Facile Transformations of Lanthanocene Alkyls to Lanthanocene Thiolate, Sulfide, and Disulfide Derivatives by Reaction with Elemental Sulfur

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Treatment of $[Cp_2Ln(\mu\text{-}Me)]_2$ with 2 equiv of elemental sulfur in toluene at room temperature leads to the formation of the methylthiolate complexes $[Cp_2Ln(\mu\text{-}SMe)]_2$ [Ln = Yb (**1a**), Y (**1b**), Er (**1c**), Dy (**1d**)] in good yields. While reaction of $Cp_2Y(^nBu)$ with elemental sulfur in 1:1 stoichiometric ratio under the same conditions yields $[(Cp_2Y)_2(\mu_3\text{-}S)(THF)]_2$ (**2a**) as the metal-containing product with the extrusion of $^nBuS^nBu$ and $^nBuSS^nBu$, the corresponding insertion intermediate $[Cp_2Y(\mu\text{-}S^nBu)]_2$ (**1e**) could be isolated only by decreasing the relative amount of S_8 under more mild reaction conditions. Furthermore, $[Cp_2Yb(\mu\text{-}SEt)]_2$ reacts with 2 equiv of sulfur to give a mixture of $[(Cp_2Yb)_2(\mu_3\text{-}S)(THF)]_2$ (**2b**) and $[Cp_2Yb(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)$ (**3**). **2b** and **3** can also be prepared from the reaction of $[Cp_2Yb(\mu\text{-}Me)]_2$ with excess elemental sulfur in THF. All these results demonstrate that lanthanocene thiolate complexes are unstable in solution with S_8, and the nature of the alkyl ligands and reaction conditions has a great influence on the final product structures from the reaction of lanthanocene alkyls with elemental sulfur and provides an easy access to trivalent lanthanocene thiolate, sulfide, and disulfide complexes as well as thioethers and organic disulfides. Complexes **1**−**3** were characterized by elemental analysis and IR and mass spectroscopies. The structures of complexes **1a**, **1e**, **2a**, **2b**, and **3** are also determined through X-ray single-crystal diffraction analysis.

Introduction

The synthesis and transformation of lanthanide complexes containing sulfur-based ligands are receiving increasing attention for both fundamental interest and potential applications in catalysis and materials science.[1−4] Insertion reactions of metal−ligand bonds are powerful tools for the construction of ancillary ligands in organolanthanide chemistry.[5] Although tellurium and selenium insertions into a lanthanide−carbon bond proved to be feasible 10 years ago,[6] surprisingly no example of the formation of thiolate ligands by the insertion of elemental sulfur into the lanthanide−carbon σ-bond has been reported. Furthermore, very little is known about the reactivity of lanthanocene thiolates in comparison with the extensive knowledge of lanthanocene derivatives containing C- or N-based anion ligands.[2,4] To our knowledge, no selective substitution of thiolate ligands has as yet been identified for lanthanocene systems.

Lanthanide thiolate complexes have previously been prepared either by classical metathetical reactions or

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by oxidative addition of organic disulfides to low-valent lanthanide species.[1,3] In continuation of our studies on insertions into lanthanide−ligand bonds,[7] we are especially interested to determine if thiolate complexes of rare earths may be synthesized by sulfur insertion into organolanthanide alkyls, because the latter route has significant advantages in that it avoids the synthesis of the intermediate organosulfurs and gives potentially easy access to compounds that are either difficult to synthesize or inaccessible by other routes.

We now report the investigation of the activation of lanthanocene alkyl complexes on elemental sulfur, indicating that lanthanocene thiolate complexes are unstable in solution with S_8, and treatment of lanthanocene alkyls with elemental sulfur allows the isolation of lanthanocene thiolates, sulfides, or disulfides depending on the nature of alkyl groups and the reaction conditions.

Experimental Section

General Procedures. All operations involving air- and moisture-sensitive compounds were carried out under an inert atmosphere of purified nitrogen using standard Schlenk techniques. The solvents THF, toluene, and *n*-hexane were refluxed and distilled over sodium benzophenone ketyl under nitrogen immediately prior to use. $[Cp_2Ln(\mu\text{-}Me)]_2$[8] and Cp_2Ln^nBu ($Cp = \eta^5\text{-}C_5H_5$)[7b,9] were prepared by literature procedures. Methyllithium, *n*-butyllithium, and EtSH were purchased from Aldrich and were used without further purification. Melting points were determined in sealed nitrogen-filled capillaries without temperature correction. Elemental analyses for C and H were carried out on a Rapid CHN-O analyzer. Infrared spectra were obtained on a Nicolet FT-IR 360 spectrometer with samples prepared as Nujol mulls. Mass spectra were recorded on a Philips HP5989A instrument operating in EI mode. Crystalline samples of the respective complexes were rapidly introduced by the direct inlet techniques with a source temperature of 200 °C. The values of *m/z* are referred to the isotopes ^{12}C, ^{1}H, ^{16}O, ^{32}S, ^{174}Yb, ^{166}Er, ^{89}Y, and ^{164}Dy. GC/MS were obtained on a Hewlett-Packard 6890/5973 instrument. ^1H NMR data were obtained on a Bruker DMX-500 NMR spectrometer and referred to residual aryl protons in C_6H_6 ($\delta = 7.15$).

Synthesis of $[Cp_2Yb(\mu\text{-}SMe)]_2$ (1a). To a solution of $[Cp_2Yb(\mu\text{-}Cl)]_2$ (0.273 g, 0.40 mmol) in toluene (40 mL) was added MeLi (1.80 M, 0.45 mL in diether) at −30 °C. After stirring for 1 h at low temperature, the mixture solution was slowly warmed to ambient temperature and the precipitate (LiCl) was removed by centrifugation. Then, to the clear solution was added S_8 (26 mg, 0.10 mmol). After stirring for 10 h, the reaction mixture was concentrated by reduced pressure to give a yellow powder. Recrystallization of the powder from the mixture solvent of THF and hexane at −15 °C afforded **1a** as orange-red crystals. Yield: 0.200 g (70%). Mp: 225−228 °C. Anal. Calcd for $C_{22}H_{26}S_2Yb_2$: C, 37.71; H, 3.74. Found: C, 37.65; H, 3.70. IR (Nujol, cm^{-1}): 3085 w, 1460 s, 1377 s, 1307 m, 1148 m, 1009 s, 890 m, 779 m, 726 m, 663 m. ^1H NMR (C_6H_6): δ −53.19 (s, 10H, $2C_5H_5$), 85.19 (s, 3H, CH_3). EI-MS: *m/z* [fragment, relative intensity (%)] = 700 (M − 2, 5), 653 (M − 2 − SMe, 12), 634 (M − 2 − CpH, 58), 620 (M − CpH − CH_4, 3), 604 (M − CpH − $2CH_4$, 6), 587 (M − 2 − CpH − SMe, 8), 570 (M − 2CpH, 6), 554 (M − 2CpH − CH_4, 10), 350 (M/2 − 1, 6) 304 (Cp_2Yb, 55), 239 (CpYb, 75), 65 (CpH, 100).

Synthesis of $[Cp_2Y(\mu\text{-}SMe)]_2$ (1b). To a solution of $[Cp_2Y(\mu\text{-}Cl)]_2$ (0.232 g, 0.46 mmol) in toluene (40 mL) was added MeLi (1.80 M, 0.51 mL in diether) at −30 °C. After stirring for 1 h at low temperature, the reaction mixture was slowly warmed to ambient temperature. Then, to the mixture solution was added S_8 (29 mg, 0.11 mmol). After stirring for 10 h, the precipitate was removed by centrifugation. The solution was concentrated by reduced pressure to ca. 4 mL and a colorless solid precipitated, which was collected, washed with hexane twice, and dried in a vacuum. Yield: 0.164 g (65%). Mp: 234−237 °C. Anal. Calcd for $C_{22}H_{26}S_2Y_2$: C, 49.63; H, 4.92. Found: C, 49.48; H, 4.75. IR (Nujol, cm^{-1}): 3080 w, 1460 s, 1377 s, 1300 w, 1154 s, 1009 s, 891 m, 777 m, 722 m, 663 m. ^1H NMR (C_6H_6): δ 6.14 (s, 10H, $2C_5H_5$), 2.18 (s, 3H, CH_3). EI-MS: *m/z* [fragment, relative intensity (%)] = 532 (M, 22), 502 (M − 2Me, 4), 485 (M − SMe, 52), 467 (M − Cp, 85), 452 (M − Cp − Me, 8), 437 (M − Cp − 2Me, 14), 419 (M − SMe − CpH, 28), 387 (M − 2Cp − Me, 11), 372 (M − 2Cp − 2Me, 9), 265 (M/2 − 1, 8), 219 (Cp_2Y, 90), 154 (CpY, 10), 65 (Cp, 40).

Synthesis of $[Cp_2Er(\mu\text{-}SMe)]_2$ (1c). Following the procedure described above for **1b**, reaction of $[Cp_2Er(\mu\text{-}Cl)]_2$ (0.260 g, 0.39 mmol) with MeLi (1.80 M, 0.43 mL in diether) and subsequently with S_8 (25 mg, 0.097 mmol) gave complex **1c** as a pink powder. Yield: 0.172 g (64%). Mp: 227−230 °C. Anal. Calcd for $C_{22}H_{26}S_2Er_2$: C, 38.35; H, 3.80. Found: C, 38.29; H, 3.75. IR (Nujol, cm^{-1}): 3080 w, 1618 w, 1460 s, 1377 s, 1295 w, 1154 s, 1009 s, 891 m, 777 m, 722 m, 663 m. EI-MS: *m/z* [fragment, relative intensity (%)] = 686 (M, 15), 656 (M − 2Me, 4), 639 (M − SMe, 48), 621 (M − Cp, 85), 606 (M − Cp − Me, 9), 591 (M − Cp − 2Me, 15), 574 (M − SMe − Cp, 28), 541 (M − 2Cp − Me, 11), 462 (M − 2Cp − 2SMe, 7), 342 (M/2 − 1, 8), 296 (Cp_2Er, 90), 231 (CpEr, 10), 65 (Cp, 80).

Synthesis of $[Cp_2Dy(\mu\text{-}SMe)]_2$ (1d). Following the procedure described above for **1b**, reaction of $[Cp_2Dy(\mu\text{-}Cl)]_2$ (0.269 mg, 0.41 mmol) with MeLi (1.80 M, 0.46 mL in diether) and subsequently with S_8 (26 mg, 0.10 mmol) gave complex **1d** as a pale yellow powder. Yield: 0.181 g (65%). Mp: 236−240 °C. Anal. Calcd for $C_{22}H_{26}S_2Dy_2$: C, 38.88; H, 3.86. Found: C, 38.81; H, 3.79. IR (Nujol, cm^{-1}): 3080 w, 1460 s, 1377 s, 1295 w, 1154 s, 1009 s, 891 w, 777 m, 722 s, 663 m. EI-MS: *m/z* [fragment, relative intensity (%)] = 680 (M − 2, 16), 652 (M − 2Me, 4), 635 (M − SMe, 50), 617 (M − Cp, 80), 587 (M − Cp − 2Me, 14), 570 (M − SMe − Cp, 26), 537 (M − 2Cp − Me, 11), 522 (M − 2Cp − 2Me, 9), 455 (M − 2Cp − 2SMe, 7), 340 (M/2 − 1, 8)), 294 (Cp_2Dy, 50), 229 (CpDy, 10), 65 (Cp, 90).

Synthesis of $[Cp_2Y(\mu\text{-}S^nBu)]_2$ (1e). To a solution of $[Cp_2Y(\mu\text{-}Cl)]_2$ (0.348 g, 0.68 mmol) in toluene (50 mL) was added ^{n}BuLi (1.60 M, 0.86 mL in cyclohexane) at −30 °C. After stirring for 3 h, to the mixture was added S_8 (39 mg, 0.15 mmol) at −5 °C. After stirring 5 h at low temperature, the reaction mixture was then warmed to ambient temperature and stirred overnight. The precipitate was removed by centrifugation. The solution was concentrated by reduced pressure to ca. 6 mL, and a colorless solid precipitated. Recrystallization of the solid in toluene/THF at −15 °C gave colorless crystals of **1e**. Yield: 0.211 g (50%). Mp: 230−235 °C. Anal. Calcd for $C_{28}H_{38}S_2Y_2$: C, 54.55; H, 6.21. Found: C, 54.40; H, 6.15. IR (Nujol, cm^{-1}): 3089 w, 1464 s, 1377 s, 1264w, 1154 s, 1011 s, 779 m, 636 m. ^1H NMR (C_6H_6): δ 6.25 (s, 10 H, $2C_5H_5$), 2.81 (t, 2H, SCH_2), 1.42 (m, 2H, CH_2), 1.34 (m, 2H, CH_2CH_3), 0.92 (t, 3H, CH_3). EI-MS: *m/z* [fragment, relative intensity (%)] = 616 (M, 20), 551 (M − Cp, 83), 527 (M − S ^{n}Bu, 48), 502 (M − 2^{n}Bu, 4), 494 (M − Cp − ^{n}Bu, 8), 437 (M − Cp − 2^{n}Bu, 14), 461 (M − S^{n}Bu − CpH, 25), 429 (M − 2Cp − ^{n}Bu, 11), 372 (M − 2Cp − 2 ^{n}Bu, 9), 307 (M/2 − 1, 8), 219 (Cp_2Y, 90), 154 (CpY, 10), 65 (Cp, 50).

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Synthesis of [(Cp$_2$Y)$_2$(μ_3-S)(THF)]$_2$ (2a). To a solution of [Cp$_2$Y(μ-Cl)]$_2$ (0.213 g, 0.42 mmol) in 40 mL of toluene was added ^{n}BuLi (1.60 M, 0.53 mL in cyclohexane) at −30 °C. After stirring for 30 min at low temperature, the reaction solution was slowly warmed to room temperature and stirred for 3 h. Then, to the mixture was added S$_8$ (27 mg 0.11 mmol) at ambient temperature. After stirring 12 h, the precipitate was removed by centrifugation. Removal of the solvent gave a white solid. Diffusion of hexane into a solution of **2a** in THF afforded pale yellow crystals. Yield: 70 mg (30%). Mp: 285 °C. Anal. Calcd for $C_{48}H_{56}O_2S_2Y_4$: C, 53.15; H, 5.20. Found: C, 52.95; H, 5.12. IR (Nujol, cm^{-1}): 3081 w, 1338 m, 1246 w, 1172 w, 1072 w, 1016 s, 913 m, 784 s, 768 m, 722 w, 663 m. EI-MS: *m/z* [fragment, relative intensity (%)] = 676 (M − 2THF − 4CpH, 2), 472 (M/2 − THF + 2, 7), 407 (M/2 − THF − Cp + 2, 28), 341 (M/2 − THF − 2Cp + 1, 26), 219 (Cp$_2$Y, 90), 154 (CpY, 7), 66 (CpH, 90).

Synthesis of [(Cp$_2$Yb)$_2$(μ_3-S)(THF)]$_2$ (2b) and [Cp$_2$Yb(THF)]$_2$(μ-η^2:η^2-S$_2$) (3). To a solution of [Cp$_2$Yb(μ-SEt)]$_2$ (0.293 g, 0.40 mmol) in THF (32 mL) was added S$_8$ (26 mg, 0.10 mmol). After stirring for 3 h, there is a progressively deepening color. Several days later, a mixture containing red crystals of complex **2b** (0.108 g, 38% yield based on metal) and dark green crystals of **3** (97 mg, 30% yield) was obtained at room temperature, which were separated by picking large crystals, and the pure compounds were used for characterization purposes.

Anal. Calcd for complex **2b**, $C_{48}H_{56}O_2S_2Yb_4$: C, 40.56; H, 3.97. Found: C, 40.46; H, 3.85. IR (Nujol, cm^{-1}): 3080 w, 1338 m, 1246 w, 1172 w, 1072 w, 1016 s, 912 m, 784 s, 763 m, 722 m, 663 w. EI-MS: *m/z* [fragment, relative intensity (%)] = 639 (M/2 − THF − 1, 3), 574 (M/2 − THF − CpH, 10), 510 (M/2 − THF − 2Cp, 26), 304 (Cp$_2$Yb, 90), 239 (CpYb, 7), 174 (Yb, 36), 66 (CpH, 90). Mp: 260 °C (dec).

Anal. Calcd for complex **3**, $C_{28}H_{36}O_2S_2Yb_2$: C, 41.27; H, 4.45. Found: C, 41.46; H, 4.38. IR (Nujol, cm^{-1}): 3081 w, 1338 m, 1246 w, 1172 w, 1072 w, 1016 s, 913 m, 784 s, 768 m, 723 m, 663 w. EI-MS: *m/z* [fragment, relative intensity (%)] = 672 (M − 2THF, 10), 607 (M − 2THF − Cp, 6), 542 (M − 2THF − 2Cp, 9), 412 (Yb$_2$S$_2$, 23), 380 (Yb$_2$S, 12), 336 (M/2, 46), 304 (Cp$_2$Yb, 90), 239 (CpYb, 7), 65 (Cp, 95). Mp: 195 °C (dec).

X-ray Data Collection, Structure Determination, and Refinement. Suitable single crystals of complexes **1a**, **1e**, **2a**, **2b**, and **3** were sealed under argon in Lindemann glass capillaries for X-ray structural analysis. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. During the collection of the intensity data, no significant decay was observed. For **1a**, frames were integrated to the maximum 2θ angle of 52.02° with the Siemens SAINT program to yield a total of 28 570 reflections, of which 12 276 were independent (R_{int} = 0.0887). For **1e**, frames were integrated to the maximum 2θ angle of 52.02° with the Siemens SAINT program to yield a total of 6328 reflections, of which 2751 were independent (R_{int} = 0.0556). For **2a**, frames were integrated to the maximum 2θ angle of 50.02° with the Siemens SAINT program to yield a total of 9799 reflections, of which 4179 were independent (R_{int} = 0.1192). For **2b**, frames were integrated to the maximum 2θ angle of 50.02° with the Siemens SAINT program to yield a total of 9652 reflections, of which 4121 were independent (R_{int} = 0.0468). For **3**, frames were integrated to the maximum 2θ angle of 50.02° with the Siemens SAINT program to yield a total of 5793 reflections, of which 4227 were independent (R_{int} = 0.0224). The final unit cell parameters were determined from the full-matrix least-squares on F^2 refinement of three-dimensional centroids of 12 276 reflections for **1a**, 2751 reflections for **1e**, 4179 reflections for **2a**, 4121 reflections for **2b**, and 4227 reflections for **3**. The intensities were corrected for Lorentz−polarization effects and empirical absorption with the SADABS program.[10] A summary of the crystallographic data and selected experimental information is given in Table 1.

The structures were solved by the direct method using the SHELXL-97 program.[11] All non-hydrogen atoms were found from the difference Fourier syntheses. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms, but were not included in the refinement. The absolute structure of **3** was determined by the refinement. All calculations were performed using the Bruker Smart program.

Results and Discussion

Insertion of Elemental Sulfur into the Ln−C Bond of [Cp$_2$Ln(μ-Me)]$_2$. The reaction of [Cp$_2$LnCl]$_2$ with 2 equiv of MeLi and subsequently with elemental sulfur provided the dinuclear products [Cp$_2$Ln(μ-SMe)]$_2$ [Ln = Yb (**1a**), Y (**1b**), Er (**1c**), Dy (**1d**)], as shown in eq 1. Complexes **1a**−**d** could also be obtained by the direct reaction of [Cp$_2$Ln(μ-Me)]$_2$ with 2 equiv of elemental sulfur in toluene at room temperature in good yields.

$$[\mathrm{Cp_2LnCl}]_2 \xrightarrow[\text{toluene}]{\text{2LiMe, -30 °C}} [\mathrm{Cp_2LnMe}]_2 \xrightarrow[\text{toluene}]{\text{1/4S}_8\text{, r. t.}} [\mathrm{Cp_2Ln(\mu{-}SMe)}]_2 \qquad (1)$$

Ln = Yb(**1a**), Y(**1b**), Er(**1c**), Dy(**1d**)

The formation of **1a**−**d** represents the first insertion of a sulfur atom into lanthanide−carbon bonds. Examples of insertion of a single sulfur atom from elemental sulfur into a metal−carbon bond are also rare in transition metal chemistry.[12,13] In most cases elemental sulfur does not undergo the insertion into the transition-metal−carbon bond. For example, only one sulfur atom insertion has occurred into the M−H bond without the sulfur insertion into the Pt−C bond even under more drastic conditions when excess S$_8$ is added to a benzene or THF solution of Pt(Cy$_2$PCH$_2$CH$_2$PCy$_2$)(R)H (R = Me, CH$_2$^{t}Bu, Ph).[14]

Complexes **1a**−**d** are air- and moisture-sensitive. They are soluble in THF and toluene, but less soluble in *n*-hexane. All the methylthiolate complexes were characterized by elemental analysis and IR and MS spectroscopy, which were in good agreement with the proposed structure. The spectroscopic properties of **1a**−**d** are very similar, indicating that they have the same structures. Only one of them, **1a**, was characterized crystallographically. In the mass spectra, all the compounds clearly display their molecular ions which are characterized by the loss of the cyclopentadienyl group from the molecular ion with the [M − Cp]$^+$ ion as a strong peak.

Complex **1a** crystallizes from the solvent mixture of tetrahydrofuran and hexane in the monoclinic system, space group *C*2/*c*. An ORTEP diagram of **1a** is shown in Figure 1. Selected bond distances and angles are given in Table 2. The X-ray structure of **1a** definitively proves that only one sulfur atom was inserted into the

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Table 1. Crystal and Data Collection Parameters of Complexes 1a, 1e, 2a, 2b, and 3

	1a	**1e**	**2a**	**2b**	**3**
formula	$C_{22}H_{26}S_2Yb_2$	$C_{28}H_{38}S_2Y_2$	$C_{48}H_{56}O_2S_2Y_4$	$C_{48}H_{56}O_2S_2Yb_4$	$C_{28}H_{36}O_2S_2Yb_2$
molecular weight	700.63	616.52	1084.69	1421.21	814.77
cryst color	orange	colorless	pale yellow	orange	dark green
crystal dimens (mm)	0.25 × 0.08 × 0.05	0.25 × 0.20 × 0.20	0.15 × 0.10 × 0.04	0.20 × 0.15 × 0.10	0.20 × 0.08 × 0.05
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*P*2(1)/*c*	*P*2(1)/*n*	*P*2(1)/*n*	*P*2(1)
unit cell dimensions					
a (Å)	29.059(7)	9.181(4)	11.064(2)	10.969(4)	8.132(3)
b (Å)	27.865(7)	17.772(9)	19.121(4)	19.069(8)	21.599(8)
c (Å)	17.086(4)	8.877(4)	111.450(2)	11.416(5)	8.376(3)
β (deg)	115.418(3)	104.688(7)	101.570(4)	101.459(7)	109.020(5)
V (Å^3)	12496(5)	1401.0(12)	2373.1(8)	2340.3(16)	1390.8(9)
Z	20	2	2	2	2
D_c (g.cm^{-3})	1.862	1.461	1.518	2.017	1.946
μ (mm^{-1})	7.608	4.284	4.965	8.043	6.856
F(000)	6600	632	1096	1344	784
radiation (λ =0.710730 Å)	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
temperature (K)	298.2	298.2	298.2	298.2	298.2
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
θ range (deg)	1.41 to 26.01	2.29 to 26.01	2.13 to 25.01	2.11 to 25.01	1.89 to 25.01
h,k,l range (λ = 0.710730 Å)	$-35\le h\le 32$, $-34\le k\le 32$ $-20\le l\le 21$	$-10\le h\le 11$, $-21\le k\le 21$ $-7\le l\le 10$	$-10\le h\le 13$ $-17\le k\le 22$ $-13\le l\le 13$	$-13\le h\le 12$ $-22\le k\le 19$ $-10\le l\le 13$	$-9\le h\le 9$ $-25\le k\le 24$ $-8\le l\le 9$
no. of reflns measd	28 570	6328	9799	9652	5793
no. of unique reflns	12276 (R_{int} = 0.0887)	2751 (R_{int} = 0.0556)	4179 (R_{int} = 0.1192)	4121 (R_{int} = 0.0468)	4227 (R_{int} = 0.0224)
completeness to θ	99.8% (θ = 26.01)	99.8% (θ = 26.01)	99.7% (θ =25.01)	99.8% (θ =25.01)	99.8% (θ =25.01)
max. and min. transmn	0.7022 and 0.2521	0.4812 and 0.4139	0.8261 and 0.5230	0.5001 and 0.2961	0.7256 and 0.3409
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	12276/0/586	2751/0/145	4179/0/253	4121/0/253	4227/1/258
goodness-of-fit on F^2	0.843	0.945	0.763	1.012	1.140
final *R* indices [$I>2\sigma(I)$]	$R_1 = 0.0431$, $wR_2 = 0.0865$	$R_1 = 0.0438$, $wR_2 = 0.0919$	$R_1 = 0.0576$, $wR_2 = 0.1076$	$R_1 = 0.0366$, $wR_2 = 0.0666$	$R_1 = 0.0349$, $wR_2 = 0.0827$
R indices (all data)	$R_1 = 0.1164$, $wR_2 = 0.1043$	$R_1 = 0.0890$, $wR_2 = 0.1057$	$R_1 = 0.1867$, $wR_2 = 0.1318$	$R_1 = 0.0637$, $wR_2 = 0.0751$	R_1=0.0364, $wR_2 = 0.0755$
largest diff peak and hole (e·Å^{-3})	1.348 and −1.138	0.569 and −0.570	0.507 and −0.439	1.156 and −0.647	1.336 and −1.309

Yb−C bond, giving a thiolate ligand. Complex **1a** is a solvent-free dimeric structure with each ytterbium atom bonded to two η^5-cyclopentadienyl rings and two bridging sulfur atoms. The coordination number of each Yb atom is 8. The Yb_2S_2 unit is planar. The average Yb−S distance of 2.706(4) Å is comparable with the value found in the related thiolate-bridged complex $[Cp_2Yb(\mu\text{-}S^nBu)]_2$, 2.707(3) Å.[1c] The S−C bond distances of 1.815(11) and 1.853(12) Å are in the normal range for an sp^3 sulfur−carbon single bond[15] and are similar to the distances reported in other complexes containing SR groups.[1c] In the Yb_2S_2 bridging unit, the average angles of Yb−S−Yb and S−Yb−S are respectively 96.43(11)° and 83.56(10)°, which are similar to the corresponding values in $[Cp_2Yb(\mu\text{-}S^nBu)]_2$,[1c] but very different from the observations in bridging complex $[(Me_3CC_5H_4)_2Ce(\mu\text{-}SCHMe_2)]$.[1d]

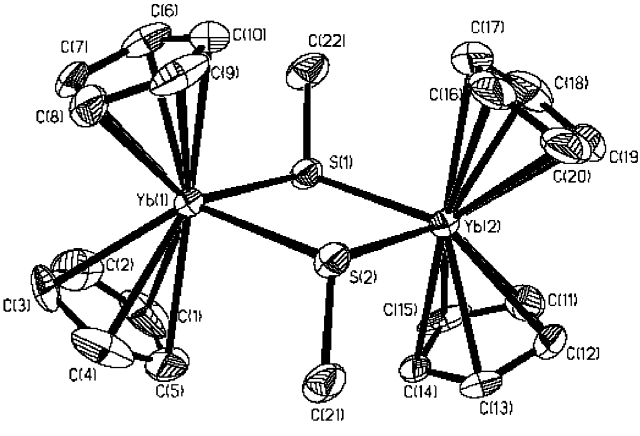


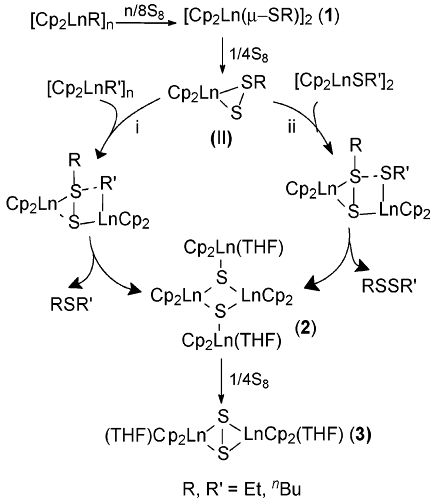
Figure 1. ORTEP diagram of $[(C_5H_5)_2Yb(\mu\text{-}SMe)]_2$ (**1a**) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.

Table 2. Bond Lengths [Å] and Angles [deg] for Complex 1a

Yb(1)−S(1)	2.713(4)	Yb(2)−S(1)	2.698(3)
Yb(1)−S(2)	2.699(3)	Yb(2)−S(2)	2.712(3)
S(1)−C(22)	1.850(12)	S(2)−C(21)	1.820(12)
Yb(1)−C(1)	2.609(14)	Yb(2)−C(11)	2.557(14)
Yb(1)−C(2)	2.573(19)	Yb(2)−C(12)	2.584(13)
Yb(1)−C(3)	2.584(16)	Yb(2)−C(13)	2.595(12)
Yb(1)−C(4)	2.574(16)	Yb(2)−C(14)	2.580(10)
Yb(1)−C(5)	2.609(16)	Yb(2)−C(15)	2.582(12)
Yb(1)−C(6)	2.587(13)	Yb(2)−C(16)	2.579(14)
Yb(1)−C(7)	2.575(14)	Yb(2)−C(17)	2.622(15)
Yb(1)−C(8)	2.549(15)	Yb(2)−C(18)	2.594(15)
Yb(1)−C(9)	2.593(13)	Yb(2)−C(19)	2.574(16)
Yb(1)−C(10)	2.593(13)	Yb(2)−C(20)	2.564(15)
S(2)−Yb(1)−S(1)	83.6(1)	S(1)−Yb(2)−S(2)	83.6(1)
C(22)−S(1)−Yb(2)	116 (1)	C(21)−S(2)−Yb(2)	117.5(5)
Yb(2)−S(1)−Yb(1)	96.4(1)	C(21)−S(2)−Yb(1)	114.2(5)
C(22)−S(1)−Yb(1)	14.0(5)	Yb(1)−S(2)−Yb(2)	96.4(1)

Activation of $Cp_2Ln(^nBu)$ on Elemental Sulfur. To understand the factors affecting the insertion of sulfur into the lanthanide−carbon bond, the reactivity of lanthanocene *n*-butyl complexes with elemental sulfur was also studied. In contrast to the simple insertion reaction observed in the formation of complexes **1a**−**d**,

Scheme 1. Proposed Pathway for the Formation of 1−3



the reaction of $Cp_2Y(^nBu)$ (prepared in situ from Cp_2YCl and Li^nBu) with 1 equiv of sulfur under the same conditions did not result in the expected $[Cp_2Y(\mu\text{-}S^nBu)]_2$ but instead resulted in the tetranuclear sulfido-bridged complex $[(Cp_2Y)_2(\mu_3\text{-}S)(THF)]_2$ (**2a**), with the byproducts $^nBuS^nBu$ and $^nBuSS^nBu$ in 3:2 identified by GC/MS (eq 2). The corresponding insertion intermediate $[Cp_2Y(\mu\text{-}S^nBu)]_2$ (**1e**) could be isolated only in the presence of excess $Cp_2Y(^nBu)$ under more mild reaction conditions (eq 3).

$$[\mathrm{Cp_2YCl}]_2 \xrightarrow[\text{(2) } 1/4\mathrm{S_8}\text{, r. t.}]{\text{(1) Li}^n\text{Bu, toluene, -30 °C}} [(\mathrm{Cp_2Ln})_2(\mathrm{THF})(\mu\text{-S})]_2 + {}^n\mathrm{BuS}^n\mathrm{Bu} + {}^n\mathrm{BuSS}^n\mathrm{Bu} \qquad (2)$$

$$[\mathrm{Cp_2YCl}]_2 \xrightarrow[\text{(2) } 1/4.5\mathrm{S_8}\text{, -5 °C}]{\text{(1) Li}^n\text{Bu, toluene, -30 °C}} [\mathrm{Cp_2Y}(\mu\text{-S}^n\mathrm{Bu})]_2 \qquad (3)$$

Presumably, the formation of **2a** may result from the competitive reaction of $[Cp_2Y(\mu\text{-}S^nBu)]_2$ with elemental sulfur, which leads to the conversion of $[Cp_2Y(\mu\text{-}S^nBu)]_2$ to the alkylperthio intermediate $Cp_2YS_2{}^nBu$. The subsequent donating coordination of the resultant alkylperthio to a second Y center followed by the intermolecular elimination of $^nBu_2S$ or $^nBu_2S_2$ leads to the formation of the S^{2-} ligand. Since the bound alkylperthio group may be further attacked by either $Cp_2Y(^nBu)$ or $[Cp_2Y(\mu\text{-}S^nBu)]_2$, two competitive elimination products, thioether (pathway i) and dialkyl disulfide (pathway ii), were observed (Scheme 1). The analogous preferential formation of the alkylperthio group has been confirmed in the insertion of S into W−C bonds of $CpW(NO)(CH_2SiMe_3)_2$,[13] but attempts to isolate the intermediate (**II**) were unsuccessful.

Consistent with this hypothesis, five organosulfur elimination products, ^nBuSEt, $EtSS^nBu$, and EtSSEt as major species and $^nBuS^nBu$ and $^nBuSS^nBu$ as minor products, were unambiguously detected and identified by GC/MS, when a mixture of $[Cp_2Y(\mu\text{-}SEt)]_2$ and $Cp_2Y(^nBu)$ was treated with 1 equiv of elemental sulfur (based on metal) in which $[(Cp_2Y)_2(\mu_3\text{-}S)(THF)]_2$ was also found to be the principal metal-containing product. On the other hand, we can exclude the possibility that the observed four-membered complex is formed via a thermally induced decomposition, on the basis of two facts: that no elimination product EtSEt is observed in the above reaction and that $[Cp_2Y(\mu\text{-}S^nBu)]_2$ is thermally stable.[1c] Further evidence that the driving force is probably the further interaction of the putative thiolate intermediate $[Cp_2Y(\mu\text{-}S^nBu)]_2$ with elemental sulfur on going from Cp_2Y^nBu to $[(Cp_2Y)_2(\mu_3\text{-}S)(THF)]_2$ was obtained from experiments entailing a similar transformation of $[Cp_2Yb(\mu\text{-}SMe)]_2$ in the presence of excess elemental sulfur.

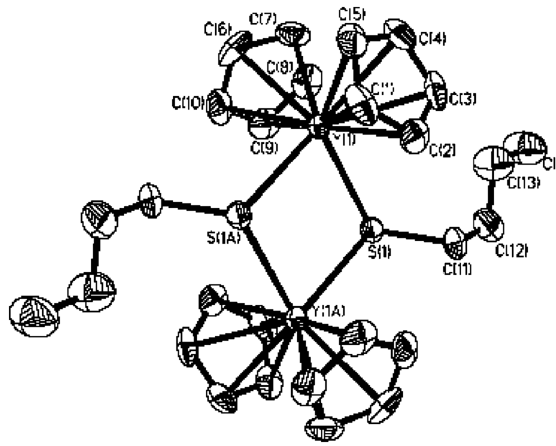


Figure 2. ORTEP diagram of $[(C_5H_5)_2Y(\mu\text{-}S^nBu)]_2$ (**1e**) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.

The formation of ^nBuSEt and $^nBuS^nBu$ is noteworthy since elimination reactions that form thioethers are rare; all previous examples of such reactions are restricted to redox-active metals.[12c,16] To our knowledge, there is no evidence to indicate that the intermolecular elimination of unsymmetrical thioethers can occur from the redox-inactive metal coordination sphere. The present results suggest that the lanthanide-based sulfur insertion/elimination reactions might be a potential method for the syntheses of thioethers and organic disulfides, especially for the syntheses of unsymmetrical thioethers and organic disulfides.

Complex **1e** is isostructural to a known derivative of ytterbium (Figure 2),[1c] in which a newly formed butylthiolate ligand is clearly established. All bond parameters for **1e** are in normal ranges (Table 3).

Figure 3 shows the molecular structure of **2a**. Selected bond distances and angles are listed in Table 4. X-ray analysis shows that complex **2a** is a centrosymmetric square-planar tetrametallic structure in that each S^{2-} ligand bridges three metal atoms, which is markedly different from the observation in $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}S)$, indicating that the steric bulk of ancillary ligands plays a significant role in determining the structure.[17] Two yttrium atoms are respectively coordinated by two η^5-cyclopentadienyl rings, one bridging S and one O atom of THF, while the other two yttrium atoms are respectively coordinated by two η^5-cyclopentadienyl groups and two bridging S atoms. The bridging Y_4S_2 unit is planar. The complex has no unusual distances

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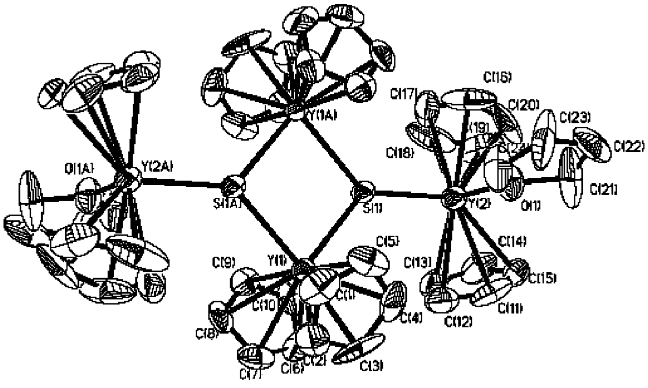

Figure 3. ORTEP diagram of $[(Cp_2Y)_2(\mu_3\text{-}S)(THF)]_2$ (**2a**) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.

Table 3. Bond Lengths [Å] and Angles [deg] for Complex 1e

Y(1)−S(1A)	2.7409(16)	S(1)−C(11)	1.819(6)
Y(1)−S(1)	2.7491(18)	S(1)−Y(1A)	2.7409(16)
Y(1)−C(1)	2.626(5)	Y(1)−C(6)	2.604(5)
Y(1)−C(2)	2.607(5)	Y(1)−C(7)	2.591(5)
Y(1)−C(3)	2.609(5)	Y(1)−C(8)	2.615(6)
Y(1)−C(4)	2.624(5)	Y(1)−C(9)	2.646(6)
Y(1)−C(5)	2.619(6)	Y(1)−C(10)	2.644(5)
S(1A)−Y(1)−S(1)	85.7(1)	C(11)−S(1)−Y(1)	118.9(2)
C(11)−S(1)−Y(1A)	115.0(2)	Y(1A)−S(1)−Y(1)	94.3(1)

Table 4. Bond Lengths [Å] and Angles [deg] for Complex 2a

Y(1)−S(1A)	2.698(2)	S(1)−S(1A)	3.684(10)
Y(1)−S(1)	2.703(3)	Y(2)−O(1)	2.328(7)
Y(1A)−S(1)	2.698(2)	Y(2)−S(1)	2.639(3)
Y(1)−Y(1A)	3.949(15)	Y(2)−C(11)	2.624(12)
Y(1)−C(1)	2.659(12)	Y(2)−C(12)	2.661(14)
Y(1)−C(2)	2.673(12)	Y(2)−C(13)	2.630(14)
Y(1)−C(3)	2.622(11)	Y(2)−C(14)	2.631(13)
Y(1)−C(4)	2.619(11)	Y(2)−C(15)	2.629(11)
Y(1)−C(5)	2.650(11)	Y(2)−C(16)	2.609(17)
Y(1)−C(6)	2.640(11)	Y(2)−C(17)	2.59(2)
Y(1)−C(7)	2.651(11)	Y(2)−C(18)	2.62(2)
Y(1)−C(8)	2.665(10)	Y(2)−C(19)	2.637(17)
Y(1)−C(9)	2.632(10)	Y(2)−C(20)	2.626(15)
Y(1)−C(10)	2.649(10)		
S(1A)−Y(1)−S(1)	86.0(1)	Y(2)−S(1)−Y(1)	130.8(1)
Y(2)−S(1)−Y(1A)	134.8(1)	Y(1A)−S(1)−Y(1)	94.0(1)

or angles in the Cp_2Y unit. The feature of the Y−S(μ_3) bond distances is similar to the observation for $[Sm_7S_7(SePh)_6(DME)_7]^+[Hg_3(SePh)_7]^-$.[3e] When the differences in metallic radii are subtracted,[18] the Y(1)−S(1) and Y(1)−S(1A) distances (2.698(2) and 2.703(3) Å) in **2a** are in good agreement with the value found in dimeric $[Cp_2Yb(\mu\text{-}S^nBu)]_2$ (2.70 Å). S(1A)−Y(1)−S(1) and Y(1A)−S(1)−Y(1) angles of 86.0(1)° and 94.0(1)° are also similar to the corresponding values found in $[Cp_2Yb(\mu\text{-}S^nBu)]_2$, respectively.[1c] However, the Y(2)−S(1) distance of 2.639(3) Å is similar to the distance of the terminal Yb−S distance found in $Cp_2Yb[SC_6H_2(CF_3)_3](THF)$ (2.639 Å).[1e]

Activation of $[Cp_2Yb(\mu\text{-}SEt)]_2$ on Elemental Sulfur. We examine the reaction of $[Cp_2Yb(\mu\text{-}SEt)]_2$ with elemental sulfur to model the transformation of metal alkyl to metal sulfide via the formation of a metal thiolate intermediate. We have found that the reaction of $[Cp_2Yb(\mu\text{-}SEt)]_2$ with elemental sulfur in THF for a short time formed red $[(Cp_2Yb)_2(\mu_3\text{-}S)(THF)]_2$ (**2b**). However, after 3 h, another green product, $[Cp_2Yb(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}S_2)$ (**3**), began to precipitate from the deep red solution, and after 48 h, **2b** and **3** were isolated in 38 and 30% yield, respectively. It is clear that in the reaction of $[Cp_2Yb(\mu\text{-}SEt)]_2$ with elemental sulfur the first equivalent of S will be reduced to S^{2-}, with oxidative elimination of EtSSEt. The S^{2-} of **2b** reacts further with additional elemental sulfur to give **3**. Consistent with the mechanism proposed in Scheme 1, no extrusion of EtSEt is observed in the reaction of $[Cp_2Yb(\mu\text{-}SEt)]_2$ with sulfur; instead, only Et_2S_2 was isolated. Preliminary results indicate that complex **3** may also be synthesized directly by reacting $Cp_2Yb(^nBu)$ or $[Cp_2Yb(\mu\text{-}Me)]_2$ with elemental sulfur in 1:2 Yb:S ratio. However, attempts to obtain $[(Cp_2Yb)_2(S_3)(THF)]_2$ by the reaction of $[Cp_2Yb(\mu\text{-}SEt)]_2$ with 3 equiv of elemental sulfur were unsuccessful, indicating that the presence of excess sulfur gives complicated mixtures of products. Recently, two general modes of reduction of elemental sulfur by oxidation of the thiolate ligands have been described in lanthanide chemistry, where partial displacement of arylthiolates by sulfurs to give S^{2-} ligands was observed for $Ln(SAr)_3$,[3b−e] whereas YbI(SPh) and $YbI(SPh)_2$ tend to completely displace arylthiolate ligands concomitant with the partial extrusion of iodide ligands.[3a] Despite additional research efforts along these lines, however, no lanthanide alkylthiolate complex has ever been found to undergo analogous reactions.[19] Furthermore, although it has been well-known that selective substitution of the alkyl, amido, or hydrogen ligand provides an important synthetic method for organolanthanide derivatives,[20] no analogous reaction involving the thiolate ligand has been reported. The formation of **2** and **3** represents the first example of selective displacement of alkylthiolate ligands of the lanthanocene thiolate system without the extrusion of coligands.

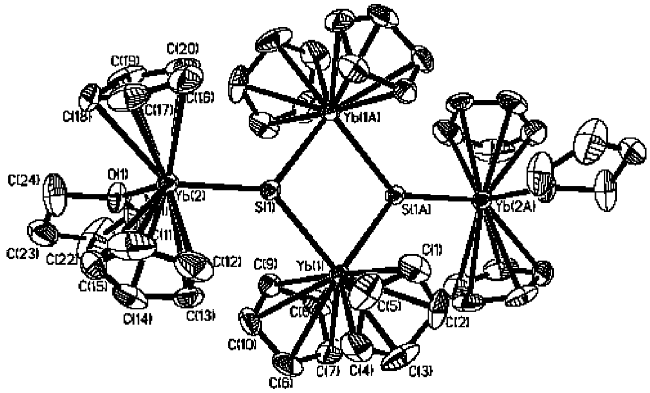

Figure 4. ORTEP diagram of $[(Cp_2Yb)_2(\mu_3\text{-}S)(THF)]_2$ (**2b**) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.

Complexes **2b** and **3** were identified by X-ray crystallographic analysis. As shown in Figure 4, complex **2b** is isostructural to **2a** and is also a square-planar

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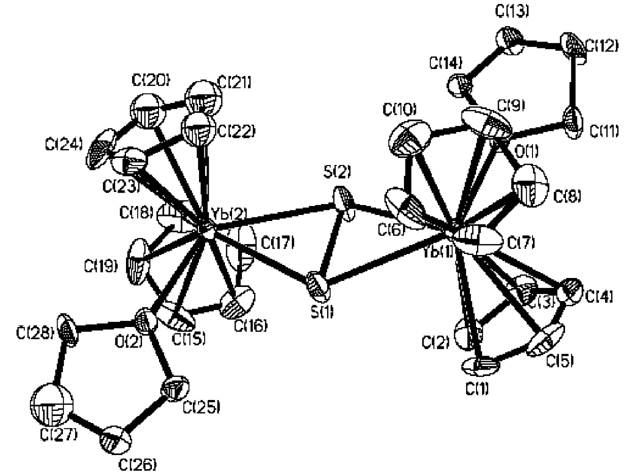

Figure 5. ORTEP diagram of [Cp$_2$Yb(THF)]$_2$(μ-η^2:η^2-S$_2$) (**3**) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.

Table 5. Bond Lengths [Å] and Angles [deg] for Complex 2b

Yb(1)–S(1A)	2.672(2)	Yb(2)–S(1)	2.615(2)
Yb(1)–S(1)	2.675(2)	Yb(2)–O(1)	2.326(6)
Yb(1A)–S(1)	2.672(2)	S(1)–S(1A)	3.655(9)
Yb(1)–Yb(1A)	3.903(10)	Yb(2)–C(11)	2.605(9)
Yb(1)–C(1)	2.617(10)	Yb(2)–C(12)	2.596(10)
Yb(1)–C(2)	2.618(11)	Yb(2)–C(13)	2.595(10)
Yb(1)–C(3)	2.618(10)	Yb(2)–C(14)	2.598(10)
Yb(1)–C(4)	2.636(11)	Yb(2)–C(15)	2.587(9)
Yb(1)–C(5)	2.615(10)	Yb(2)–C(16)	2.613(10)
Yb(1)–C(6)	2.618(9)	Yb(2)–C(17)	2.607(9)
Yb(1)–C(7)	2.639(10)	Yb(2)–C(18)	2.597(11)
Yb(1)–C(8)	2.631(10)	Yb(2)–C(19)	2.594(12)
Yb(1)–C(9)	2.609(9)	Yb(2)–C(20)	2.617(11)
Yb(1)–C(10)	2.624(9)		

S(1A)–Yb(1)–S(1)	86.2(1)	Yb(2)–S(1)–Yb(1)	134.8(1)
Yb(2)–S(1)–Yb(1A)	131.2(1)	Yb(1A)–S(1)–Yb(1)	93.8(1)

Table 6. Bond Lengths [Å] and Angles [deg] for Complex 3

Yb(1)–S(1)	2.802(5)	Yb(2)–S(1)	2.668(4)
Yb(1)–S(2)	2.670(4)	Yb(2)–S(2)	2.761(6)
S(1)–S(2)	2.115(4)	Yb(2)–O(2)	2.387(7)
Yb(1)–O(1)	2.367(7)	Yb(2)–C(15)	2.654(15)
Yb(1)–C(1)	2.631(11)	Yb(2)–C(16)	2.637(18)
Yb(1)–C(2)	2.609(14)	Yb(2)–C(17)	2.610(16)
Yb(1)–C(3)	2.626(15)	Yb(2)–C(18)	2.600(16)
Yb(1)–C(4)	2.650(16)	Yb(2)–C(19)	2.593(16)
Yb(1)–C(5)	2.634(13)	Yb(2)–C(20)	2.61(2)
Yb(1)–C(6)	2.591(15)	Yb(2)–C(21)	2.60(2)
Yb(1)–C(7)	2.581(15)	Yb(2)–C(22)	2.588(18)
Yb(1)–C(8)	2.594(15)	Yb(2)–C(23)	2.635(14)
Yb(1)–C(9)	2.648(15)	Yb(2)–C(24)	2.619(15)
Yb(1)–C(10)	2.606(18)		

S(2)–S(1)–Yb(2)	69.7(1)	S(1)–S(2)–Yb(2)	64.6(1)
S(2)–S(1)–Yb(1)	64.2(1)	Yb(1)–S(2)–Yb(2)	131.3(1)
Yb(2)–S(1)–Yb(1)	130.4(1)	S(1)–S(2)–Yb(1)	70.3(1)
S(1)–Yb(1)–S(2)	69.7(1)	S(1)–Yb(2)–S(2)	70.4(1)

tetrametallic structure in that each S^{2-} ligand bridges three metal atoms. The structural parameters of **2b** (Table 5) are very similar to those for complex **2a**. All the bond distances and angles are in normal ranges. The molecular structure of **3** is shown in Figure 5. Selected bond distances and angles are listed in Table 6. Compound **3** is the first structurally characterized lanthanocene disulfide, having a dinuclear structure with the disulfide as the η^2:η^2-bridging group. Each ytterbium atom is coordinated by two η^5-cyclopentadienyl groups, two bridging sulfur atoms, and one oxygen atom of THF. The coordination number of each Yb atom is 9. There are two distinctive metal–sulfur distances in complex **3**. The Yb(1)–S(2) and Yb(2)–S(1) distances of 2.670(4) and 2.668(4) Å are in the normal range of an Yb^{3+}–S single bond, while the Yb(1)–S(1) and Yb(2)–S(2) distances of 2.802(5) and 2.761(6) Å are longer than the corresponding values found in lanthanide disulfide (THF)$_6$Yb$_4$I$_2$(μ-η^2:η^2-S$_2$)(μ_4-S)[3a] and are between those expected for a Yb^{3+}–S single bond and a Yb^{3+}←:S donor bond.[1e,21] Obviously, the nature of the Yb–S(S$_2$$^{2-}$) bond in **3** is different from that of the M–O(O$_2$$^{2-}$) bond in peroxide complexes, where all metal–oxygen bond distances are equivalent within experimental error.[22] The S–S bond distance of 2.115(4) Å is consistent with the average value, 2.10 Å, found in (THF)$_6$Yb$_4$I$_2$(μ-η^2:η^2-S$_2$)(μ_4-S) [2.08–2.12 Å],[3a] but is slightly longer than those observed in Mn$_2$(CO)$_6$(μ-SMe)(μ-S$_2$) [2.047 Å], Mn$_2$(CO)$_6$(μ-SCH$_2$CH$_2$CH$_2$)(μ-S$_2$) [2.046 Å],[23] and [Cp*Ir(μ-SiPr)$_2$(μ-S$_2$)IrCp*][BPh$_4$] [1.997 Å].[24]

Conclusions

The work presented demonstrates that lanthanocene alkyl and thiolate complexes exhibit high activity toward element sulfur. Not only can elemental sulfur be inserted into the Ln–C σ-bond of lanthanocene alkyls, but also lanthanocene thiolate complexes are unstable in solution with S$_8$, allowing a mild and efficient transformation into lanthanocene sulfides and disulfides with the elimination of thioethers and organic disulfides. In contrast to the conversion processes of scandocene alkyls to scandocene tellurides, where the extrusion of TeR$_2$ from scandocene tellurolate intermediates is thermally or photochemical driven,[6b,c,25] several lines of experimental evidence suggest that the present conversion of lanthanocene alkyls to lanthanocene sulfides proceeds via the competitive interaction of the resultant thiolate intermediate with the remaining sulfur, followed by the intermolecular elimination of thioether or organic disulfide. The present results would seem to offer a new route to generate lanthanocene sulfide and disulfide complexes, which still remains undeveloped due to the lack of a general synthetic approach.[1b,17,26]

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Supporting Information Available: Details of crystal structure determinations and structure data for all structurally characterized complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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