

The reaction of alkyl derivatives of yttrium and lutetium with organic disulphides and diselenides: The molecular structure of $\{({}^t\text{BuC}_5\text{H}_4)_2\text{Y}(\mu\text{-SePh})\}_2 \cdot \text{C}_6\text{H}_6$

Irina P. Beletskaya

Department of Chemistry, Moscow State University, 119899 Moscow, GSP-3 (Russian Federation)

Alexander Z. Voskoboynikov and Alla K. Shestakova

State Scientific-Research Institute of Chemistry and Technology of Organoelement Compounds, Sh. Entuziastov 38, 111123 Moscow (Russian Federation)

Alexander I. Yanovsky, Georgiy K. Fukin, Lev N. Zacharov and Yuri T. Struchkov

A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, ul. Vavilova 29, 117813 Moscow (Russian Federation)

Herbert Schumann

Institut für Anorganische und Analytische Chemie der Technischen Universität Berlin, Strasse des 17. Juni 135, D-10623 Berlin (Germany)

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Abstract

The dimers $\{({}^t\text{BuC}_5\text{H}_4)_2\text{Ln}(\mu\text{-Me})\}_2$ (Ln=Y, or Lu) react with organic dichalcogenides R_2E_2 (E=S or Se; R=Ph, ${}^n\text{Bu}$, ${}^t\text{Bu}$ or CH_2Ph) to form $\{({}^t\text{BuC}_5\text{H}_4)_2\text{Ln}(\mu\text{-ER})\}_2$ complexes with Ln–S or Ln–Se bonds. The molecular structure of $\{({}^t\text{BuC}_5\text{H}_4)_2\text{Ln}(\mu\text{-SePh})\}_2 \cdot \text{C}_6\text{H}_6$ has been determined by X-ray diffraction (\bar{P} ; $a = 11.242(2)$ Å, $b = 11.388(2)$ Å and $c = 12.865(2)$ Å; $\alpha = 110.32(2)^\circ$; $\beta = 105.16(2)^\circ$; and $\gamma = 102.84(2)^\circ$; $Z = 1$; $d_{\text{calc.}} = 1.343$ g cm $^{-3}$; $R = 0.0509$ and $R_w = 0.0532$). The two yttrium atoms of the centrosymmetric dimeric molecule are bridged by two $\mu\text{-SePh}$ groups.

Key words: Sulphur; Selenium; Yttrium; Lutetium; Bridging ligand; Cyclopentadienyl; Crystal structure

1. Introduction

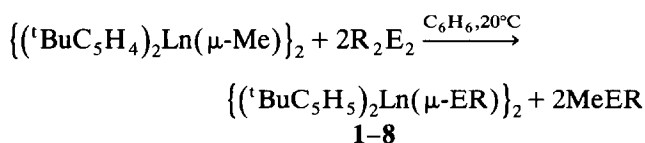
A number of organolanthanide compounds with lanthanide–sulphur, lanthanide–selenium and lanthanide–tellurium bonds has been prepared recently. The formation of Ln–E (E=S, Se or Te) bonds was achieved by three general methods. Sulphur-containing and only sometimes selenium-containing compounds were prepared by splitting Ln–C [1–4], Ln–H [5], Ln–N bonds [4,6,7] by soft E–H acids (E=S or Se). Selenium- and tellurium-containing organolanthanides were synthesized by redox reactions of complexes of divalent lan-

thanides with compounds containing E–E bonds (E=S, Se or Te) [8–11] or with elementary selenium and tellurium [12,13]. However, this method can be used only for the preparation of derivatives of samarium, europium or ytterbium, the only lanthanide metals which form stable Ln^{2+} compounds. Exchange reactions between lanthanide halides and chalcogen derivatives of electropositive metals, such as NaER (E=S, Se or Te), have been used only scarcely [6], because they usually afford the products only with very low yields. We succeeded in the preparation of chalcogen derivatives of organolanthanides by cleavage of the Ln– CH_3 σ bonds in $\{({}^t\text{BuC}_5\text{H}_4)_2\text{Ln}(\mu\text{-Me})\}_2$ (Ln=Y or Lu) by R_2E_2 (E=S or Se).

Correspondence to: Dr. I.P. Beletskaya.

2. Results and discussion

The reactions of dimeric bis(*t*-butylcyclopentadienyl)methylttrium and bis(*t*-butylcyclopentadienyl)methyltutetium with two equivalents of various organic disulphides RSSR or diphenyldiselenide PhSeSePh in benzene at 20°C produce the corresponding dimeric bis(*t*-butylcyclopentadienyl)lanthanide organosulphides or organoselenides $\{({}^t\text{BuC}_5\text{H}_4)_2\text{Ln}(\mu\text{-ER})\}_2$ with almost quantitative yields. Depending on R_2E_2 , the cleavage of the E–E bonds requires a reaction time of between several minutes and some hours to achieve completion.



$\text{Ln}=\text{Y}$ E=S R=Ph (1),

${}^n\text{Bu}$ (2), ${}^t\text{Bu}$ (3) or CH_2Ph (4)

$\text{Ln}=\text{Y}$ E=Se R=Ph (5)

$\text{Ln}=\text{Lu}$ E=S R=Ph (6) or CH_2Ph (7)

$\text{Ln}=\text{Lu}$ E=Se R=Ph (8)

The dimeric EPh-bridged complexes crystallize from the benzene solution as monosolvates $\{({}^t\text{BuC}_5\text{H}_4)_2\text{Ln}(\mu\text{-EPh})\}_2 \cdot \text{C}_6\text{H}_6$, which on drying *in vacuo* form the unsolvated compounds 1, 5, 6 and 8. These complexes were isolated as air- and moisture-sensitive colourless crystalline solids and were unambiguously identified and characterized. The formation of 2, 3, 4 and 7 was monitored by nuclear magnetic resonance (NMR).

The structure of 5 was determined by X-ray diffraction analysis. The molecular structure is depicted in Fig. 1; the bond distances are listed in Table 1. The compound forms centrosymmetric dimeric molecules with two bridging SePh ligands. The central Y_2Se_2 unit is planar, with almost identical Y–Se distances: Y(1)–Se(1), 2.915(1) Å; Y(1)–Se(1A), 2.912(1) Å. These values are somewhat larger than the sum of the covalent radii of Y and Se (2.81 Å [14]). The coordination of the yttrium atoms in 5 is that of a distorted tetrahedron Cp_2YSe_2 with Cp–Y–Se angles (Cp(1) and Cp(2) centroids of Cp rings C(1)–C(5) and C(10)–C(14) respectively) ranging from 110.2(3) to 115.5(3)°, and Se(1)–Y(1)–Se(1A) and Cp(1)–Y(1)–Cp(2) angles of 71.5(1)° and 127.7(3)° respectively. The *t*-butyl substituents in the Cp_2Y fragments have transoid orientation relative to each other, and quaternary carbon atoms are displaced from the cyclopentadienyl ring planes by 0.14(2) Å towards the yttrium atom.

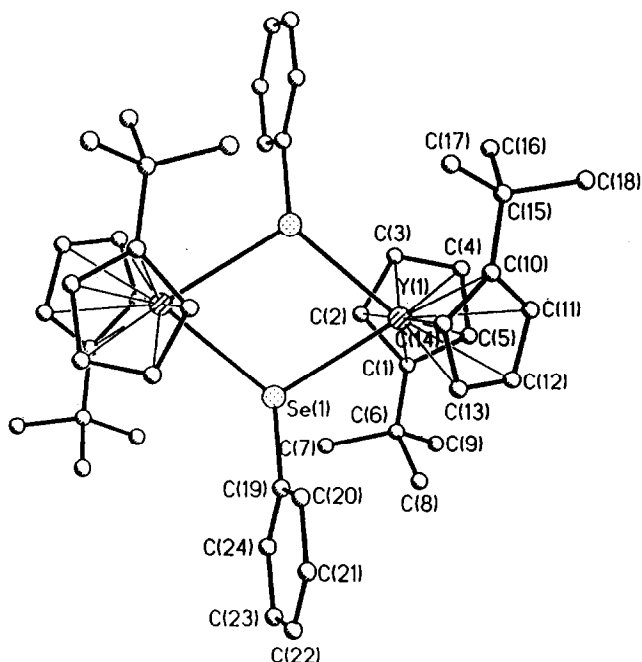


Fig. 1. Molecular structure of 5.

Each bridging selenium atom is on top of a trigonal pyramid with the two yttrium atoms and the *ipso*-carbon atom of the phenyl group (C(19)) forming the base. The angles within the Y_2SeR unit are as follows: Y(1)–Se(1)–C(19), 117.6(3)°; Y(1A)–Se(1)–C(19), 118.6(3)°; Y(1)–Se(1)–Y(1A), 108.5(3)°. The carbon

TABLE 1. Bond lengths in molecule 5

	Bond length (Å)		Bond length (Å)
Y(1)–Se(1)	2.915(1)	Y(1)–C(1)	2.701(10)
Y(1)–C(2)	2.653(12)	Y(1)–C(3)	2.612(13)
Y(1)–C(4)	2.595(10)	Y(1)–C(5)	2.620(9)
Y(1)–C(10)	2.686(13)	Y(1)–C(11)	2.628(12)
Y(1)–C(12)	2.608(10)	Y(1)–C(13)	2.607(13)
Y(1)–C(14)	2.656(13)	Y(1)–Se(1A)	2.912(1)
Se(1)–C(19)	1.930(10)	Se(1)–Y(1A)	2.912(1)
C(1)–C(2)	1.437(12)	C(1)–C(5)	1.422(16)
C(1)–C(6)	1.488(17)	C(2)–C(3)	1.423(17)
C(3)–C(4)	1.384(14)	C(4)–C(5)	1.420(15)
C(6)–C(7)	1.539(19)	C(6)–C(8)	1.522(22)
C(6)–C(9)	1.531(13)	C(10)–C(11)	1.409(12)
C(10)–C(14)	1.452(15)	C(10)–C(15)	1.488(17)
C(11)–C(12)	1.396(19)	C(12)–C(13)	1.395(15)
C(13)–C(14)	1.389(15)	C(15)–C(16)	1.521(18)
C(15)–C(17)	1.531(13)	C(15)–C(18)	1.561(18)
C(19)–C(20)	1.386(17)	C(19)–C(24)	1.363(16)
C(20)–C(21)	1.394(18)	C(21)–C(22)	1.362(30)
C(22)–C(23)	1.303(31)	C(23)–C(24)	1.399(20)
C(25)–C(26)	1.294(51)	C(25)–C(30)	1.383(43)
C(26)–C(27)	1.347(59)	C(27)–C(28)	1.288(62)
C(28)–C(29)	1.292(65)	C(29)–C(30)	1.257(60)

atom C(19) is displaced by 1.14(2) Å from the Y_2Se_2 plane. The phenyl rings are arranged above and below the Y_2Se_2 plane and the planes of both phenyl rings are almost normal (88.6(3)°) to the Y_2Se_2 plane. In this connection it is of interest that, in $(C_5H_5)_2Lu(\mu-SePh)_2Li(THF)_2$, both phenyl groups are on one side of the plane of the four-membered $LiSe_2Lu$ ring [2]. The lengths of the Y–Se bonds in **5** are in the same range as the length of the Lu–Se bonds in $(C_5H_5)_2Lu(\mu-SePh)_2Li(THF)_2$ (2.798(7) and 2.800(6) Å [2]) or the Sm–Se bond in $(C_5Me_5)_2Sm[SeC_6H_2(CF_3)_3-2,4,6](THF)$ (2.919(1) Å) [10].

3. Experimental details

All manipulations have been done either on the high vacuum line in all-glass apparatuses equipped with polytetrafluoroethylene stopcocks or in an atmosphere of thoroughly purified argon using the standard Schlenk technique, or in a Vacuum Atmospheres dry-box. Benzene for synthesis and NMR investigation (benzene- d_6) was distilled and stored over CaH_2 . Organic disulphides and Ph_2Se_2 (Merck) were used as received. The compounds $\{(tBuC_5H_4)_2Ln(\mu-Me)\}_2$ ($Ln=Y$ or Lu) were prepared by the method described by two of the present authors and coworkers [15]. 1H and ^{13}C NMR spectra were recorded with a Bruker AM 360 instrument. Electron probe X-ray analysis was done with a Phillips SEM-505 scanning electron microscope equipped with a unit for X-ray energy-dispersive analysis.

3.1. $\{(tBuC_5H_4)_2Y(\mu-SPh)\}_2$ (**1**)

A mixture of 0.69 g (1.00 mmol) $\{(tBuC_5H_4)_2Y(\mu-Me)\}_2$ with 0.44 g (2.02 mmol) of Ph_2S_2 in 15 ml of benzene was stirred at room temperature for 2 h. The reaction mixture was evaporated to about 5 ml. Crystalline $1 \cdot C_6H_6$ was separated by filtration and washed with a small amount of cold benzene. The complex loses benzene after prolonged drying under vacuum at 20–50°C to give a colourless powder **1** (yield, 0.67 g (76%); melting point (m.p.), 214–215°C). The solid could be further purified by crystallization from benzene. Anal. Calcd for $C_{48}H_{62}S_2Y_2$: C, 65.45; H 7.05. Found: C, 65.59; H, 7.09. Electron probe microanalysis: Y : S = 1 : 1. 1H NMR (C_6D_6): δ 1.38 (s, 36H, tBu); 6.25 (t, 8H, $J = 2.7$ Hz, 2,5- H_2 in C_5H_4); 6.64 (t, 8H, $J = 2.7$ Hz, 3,4- H_2 in C_5H_4); 7.41–7.56 (m, 10H, Ph ppm). ^{13}C NMR (C_6D_6): 139.4 (1-C in C_5H_4); 136.3 (1-C in Ph); 134.2 (2,6- C_2 in Ph); 128.8 (3,5- C_2 in Ph); 125.8 (4-C in Ph); 111.8 (3,4- C_2 in C_5H_4); 111.4 (2,5- C_2 in C_5H_4); 32.6 (CMe_3); 32.4 (Me) ppm.

3.2. $\{(tBuC_5H_4)_2Y(\mu-SePh)\}_2$ (**5**)

The reaction was carried out similarly to the preparation of **1**, starting from 0.35 g (0.51 mmol) of $\{(tBuC_5H_4)_2Y(\mu-Me)\}_2$ and 0.32 g (1.03 mmol) of Ph_2Se_2 in 10 ml of benzene. The reaction mixture was stirred for 5 h to give a colourless powder **5** (yield, 0.46 g (92%)); m.p., 218–219°C). Anal. Calcd for $C_{48}H_{62}Se_2Y_2$: C, 59.14; H 6.37%. Found: C, 59.23; H, 6.31. Electron probe microanalysis: Y : Se = 1 : 1. 1H NMR (C_6D_6): δ 1.36 (s) 36H, tBu); 6.28 (t, 8H, $J = 2.7$ Hz, 2,5- H_2 in C_5H_4); 6.68 (t, 8H, $J = 2.7$ Hz, 3,4- H_2 in C_5H_4); 7.33–7.40 (m, 10H, Ph) ppm. ^{13}C NMR (C_6D_6): 140.9 (1-C in C_5H_4); 135.6 (2,6- C_2 in Ph); 133.2 (1-C in Ph); 129.0 (3,5- C_2 in Ph); 126.3 (4-C in Ph); 111.8 (3,4- C_2 in C_5H_4); 110.8 (2,5- C_2 in C_5H_4); 32.6 (CMe_3); 32.0 (Me) ppm.

TABLE 2. Atomic coordinates and equivalent isotropic displacement coefficients in molecule **5**

	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	U_{eq}^a ($\times 10^{-3} \text{ \AA}^2$)
Y(1)	–2116(1)	3346(1)	3957(1)	45(1)
Se(1)	574(1)	4056(1)	4040(1)	48(1)
C(1)	–3068(9)	3017(9)	1679(8)	59(5)
C(2)	–2624(9)	4422(9)	2437(8)	62(5)
C(3)	–3440(11)	4643(10)	3112(8)	70(6)
C(4)	–4354(9)	3434(10)	2835(9)	66(5)
C(5)	–4126(10)	2437(10)	1959(9)	73(6)
C(6)	–2621(12)	2316(12)	727(9)	89(7)
C(7)	–1449(12)	3259(14)	671(10)	117(9)
C(8)	–2219(12)	1183(12)	895(9)	118(8)
C(9)	–3758(12)	1686(13)	–481(8)	128(9)
C(10)	–2866(9)	2349(9)	5386(9)	56(5)
C(11)	–3708(10)	1473(9)	4200(10)	69(6)
C(12)	–2995(12)	858(8)	3587(10)	80(6)
C(13)	–1693(11)	1365(9)	4376(10)	69(6)
C(14)	–1570(9)	2279(9)	5481(9)	59(5)
C(15)	–3299(10)	3077(10)	6339(10)	69(6)
C(16)	–3968(11)	4006(10)	6042(9)	87(7)
C(17)	–2154(12)	3909(11)	7541(10)	101(8)
C(18)	–4313(10)	2030(11)	6492(10)	98(8)
C(19)	1339(8)	2672(8)	3764(8)	50(4)
C(20)	1595(9)	2099(10)	4550(10)	75(6)
C(21)	2129(11)	1086(11)	4299(14)	105(9)
C(22)	2391(14)	673(14)	3283(19)	134(13)
C(23)	2171(14)	1235(13)	2561(14)	119(9)
C(24)	1630(10)	2249(10)	2763(9)	76(6)
C(25)	8416(35)	7747(34)	466(33)	215(24)
C(26)	8936(22)	8101(20)	1600(27)	175(14)
C(27)	8192(49)	7954(31)	2246(22)	247(33)
C(28)	6995(55)	7179(43)	1602(36)	279(50)
C(29)	6429(18)	6742(25)	461(45)	220(30)
C(30)	7106(33)	6952(29)	–136(16)	193(16)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

3.3. $\{(^t\text{BuC}_5\text{H}_4)_2\text{Lu}(\mu\text{-SPh})\}_2$ (**6**)

The reaction was carried out similarly to the preparation of **1**, starting from 0.48 g (0.56 mmol) of $\{(^t\text{BuC}_5\text{H}_4)_2\text{Lu}(\mu\text{-Me})\}_2$ and 0.25 g (1.15 mmol) of Ph_2S_2 in 10 ml of benzene. The reaction mixture was stirred for 2 h to give a colourless powder **6** (yield, 0.48 g (80%); m.p. 216–217°C. Anal. Calcd for $\text{C}_{48}\text{H}_{62}\text{Lu}_2\text{S}_2$: C, 54.75; H, 5.89%. Found: C, 54.82; H, 5.80. Electron probe microanalysis: Lu:S = 1:1. ^1H NMR (C_6D_6): δ 1.39 (s, 36H, ^tBu); 6.24 (t, 8H, $J = 2.6$ Hz, 2,5- H_2 in C_5H_4); 6.67 (t, 8H, $J = 2.6$ Hz, 3,4- H_2 in C_5H_4); 7.46–7.53 (m, 10H, Ph) ppm. ^{13}C NMR (C_6D_6): 139.2 (1-C in C_5H_4); 136.0 (1-C in Ph); 134.2 (2,6- C_2 in Ph); 128.7 (3,5- C_2 in Ph); 126.0 (4-C in Ph); 111.1 (3,4- C_2 in C_5H_4); 110.5 (2,5- C_2 in C_5H_4); 32.6 (CMe_3); 32.0 (Me) ppm.

3.4. $\{(^t\text{BuC}_5\text{H}_4)_2\text{Lu}(\mu\text{-SePh})\}_2$ (**8**)

The reaction was carried out similarly to the preparation of **1**, starting from 0.65 g (0.75 mmol) of $\{(^t\text{BuC}_5\text{H}_4)_2\text{Lu}(\mu\text{-Me})\}_2$ and 0.48 g (1.54 mmol) of Ph_2Se_2 in 15 ml of benzene. The reaction mixture was stirred for 1 h to give a colourless powder **8** (yield, 0.74 g (86%); m.p., 234–235°C). Anal. Calcd for $\text{C}_{48}\text{H}_{62}\text{Lu}_2\text{Se}_2$: C, 50.26; H, 5.41%. Found: C, 50.39; H, 5.54. Electron probe microanalysis: Lu:Se = 1:1. ^1H NMR (C_6D_6): δ 1.39 (s, 36H, ^tBu); 6.24 (t, 8H, $J = 2.6$ Hz, 2,5- H_2 in C_5H_4); 6.69 (t, 8H, $J = 2.6$ Hz, 3,4- H_2 in C_5H_4); 7.31–7.40 (m, 10H, Ph) ppm. ^{13}C NMR (C_6D_6): 139.4 (1-C in C_5H_4); 135.6 (2,6- C_2 in Ph); 133.3 (1-C in Ph); 129.0 (3,5- C_2 in Ph); 126.5 (4-C in Ph); 110.7 (3,4- C_2 in C_5H_4); 109.6 (2,5- C_2 in C_5H_4); 32.6 (CMe_3); 32.0 (Me) ppm.

3.5. X-ray diffraction study of complex $5 \cdot \text{C}_6\text{H}_6$

Crystals of $5 \cdot \text{C}_6\text{H}_6$ were grown from saturated solution of compound in benzene; single crystals were packed in thin-walled glass capillaries under argon. The crystals of $5 \cdot \text{C}_6\text{H}_6$ are triclinic; at 296 K, $a = 11.242(2)$ Å, $b = 11.388(2)$ Å, $c = 12.865(2)$ Å, $\alpha = 110.32(2)^\circ$, $\beta = 105.16(2)^\circ$, $\gamma = 102.84(2)^\circ$, $V = 1398.8(4)$ Å³, $d_{\text{calc}} = 1.343$ g cm⁻³, $Z = 1$ and the space group is \bar{P} .

The unit-cell parameters and intensities of 4353 independent reflections with $F^2 \geq 3\sigma(F^2)$ were deter-

mined using a Siemens P3/PC diffractometer ($\lambda(\text{Mo K}\alpha)$; graphite monochromator; θ - 2θ scan method; $\theta \leq 24^\circ$). The structure was solved by the direct method and refined by the full-matrix least-squares method. Hydrogen atoms were placed in the calculated positions and included in the final refinement in the "riding model" approximation with the common isotopic temperature factor (refined to $U = 0.110(7)$ Å²). Final discrepancy factors are $R = 0.0509$ and $R_w = 0.0532$. The atomic coordinates are listed in Table 2.

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