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Cocrystallization of $(\mu\text{-}S_2)^{2-}$ and $(\mu\text{-}S)^{2-}$ and Formation of an $[\eta^2\text{-}S_3N(SiMe_3)_2]$ Ligand from Chalcogen Reduction by $(N_2)^{2-}$ in a Bimetallic Yttrium Amide Complex

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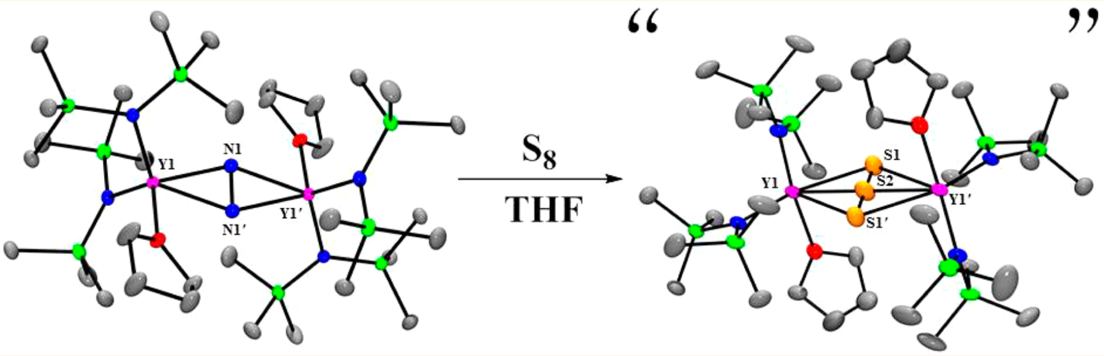
Supporting Information



ABSTRACT: The reactivity of the $(N_2)^{2-}$ complex $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**1**) with sulfur and selenium has been studied to explore the special reductive chemistry of this complex and to expand the variety of bimetallic rare-earth amide complexes. Complex **1** reacts with elemental sulfur to form a mixture of compounds, **2**, that is the first example of cocrystallized complexes of $(S_2)^{2-}$ and S^{2-} ligands. The crystals of **2** contain both the $(\mu\text{-}S_2)^{2-}$ complex $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)$ (**3**) and the $(\mu\text{-}S)^{2-}$ complex $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}S)$ (**4**), respectively. Modeling of the crystal data of **2** shows a 9:1 ratio of **3**:**4** in the crystals of **2** obtained from solutions that have 1:1 to 4:1 ratios of **3**/**4** by ^{1}H NMR spectroscopy. The addition of KC_8 to samples of **2** allows for the isolation of single crystals of **4**. The $[S_3N(SiMe_3)_2]^-$ ligand was isolated for the first time in crystals of $[(Me_3Si)_2N]_2Y[\eta^2\text{-}S_3N(SiMe_3)_2](THF)$ (**5**), obtained from the mother liquor of **2**. In contrast to the sulfur chemistry, the $(\mu\text{-}Se_2)^{2-}$ analogue of **3**, namely, $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Se_2)$ (**6**), can be cleanly synthesized in good yield by reacting **1**, with elemental selenium. The $(\mu\text{-}Se)^{2-}$ analogue of **4**, namely, $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}Se)$ (**7**), was synthesized from Ph_3PSe.

■ INTRODUCTION

Recent studies of rare-earth reductive chemistry have provided a series of $(N_2)^{2-}$ and $(N_2)^{3-}$ complexes of the rare-earth metals ligated by two bis(trimethylsilyl) ligands: $\{[(Me_3Si)_2N]_2Ln(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$[1,2] and $\{[(Me_3Si)_2N]_2Ln(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)K(THF)_x$ (Ln = rare earth; $x = 0, 6$).[3,4] The latter complexes with Ln = Dy and Tb are of interest as single-molecule magnets,[4−6] and both sets of complexes function as reducing agents. Reductions of NO and O_2 by these complexes to form the $(NO)^{2-}$ complex $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}NO)$,[7] the $(O_2)^{2-}$ complex $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)$,[8] and the oxide $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}O)$[8] have been studied in efforts to increase the number of bimetallic complexes that could be precursors to interesting single-molecule magnets. The reduction chemistry of these reduced dinitrogen complexes with sulfur and selenium has now been examined to expand the range of bridged bimetallic compounds and to determine if chalcogen congeners of the $(\mu\text{-}O_2)^{2-}$ and $(\mu\text{-}O)^{2-}$ bimetallic amide complexes could be made in this way. It was also of interest to determine if the bis(amide) rare-earth reduction system could provide access to ligands like the $(\mu\text{-}S_3)^{2-}$ moiety isolated in the bimetallic bis(pentamethylcyclopentadienyl) complex $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^1{:}\eta^3\text{-}S_3)$,[9] synthesized from $(C_5Me_5)_2Sm(THF)_2$ and sulfur or more complicated lanthanide chalcogenides like the fascinating clusters derived from $Ln(EPh)_3$ and chalcogens (E = S, Se).[10−12]

Reduction of sulfur and selenium by $(N_2)^{2-}$ is observed, but as reported here, the sulfur reaction is complicated by the fact that the $(\mu\text{-}S_2)^{2-}$and $(\mu\text{-}S)^{2-}$ complexes cocrystallize. Cocrystallization of similar ligands is a general problem in any area of chemistry that relies on X-ray crystallography for characterization. This has been particularly problematic in some inorganic systems where variable X-ray data due to different mixtures of complexes have been mistaken for "bond stretch

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Table 1. Crystal Data and Structure Refinement Parameters for **2** and **4**–**7**

	2	**4**	**5**	**6**	**7**
empirical formula	$C_{32}H_{88}N_4O_2S_2Si_8Y_2$	$C_{32}H_{88}N_4O_2SSi_8Y_2$	$C_{22}H_{62}N_3OS_3Si_6Y$	$C_{32}H_{88}N_4O_2Se_2Si_8Y_2$	$C_{32}H_{88}N_4O_2SeSi_8Y_2$
fw	1027.72	995.66	738.37	1121.52	1042.56
temperature (K)	143(2)	143(2)	88(2)	133(2) K	143(2)
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	10.6928(8)	10.429(4)	8.8099(5)	10.8331(9)	10.4235(8)
b (Å)	12.0462(9)	12.160(4)	10.0494(6)	11.9995(10)	12.1854(10)
c (Å)	12.1372(9)	12.166(4)	23.8094(14)	12.0793(10)	12.1499(10)
α (deg)	60.9538(8)	61.535(4)	101.0619(8)	61.5418(9)	61.9740(9)
β (deg)	79.5414(9)	80.236(5)	90.9696(8)	80.0644(10)	80.5568(10)
γ (deg)	88.4501(9)	89.078(5)	101.7946(8)	87.4348(10)	88.8205(10)
volume (Å^3)	1340.63(17)	1332.9(8)	2021.6(2)	1358.5(2)	1340.96(19)
Z	1	1	2	1	1
ρ_{calcd} (Mg m^{-3})	1.273	1.240	1.213	1.371	1.291
μ (mm^{-1})	2.440	2.414	1.794	3.671	3.039
R1[a]	0.0471	0.0413	0.0365	0.0324	0.0278
wR2[b]	0.1232	0.1002	0.0805	0.0773	0.0696

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

isomerism”.[13] Because $(S_2)^{2-}$ and S^{2-} ligands are of general interest in inorganic and particularly bioinorganic chemistry,[14−16] it is important to be aware of this cocrystallization possibility. Reduction of selenium to form $(Se_2)^{2-}$ and Se^{2-} analogues is reported for comparison. The isolation of a new aminotrisulfide ligand, $[S_3N(SiMe_3)_2]^-$, is also described.

EXPERIMENTAL SECTION

All syntheses and manipulations described below were conducted under nitrogen or argon with rigorous exclusion of air and water using glovebox, Schlenk-line, and high-vacuum-line techniques. Solvents were sparged with UHP argon and dried over columns containing Q-5 and molecular sieves. Benzene-d_6 was dried over sodium−potassium alloy, degassed using three freeze−pump−thaw cycles, and vacuum-transferred before use. Potassium and sodium were washed with hexane and scraped to provide fresh surfaces before use. $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**1**)[3] and KC_8[17] were prepared according to literature methods. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were obtained on a Bruker CRYO500 MHz spectrometer at 25 °C in benzene-d_6 unless otherwise stated. IR samples were prepared as KBr pellets on a Varian 1000 FT-IR system. Elemental analyses were performed on a PerkinElmer series II 2400 CHNS analyzer.

Reaction of $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (1) with S_8. The addition of S_8 (12 mg, 0.047 mmol) to a stirred pale-blue solution of **1** (148 mg, 0.15 mmol) in tetrahydrofuran (THF; 10 mL) in a nitrogen-filled glovebox caused an immediate color change to green. The solution became yellow after 20 min. After 1 h, the solvent was removed under reduced pressure to produce a yellow solid, which was redissolved in a minimal amount of hexane and stored at −30 °C. After 1 day, yellow crystals of a material designated as **2** (90 mg) were isolated. X-ray crystallography and NMR spectroscopy revealed these crystals to be a mixture of $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)$ (**3**) and $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}S)$ (**4**). ^{1}H NMR: δ 0.46 [s, 72H, N(SiMe$_3$)-**3**], 0.45 [s, 72H, N(SiMe$_3$)-**4**]. ^{13}C NMR: δ 5.94 [s, N(SiMe$_3$)-**3**], 5.77 [s, N(SiMe$_3$)-**4**]. An additional crop of colorless crystals was isolated from the concentrated mother liquor of **2** at −30 °C after several weeks and identified as $[(Me_3Si)_2N]_2Y[\eta^2\text{-}S_3N(Me_3Si)_2](THF)$ (**5**) by X-ray crystallography.

$\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}S)$ (4). A yellow solution of **2** (163 mg) in THF (7 mL) was treated with KC_8 (13 mg, 0.010 mmol) and stirred. After 1 h, the reaction mixture was filtered to remove black solids. THF was removed under vacuum, and the product was extracted with toluene (18 mL). The extract was centrifuged to remove pale insoluble material, and the supernatant was concentrated to 2 mL and stored at −35 °C to provide a small amount of colorless X-ray-quality crystals (10 mg) of **4** after several days. ^{1}H NMR: δ 0.45 [s, 72H, N(SiMe$_3$)].

$\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Se_2)$ (6). Elemental selenium (79 mg, 1.0 mmol) was added to a stirred solution of **1** (400 mg, 0.40 mmol) in THF (15 mL), and the reaction mixture became orange overnight. THF was removed under vacuum to yield orange solids, which were dissolved in hexane (50 mL). The orange solution was stored at −30 °C. Within 1 day, orange X-ray-quality crystals of **6** were obtained (340 mg, 75%). ^{1}H NMR: δ 4.05 (m, 8H, THF), 1.32 (m, 8H, THF), 0.48 [s, 72H, N(SiMe$_3$)]. ^{13}C NMR: δ 6.04 [s, N(SiMe$_3$)]. IR: 2948s, 2896s, 1456m, 1245s, 977s, 867s, 775s, 662s, 610s cm^{-1}. Anal. Calcd for $\{[(Me_3Si)_2N]_2Y\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Se_2)(THF)_{1.7}$ [**6**·(THF)$_{-0.3}$]: C, 33.63; H, 7.84; N, 5.09. Found: C, 33.45; H, 7.85; N, 4.80.

$\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}Se)$ (7). Ph_3PSe (18 mg, 0.050 mmol) was added to a stirred solution of **1** (50 mg, 0.050 mmol) in toluene (5 mL), and the stirred reaction mixture turned colorless overnight. The colorless solution was concentrated to 3 mL and stored at −30 °C. After 3 days, colorless X-ray-quality crystals of **7** were obtained (35 mg, 67%). ^{1}H NMR: δ 0.46 [s, 72H, N(SiMe$_3$)]. ^{13}C NMR: δ 5.79 [s, N(SiMe$_3$)]. Ph_3P was also observed by NMR spectroscopy. IR: 2949s, 2894s, 1444m, 1245s, 966s, 830s, 774s, 666s, 610s cm^{-1}. Anal. Calcd for $C_{32}H_{88}N_4O_2SeSi_8Y_2$ (**7**): C, 36.87; H, 8.51; N, 5.37. Found: C, 36.44; H, 8.50; N, 5.25.

X-ray Data Collection, Structure Determination, and Refinement. Crystallographic information for complexes **2** and **4**−**7** is summarized in Table 1, and further details can be found in the Supporting Information (SI). Crystallographic data for **2** show three areas of electron density bridging the metal centers. The structure was modeled using two components with partial site-occupancy factors and solved as a 8.6:1.4 mixture of $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)$ (**3**) and $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}S)$ (**4**), respectively (Figure 1).

RESULTS

Synthesis of Sulfur Products. The addition of elemental sulfur to a pale-blue THF solution of the $(N_2)^{2-}$ complex $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**1**) caused an immediate color change. Removal of the solvent from the solution after 1 h and recrystallization from hexane yielded yellow crystals of a material designated as **2**. The ^{1}H NMR spectrum of **2** in benzene-d_6 contained two resonances of different intensity in the region associated with the $[N(SiMe_3)_2]^-$ ancillary ligands, 0.46 and 0.45 ppm, which suggested the presence of two different complexes. X-ray crystallographic analysis of the yellow crystals revealed a bimetallic entity containing two

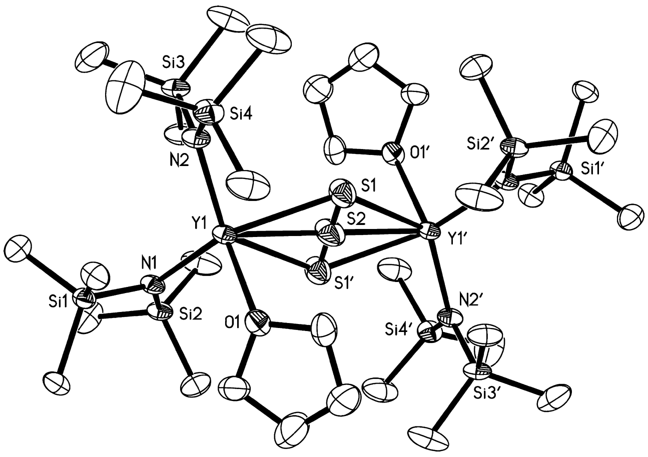
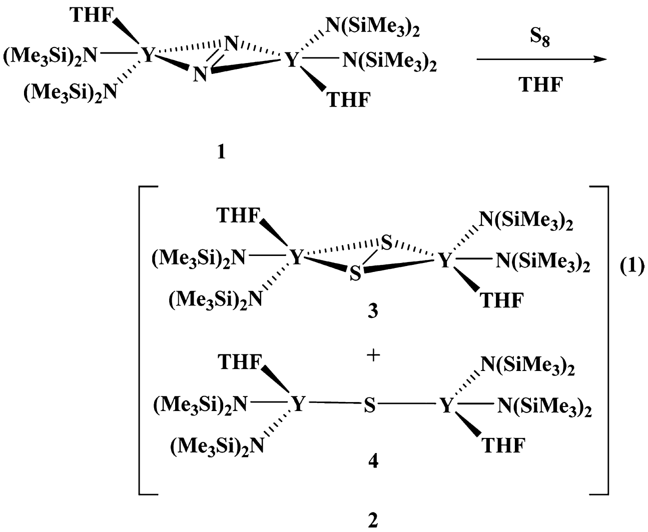


Figure 1. Thermal ellipsoid plot of **2** identified as a mixture of $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)$ (**3**) and $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}S)$ (**4**), drawn at the 50% probability level. The partial site occupancy of S1:S2 was modeled with an 8.6:1.4 mixture of $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)$ (**3**) and $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}S)$ (**4**), respectively. Hydrogen atoms are omitted for clarity.

$\{[(Me_3Si)_2N]_2Y(THF)\}^+$ units with three areas of electron density between the metal centers (Figure 1). A model for the crystallographic data for **2** with disulfide, $(S_2)^{2-}$, and monosulfide, S^{2-}, bridging moieties, i.e., a mixture of $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)$ (**3**) and $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}S)$ (**4**), in an 8.6:1.4 ratio gave an acceptable refinement (eq 1).



Varying the reaction time, temperature, sulfur equivalents, and crystallization solvent of the reaction in eq 1 did not lead to pure samples of either the disulfide **3** or the monosulfide species **4**. A slight excess of sulfur [2.4 equiv of S per $(N_2)^{2-}$] consistently gave better yields of **2**. The ratio of the two $N(SiMe_3)_2$ NMR peaks for **3** and **4** varied from 1:1 to 4:1 in multiple reactions, but each batch of crystals examined refined to an approximate 9:1 mixture. Repeated crystallizations did not yield a mother liquor of just **4** but instead led to other products (*vide infra*). Reactions using Ph_3PS as the sulfur source required heat to proceed and generated **4**, as identified by NMR spectroscopy, as well as the expected Ph_3P byproduct. However, decomposition of the $(N_2)^{2-}$ starting material also occurred during the heating process, and **4** could not be isolated cleanly via this route.

Reactions were also performed using the $(N_2)^{3-}$ radical complex $\{[(Me_3Si)_2N]_2(THF)Y\}_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}N_2)K$[2] to see if the enhanced reducing power of the trianionic dinitrogen ligand could cleanly reduce sulfur to form a pure product. The addition of sulfur to $\{[(Me_3Si)_2N]_2(THF)Y\}_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}N_2)K$ produced the reduced sulfur products **3** and **4**, again as a mixture observed by NMR spectroscopy with roughly a 2:1 ratio of **3**/**4**. In addition, NMR evidence for the known $(N_2H_2)^{2-}$-containing compound $\{[(Me_3Si)_2N]_2(THF)Y\}_2(\mu\text{-}N_2H_2)$[18] as well as another $[N(SiMe_3)_2]^-$-ligated product was also observed, making this reaction more complicated than the reaction of sulfur with **1**.

However, the addition of excess KC_8 to a THF solution of crystalline **2** causes the resonance at 0.46 ppm to diminish while the 0.45 ppm resonance remains. Crystallization of this sample from THF gave small amounts of colorless crystals of $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}S)$ (**4**; Figure 2).

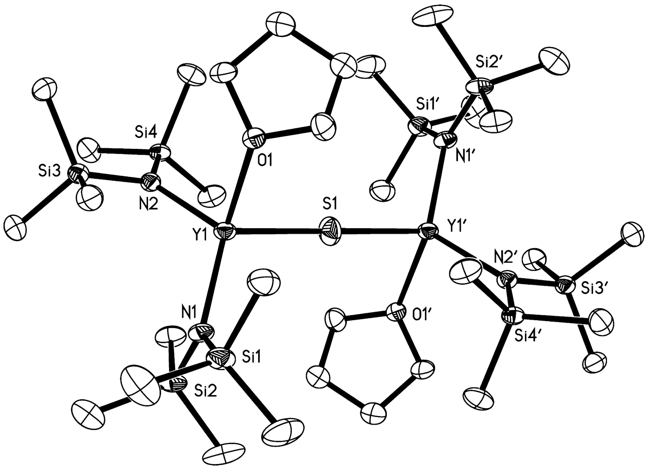


Figure 2. Thermal ellipsoid plot of $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}S)$ (**4**), drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

The ^1H NMR spectrum of these crystals contained only the 0.45 ppm resonance of the mixture found in **2**, and hence this resonance is assigned to **4**. Attempts to oxidize the S^{2-} component of **2** to form **3** using $AgBPh_4$ yielded NMR resonances consistent with the known cationic complex $\{[(Me_3Si)_2N]_2Y(THF)_2\}\{BPh_4\}$.[8] The addition of AgOTf to **2** resulted in isolation of the previously identified cyclic silver cluster, $Ag_4[N(SiMe_3)_2]_4$, as determined by X-ray crystallography.[19]

A second crystallization of the mother liquor of **2** yielded, in addition to more crystals of **2**, some colorless crystals that were analyzed by X-ray diffraction and found to be $[(Me_3Si)_2N]_2Y[\eta^2\text{-}S_3N(SiMe_3)_2](THF)$ (**5**; Figure 3). Complex **5**, to our knowledge, contains the first example of the $[S_3N(SiMe_3)_2]^-$ ligand. The closest examples of S_3NR_2 moieties of any kind in the crystallographic literature are organic compounds: a bis(fluorosilylamino)trisulfide, $[(^tBu_2FSi)NBu^t]SSS[^tBuN(SiF^tBu_2)]$, isolated in 1973 from sulfur and the lithium salt of the amine,[20] and the benzylidenimine trisulfide, (PhCHN)SSS(NCHPh), identified in 1991 from the reaction of sulfur with benzylamine in the presence of lead oxide.[21]

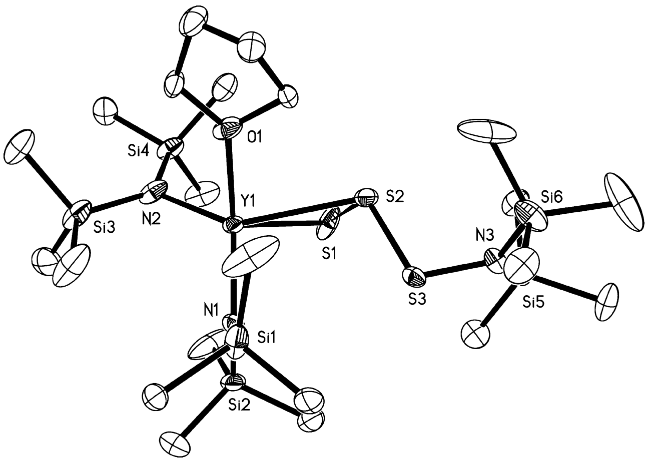


Figure 3. Thermal ellipsoid plot of $[(Me_3Si)_2N]_2Y[\eta^2\text{-}S_3N(SiMe_3)_2](THF)$ (**5**), drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Synthesis of Selenium Products. In contrast to the reaction of the $(N_2)^{2-}$ complex **1** with elemental sulfur, 2 equiv of elemental selenium react cleanly with **1** to yield the selenium analogue of **3**, namely, the $(Se_2)^{2-}$ species $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Se_2)$ (**6**; Figure 4 and eq 2). No contamination of a Se^{2-} complex analogous to **4** was observed in this reaction.

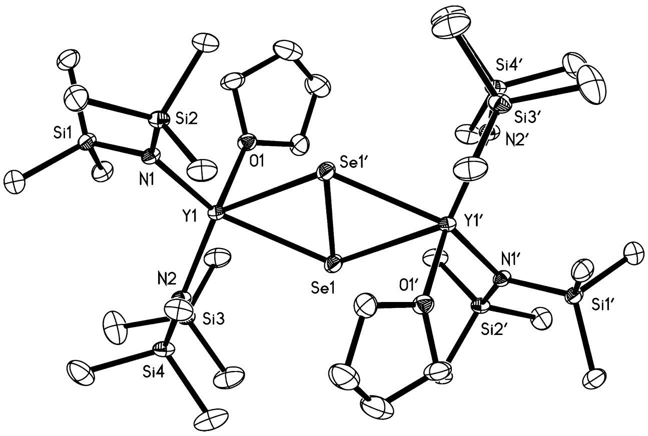
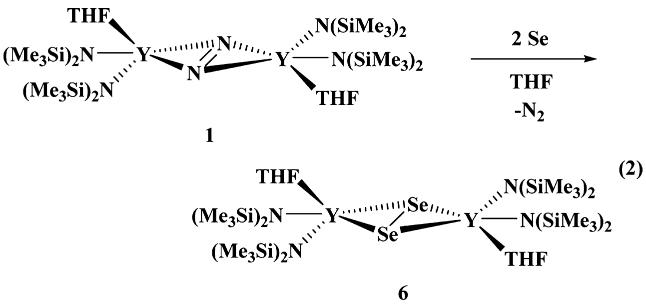


Figure 4. Thermal ellipsoid plot of $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Se_2)$ (**6**), drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.



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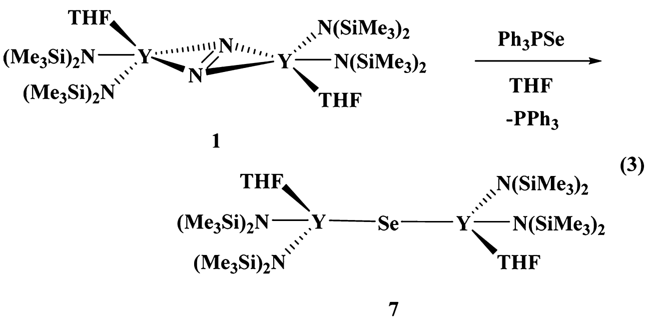
(2)



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(3)

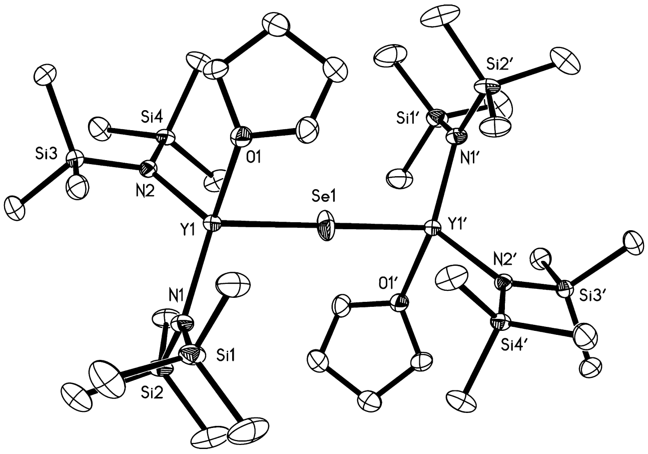
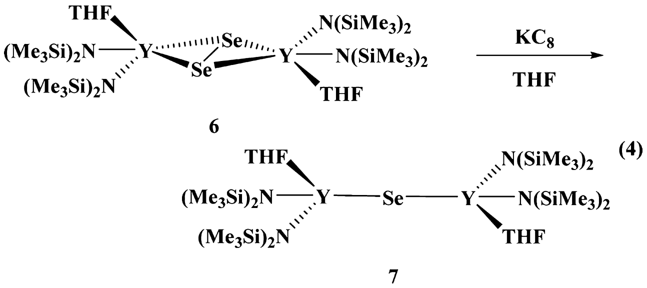


Figure 5. Thermal ellipsoid plot of $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-Se})$ (**7**), drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

The selenium analogue of **4** can also be synthesized by $(N_2)^{2-}$ reduction via **1** by reaction with 1 equiv of Ph_3PSe (eq 3). No heating is required for this reaction, as was necessary for the sulfur analogue, and the Se^{2-} complex $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-Se})$ (**7**; Figure 5) can be obtained as a pure crystalline product. The addition of KC_8 to the $(Se_2)^{2-}$ complex **6** yields the Se^{2-} complex **7** (eq 4), as determined by NMR spectroscopy. The addition of $AgBPh_4$ to **6** also parallels the sulfur reactivity and yields the known cationic complex $\{[(Me_3Si)_2N]_2Y(THF)_2\}\{BPh_4\}$ (eq 5).[8]



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(4)

Structure. The structures of **2** and **4**–**7** are compared in Table 2. Additional comparisons with the oxygen analogues, $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)$ (**8**) and $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-O})$ (**9**), are presented in Table 3.[8] The $\{[(Me_3Si)_2N]_2Y(THF)\}^+$ units are similar in all of the complexes, both bimetallic and monometallic. This is clearly a flexible metal fragment that can bind a variety of ligands.

The Y–S and Y–Se distances in the $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-E})$ complexes **4** and **7** are consistent with the 0.14 Å difference in the ionic radii between S^{2-} and Se^{2-} using the radii of Shannon.[22] A direct comparison with the oxygen analogue, the O^{2-} complex $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-O})$[8]

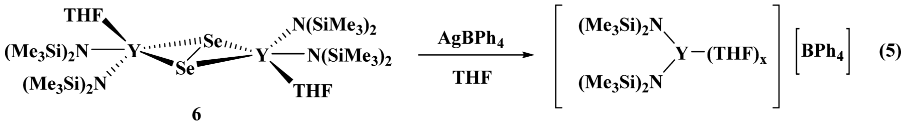

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for Complex 2, $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}S)$ (4), $[(Me_3Si)_2N]_2Y[\eta^2\text{-}S_3N(SiMe_3)_2](THF)$ (5), $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Se_2)$ (6), and $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}Se)$ (7), Where E = S (2, 4, and 5) or Se (6 and 7)

	Y−E	Y−N	Y−O	N−Y−N	N−Y−E	Y−E−Y′
Complex **2**: $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)$ (**3**)/ $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}S)$ (**4**)	2.508(3), 2.705(1)	2.231(3), 2.238(3)	2.350(2)	116.36(11)	136.80(7), 90.74(8), 115.63(7), 112.13(8)	180.0, 134.22(6)
$\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}S)$ (**4**)	2.525(7)	2.221(2), 2.234(2)	2.353(2)	116.61(9)	113.39(7), 109.66(7)	180.0
$[(Me_3Si)_2N]_2Y[\eta^2\text{-}S_3N(SiMe_3)_2](THF)$ (**5**)	2.673(6), 2.840(6)	2.205(2), 2.231(2)	2.350(2)	119.71(7)	105.26(5), 103.76(5), 137.21(5), 99.03(5)	
$\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Se_2)$ (**6**)	2.861(4), 2.911(4)	2.234(2), 2.236(2)	2.354(2)	115.58(8)	139.12(6), 89.91(6), 135.81(6), 93.98(5)	130.90(1)
$\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}Se)$ (**7**)	2.654(2)	2.219(2), 2.229(2)	2.354(1)	116.93(6)	112.35(4), 109.09(4)	180.0

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for the E^{2-} and $(E_2)^{2-}$ Analogues of $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}E)$ and $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}E_2)$, Where E = O, S, or Se

		E−E	Y−E	Y−Y	E−Y−E′	Y−E−Y′
E^{2-}	$\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}O)$ (**9**)		2.035(3),[a] 2.086(3)	4.091		166.23(14)
	$\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}S)$ (**4**)		2.525(7)	5.050		180
	$\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}Se)$ (**7**)		2.654(2)	5.309		180
$(E_2)^{2-}$	$\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)$ (**8**)	1.535(3)	2.206(2), 2.240(2)	4.173	40.38(7)	139.62(7)
	$\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)$ (**3**; as a portion of complex **2**)	2.118(2) (S1−S1′)	2.705(1) (S1−Y1)	5.016	45.78(5) (S1−Y1−S1′)	134.22(6) (Y1−S1−Y1′)
	$\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Se_2)$ (**6**)	2.399(5)	2.861(4), 2.911(4)	5.250	49.10(1)	130.90(1)

[a] Oxygen is disordered in the structure.

(**9**), is not possible because this structure contains a disordered oxide bridge.

Direct structural comparisons of the $(E_2)^{2-}$ series $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}E_2)$, where E = O, S, or Se, are complicated by the fact that the $(S_2)^{2-}$ structure is known only as the 86% component in a model of the cocrystallized mixture **2**. With this caveat and using the Shannon O^{2-} radius that is 0.44 Å smaller than S^{2-},[22] the Y−E bond lengths follow the expected trends for the increasing size of O, S, and Se from the peroxide **8** to the disulfide **3** in complex **2** to the diselenide **6**. The E−Y−E′ angles also increase as expected as the atoms of the diatomic bridge get larger: **8**, 40.38(7)°; **3**, 45.78(5)°; **6**, 49.10(1)°. An increase in the Y···Y distances is also observed: **8**, 4.173 Å; **3**, 5.016 Å; **6**, 5.250 Å. The 2.118(2) Å S1−S1′ and 2.399(5) Å Se1−Se1′ distances in **2** and **6**, respectively, are consistent with other $(S_2)^{2-}$ and $(Se_2)^{2-}$ distances in the literature.[14,23−25]

In **5**, the $[\eta^2\text{-}S_3N(SiMe_3)_2]^-$ anion ligates the $\{[(Me_3Si)_2N]_2Y(THF)\}^+$ unit through two of the three sulfur atoms in the chain. The terminal sulfur, S1, has the shorter Y−S distance, 2.673(6) Å, in comparison with the 2.840(6) Å length for Y−S2. The 2.052(1) Å S1−S2 distance is only slightly shorter than the 2.0823(8) Å S2−S3 length, and both are in the range defined by $[(^tBu_2FSi)NBu^t]SSS[^tBuN(SiF^tBu_2)]$ [2.102(1) Å][20] and (PhCHN)SSS(NCHPh) [2.051(1) Å].[21] The 1.704(2) Å S−N distance in **5** is also similar to those in these two organic complexes, 1.668(2) and 1.680(2) Å, in the former[14] and 1.661(3) Å in the latter.[20,21]

Three examples were found in the crystallographic literature in which an S_3 unit is bound η^2 to one metal and η^1 to another atom: $(C_5H_5)_2Ru_2(CO)S_5$,[26] $(C_5H_4{}^tBu)_3Nb_3S_{12}$,[27] and $(C_5H_5)Ti(C_5H_5S_5)$.[28] The first two examples have an S_3 ligand bridging two metal centers in polymetallic complexes, and the third example has a TiS_3C linkage formed by thermal rearrangement of $(C_5H_5)_2TiS_5$.[29] In all of these metal complexes, the S−S distance between the two sulfur atoms bound to the metal center is shorter than that observed in **5** [2.052(1) Å]: Ru, 2.014(7) Å; Nb, 2.038 Å; Ti, 2.025(3) Å. The niobium complex shows a similar difference in the metal−sulfur distances (2.481 and 2.600 Å, i.e., 0.119 Å) compared to **5** [2.673(6) and 2.840(6) Å, i.e., 0.167 Å], but the two S−S distances in the $(S_3)^{2-}$ unit of the niobium complex are nearly the same (2.038 and 2.042 Å). In the ruthenium complex, the metal−sulfur distances are closer in length to one another, 2.255(4) and 2.362(6) Å, than those in **5** and the S−S distances are more disparate, 2.014(7) versus 2.110(5) Å.[26] The titanium complex has 2.358(3) and 2.474(3) Å Ti−S distances with a 2.025(3) Å S−S bond between the two coordinating sulfur atoms and a 2.061(3) Å S−S bond involving the third sulfur attached to the C_5H_5 ring. Hence, there is substantial variation in the coordination parameters of the η^2-S_3 units in the three previously known metal complexes and **5**.

DISCUSSION

The $(N_2)^{2-}$ ligand in $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (**1**) is capable of reducing sulfur and selenium to make analogues of the $(O_2)^{2-}$ complex $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)$ (**8**) and the O^{2-} complex $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}O)$ (**9**).[8] The selenium complexes **6** and **7** constitute direct parallels with the oxides, but the sulfur system is more complicated because the two analogous complexes cocrystallize with both $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}S_2)$ (**3**) and $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}S)$ (**4**) in the same crystal. Cocrystallization of two similarly ligated complexes is well-known,[13,30] but few reports involve sulfur. The closest examples we could find in the literature involved side-by-side cocrystallization of two closely related sulfur complexes in the crystal lattice. The fulvalene (Fv) tungsten complexes of $(S_2)^{2-}$ and two $(SH)^-$ ligands, $FvW_2(\mu\text{-}S_2)(CO)_6$ and $FvW_2(SH)_2(CO)_6$,[31] crystallize as two separate molecules in the same unit cell with both tungsten centers on the same side of the Fv moiety in the former complex and a trans arrangement of the tungsten atoms across the Fv moiety in the latter. Bis(4-aminophenyl) disulfide, $(p\text{-}NH_2Ph)_2(\mu\text{-}S_2)$, crystallizes alongside 4-aminothiophenol, $p\text{-}NH_2PhSH$,[32] in the same unit cell. However, cocrystallization of the $S^{2-}/(S_2)^{2-}$ pair in complexes that overlay in all other components has not been reported to our knowledge. We are grateful to a reviewer for pointing out that, in the nitrogen-anchored tris(aryloxide)-chelated uranium selenide system, <7% of the bis$(Se)^{2-}$-bridged uranium(V) complex, $\{[(^{Ad}ArO)_3N]U\}_2(\mu\text{-}Se)_2$, crystallizes with the $U^{IV}(Se_4)^{2-}$ complex, $\{[(^{Ad}ArO)_3N]U\}_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-}Se_4)$, and the solvated analogue of the latter complex, $\{[(^{Ad}ArO)_3N]U(THF)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Se_4)$, crystallizes with 5.5% of the $(Se_3)^{2-}$ complex, $\{[(^{Ad}ArO)_3N]U(THF)\}_2(\mu\text{-}Se_3)$.[30]

It is interesting to note that among all of the bimetallic $\{[(Me_3Si)_2N]_2Y(THF)\}^+$ complexes,[3,8,18,33] including **2**, **4**, and **6**–**9**, only the S^{2-} and $(S_2)^{2-}$ complexes cocrystallize. One difference in the $(O_2)^{2-}$ complex **8** is that it was crystallized with a toluene of solvation, which gives it unit cell parameters quite different from those of the O^{2-} complex **9**.[8] Attempts to obtain the $(S_2)^{2-}$ complex **4** in pure form by crystallizing **2** in the presence of toluene were unsuccessful. One difference between the **3**/**4** pair and the **8**/**9** pair is that **3** and **4** have similar Y···Y distances, 5.016 and 5.050 Å, respectively, while the distances for **8** and **9** are not as close, 4.091 and 4.173 Å, respectively. The **6**/**7** selenium pair are intermediate in this regard, 5.250 and 5.309 Å, respectively.

Sulfur is well-known to adopt a variety of forms upon reduction including S^{2-}, $(S_2)^{2-}$, and $(S_3)^{2-}$ in lanthanide-containing complexes.[9−12,14,34,35] Hence, the formation of **2**–**4** is not unexpected. However, other sulfur insertion chemistry occurs in this system, as demonstrated by the isolation of $[(Me_3Si)_2N]_2Y[\eta^2\text{-}S_3N(SiMe_3)_2](THF)$ (**5**). In this case, not only has sulfur been homologated to make an S_3 chain but an N–S bond is also formed. Relatively few polysulfur amines have been crystallographically characterized. The route leading to the $[\eta^2\text{-}S_3N(SiMe_3)_2]^-$ ligand, the first of its kind to our knowledge, is unknown. It seems unlikely that sulfur would insert into a strong $Y\text{–}N[N(SiMe_3)_2]$ bond or that an $[N(SiMe_3)_2]^-$ ligand would attack $(S_2)^{2-}$ followed by S insertion. The ubiquitous $HN(SiMe_3)_2$, which is typically formed as a byproduct in reactions of rare-earth complexes of bis(trimethylsilyl)amide ligands, could be involved in the reaction, but this does not explain the presence of three sulfur atoms.

Examination of the analogous selenium reactions reveals a pattern that differs from both the oxygen and sulfur congeners. Elemental selenium can be used to completely convert the $(N_2)^{2-}$ complex **1** to $(Se_2)^{2-}$ complex $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Se_2)$ (**6**). While this is consistent with the quantitative formation of the $(O_2)^{2-}$ complex $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)$ (**8**) from O_2, the analogous sulfur reaction gives S^{2-} as well as $(S_2)^{2-}$. Ph_3PSe can be used to form the Se^{2-} complex $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}Se)$ (**7**), while similar oxygen and sulfur delivery reagents were unsuccessful routes to **9** and **4**, respectively.

CONCLUSION

The $(N_2)^{2-}$ ligand in $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (**1**) can effectively reduce both sulfur and selenium to make $(\mu\text{-}E)^{2-}$ and $(\mu\text{-}E_2)^{2-}$ complexes (E = S, Se) analogous to previously identified oxygen compounds, although Ph_3PSe is a better source for the Se^{2-} compound. The existence of this series demonstrates the coordinative flexibility of the $\{[(Me_3Si)_2N]_2Y(THF)\}^+$ cation for making bimetallic bridged species. The sulfur reactions provided the first example of cocrystallization of complexes of S^{2-} and $(S_2)^{2-}$ anions, which demonstrates that complexes of these two anions could be difficult to separate and could have very similar structures such that they could be mistaken for each other or a mixture of the two in metallosulfur chemistry. This pair of ions should be added to the list already identified through the bond stretch isomerism saga.[13] These studies also revealed the existence of the $[S_3N(SiMe_3)_2]^-$ ligand and showed another way in which the $[N(SiMe_3)_2]^-$ ligand can be more than an ancillary ligand.[3,36]

ASSOCIATED CONTENT

Supporting Information

Additional experimental details, crystallographic data collection, structure solution, and refinement and X-ray diffraction details in CIF format of compounds **2** and **4**–**7** (CCDC 1015155–1015159). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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DEDICATION

Dedicated to the memory of the man who always said “First comes the synthesis” and who inspired us all in many ways.

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■ NOTE ADDED IN PROOF

We were recently informed of an example of a rare earth complex with $(O_2)^{2-}$ and O^{2-} ligands co-crystallized in $[(C_5H_5)_2Yb(THF)]_2(\mu\text{-}O)_{2/3}(\mu\text{-}O_2)_{1/3}$: Deacon, G. B.; Forsyth, C. M.; Freckmann, D.; Junk, P. C.; Konstas, K.; Luu, J.; Meyer, G.; Werner, D. *Aust. J. Chem.* in press, DOI: 10.1071/CH14410.