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Notes

The Reactivity of $(CH_3C_5H_4)_2LnNPh_2(THF)$ (Ln = Y, Yb) with CS_2 and PhNCS: Synthesis and Crystal Structures

Huanrong Li,[†] Yingming Yao,[†] Qi Shen,*[,†,‡] and Linhong Weng[§]

Department of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215006, People's Republic of China, State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China, and Department of Chemistry, Fudan University, Shanghai 200433, People's Republic of China

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*Summary: The insertion reactions of CS_2 and phenyl isothiocyanate into the Ln−N bond of lanthanocene diphenylamide were first studied, and the insertion products, viz., $[(CH_3C_5H_4)_2Y(\eta^2\text{-}S_2CNPh_2)]_2\cdot CH_3C_6H_5$ (**1**), $[(CH_3C_5H_4)_2Yb(\eta^2\text{-}S_2CNPh_2)]$ (**2**), and $\{(CH_3C_5H_4)_2Y[\eta^2\text{-}SC(NPh_2)NPh]\}$ (**3**), were obtained. All the new complexes were characterized by single-crystal X-ray diffraction. Both **1** and **3** have dimeric structure, which have an interlinked tricycle formed via two bridged S atoms, while **2** exists as a monomer.*

Introduction

The insertion reactions of CS_2 into the M−X bonds of various main-group-metal or transition-metal complexes have been studied extensively, and a variety of products, such as coordinated dithioesters, dithiocarbaminates, or similar types of compounds, can be obtained, depending on the nature of M−X.[1] For example, the complexes $[Fe(\eta^5\text{-}C_5H_5)(C{\equiv}CR)(PPh_3)]$ (R = Ph, ^tBu), $Cp^*W(NO)(OCMe_3)(NHCMe_3)$, and $Re(OCH_3)(CO)_3(PMe_3)_2$ react with CS_2 to form the corresponding insertion products $[Fe(\eta^5\text{-}C_5H_5)(S_2CC{\equiv}CR)(PPh_3)]$,[2] $Cp^*W(NO)(\eta^2\text{-}S_2CNHCMe_3)(OCMe_3)$,[3] and $Re(\eta^2\text{-}S_2COCH_3)(CO)_3(PMe_3)_2$,[4] respectively.

However, the reactivity of organolanthanide compounds with CS_2 has still remained poorly explored. Up to date, it is known only that organolanthanide compounds containing a Ln−C bond, $Cp_2^*Sm(\eta^3\text{-}CH_2CHCHCH_3)$ and $Cp_2^*YCH_2Ph$, can react with CS_2 to afford the corresponding dithioesters $Cp_2^*Sm(\eta^2\text{-}S_2CCH_2CHCHCH_3)$[5] and $Cp_2^*Y(\eta^2\text{-}S_2CH_2Ph)$.[6]

For some time now, we have engaged in studies on the reactivity of organolanthanide amide with small molecules.[7−9] As part of our studies, we have recently found that lanthanocene diphenylamide, $(CH_3C_5H_4)_2LnNPh_2(THF)$ (Ln = Y, Yb), is also able to react with CS_2 to give the corresponding dithiocarbaminate, $[(CH_3C_5H_4)_2Y(\eta^2\text{-}S_2CNPh_2)]_2\cdot CH_3C_6H_5$ (**1**) and $[(CH_3C_5H_4)_2Yb(\eta^2\text{-}S_2CNPh_2)]$ (**2**). In addition, the reaction of $(CH_3C_5H_4)_2YNPh_2(THF)$ with PhNCS was also examined, as PhNCS is an isoelectronic analogue of CS_2. The reaction gives an insertion product, $\{(CH_3C_5H_4)_2Y[\eta^2\text{-}SC(NPh_2)NPh]\}$ (**3**), in good yield. Here we report the results.

Experimental Section

All manipulations were performed under a pure argon atmosphere using standard Schlenk techniques. Solvents were refluxed and distilled from sodium/benzophenone ketyl prior to use. CS_2 and PhNCS were dried over 3 Å molecular sieves for a week before distillation. $(CH_3C_5H_4)_2LnNPh_2(THF)$ (Ln = Y, Yb) was prepared according to a literature method.[9]

Melting points were determined in a sealed argon-filled capillary and are uncorrected. Lanthanide metal analyses were carried out by complexometric titration. Carbon, hydrogen, and nitrogen analyses were performed on a Carlo Erba 1110 spectrometer by direct combustion. The ^1H and ^{13}C NMR spectra were recorded on an INOVA-400 instrument using benzene-d_6 as solvent. The IR spectra were recorded on a Magna-550 spectrometer as KBr pellets.

Preparation of $[(CH_3C_5H_4)_2Y(\eta^2\text{-}S_2CNPh_2)]_2\cdot CH_3C_6H_5$ (1). To a solution of $(CH_3C_5H_4)_2YNPh_2(THF)$ (20 mL, 5.4 mmol) in toluene was added CS_2 in excess (5 mL) at room temperature. The color of the solution immediately changed from yellowish to dark red. The reaction mixture was stirred for 5 min and then concentrated to about 10 mL under reduced pressure. Red crystals of **1** suitable for X-ray single-crystal structure determination were obtained at −10 °C for 2 days. Yield: 2.57 g (88.5%). Mp: 146−149 °C (dec). Anal. Calcd for $C_{57}H_{56}N_2S_4Y_2$: C, 63.68; H, 5.25; N, 2.61; Y, 16.54. Found: C, 63.50; H, 5.19; N, 2.54; Y, 16.47. ^1H NMR: δ 7.28−7.41 (m,

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* To whom correspondence should be addressed. E-mail: qshen@suda.edu.cn. Fax: 0086-512-65112371.

[†] Suzhou University.

[‡] Shanghai Institute of Organic Chemistry.

[§] Fudan University.

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Table 1. Crystal Data and Structure Refinement for Complexes 1, 2, and 3

	1	2	3
formula	$C_{57}H_{56}N_2S_4Y_2$	$C_{25}H_{24}NS_2Yb$	$C_{62}H_{58}N_4S_2Y_2$
fw	1075.10	575.61	1101.06
T (K)	293(2)	293(2)	293(2)
cryst syst	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$Pnma$	$P2_1/n$
a (Å)	13.104(2)	9.667(12)	15.4885(17)
b (Å)	13.553(2)	11.462(15)	9.5787(11)
c (Å)	16.893(3)	21.00(3)	18.2814(19)
α (deg)	67.1655(3)	90.00	90.00
β (deg)	71.210(3)	90.00	103.695(2)
γ (deg)	73.545(4)	90.00	90.00
V (Å^3)	2574.1(8)	2327(5)	2635.1(5)
Z	2	2	4
F(000)	1108	1132	1136
D(calc) (Mg/m^3)	1.387	1.643	1.388
μ (mm^{-1})	2.444	4.209	2.314
diffractometer	BRUKER SMART 1000	BRUKER SMART 1000	BRUKER SMART 1000
radiation	Mo Kα	Mo Kα	Mo Kα
θ range (deg)	1.35–26.40	2.02–25.01	1.55–26.38
cryst size (mm)	0.45 × 0.35 × 0.30	0.40 × 0.35 × 0.25	0.45 × 0.10 × 0.05
no.of reflns collected	10 303	7639	12 712
no. of obsd ($I > 2\sigma(I)$)	6308	2147	5363
no. of variables	586	152	432
R_F, R_{wF}	0.0531, 0.1430	0.0615, 0.1202	0.0346, 0.0628
goodness of fit	0.982	1.252	0.930

25H, *Ph*), 5.87–6.10 (m, 16H, $CH_3C_5H_4$), 2.34 (s, 3H, $CH_3C_6H_5$), 2.22 (s, 12H, $CH_3C_5H_4$). ^{13}C NMR: δ 209.43 (CS_2), 145.90, 137.20, 129.97, 129.76, 128.44, 125.70, 122.46, 118.49 (*Ph*), 112.97, 110.68, 108.43 ($CH_3C_5H_4$), 21.89 ($CH_3C_6H_5$), 16.06 ($CH_3C_5H_4$). IR (KBr pellet, cm^{-1}): 3061 (m), 2924 (w), 1610 (s), 1589 (m), 1490 (s), 1334 (s), 1302 (s), 1265 (s), 1049 (s), 1031 (m), 886 (m), 780 (s), 753 (s), 669 (s), 651 (s), 617 (s).

Preparation of [$(CH_3C_5H_4)_2Yb(\eta^2\text{-}S_2CNPh_2)$] (2). To a solution of $(CH_3C_5H_4)_2YbNPh_2(THF)$ (10 mL, 1.50 mmol) in toluene was added an excess of CS_2. After stirring at room temperature for 5 min, the solution was concentrated to about 6 mL and allowed to crystallize at −10 °C. Red crystals were isolated. Yield: 0.74 g (85.7%). Mp: 138–141 °C (dec). Anal. Calcd for $C_{25}H_{24}NS_2Yb$: C, 52.16; H, 4.20; N, 2.43; Yb, 30.05. Found: C, 52.07; H, 4.12; N, 2.36; Y, 29.98. ^{1}H NMR: δ 6.46–7.21 (m, 10H, *Ph*), −11.93 (s, 6H, $CH_3C_5H_4$), −41.92 (s, 4H, $CH_3C_5H_4$), −46.70(s, 4H, $CH_3C_5H_4$). IR (KBr pellet, cm^{-1}): 3057 (w), 1588 (m), 1489 (s), 1347 (s), 1303 (s), 1260 (s), 1157 (s), 1048 (s), 1027 (s), 881 (s), 751 (s), 698 (s).

Preparation of $\{(CH_3C_5H_4)_2Y[\eta^2\text{-}SC(NPh_2)NPh]\}_2$ (3). To a solution of $(CH_3C_5H_4)_2YNPh_2(THF)$ (17 mL, 4.59 mmol) in toluene was added 0.54 mL of phenyl isothiocyanate (PhNCS) (4.59 mmol). After the reaction mixture was stirred at room temperature overnight, the solution was concentrated and cooled to −10 °C for crystallization. Colorless crystals of complex **3** were obtained. Yield: 1.52 g (60.1%). Mp: 169–172 °C (dec). Anal. Calcd for $C_{62}H_{58}N_4S_2Y_2$: C, 67.63; H, 5.31; N, 5.09; Y, 16.15. Found: C, 67.46; H, 5.25; N, 4.98; Y, 16.07. ^{1}H NMR: δ 7.03–7.26 (m, 30H, *Ph*), 5.84–6.11 (m, 16H, $CH_3C_5H_4$), 2.20 (s, 12H, $CH_3C_5H_4$). ^{13}C NMR: δ 149.09, 135.07, 129.74, 128.73, 124.80, 123.05, 122.71, 119.67 (*Ph*), 113.11, 112.50, 110.27 ($CH_3C_5H_4$), 16.75 ($CH_3C_5H_4$). IR (KBr pellet, cm^{-1}): 3062 (w), 1709 (s), 1592 (m), 1490 (s), 1414 (s), 1290 (m), 690 (s), 590 (s).

X-ray Data Collection and Structure Determination. Suitable crystals of complexes **1**–**3** were selected and sealed in a thin-walled glass capillaries for X-ray structure analyses. The diffraction data were collected at room temperature on a Bruker SMART 1000 diffractometer using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. Intensity data were corrected for Lorentz–polarization and empirical absorption effects. A summary of crystallographic data is given in Table 1.

The structures were solved by direct methods and refined with full-matrix least squares on F^2. All computations were performed on an IBM-compatible PC with the SHELX-97 package.[10] In the final cycles, the non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in idealized positions.

Results and Discussion

Syntheses and Molecular Structures of [$(CH_3\text{-}C_5H_4)_2Y(\eta^2\text{-}S_2CNPh_2)]_2\cdot CH_3C_6H_5$ (1) and ($CH_3\text{-}C_5H_4)_2Yb(\eta^2\text{-}S_2CNPh_2$) (2). Reaction of excess CS_2 with a solution of $(CH_3C_5H_4)_2LnNPh_2(THF)$ (Ln = Y, Yb) in toluene for 5 min at room temperature gave a red-colored complex with the constitution of a 1:1 adduct of $(CH_3C_5H_4)_2LnNPh_2$ (Ln = Y, Yb) and CS_2 according to their elemental analyses and spectral data. The IR spectra of the two products display ν(CS) absorption peaks at 1031 and 886 cm^{-1} for **1**, which are comparable to those of related trithiocarbonate complexes,[13] and at 1157 and 1048 cm^{-1} for **2**, which can be attributed to the symmetric and asymmetric stretching frequencies of the C–S bond in $[S_2CNPh_2]^-$ fragments, respectively. These data are also comparable to those observed in the related CS_2 insertion products, such as Cp*W(NO)(η^2-$S_2CNHCCMe_3$)($OCMe_3$),[3] Cp*W(NO)(η^2-S_2CPh)(Ph),[14] and $Me_2Al(\mu\text{-i-}Pr_2N)_2Mg[SC(CH_3)S]$.[15] These results obviously indicate a new C–N bond is formed via the insertion reaction of CS_2 into the Ln–N bond of organolanthanide amide in these reactions and the new ligand dithiocarbaminate group, $[Ph_2NCS_2\ ]^-$, is coordinated to the central metal Y or Yb in an η^2 manner (eqs 1 and 2). Although the analogous dithiocarbaminate

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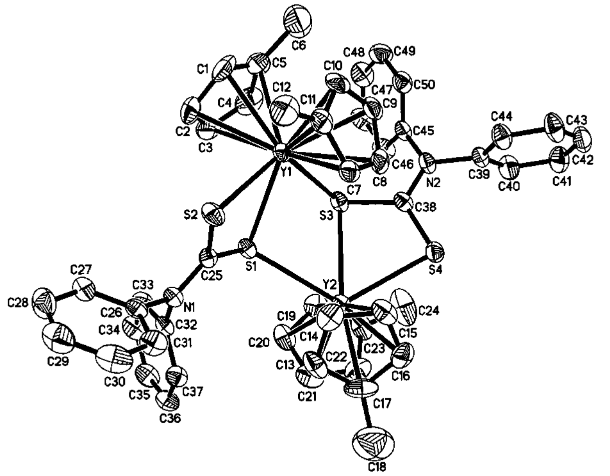

Figure 1. ORTEP diagram of the molecular structure of $[(CH_3C_5H_4)_2Y(\eta^2\text{-}S_2CNPh_2)]_2\cdot CH_3C_6H_5$ (**1**).

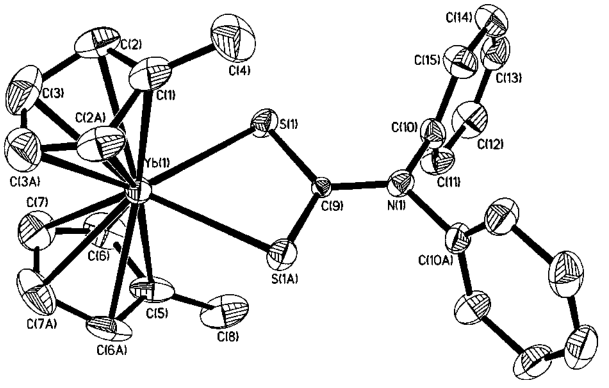

Figure 2. ORTEP diagram of the molecular structure of $[(CH_3C_5H_4)_2Yb(\eta^2\text{-}S_2CNPh_2)]$ (**2**).

derivatives $(Me_5C_5)_2Ln(S_2CNEt_2)$ (Ln = Yb, Nd) and $(Me_5C_5)_2Nd(S_2CNMe_2)$ have been reported in the literatures, the synthetic routes are quite different. The former was formed via metathesis reaction of $Na(OEt_2)_2(Me_5C_5)_2LnCl_2$ with NaS_2CNEt_2,[11] and the latter was obtained by redox reaction of divalent neodymium complex $[(Me_5C_5)_2NdCl_2][K(THF)]$ with $[Me_2NC(S)S]_2$.[12] To our knowledge, this is the first example of the insertion reaction of CS_2 into the Ln−N bond of organolanthanide amide.

$$2(CH_3C_5H_4)_2YNPh_2(THF) + 2CS_2 \xrightarrow{\text{toluene}} [(CH_3C_5H_4)_2Y(S_2CNPh_2)]_2\cdot CH_3C_6H_5 \quad (1)$$

$$(CH_3C_5H_4)_2YbNPh_2(THF) + CS_2 \rightarrow (CH_3C_5H_4)_2Yb(S_2CNPh_2) \quad (2)$$

To understand the solid-state structures of these complexes further, their single-crystal structures were determined. The results show that complex **1** is a dimer, while complex **2** exists as a monomer. The molecular structures are shown in Figures 1 and 2, and selected bond distances and angles are listed in Tables 2 and 3, respectively.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 1[a]

Y(1)−C(1)	2.618(6)	Y(1)−C(2)	2.634(6)
Y(1)−C(3)	2.646(6)	Y(1)−C(4)	2.655(7)
Y(1)−C(5)	2.659(6)	Y(1)−C(7)	2.692(5)
Y(1)−C(8)	2.647(5)	Y(1)−C(9)	2.608(5)
Y(1)−C(10)	2.653(5)	Y(1)−C(11)	2.710(5)
Y(1)−S(1)	2.8595(14)	Y(1)−S(2)	2.8754(16)
Y(2)−S(3)	2.9023(15)	Y(2)−S(4)	2.8659(15)
S(1)−C(25)	1.737(5)	S(2)−C(25)	1.704(5)
S(3)−C(38)	1.729(5)	S(4)−C(38)	1.697(5)
Y(1)−Cp(1)	2.365(2)	Y(1)−Cp(2)	2.376(2)
Y(2)−Cp(3)	2.390(2)	Y(2)−Cp(4)	2.395(2)
S(1)−Y(1)−S(2)	61.93(4)	S(4)−Y(2)−S(3)	61.56(4)
Y(1)−S(1)−Y(2)	102.84(4)	Y(2)−S(3)−Y(1)	99.36(4)
Cp(1)−Y(1)−Cp(2)	125.3(2)	Cp(3)−Y(2)−Cp(4)	125.1(2)

[a] Cp(1) represents the centroid of C(1)−C(5) ring; Cp(2) represents the centroid of C(7)−C(11) ring; Cp(3) represents the centroid of C(13)−C(17) ring; Cp(4) represents the centroid of C(19)−C(23) ring.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex 2[a]

Yb(1)−C(1)	2.608(14)	Yb(1)−C(2)	2.591(11)
Yb(1)−C(2)#1	2.591(11)	Yb(1)−C(3)	2.534(12)
Yb(1)−C(3)#1	2.534(12)	Yb(1)−C(5)	2.620(16)
Yb(1)−C(6)	2.570(11)	Yb(1)−C(6)#1	2.570(12)
Yb(1)−C(7)	2.542(12)	Yb(1)−C(7)#1	2.542(12)
Yb(1)−S(1)	2.695(3)	Yb(1)−S(1)#1	2.695(3)
S(1)−C(9)	1.716(6)	C(9)−S(1)#1	1.716(6)
N(1)−C(9)	1.341(15)	Yb(1)−Cp(1)	2.286(7)
Yb(1)−Cp(2)	2.283(7)		
S(1)−Yb(1)−S(1)#1	67.63(14)	Cp(1)−Yb(1)−Cp(2)	134.3(7)
S(1)#−C(9)−S(1)	121.9(6)		

[a] Cp(1) represents the centroid of C(1)−C(3A) ring; Cp(2) represents the centroid of C(5)−C(7A) ring.

Complex **1** is composed of two $[(CH_3C_5H_4)_2Y(S_2CNPh_2)]$ units linked by two sulfur atoms, and the central metal Y is coordinated by two $CH_3C_5H_4$ rings and three S atoms to give the formal coordination number of nine. The eight atoms Y(1), S(2), C(25), S(1), Y(2), S(3), C(38), and S(4) form an interlinked tricycle via two bridged S atoms. The bridged Y−S bonds are asymmetric, and their lengths are 2.8595(14) Å for Y(1)−S(1), 3.033(1) Å for Y(1)−S(3), 2.931(1) Å for Y(2)−S(1), and 2.9023(15) Å for Y(2)−S(3), respectively, giving an average of 2.932 Å, which is somewhat longer than that of the terminal Y−S bond length (2.871 Å). This is reasonable because the bridged bond length is normally longer than that of the terminal bond. The C−S bond distances in **1** are intermediate between single- and double-bond distances.[18] These parameters show that the electrons are delocalized over the YS_2C four-member ring, which supports the structure proposed on the basis of the analytical and spectral data. The average Y−C(Cp) distance, 2.6522 Å, is in the range of values found in other ytterbocene complexes, $[(MeC_5H_4)_2Y(\mu\text{-}OPr\text{-}i)]_2$, 2.6662 Å;[16] $[(MeC_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$, 2.651 Å;[17] $(MeC_5H_4)_2Y(THF)[OCN(Pr\text{-}i)_2NPh]$, 2.674 Å.[8]

The coordination polyhedron formed in complex **2** has previously been observed in $(Me_5C_5)_2Yb(S_2CNEt_2)$,[11] although the mode of formation for complex **2** is novel. There is the expected pattern of delocalization within the YbS_2C ring. The dithiocarbamate group is symmetrically coordinated to ytterbium, and the Yb−S and S−C bond lengths (2.695(3), 1.716(6) Å) are comparable with those found in $(Me_5C_5)_2Yb(S_2CNEt_2)$ (2.70(1), 1.71(1) Å), respectively.[11]

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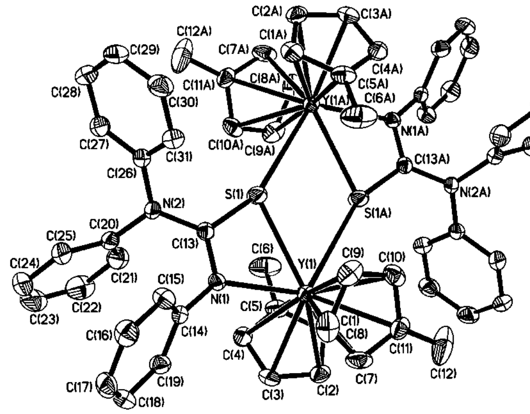

Figure 3. ORTEP diagram of the molecular structure of $\{(CH_3C_5H_4)_2Y[\eta^2\text{-}SC(NPh_2)NPh]\}_2$ (**3**).

Synthesis and Molecular Structure of $\{(CH_3C_5H_4)_2Y[\eta^2\text{-}SC(NPh_2)NPh]\}_2$ (3). The reaction of $(CH_3C_5H_4)_2YNPh_2(THF)$ with PhNCS goes smoothly. The insertion product, $\{(CH_3C_5H_4)_2Y[\eta^2\text{-}SC(NPh_2)NPh]\}_2$ (**3**), which was identified by elemental analyses, was isolated in good yield. In the IR spectrum of **3**, the two strong absorptions at 1490 and 1028 cm^{-1} can be assigned to the bidentate CN and CS vibrations in the *N*-phenylthioacetamide ligand, respectively,[19] which indicates that a new thioamido ligand, $[SC(NPh_2)NPh]^-$, is formed by the transfer of the $-NPh_2$ group to the isothiocyanate carbon atom, as shown in eq 3.

$$2(CH_3C_5H_4)_2YNPh_2(THF) + 2PhNCS \rightarrow \{(CH_3C_5H_4)_2Y[\eta^2\text{-}SC(NPh_2)NPh]\}_2 \quad (3)$$

The estimations from the IR spectrum have also been unambiguously verified by X-ray crystal structure analysis of **3**.

X-ray determination indicates that complex **3** has a dimeric structure, as shown in Figure 3, in which two $(CH_3C_5H_4)_2Y$ fragments connect with two $[SC(SPh)NPh]^-$ units. The six atoms Y(1), N(1), C(13), S(1), Y(1A), N(1A), C(13A), and S(1A) form an interlinked tricyclic structure via two bridged S atoms. Its coordination geometry is similar to that in complex **1**. Selected bond distances and angles are given in Table 4.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex 3[a]

Y(1)−C(1)	2.634(3)	Y(1)−C(2)	2.629(3)
Y(1)−C(3)	2.614(3)	Y(1)−C(4)	2.648(3)
Y(1)−C(5)	2.674(3)	Y(1)−C(7)	2.609(3)
Y(1)−C(8)	2.603(3)	Y(1)−C(9)	2.621(3)
Y(1)−C(10)	2.645(3)	Y(1)−C(11)	2.653(3)
Y(1)−S(1)	2.7847(8)	Y(1)−N(1)	2.445(8)
S(1)−Y(1)#1	3.1915(8)	S(1)−C(13)	1.727(3)
N(1)−C(13)	1.304(3)	Y(1)−Cp(1)	2.359(1)
Y(1)−Cp(2)	2.348(1)		
N(1)−Y(1)−S(1)	58.45(5)	Cp(1)−Y(1)−Cp(2)	128.3(1)
Y(1)−S(1)−Y(1)#1	119.41(2)	N(1)−C(13)−S(1)	115.31(19)

[a] Cp(1) represents the centroid of C(1)−C(5) ring; Cp(2) represents the centroid of C(7)−C(11) ring.

The N(1)−C(13) and C(13)−S(1) bond lengths in complex **3**, 1.304(3) and 1.727(3) Å, are intermediate between the corresponding single- and double-bond distances.[18] These bond parameters indicate substantial electronic delocalization over the S−C−N unit. The observed Y(1)−N(1) (2.445(2) Å) bond distance is in agreement with that of the Nd−N bond (2.534(4) Å) in $(CH_3C_5H_4)_2Nd[\eta^2\text{-}SC(SPh)NPh](THF)$,[20] if the difference in ionic radii is considered. The average Y−S bond distance, 2.988 Å, is longer than that of the Nd−S (2.881 Å) bond in $(CH_3C_5H_4)_2Nd[\eta^2\text{-}SC(SPh)NPh](THF)$,[20] although the ionic radius for Y^{3+} (1.075 Å) is smaller than that for Nd^{3+} (1.163 Å).[21] This can be attributed to the formation of the bridged bond in complex **3**. The Y−C(Cp) distances range from 2.603(3) to 2.674(3) Å, giving an average distance of 2.633(3) Å, which is comparable to that in complex **1**. The Cp(1)(centroid)−Y−Cp(2)(centroid) angle in complex **3**, 128.3(1)°, is similar to those found in the following complexes, $[(MeC_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$, 128.1°;[17] $(MeC_5H_4)_2Y(THF)[OCN(Pr\text{-}i)_2NPh]$, 127.5°;[8] $[(C_5H_5)_2Y(\mu\text{-}Me)]_2$, 128.9°.[22]

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Supporting Information Available: Tables of crystal data, atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for complexes **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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