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Activation of Bis(guanidinate)lanthanide Alkyl and Aryl Complexes on Elemental Sulfur: Synthesis and Characterization of Bis(guanidinate)lanthanide Thiolates and Disulfides

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The treatment of $[(Me_3Si)_2NC(NCy)_2]_2Ln(\mu\text{-}Cl)_2Li(THF)_2$ with 1 equiv of BnK (Bn = benzyl) in toluene affords $[(Me_3Si)_2NC(NCy)_2]_2LnBn$ [Ln = Er (**1-Er**), Y (**1-Y**)] in good yields. Similarly, $[(Me_3Si)_2NC(NCy)_2]_2Ln{}^tBu$ [Ln = Er (**2-Er**), Yb (**2-Yb**)] are obtained in satisfactory yields by the reaction of $[(Me_3Si)_2NC(NCy)_2]_2Ln(\mu\text{-}Cl)_2Li(THF)_2$ with ${}^tBuLi$ in hexane. **1** reacts with $^1/_8$ equiv of S_8 in toluene to form the sulfur insertion products $\{[(Me_3Si)_2NC(NCy)_2]_2Ln(\mu\text{-}SBn)\}_2$ [Ln = Er (**3-Er**), Y (**3-Y**)], while the reaction of **2** with elemental sulfur under the same conditions affords the oxidation products $\{[(Me_3Si)_2NC(NCy)_2]_2Ln\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)$ [Ln = Er (**4-Er**), Yb (**4-Yb**)] regardless of the equivalency of S_8 employed. Disulfide complexes **4** can also be obtained by the reaction of **3** with $^1/_4$ equiv of S_8. Furthermore, the treatment of $[(Me_3Si)_2NC(NCy)_2]_2Ln(\mu\text{-}Cl)_2Li(THF)_2$ with 1 equiv of ${}^nBuLi$ in hexane, followed by reaction with $^1/_8$ equiv of S_8, affords the dinuclear thiolate complexes $\{[(Me_3Si)_2NC(NCy)_2]_2Ln(\mu\text{-}S{}^nBu)\}_2$ [Ln = Y (**5-Y**), Er (**5-Er**)] in good yields. However, under the same conditions, $[(Me_3Si)_2NC(NCy)_2]_2Yb(\mu\text{-}Cl)_2Li(THF)_2$ reacts with ${}^nBuLi$ and S_8 to give $\{[(Me_3Si)_2NC(NCy)_2]_2Yb\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)$ (**4-Yb**) as the main metal-containing product. $[(Me_3Si)_2NC(NCy)_2]_2LnPh$ (generated in situ from $[(Me_3Si)_2NC(NCy)_2]_2Ln(\mu\text{-}Cl)_2Li(THF)_2$ and PhLi) also undergoes sulfur insertion, affording $\{[(Me_3Si)_2NC(NCy)_2]_2Ln(\mu\text{-}SPh)\}_2$ [Ln = Er (**6-Er**), Yb (**6-Yb**)] in good yields. All of the complexes were characterized by spectroscopic and elemental analyses. The structures of all of these compounds, except **3-Y**, are also determined by single-crystal X-ray diffraction analysis. Surprisingly, **3**, **5**, and **6** bear the same space group and very similar cell parameters, despite the different thiolate ligands.

Introduction

Organometallic complexes bearing sulfur-containing ligands have received considerable attention because of their involvement in industrially relevant or enzyme-catalyzed processes.[1,2] Moreover, they can also serve as intermediates in organic synthesis or precursors for materials with interesting properties.[3,4] Because stability and reactivity as well as biological and/or physical properties of molecules containing sulfur are crucial for final application, significant effort continues to be given over to the development of new complexes containing sulfur and versatile strategies for their construction. Controlling the metal coordination environment and properties through variation of supporting ligation is a common theme in organometallic

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chemistry. Considerable recent interest has focused on the development of guanidinate anions as sterically and electronically flexible ligands for the design of new organometallic complexes.[5] These compounds have been shown as exceptional catalysts in the transformation of organic functionalities and the polymerization of a variety of polar monomers and olefins.[6−8] Moreover, guanidinate complexes bear an application potential as photoelectric materials[9] and precursors for ALD and MOCVD processes.[10] Despite significant recent advances in this area, the synthesis of thiolate complexes containing the guanidinate coligand has no precedent.[5]

Furthermore, the basic chemistry of organolanthanides containing thiolate and disulfide ligands remains relatively little explored,[11,12] in comparison to the impressive development of their transition-metal counterparts. A major reason may be attributed to the difficulties encountered in their synthesis due to the intrinsic low affinity of these metals to the soft sulfur-containing ligands. Recently, we have reported that sulfur insertion into the Ln−C bond is a feasible route to formation of the Ln−S bond.[13] As part of a continuing effort in our laboratory toward the development of new methods for the synthesis of organolanthanide thiolate and disulfide complexes, we became interested in comparing the reactivity of complexes with alternative spectator ligand systems with that of bis(cyclopentadienyl) and related systems and further revealing the versatility of the sulfur insertion into Ln−C (Ln = lanthanide metal or yttrium) bonds.

In this paper, we describe the synthesis of bis(guanidinate)lanthanide(III) alkyl and aryl complexes and their reactivity behavior toward elemental sulfur, which provide a simple and efficient method for the preparation of unreported bis(guanidinate)lanthanide thiolate and disulfide complexes that would be difficult to prepare by classical metathetical reactions.

Experimental Section

General Procedure. All operations involving air- and moisture-sensitive compounds were carried out under an inert atmosphere of purified nitrogen using standard Schlenk techniques. Tetrahydrofuran (THF), toluene, and *n*-hexane were refluxed and distilled over sodium benzophenone ketyl under nitrogen immediately prior to use. $[(Me_3Si)_2NC(NCy)_2]_2Ln(\mu\text{-}Cl)_2Li(THF)_2$[14] and BnK[15] were prepared according to the literature procedures. ^{n}BuLi, ^{t}BuLi, and PhLi were purchased from Aldrich and used as received without further purification. Elemental sulfur was treated under vacuum for 30 min immediately prior to use. Elemental analysis for C, H, and N was carried out on a Rapid CHN-O analyzer. IR spectra were obtained on a Nicolet FT-IR 360 spectrometer with samples prepared as Nujol mulls. ^{1}H NMR data were obtained on a Jeol ECA-400 NMR spectrometer. The UV−visible spectra were recorded on a Shimadzu UV-2550 spectrometer.

Synthesis of $[(Me_3Si)_2NC(NCy)_2]_2ErBn$ (1-Er). To a toluene (30 mL) solution of $[(Me_3Si)_2NC(NCy)_2]_2Er(\mu\text{-}Cl)_2Li(THF)_2$ (0.360 g, 0.320 mmol) was added BnK (41.8 mg, 0.320 mmol) at −30 °C. The mixture was allowed to slowly warm to room temperature and stirred for 12 h. The volatiles were removed under vacuum, and the solid was extracted with toluene (30 mL × 2).

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The extraction was concentrated to 3 mL, and cooling the solution at −15 °C for several weeks yielded pink crystals of **1-Er**. The crystals isolated were fast-washed with hexane and then dried under a vacuum. Yield: 0.263 g (82%). Anal. Calcd for $C_{45}H_{87}N_6Si_4Er$: C, 54.49; H, 8.84; N, 8.47. Found: C, 54.27; H, 8.71; N, 8.63. IR (Nujol, cm^{-1}): 2922 s, 2854 s, 1637 s, 1459 s, 1378 s, 1304 m, 1254 s, 1198 w, 1137 m, 933 s, 835 w, 723 s, 641 m.

Synthesis of $[(Me_3Si)_2NC(NCy)_2]_2YBn$ (1-Y). Following the procedure described above for **1-Er**, the reaction of $[(Me_3Si)_2NC(NCy)_2]_2Y(\mu\text{-}Cl)_2Li(THF)_2$ (0.605 g, 0.579 mmol) with BnK (75.4 mg, 0.579 mmol) gave complex **1-Y** as colorless crystals. Yield: 0.386 g (73%). Anal. Calcd for $C_{45}H_{87}N_6Si_4Y$: C, 59.17; H, 9.60; N, 9.20. Found: C, 58.93; H, 9.51; N, 9.35. IR (Nujol, cm^{-1}): 2925 s, 2859 s, 1631 s, 1454 s, 1377 s, 1304 m, 1251 s, 1197 w, 1134 m, 932 s, 831 w, 721 s, 640 m. ^1H NMR (C_6D_6, 400 MHz, 25 °C): δ 7.28−7.25 (m, 2H, C_6H_5), 7.16−7.11 (m, 2H, C_6H_5), 7.07−7.00 (m, 1H, C_6H_5), 3.33−3.39 (m, 4H, NC*H*[Cy]), 2.11 (s, 2H, $CH_2C_6H_5$), 1.95−1.22 (m, 40H, CH_2[Cy]), 0.30 (s, 36H, $SiMe_3$).

Synthesis of $[(Me_3Si)_2NC(NCy)_2]_2Er^tBu$ (2-Er). To a hexane (50 mL) solution of $[(Me_3Si)_2NC(NCy)_2]_2Er(\mu\text{-}Cl)_2Li(THF)_2$ (1.704 g, 1.52 mmol) was added ^{t}BuLi (0.89 mL of a 1.70 M solution in pentane, 1.52 mmol) at −20 °C. The mixture was allowed to slowly warm to room temperature and stirred for 12 h. The mixture was centrifuged, and the precipitate was further extracted with hexane (50 mL × 2). The combined extraction was concentrated to 10 mL. Cooling the solution at −15 °C for several weeks yielded yellow crystals of **2-Er**. Yield: 1.208 g (83%). Anal. Calcd for $C_{42}H_{89}N_6Si_4Er$: C, 52.67; H, 9.37; N, 8.77. Found: C, 52.41; H, 9.25; N, 8.89. IR (Nujol, cm^{-1}): 2954 s, 2848 s, 1637 s, 1460 s, 1377 s, 1252 s, 1136 m, 1003 m, 943 s, 841 w, 641 m.

Synthesis of $[(Me_3Si)_2NC(NCy)_2]_2Yb^tBu$ (2-Yb). Following the procedure described above for **2-Er**, the reaction of $[(Me_3Si)_2NC(NCy)_2]_2Yb(\mu\text{-}Cl)_2Li(THF)_2$ (4.455 g, 3.95 mmol) with ^{t}BuLi (2.32 mL of a 1.70 M solution in pentane, 3.95 mmol) in hexane gave **2-Yb** as blue crystals. Yield: 3.083 g (81%). Anal. Calcd for $C_{42}H_{89}N_6Si_4Yb$: C, 52.35; H, 9.31; N, 8.72. Found: C, 52.19; H, 9.16; N, 8.81. IR (Nujol, cm^{-1}): 2950 s, 2845 s, 1637 s, 1462 s, 1377 s, 1250 s, 1136 m, 999 m, 943 s, 840 w, 641 m. UV−vis ($C_6H_5CH_3$, λ_{max}): 386, 616 nm.

Synthesis of $\{[(Me_3Si)_2NC(NCy)_2]_2Er(\mu\text{-}SBn)\}_2$ (3-Er). Method A. To a toluene (30 mL) solution of **1-Er** (0.401 g, 0.404 mmol) was added elemental sulfur S_8 (12.9 mg, 0.0505 mmol) at 0 °C. After stirring for 24 h, the solution was concentrated to 3 mL and cooled at −15 °C to afford pink crystals of **3-Er**. Yield: 0.323 g (78%). Anal. Calcd for $C_{90}H_{174}N_{12}S_2Si_8Er_2$: C, 52.79; H, 8.56; N, 8.21. Found: C, 52.67; H, 8.49; N, 8.33. IR (Nujol, cm^{-1}): 2940 s, 2848 s, 1634 s, 1455 s, 1378 s, 1252 s, 1178 w, 1132 m, 999 w, 933 s, 841 w, 727 s, 641 m.

Method B. To a toluene (30 mL) solution of $[(Me_3Si)_2NC(NCy)_2]_2Er(\mu\text{-}Cl)_2Li(THF)_2$ (0.683 g, 0.608 mmol) was added BnK (79.2 mg, 0.608 mmol) at −30 °C. The mixture was allowed to slowly warm to room temperature and stirred for 3 h. Then, to the solution was added elemental sulfur S_8 (19.5 mg, 0.076 mmol) at 0 °C, and the reaction mixture was stirred for 16 h. The volatiles were removed under vacuum, and the solid was extracted with toluene (30 mL × 2). The extraction was concentrated to ca. 3 mL and cooled at −15 °C to afford pink crystals of **3-Er**. Yield: 0.468 g (75%).

Synthesis of $\{[(Me_3Si)_2NC(NCy)_2]_2Y(\mu\text{-}SBn)\}_2$ (3-Y). Following the procedure described above for **3-Er** (method A), the reaction of **1-Y** (0.322 g, 0.353 mmol) with elemental sulfur S_8 (11.3 mg, 0.044 mmol) gave **3-Y** as colorless crystals. Yield: 0.237 g (71%). Anal. Calcd for $C_{90}H_{174}N_{12}S_2Si_8Y_2$: C, 57.16; H, 9.27; N, 8.89. Found: C, 56.88; H, 9.13; N, 9.02. IR (Nujol, cm^{-1}): 2947 s, 2845 s, 1631 s, 1458 s, 1378 s, 1249 s, 1171 w, 1130 m, 1002 w, 931 s, 840 w, 724 s, 640 m. ^1H NMR (C_6D_6, 400 MHz, 25 °C): δ 7.35−7.30 (m, 4H, C_6H_5), 7.22−7.16 (m, 4H, C_6H_5), 7.13−7.08 (m, 2H, C_6H_5), 4.48 (s, 4H, SCH_2), 3.42−3.37 (m, 8H, NC*H*[Cy]), 2.03−1.31 (m, 80H, CH_2[Cy]), 0.34 (s, 72H, $SiMe_3$).

Synthesis of $\{[(Me_3Si)_2NC(NCy)_2]_2Er\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)\cdot 2THF$ (4-Er·2THF). Method A. To a toluene (30 mL) solution of **2-Er** (0.351 g, 0.366 mmol) was added elemental sulfur S_8 (23.5 mg, 0.0916 mmol) at 0 °C. After stirring for 36 h, the volatiles were removed under a vacuum. The residue was dissolved in 10 mL of THF. Cooling the solution at −15 °C for several days yielded yellow crystals of **4-Er·2THF**. Yield: 0.305 g (83%). Anal. Calcd for $C_{84}H_{176}N_{12}O_2S_2Si_8Er_2$: C, 50.20; H, 8.83; N, 8.36. Found: C, 50.51; H, 8.98; N, 8.21. IR (Nujol, cm^{-1}): 2904 s, 2853 s, 1635 s, 1458 s, 1377 s, 1250 m, 999 m, 935 s, 838 w, 727 s, 687 m, 641 m.

Method B. Following the procedure described above for **4-Er·2THF** (method A), the reaction of **3-Er** (0.306 g, 0.149 mmol) with elemental sulfur S_8 (9.56 mg, 0.037 mmol), followed by crystallization from THF, gave orange crystals of **4-Er·2THF**. Yield: 0.258 g (86%).

Synthesis of $\{[(Me_3Si)_2NC(NCy)_2]_2Yb\}_2(\mu-\eta^2{:}\eta^2\text{-}S_2)\cdot 2THF$ (4-Yb·2THF). Method A. Following the procedure described above for **4-Er·2THF** (method A), **2-Yb** (0.468 g, 0.486 mmol) reacted with elemental sulfur S_8 (31.1 mg, 0.121 mmol) to give orange crystals of **4-Yb·2THF**. Yield: 0.402 g (82%). Anal. Calcd for $C_{84}H_{176}N_{12}O_2S_2Si_8Yb_2$: C, 49.91; H, 8.78; N, 8.32. Found: C, 50.22; H, 8.95; N, 8.16. IR (Nujol, cm^{-1}): 2905 s, 2855 s, 1637 s, 1456 s, 1377 s, 1252 m, 1132 w, 999 m, 938 s, 835 w, 722 s, 685 m, 641 m.

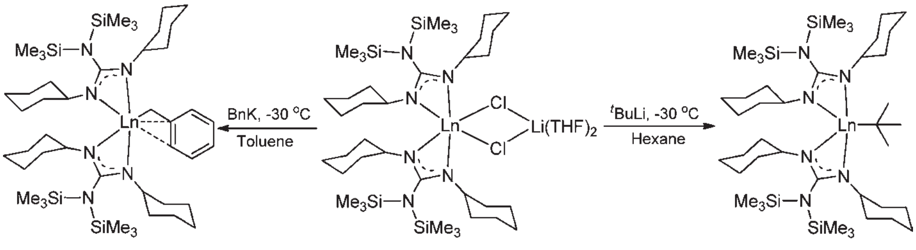
Method B. To a toluene (30 mL) solution of $[(Me_3Si)_2NC(NCy)_2]_2Yb(\mu\text{-}Cl)_2Li(THF)_2$ (0.675 g, 0.598 mmol) was added Li^{n}Bu (0.37 mL of a 1.60 M solution in hexane, 0.598 mmol) at −30 °C. The solution became turbid immediately. Then, the mixture was allowed to warm to room temperature and stirred for 12 h. The solution changed from yellow to red slowly. Then, to the solution was added elemental sulfur S_8 (19.1 mg, 0.0748 mmol) at 0 °C, and the reaction mixture was stirred for 16 h. The precipitate (LiCl) was removed by centrifugation, and removal of the volatiles gave a yellow solid. It crystallized in THF to give yellow crystals of **4-Yb·2THF**. Yield: 0.429 g (71%).

Synthesis of $\{[(Me_3Si)_2NC(NCy)_2]_2Y(\mu\text{-}S^nBu)\}_2$ (5-Y). To a toluene (30 mL) solution of $[(Me_3Si)_2NC(NCy)_2]_2Y(\mu\text{-}Cl)_2Li(THF)_2$ (0.751 g, 0.719 mmol) was added Li^{n}Bu (0.45 mL of a 1.60 M solution in hexane, 0.719 mmol) at −30 °C. The mixture was allowed to slowly warm to room temperature and stirred for 3 h. Then, to the solution was added elemental sulfur S_8 (23.0 mg, 0.0899 mmol) at 0 °C, and the reaction mixture was stirred for 16 h. The precipitate (LiCl) was removed by centrifugation, and the solution was concentrated to ca. 10 mL and cooled at −15 °C to afford colorless crystals of **5-Y**. Yield: 0.525 g (80%). Anal. Calcd for $C_{84}H_{178}N_{12}S_2Si_8Y_2$: C, 55.34; H, 9.84; N, 9.22. Found: C, 55.26; H, 9.75; N, 9.45. IR (Nujol, cm^{-1}): 2923 s, 2853 s, 1635 s, 1456 s, 1377 s, 1298 w, 1252 m, 1219 w, 1118 w, 1070 m, 956 s, 890 w, 840 m, 721 s, 693 m, 640 m. ^1H NMR (C_6D_6, 400 MHz, 25 °C): δ 3.48−3.42 (m, 8H, NC*H*[Cy]), 2.76 (t, 4H, SCH_2), 2.05−1.38 (m, 88H, CH_2[Cy and $Me(CH_2)_2$]), 1.05 (s, 6H, $S(CH_2)_3Me$), 0.39 (s, 72H, $SiMe_3$).

Synthesis of $\{[(Me_3Si)_2NC(NCy)_2]_2Er(\mu\text{-}S^nBu)\}_2$ (5-Er). Following the procedure described above for **5-Y**, the reaction of $[(Me_3Si)_2NC(NCy)_2]_2Er(\mu\text{-}Cl)_2Li(THF)_2$ (0.349 g, 0.311 mmol) with Li^{n}Bu (0.19 mL of a 1.60 M solution in hexane, 0.311 mmol) and subsequently with elemental sulfur S_8 (9.95 mg, 0.0389 mmol) gave complex **5-Er** as pink crystals. Yield: 0.224 g (73%). Anal. Calcd for $C_{84}H_{178}N_{12}S_2Si_8Er_2$: C, 50.96; H, 9.06; N, 8.49. Found: C, 50.74; H, 8.91; N, 8.59. IR (Nujol, cm^{-1}): 2930 s, 2858 s, 1637 s, 1455 s, 1378 s, 1301 m, 1240 s, 1173 w, 1127 m, 1070 w, 1009 s, 938 s, 835 w, 722 s, 641 m.

Synthesis of $\{[(Me_3Si)_2NC(NCy)_2]_2Yb(\mu\text{-}S^nBu)\}_2$ (5-Yb). To a toluene (15 mL) solution of ^{n}BuSH (0.42 mL, 3.90 mmol) was added Li^{n}Bu (2.44 mL of a 1.60 M solution in hexane, 3.90 mmol) at 0 °C. The mixture was allowed to slowly warm to room temperature and stirred for 1 h. Then, to the solution was added a toluene (60 mL) solution of $[(Me_3Si)_2NC(NCy)_2]_2Yb(\mu\text{-}Cl)_2Li(THF)_2$

Scheme 1



Ln = Er(**1-Er**), Y(**1-Y**)

Ln = Er(**2-Er**), Yb(**2-Yb**)

(4.397 g, 3.90 mmol), and the reaction mixture was stirred at 80 °C for 72 h. The precipitate was removed by centrifugation. Removal of the solvents gave a tar residue, which was dissolved in 10 mL of hot hexane. Cooling the solution to room temperature gave a mixture containing primarily yellow crystals of the starting material $[(Me_3Si)_2NC(NCy)_2]_2Yb(\mu\text{-}Cl)_2Li(THF)_2$ and a small amount of red crystals of **5-Yb** (0.465 g, 12%). These were separated by picking large crystals, and the pure compounds were used for characterization purposes. Anal. Calcd for $C_{84}H_{178}N_{12}S_2Si_8Yb_2$: C, 50.66; H, 9.01; N, 8.44. Found: C, 50.43; H, 8.93; N, 8.57. IR (Nujol, cm^{-1}): 2918 w, 1633 m, 1603 m, 1547 m, 1469 s, 1373 s, 1306 m, 1250 s, 1219 w, 1118 w, 1070 m, 956 s, 890 w, 839 m, 767 m, 640 m.

Synthesis of $\{[(Me_3Si)_2NC(NCy)_2]_2Er(\mu\text{-}SPh)\}_2$ (6-Er). Following the procedure described above for **5-Y**, the reaction of $[(Me_3Si)_2NC(NCy)_2]_2Er(\mu\text{-}Cl)_2Li(THF)_2$ (0.357 g, 0.318 mmol) with PhLi (0.23 mL of a 1.38 M solution in butyl ether, 0.318 mmol) and subsequently with elemental sulfur S_8 (10.2 mg, 0.0397 mmol) gave complex **6-Er** as pink crystals. Yield: 0.283 g (88%). Anal. Calcd for $C_{88}H_{170}N_{12}S_2Si_8Er_2$: C, 52.33; H, 8.48; N, 8.32. Found: C, 52.22; H, 8.35; N, 8.43. IR (Nujol, cm^{-1}): 2930 s, 2858 s, 1634 s, 1460 s, 1378 s, 1301 m, 1250 s, 1178 w, 1132 m, 999 w, 938 s, 835 w, 722 s, 641 m.

Synthesis of $\{[(Me_3Si)_2NC(NCy)_2]_2Yb(\mu\text{-}SPh)\}_2$ (6-Yb). Following the procedure describedabove for **5-Y**, the treatment of $[(Me_3Si)_2NC(NCy)_2]_2Yb(\mu\text{-}Cl)_2Li(THF)_2$ (0.707 g, 0.626 mmol) with PhLi (0.45 mL of a 1.38 M solution in butyl ether, 0.626 mmol), followed by reaction with elemental sulfur S_8 (20.0 mg, 0.0783 mmol), gave complex **6-Yb** as red crystals. Yield: 0.528 g (83%). Anal. Calcd for $C_{88}H_{170}N_{12}S_2Si_8Yb_2$: C, 52.03; H, 8.44; N, 8.27. Found: C, 51.86; H, 8.31; N, 8.43. IR (Nujol, cm^{-1}): 2912 s, 2854 s, 1637 s, 1458 s, 1378 s, 1253 s, 1186 w, 999 w, 938 s, 840 w, 718 s, 641 m.

X-ray Data Collection, Structure Solution, and Refinement for 1−6. This information is available in the Supporting Information.

Results and Discussion

Synthesis and Structure of Bis(guanidinate)lanthanide Benzyl and *tert*-Butyl Complexes. The reaction of $[(Me_3Si)_2NC(NCy)_2]_2Ln(\mu\text{-}Cl)_2Li(THF)_2$ with 1 equiv of BnK in toluene afforded the benzyl complexes $[(Me_3Si)_2NC(NCy)_2]_2LnBn$ [Ln = Er (**1-Er**), Y (**1-Y**)] in good yields. Similarly, the treatment of $[(Me_3Si)_2NC(NCy)_2]_2Ln(\mu\text{-}Cl)_2Li(THF)_2$ with ᵗBuLi in hexane gave the bis(guanidinate)lanthanide *t*-butyl complexes $[(Me_3Si)_2NC(NCy)_2]_2Ln^tBu$ [Ln = Er (**2-Er**), Yb (**2-Yb**)] in satisfactory yields (Scheme 1).

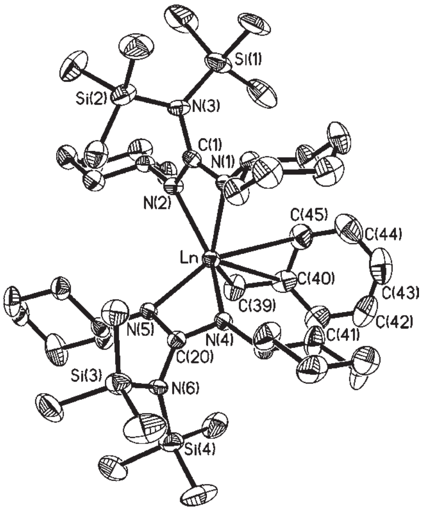


Figure 1. ORTEP diagram of $[(SiMe_3)_2NC(NCy)_2]_2LnBn$ [Ln = Er (**1-Er**), Y (**1-Y**)] with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **1-Er**: Er−N(1) 2.325(3), Er−N(2) 2.354(3), Er−C(1) 2.781(4), N(1)−C(1) 1.340(4), N(2)−C(1) 1.330(4), Er−C(39) 2.426(4), Er−C(40) 2.840(5), Er−C(45) 2.975(5); N(1)−Er−N(2) 57.07(10), N(2)−C(1)−N(1) 113.7(3), C(1)−N(1)−Er 94.9(2), C(1)−N(2)−Er 93.9(2), C(40)−C(39)−Er 90.6(3), C(39)−Er−C(40) 30.8(1). For **1-Y**: Y−N(1) 2.344(4), Y−N(2) 2.296(4), Y−C(1) 2.758(5), N(1)−C(1) 1.312(6), N(2)−C(1) 1.334(5), Y−C(39) 2.427(6), Y−C(40) 2.835(7), Y−C(45) 2.922(7); N(1)−Y−N(2) 57.1(1), N(2)−C(1)−N(1) 113.9(5), C(1)−N(1)−Y 93.6(3), C(1)−N(2)−Y 95.2(3), C(40)−C(39)−Y 90.9(4), C(39)−Y−C(40) 30.2(2).

Complexes **1** and **2** are air- and moisture-sensitive and are readily soluble in THF and toluene and moderately soluble in hexane. They are characterized by elemental analysis and IR spectroscopy, which were in good agreement with the proposed structure. The molecular structures of **1** and **2** were further determined by X-ray diffraction. Both complexes **1** and **2** are mononuclear structures. Complex **1-Er** crystallizes in a monoclinic system and space group $P2_1/n$, while complex **1-Y** crystallizes in a triclinic system and space group $P\bar{1}$. In **1-Er**, the benzyl ligand adopts an η^3-coordination mode (Figure 1),[16] which is different from the observations in $[HC(MeCNAr)_2]La(\eta^2\text{-}CH_2Ph)_2(THF)$[17a] and $(C_5Me_5)_2Sm(\eta^1\text{-}CH_2C_6H_5)(THF)$.[17b] The bond length of Er−C(40), 2.840(5) Å, and the bond angle of C(40)−C(39)−Er, 90.6(3)°, suggest a strong interaction between Er and C(40). The structural parameters of **1-Y** are very similar to those of complex **1-Er**. When the differences in metallic radii are subtracted,[18] the Ln−N and Ln−C distances of **1-Er** and **1-Y** are in good agreement with each other. Complexes **2-Er** and **2-Yb** are isostructural to $[(Me_3Si)_2NC(NCy)_2]_2Y^tBu$ (Figure 2).[19] The short distances of Er−C(42) and Yb−C(42),

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(16) Ge, S. Z.; Meetsma, A.; Hessen, B. *Organometallics* **2008**, *27*, 5339.

(17) (a) Bambirra, S.; Perazzolo, F.; Boot, S. J.; Sciarone, T. J. J.; Meetsma, A.; Hessen, B. *Organometallics* **2008**, *27*, 704. (b) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *Organometallics* **1991**, *10*, 134.

(18) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(19) Trifonov, A. A.; Lyubov, D. M.; Fedorova, E. A.; Fukin, G. K.; Schumann, H.; Muhle, S.; Hummert, M.; Bochkarev, M. N. *Eur. J. Inorg. Chem.* **2006**, 747.

3.018(17) and 3.08(3) Å, indicate an agostic interaction between the lanthanide ion and one methyl of *tert*-butyl.

Reaction of Bis(guanidinate)lanthanide Benzyl Complexes with Elemental Sulfur. Bis(guanidinate)lanthanide benzyl complexes $[(Me_3Si)_2NC(NCy)_2]_2LnBn$ (**1**) reacted with $^1/_8$ equiv of S_8 to form the dinuclear bis(guanidinate)-lanthanide thiolate complexes $\{[(Me_3Si)_2NC(NCy)_2]_2Ln(\mu\text{-SBn})\}_2$ [Ln = Er (**3-Er**), Y (**3-Y**)], as shown in Scheme 2. The formation of **3** is interpreted as one sulfur atom insertion into the Ln−C σ bond of **1**.

In order to simplify manipulation of the sulfur insertion process, we examined the reaction of the in situ generated **1-Er** with elemental sulfur. It was found that the treatment of $[(Me_3Si)_2NC(NCy)_2]_2Er(\mu\text{-Cl})_2Li(THF)_2$ and 1 equiv of BnK, followed by reaction with elemental sulfur, could also give **3-Er** without any obvious loss of yield.

Complex **3-Er** was characterized by X-ray diffraction analysis, and selected bond distances and angles are given in Table 1. As shown in Figure 3, the X-ray structure of **3-Er** definitively proves that one sulfur atom is inserted into an Er−C bond. **3-Er** is a solvent-free dimeric structure, with each Er atom bonded to two chelating η^3-guanidinate ligands and two sulfur atoms of two bridging thiolate anions. The bond lengths and angles within the guanidinate[5a] and thiolate[12] ligands are in the normal range (Table 1). The Ln_2S_2 unit is planar.

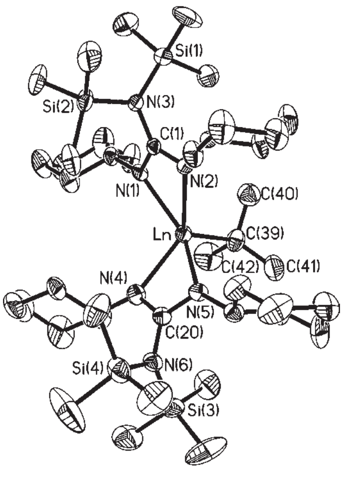


Figure 2. ORTEP diagram of $[(SiMe_3)_2NC(NCy)_2]_2Ln^tBu$ [Ln = Er (**2-Er**), Yb (**2-Yb**)] with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **2-Er**: Er−N(1) 2.375(8), Er−N(2) 2.282(8), Er−C(1) 2.778(9), N(1)−C(1) 1.326(11), N(2)−C(1) 1.328(12), Er−C(39) 2.387(12); N(1)−Er−N(2) 56.7(3), N(2)−C(1)−N(1) 113.1(8), C(1)−N(1)−Er 92.9(6), C(1)−N(2)−Er 97.1(6). For **2-Yb**: Yb−N(1) 2.282(5), Yb−N(2) 2.312(6), Yb−C(1) 2.721(8), N(1)−C(1) 1.345(8), N(2)−C(1) 1.343(8), Yb−C(39) 2.509(16); N(1)−Yb−N(2) 58.4(2), N(2)−C(1)−N(1) 113.1(6), C(1)−N(1)−Yb 94.8(4), C(1)−N(2)−Yb 93.6(5).

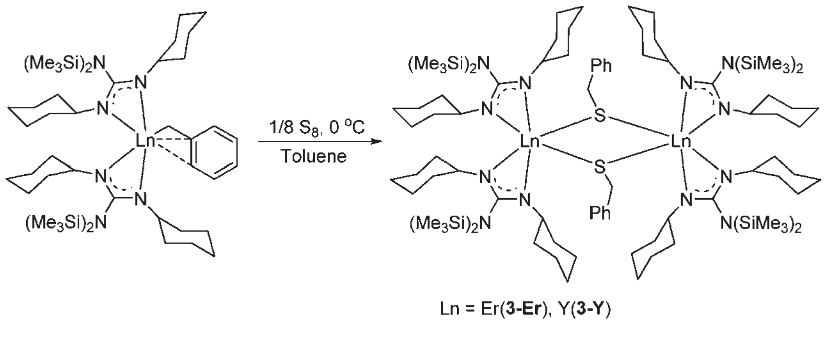
Reaction of Bis(guanidinate)lanthanide *tert*-Butyl Complexes with Elemental Sulfur. To investigate the influence of alkyl groups on the sulfur insertion, the reaction of the corresponding bulky *tert*-butyl complexes **2** with elemental sulfur was allowed to proceed under the same conditions. In contrast to **1**, the expected $\{[(Me_3Si)_2NC(NCy)_2]_2Ln(\mu\text{-S}^tBu)\}_2$ were not isolated; instead, $\{[(Me_3Si)_2NC(NCy)_2]_2Ln\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)$ [Ln = Er (**4-Er**), Yb (**4-Yb**)] were obtained in 35−41%, with the byproducts $^tBuS^tBu$ and $^tBuSS^tBu$ in a 1:4 ratio identified by gas chromatography/mass spectrometry (GC/MS). Employment of **2** and S_8 in a 4:1 ratio led to the isolation of **4** in high yields (Scheme 3). The color change from blue to orange within hours in the reaction of **2-Yb** with S_8 indicated that sulfur insertion into the Ln−C(^{t}Bu) σ bond was very slow probably because of the large steric hindrance of the ^{t}Bu group. Because the thiolate complex is sensitive to S_8 in solution as proven previously,[13b,20] this should create an opportunity for the competitive interaction of the resulting thiolate intermediate with the remaining sulfur, leading to the formation of disulfides as the main products.

$$\textbf{3-Er} + \frac{1}{4}S_8 \xrightarrow{0\ ^\circ\text{C, toluene}} \textbf{4-Er} \qquad (1)$$

We examine the reaction of **3-Er** with elemental sulfur to model the transformation of metal *tert*-butyl to metal disulfide via the formation of a metal thiolate intermediate. We have found that the reaction of **3-Er** with $^1/_4$ equiv of S_8 in toluene formed **4-Er** in 86% (eq 1). In contrast to the observation in the reaction of $[Cp_2Yb(\mu\text{-SEt})]_2$ with elemental sulfur,[13b] wherein a ca. 4:3 mixture of $[(Cp_2Yb)_2(\mu_3\text{-S})(THF)]_2$ and $[Cp_2Yb(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)$ is obtained, no metal sulfide was obtained in the present cases. It is clear that replacement of cyclopentadienyl by the $(Me_3Si)_2NC(NCy)_2$ group improves the chemoselectivity of the reaction of lanthanide thiolates with elemental sulfur.

Complexes **4** were characterized by X-ray diffraction and identified as dimers (Figure 4). In contrast to the observation that the interlinked bicyclic Ln_2S_2 fragment is generally puckered with a significant dihedral angle between two MS_2 planes in other disulfide complexes, such as $[Cp_2Yb(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)$ (161.3°),[13b] $(THF)_6Yb_4(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)_4(\mu_4\text{-S})(SC_6F_5)_2$ (average 96.2°),[20a] and $(THF)_6Yb_4I_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)_4(\mu_4\text{-S})$ (average 95.2°),[20b] in **4-Er** and **4-Yb**, the Ln_2S_2 unit is coplanar. In addition, for **4**, all Ln−S bond

Scheme 2



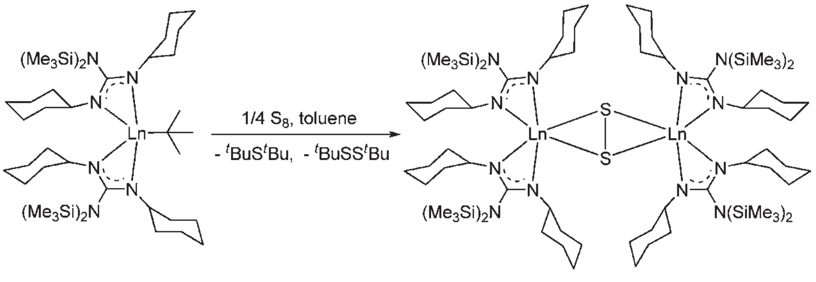
Ln = Er(**3-Er**), Y(**3-Y**)

Table 1. Bond Lengths [Å] and Angles [deg] for Complexes **3**, **5**, and **6**[a]

bond distances/angles	**3-Er**	**5-Y**	**5-Er**	**5-Yb**	**6-Er**	**6-Yb**
Ln(1)−N(1)	2.388(5)	2.356(6)	2.350(4)	2.309(8)	2.372(10)	2.320(7)
Ln(1)−N(2)	2.328(5)	2.411(6)	2.394(4)	2.320(9)	2.320(9)	2.354(8)
Ln(1)−C(1)	2.807(6)	2.844(6)	2.793(5)	2.741(11)	2.773(13)	2.770(11)
Ln(1)−S(1)	2.815(2)	2.831(3)	2.817(2)	2.808(4)	2.849(5)	2.826(4)
Ln(2)−S(1)	2.832(2)	2.804(3)	2.801(2)	2.784(4)	2.798(5)	2.804(4)
S(1)−C(39)	1.813(6)	1.789(9)	1.731(7)	1.785(8)	1.773(10)	1.774(8)
N(1)−C(1)	1.310(7)	1.340(8)	1.325(7)	1.322(10)	1.318(14)	1.341(13)
N(2)−C(1)	1.355(7)	1.357(8)	1.315(7)	1.329(10)	1.316(14)	1.359(12)
Ln(1)−N(1)−C(1)	94.2(4)	96.8(5)	94.8(3)	94.1(7)	93.0(8)	94.5(6)
N(1)−C(1)−N(2)	113.6(5)	113.1(8)	115.8(5)	114.8(11)	115.1(11)	114.7(9)
C(1)−N(2)−Ln(1)	95.7(4)	93.8(5)	93.1(3)	93.4(7)	95.4(8)	92.5(6)
N(2)−Ln(1)−N(1)	56.44(16)	56.3(2)	56.25(15	57.7(3)	56.5(3)	58.2(2)
Ln(1)−S(1)−Ln(2)	114.79(5)	114.72(6)	114.49(4)	115.22(6)	116.50(9)	116.68(8)
S(1)−Ln(2)−S(1A)	65.43(7)	65.63(9)	65.72(6)	65.09(11)	64.14(15)	63.58(11)
Ln(2)−S(1A)−Ln(1)	114.79(5)	114.72(6)	114.49(4)	115.22(6)	116.50(9)	116.68(8)
S(1A)−Ln(1)−S(1)	64.98(7)	64.93(9)	65.29(6)	64.47(12)	62,86(16)	63.05(11)

[a] A: $-x+1, -y+1, z$.

Scheme 3



Ln = Er(**4-Er**), Yb(**4-Yb**)

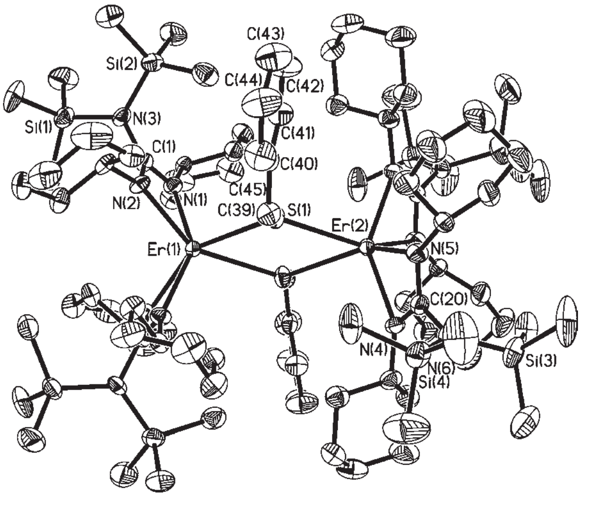


Figure 3. ORTEP diagram of **3-Er** with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.

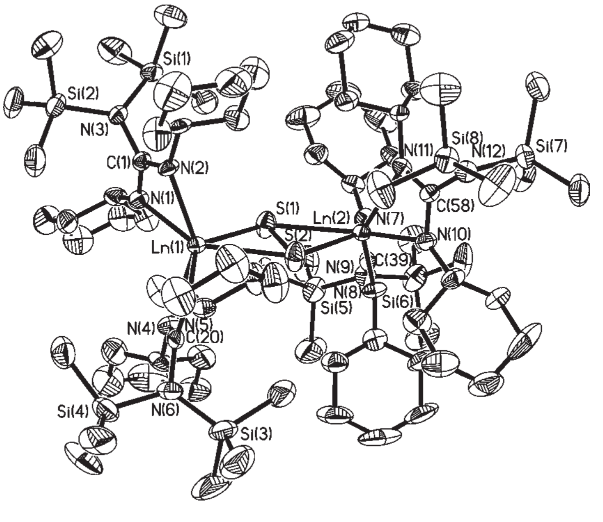


Figure 4. ORTEP diagram of $\{[(SiMe_3)_2NC(NCy)_2]_2Ln\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)$ [Ln = Er (**4-Er**), Yb (**4-Yb**)] with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **4-Er**: Er(1)−N(1) 2.303(8), Er(1)−N(2) 2.315(8), Er(1)−C(1) 2.712(10), N(1)−C(1) 1.309(12), N(2)−C(1) 1.498(13), Er(1)−S(1) 2.688(5), Er(1)−S(2) 2.667(7), Er(2)−S(1) 2.692(7), Er(2)−S(2) 2.667(5), S(1)−S(2) 2.120(6); N(1)−Er(1)−N(2) 57.7(3), N(2)−C(1)−N(1) 115.9(8), C(1)−N(1)−Er(1) 93.2(6), C(1)−N(2)−Er(1) 92.3(5), Er(1)−S(1)−Er(2) 132.2(2), Er(1)−S(2)−Er(2) 134.4(2), S(1)−Er(1)−S(2) 46.6(1), S(1)−Er(2)−S(2) 46.6(1). For **4-Yb**: Yb(1)−N(1) 2.306(6), Yb(1)−N(2) 2.299(6), Yb(1)−C(1) 2.721(8), N(1)−C(1) 1.290(10), N(2)−C(1) 1.320(10), Yb(1)−S(1) 2.671(3), Yb(1)−S(2) 2.652(3), Yb(2)−S(1) 2.670(3), Yb(2)−S(2) 2.645(3), S(1)−S(2) 2.114(3); N(1)−Yb(1)−N(2) 57.0(2), N(2)−C(1)−N(1) 114.7(7), C(1)−N(1)−Yb(1) 94.1(5), C(1)−N(2)−Yb(1) 93.6(5), Yb(1)−S(1)−Yb(2) 132.0(1), Yb(1)−S(2)−Yb(2) 134.2(1), S(1)−Yb(1)−S(2) 46.8(1), S(1)−Yb(2)−S(2) 46.9(1).

distances are very similar, but for $[Cp_2Yb(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)$, there are two distinctive metal−sulfur distances: one is in the normal range of an Yb^{3+}−S single bond and another is between those expected for an Yb^{3+}−S single bond and an Yb^{3+} ← :S donor bond.

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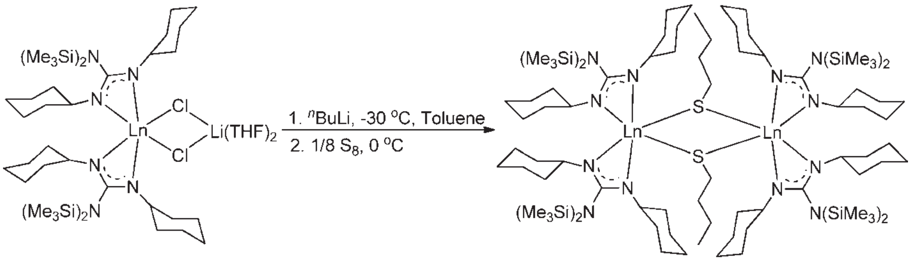
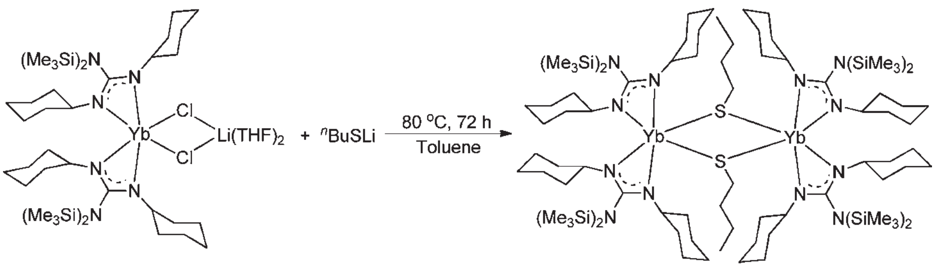
(20) (a) Melman, J. H.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **2002**, *41*, 3528. (b) Melman, J. H.; Fitzgerald, M.; Freedman, D.; Emge, T. J.; Brennan, J. G. *J. Am. Chem. Soc.* **1999**, *121*, 10247. (c) Freedman, D.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1999**, *38*, 4400. (d) Freedman, D.; Melman, J.; Emge, T.; Brennan, J. G. *Inorg. Chem.* **1998**, *37*, 4162. (e) Melman, J. H.; Emge, T. J.; Brennan, J. G. *Chem. Commun.* **1997**, 2269.

Scheme 4



Ln = Y (**5-Y**), Er (**5-Er**)

Scheme 5



5-Yb, 12%

The Yb−S distances in **4-Yb** range from 2.645(3) to 2.671(3) Å, and the average value of 2.660(3) Å is shorter than that in $[Cp_2Yb(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)$, average 2.725(5) Å.

Reactions of Bis(guanidinate)lanthanide *n*-Butyl Complexes with Elemental Sulfur. To extend the scope of bis(guanidinate)lanthanide alkyls, the reaction of the corresponding *n*-butyl complexes (prepared in situ) with elemental sulfur was further studied. As expected, the dinuclear thiolate complexes $\{[(Me_3Si)_2NC(NCy)_2]_2Ln(\mu\text{-}S^nBu)\}_2$ [Ln = Y (**5-Y**), Er (**5-Er**)] were obtained in good yields when $[(Me_3Si)_2NC(NCy)_2]_2Ln(\mu\text{-}Cl)_2Li(THF)_2$ were treated with 1 equiv of ^{n}BuLi and subsequently with $^1/_8$ equiv of S_8 under the same conditions (Scheme 4). However, the reaction of $[(Me_3Si)_2NC(NCy)_2]_2Yb(\mu\text{-}Cl)_2Li(THF)_2$ with ^{n}BuLi, followed by treatment with S_8 under the same conditions, gave $\{[(Me_3Si)_2NC(NCy)_2]_2Yb\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)$ (**4-Yb**) as the main metal-containing product. Presumably, the formation of **4-Yb** might result from the reduction of $[(Me_3Si)_2NC(NCy)_2]_2Yb(\mu\text{-}Cl)_2Li(THF)_2$ with ^{n}BuLi[21] and subsequent oxidation of the insulting divalent ytterbium intermediate with elemental sulfur.[22]

Given that lanthanide thiolate complexes are readily synthesized by protolysis of organolanhanide complexes with thiols or by the metathesis reaction of lanthanide halides with alkali metal thiolates, the alternative routes to $\{[(Me_3Si)_2NC(NCy)_2]_2Ln(\mu\text{-}S^nBu)\}_2$ were tested. However, the treatment of $[(Me_3Si)_2NC(NCy)_2]_2LnN(SiMe_3)_2$ and $[(Me_3Si)_2NC(NCy)_2]_2LnCp$[23] with thiols led to only the recovery of starting materials, while the reaction of **1-Er** or **2-Yb** with ^{n}BuSH led to the formation of a complex mixture.

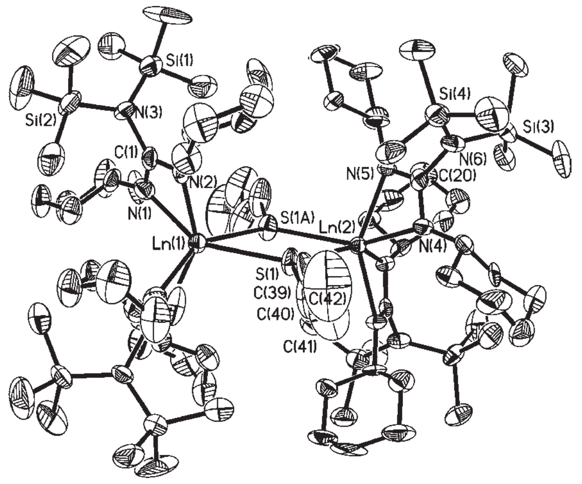


Figure 5. ORTEP diagram of $\{[(SiMe_3)_2NC(NCy)_2]_2Ln(\mu\text{-}S^nBu)\}_2$ [Ln = Y (**5-Y**), Er (**5-Er**), Yb (**5-Yb**)] with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.

Moreover, only a mixture of **5-Yb** and starting materials was obtained in the reaction of $[(Me_3Si)_2NC(NCy)_2]_2Yb(\mu\text{-}Cl)_2Li(THF)_2$ and *n*-butyl thiolate lithium in toluene even with prolonged heating (Scheme 5).

As shown in Figure 5, the geometry and stereochemistry of **5** are not particularly different from those observed in **3**. In particular, the bonding mode of the thiolates to metal ions is quite similar. The bond lengths in **5** are essentially identical with the distances in **3**. The average Y−S bond length of 2.818(3) Å for **5-Y** is longer than the values found in lanthanocene thiolates, such as $[(C_5H_5)_2Y(\mu\text{-}S^nBu)]_2$ (2.745 Å)[13b] and $[(C_5H_4SiMe_2{}^tBu)_2Y(\mu\text{-}S^nBu)]_2$ (2.749 Å).[13a] Moreover, the Y−S−Y bond angle of 114.7(1)° in **5-Y** is significantly larger than the corresponding values observed in $[(C_5H_4)_2Y(\mu\text{-}S^nBu)]_2$ (94.3°) and $[(C_5H_4SiMe_2{}^tBu)_2Y(\mu\text{-}S^nBu)]_2$ (95.3°), while the S−Y−S angle of 65.6(1)° is smaller than

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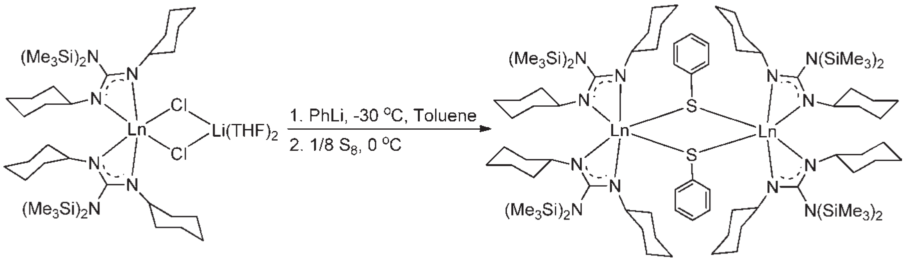
(21) (a) Zhou, X. G.; Zhang, L. B.; Zhu, M.; Cai, R. F.; Weng, L. H. *Organometallics* **2001**, *20*, 5700. (b) Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 292.

(22) Evans, W. J.; Rabe, G. W.; Ziller, J. W.; Doedens, R. J. *Inorg. Chem.* **1994**, *33*, 2719.

(23) For the synthesis of $[(SiMe_3)_2NC(NCy)_2]_2LnN(SiMe_3)_2$ and $[(SiMe_3)_2NC(NCy)_2]_2LnCp$, see the Supporting Information.

Scheme 6



Ln = Er (**6-Er**), Yb (**6-Yb**)

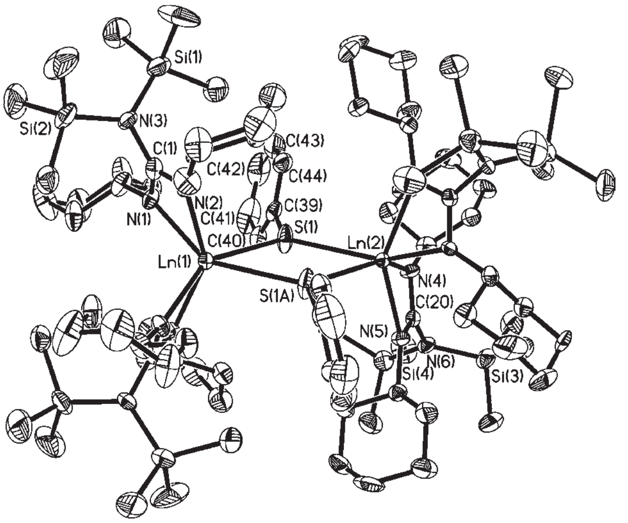


Figure 6. ORTEP diagram of $\{[(SiMe_3)_2NC(NCy)_2]_2Ln(\mu\text{-}SPh)\}_2$ [Ln = Er (**6-Er**), Yb (**6-Yb**)] with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.

those found in the above yttrocene thiolate complexes. These differences may be attributed to the larger steric hindrance of the guanidinate ligand compared with C_5H_5 and $C_5H_4SiMe_2{}^tBu$.

Reactions of Bis(guanidinate)lanthanide Phenyl Complexes with Elemental Sulfur. To better understand the influence of the alkyl ligands and to further develop the insertion reaction, we present an extension of this reaction to lanthanide aryl complexes. The treatment of $[(Me_3Si)_2NC(NCy)_2]_2LnPh$ (generated in situ from $[(Me_3Si)_2NC(NCy)_2]_2Ln(\mu\text{-}Cl)_2Li(THF)_2$ and PhLi) with $^1/_8$ equiv of S_8 under the same conditions afforded the corresponding insertion products $\{[(Me_3Si)_2NC(NCy)_2]_2Ln(\mu\text{-}SPh)\}_2$ [Ln = Er (**6-Er**), Yb (**6-Yb**)] in good yields (Scheme 6). The formation of **6** represents the first insertion of sulfur into the Ln−C(sp^2) σ bond. This proves that organolanthanide aromatic thiolate complexes can also be synthesized by this synthetic strategy.

The bonding modes were proven by single-crystal X-ray diffraction on complexes **6**. Selected bond distances and angles are listed in Table 1. Compounds **6-Er** and **6-Yb** are isostructural (Figure 6). Complexes **6-Er** and **6-Yb** have no unusual distances or angles. Surprisingly, **3**, **5**, and **6** crystallize in the same space group and have very similar cell parameters, despite the different thiolate ligands. This phenomenon is very rare. Thus, we surmise that the different reactivity behaviors and structural features of these bis(guanidinate)lanthanide complexes are largely a consequence of the less basicity and larger steric hindrance of $(Me_3Si)_2NC(NCy)_2$ compared to cyclopentadienyls.

Conclusion

In summary, both sulfur insertion into the Ln−C bond and selective oxidation of thiolate ligands of bis(guanidinate)lanthanide(III) complexes have been established that provide a simple and efficient method for the preparation of unreported bis(guanidinate)lanthanide thiolate and disulfide complexes, respectively, that would be difficult to prepare otherwise. The chemistry shown herein provides a new opportunity to gain more insight into the reactivity of guanidinate lanthanide complexes and illustrates intriguing supporting-ligand effects on the structure and/or properties of lanthanide thiolate and disulfide complexes.

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Supporting Information Available: X-ray crystallographic data in CIF format, experimental procedures, ORTEP diagrams for **S1-Ln** and **S2-Yb**, and X-ray structure determination details and crystal and data collection parameters for **1**−**6** and **S1-2**. This material is available free of charge via the Internet at http://pubs.acs.org.