750(3)	10264(3)	58(1)
O(2)	4190(3)	5225(3)	10991(2)	52(1)
O(3)	3522(3)	4876(3)	9238(3)	60(2)
C(1)	5278(8)	3168(6)	9836(6)	77(4)
C(2)	4920(7)	2469(5)	10130(5)	62(3)
C(4)	4664(8)	3422(6)	10890(6)	73(3)
C(1')	4302(47)	3165(35)	9878(33)	87(21)
C(2')	4131(42)	2621(34)	10538(31)	78(19)
C(4')	5789(68)	3371(51)	10740(52)	153(37)
C(3)	4983(8)	2642(6)	10868(6)	100(3)
C(5)	3161(6)	5137(5)	11011(5)	56(3)
C(7)	3859(8)	5517(6)	12133(6)	69(3)
C(8)	4642(7)	5411(6)	11697(5)	66(3)
C(5')	3931(49)	4527(39)	11523(37)	110(26)
C(7')	3311(41)	5757(29)	11866(29)	67(16)
C(8')	4175(37)	5804(31)	11447(28)	64(16)
C(6)	3102(7)	5044(6)	11804(5)	86(3)
C(9)	3015(7)	4207(6)	9007(6)	68(3)
C(10)	1977(9)	4439(7)	8890(8)	87(4)
C(11)	2029(8)	5178(6)	8558(7)	72(3)
C(12)	2963(7)	5468(6)	8884(6)	70(4)
C(9')	3214(65)	4709(57)	8634(54)	167(38)
C(10')	2187(35)	4448(28)	8525(32)	65(16)
C(11')	1849(20)	5102(17)	8938(17)	14(9)
C(12')	2637(50)	4990(43)	9541(40)	131(28)
Cu(1)	1272(1)	3716(1)	6977(1)	51(1)
Ge(1)	2771(1)	3335(1)	6725(1)	14(1)
Ge(2)	-278(1)	4044(1)	7164(1)	42(1)
C(13)	2834(5)	2792(4)	5837(3)	41(2)
C(14)	3358(5)	2165(4)	5780(4)	55(2)
C(15)	3450(6)	1856(5)	5119(5)	66(2)
C(16)	3018(6)	2170(5)	4498(4)	64(2)
C(17)	2493(6)	2784(5)	4538(4)	61(2)
C(18)	2401(5)	3089(4)	5197(4)	56(2)
C(19)	3660(5)	4144(4)	6560(3)	40(2)
C(20)	4377(5)	4062(5)	6136(4)	60(2)
C(21)	4934(6)	4643(5)	5958(5)	70(2)
C(22)	4771(7)	5318(5)	6203(5)	70(3)
C(23)	4072(6)	5427(5)	6634(5)	67(2)
C(24)	3514(5)	4840(4)	6807(4)	51(2)
C(25)	3515(5)	2688(4)	7429(3)	43(2)
C(26)	4493(6)	2706(4)	7606(4)	56(2)
C(27)	4961(6)	2222(5)	8090(5)	69(2)
C(28)	4474(8)	1702(5)	8406(4)	73(3)
C(29)	3494(9)	1673(6)	8235(5)	99(3)
C(30)	3018(7)	2164(6)	7770(5)	82(3)
C(31)	-1066(5)	3186(4)	7375(3)	42(2)
C(32)	-626(6)	2563(5)	7655(4)	62(2)
C(33)	-1161(9)	1947(5)	7792(5)	82(3)
C(34)	-2128(8)	1951(5)	7643(5)	71(3)
C(35)	-2573(7)	2560(5)	7364(5)	75(3)
C(36)	-2048(6)	3170(4)	7234(4)	60(2)
C(37)	-1068(5)	4479(4)	6326(4)	45(2)
C(38)	-788(7)	4376(4)	5666(4)	72(3)
C(39)	-1353(10)	4622(6)	5051(5)	99(4)
C(40)	-2185(10)	4981(6)	5099(6)	97(4)
C(41)	-2468(7)	5118(5)	5746(5)	81(3)
C(42)	-1913(6)	4856(4)	6351(4)	59(2)
C(43)	-487(4)	4710(4)	7946(4)	38(2)
C(44)	-492(5)	5463(4)	7854(4)	46(2)

Table 2 (continued)

	x	y	z	U_{eq}^a
C(45)	-595(5)	5930(4)	8410(4)	55(2)
C(46)	-717(5)	5668(5)	9070(4)	55(2)
C(47)	-710(5)	4927(5)	9169(4)	50(2)
C(48)	-596(5)	4458(4)	8625(4)	44(2)
O(45)	2088(8)	2920(6)	-89(6)	171(4)
C(49S)	2166(11)	2521(9)	524(8)	167(6)
C(50S)	1274(11)	2129(9)	497(10)	176(7)
C(51S)	943(16)	2073(13)	-235(12)	219(10)
C(52S)	1409(21)	2585(13)	-614(10)	239(12)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

clinic, space group $P2_1/n_1$, $a = 14.096(4)$ Å, $b = 18.347(3)$ Å, $c = 19.025(4)$ Å, $\beta = 97.77(2)^\circ$, $V = 4875(2)$ Å³, $Z = 2$ for above-mentioned formula, $D_{calc} = 1.426$ g cm⁻³, $\mu = 2.647$ mm⁻¹. The structure of **1** was solved by direct methods. Besides the [Yb(THF)₆]²⁺ and (Ph₃Ge)₂Cu⁻ ions the crystal structure of **1** contains solvating THF molecules. The THF molecules in the cation [Yb(THF)₆]²⁺ are disordered on two positions. For all three symmetrically independent THF molecules the refined multiplicities of these two positions are different: 0.85 and 0.15 for O1–C4, 0.84 and 0.16 for O2–C8, and 0.83 and 0.17 for O3–C12 THF molecules. The second value corresponds to the positions denoted by dashed lines in Fig. 1. The C atoms of disordered THF molecules were refined isotropically and other non-H atoms were refined anisotropically. The positions of H atoms were calculated on the basis of geometrical conditions and refined in the riding model with isotropic parameters $U = 1.2U_{eq}$, where U_{eq} is the equivalent isotropic parameter of the bonded C atom. The final refinements converged at $R = 0.038$, $R_w = 0.086$, $S = 0.88$ for observed reflections. The weight scheme was $w = 1/[\sigma^2(F_o^2) + (0.054P)^2 + 19.4082P]$ ($P = (F_o^2 + 2F_c^2)/3$). The $(\Delta/\sigma)_{av}$ value in the final cycle is 0.002. The largest peaks in the final difference maps are 0.551, -0.524 (e⁻ Å⁻³). All calculations were performed using SHELXTL-PLUS [15] and the SHELX93 package. Selected interatomic distances and bond angles, and atomic coordinates with their temperature factors in **1** are given in Tables 1 and 2 respectively.

3.2. Preparation of **1**

(a) A mixture of Ph₃GeCu(PPh₃)₃ (1.74 g, 1.51 mmol), Yb in the form of filings (2.84 g, 16.42 mmol) and YbI₂(THF)₄ (0.03 g, 0.04 mmol) in 20 ml of THF was magnetically stirred for ca. 60 h at room temperature. The resulting dark-brown solution was separated from ytterbium excess and formed metallic copper (0.045 g, 93.9%). THF was removed from the

reaction solution and the residue was washed with hexane (5×15 ml), dried in vacuum to yield 0.57 g, (72.3%) of **1**, m.p. (dec.): 155–160°C. Anal. Calcd. for $C_{104}H_{124}Cu_2Ge_3O_8Yb_1$: Cu, 6.07; Yb, 8.27. Found: Cu, 6.55; Yb, 7.90. IR (Nujol, cm^{-1}): (Ph–Ge) 3040, 1480, 1425, 1085, 1065, 1020, 995, 730, 690, 460; (coordinated THF) 1040, 860; (solvent) 1070, 910. In the hexane washings 1.07 g (90.7%) of PPh_3 was found.

(b) The mixture of $(Ph_3Ge)_2Yb(THF)_4 \cdot \frac{1}{2}C_6H_6$ (1.10 g, 0.99 mmol) and $Ph_3GeCu(PPh_3)_3$ (2.30 g, 1.99 mmol) in 30 ml of THF was kept at room temperature for 30 h. The solution gradually became dark-brown. THF was removed from the reaction solution and the residue was washed with hexane (5×15 ml), dried in vacuum to yield 1.77 g, (85.1%) of **1**, m. p. (dec.): 155–160°C. Anal. Found: Cu, 6.42; Yb, 8.00. The IR spectrum of the product is identical to the spectrum of complex **1** obtained by the reaction of $Ph_3GeCu(PPh_3)_3$ with Yb. In the hexane washings, 1.52 g (97.4%) of PPh_3 was found.

(c) The mixture of $(Ph_3Ge)_2Yb(THF)_4 \cdot \frac{1}{2}C_6H_6$ (1.40 g, 1.26 mmol) and $PhC\equiv CCu$ (0.22 g, 1.34 mmol) in 20 ml of THF was magnetically stirred at room temperature for 6 h. The yellow deposit of $PhC\equiv CCu$ was dissolved and the solution became dark-brown. After the separation of the traces of unreacted $PhC\equiv CCu$, the reaction solution was concentrated to 10 ml and kept at 0°C for 20 h to yield 0.82 g (62.1%) of **1** as pale-brown crystals, m.p. (dec.): 155–160°C. Anal. Found: Cu, 6.35; Yb, 7.95. The IR spectrum of the product is identical to the spectra of the samples of complex **1** obtained by the reaction of $Ph_3GeCu(PPh_3)_3$ with Yb and by the reaction of $(Ph_3Ge)_2Yb(THF)_4 \cdot \frac{1}{2}C_6H_6$ with $Ph_3GeCu(PPh_3)_3$.

The mother solution was concentrated to 5 ml, centrifuged and evaporated to dryness to yield 0.14 g (59.1%) of $(PhC\equiv C)_2Yb$. The IR data and elemental analysis of the compound are in accordance with the appropriate data for bis(phenylethynty)ytterbium, synthesized by reported method [14].

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