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Facile Construction of Yttrium Pentasulfides from Yttrium Alkyl Precursors: Synthesis, Mechanism, and Reactivity

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Supporting Information

ABSTRACT: Treatment of the yttrium dialkyl complex Tp^{Me2}Y(CH₂Ph)₂(THF) (Tp^{Me2} = tri(3,5 dimethylpyrazolyl)borate, THF = tetrahydrofuran) with S₈ in a 1:1 molar ratio in THF at room temperature afforded a yttrium pentasulfide Tp^{Me2}Y(κ_4 -S₅) (THF) (1) in 93% yield. The yttrium



 $Tp^{Me2}Y(\kappa_4-S_5)$ (THF) (1) in 93% yield. The yttrium monoalkyl complex $Tp^{Me2}CpYCH_2Ph(THF)$ reacted with S_8 in a 1:0.5 molar ratio under the same conditions to give another yttrium pentasulfide $[(Tp^{Me2})_2Y]^+[Cp_2Y(\kappa_4-S_5)]^-$ (10) in low yield. Further investigations indicated that the S_5^{2-} anion facilely turned into the corresponding thioethers or organic disulfides, and released the redundant S_8 , when it reacted with some electrophilic reagents. The mechanism for the formation of the S_5^{2-} ligand has been investigated by the controlling of the reaction stoichiometric ratios and the stepwise reactions.

INTRODUCTION

Study of the synthesis and reactivity of metal sulfur clusters $M_x S_y$ has been a long-standing research subject of organometallic and bioinorganic scientists to mimic the ability of nitrogenases.¹ Plenty of transition-metal sulfur clusters have been synthesized and widely applied in synthetic, catalytic, and material chemistry during the past century.² Among these studies, transition-metal polysulfide $(S_x^{2-}, x \ge 2)$ have also attracted much attention not only regarding their structure and reactivity but also owing to their potential uses.³ For example, they can be used as catalysts and intermediates in enzymatic processes or in industrial catalytic reactions, such as the hydrodesulfurization (HDS) of fossil fuels.⁴ Now the metal species have been extended to most of d-block elements and some main group elements, and the number of the MS_x ring is expanded to 9.5 In contrast, the rare-earth metal polysulfides are far less common. The polysulfido (S_r^{2-}) ions are generally viewed as a soft ligand, but the rare-earth metal ions are classically hard Lewis acids. So the rare-earth metal-sulfur coordination is regarded as a less favorite combination.⁶ The rare-earth metal polysulfides mainly focus on their disulfides. The examples of rare-earth metal polysulfides $(S_x^{2-}, x > 2)$ are rarely reported. The known example is $[(C_5Me_5)_2Sm](S_3)$ -(THF), which was obtained by treatment of $(C_5Me_5)_2Sm$ -(THF)₂ with elemental sulfur.⁸ Recently, Evans et al. reported a yttrium complex with a RS₃⁻ ligand $[(Me_3Si)_2N]_2Y[\eta^2$ - $S_3N(SiMe_3)_2$ (THF), a byproduct from the reaction of $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu-\eta^2:\eta^2-N_2)$ with elemental S.⁹ To the best our knowledge, only one rare-earth metal pentasulfides Sm complex $(Tp^{iPr2})(\kappa-3,5-^{i}Pr_2Hpz)(S_5)^{10a}$ and one actinide complex $Cp^*_2Th(S_5)^{10b}$ have been reported.

Recently, we have been investigating the reactivity of rareearth metal alkyl complexes toward some organic small molecules¹¹ and found that $Tp^{Me2}Y(CH_2Ph)_2(THF)$ can cleave the C=S bond of isothiocyanate^{11a} or promote the threecomponent combination and ring-opening of 1-methylbenzimidazole beyond C–H activation,^{11b} and Tp^{Me2}CpYCH₂Ph-(THF) can activate 1-methylimidazole to construct a C==C bond through multiple C–H activations or activate benzonitrile to give the imine-enamine tautomer products after insertion.^{11c} Encouraged by these results that these alkyl complexes activated unsaturated organic small molecules, now we aim to study their reactivity toward some inorganic small molecules such as S₈, Se, P₄, etc. Herein, we wish to report the synthesis, structure, and reactivity of the rare-earth metal pentasulfides, and the findings that the S₅^{2–} anion facilely turned into thioethers or organic disulfides and S₈. Moreover, the mechanism for the formation of the rare-earth metal pentasulfides was also investigated by the stepwise reactions, and the rare-earth metal thiolate, sulfide, and disulfide 2–4 have been obtained as the key intermediates.

RESULTS AND DISCUSSION

The yttrium dialkyl complex Tp^{Me2}Y(CH₂Ph)₂(THF) (Tp^{Me2} = tri(3,5 dimethylpyrazolyl)borate)^{11a} reacted with S₈ in a 1:1 molar ratio in THF at room temperature for 12 h to give a structural characterized yttrium pentasulfide Tp^{Me2}Y(κ_4 -S₅)-(THF) (1) in 93% isolated yield (Scheme 1).



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Two organic products BnSBn and BnSSBn have been determined by the GC/MS method. The composition of 1 has been proven by elemental analysis and ¹H and ¹³C NMR spectroscopy, and its molecular structure has also been established by single-crystal X-ray diffraction analysis. The important bond lengths and angles were compiled in Figure 1.



Figure 1. Molecular structure of **1** with ellipsoids set at 30% probability. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Y1–S1 2.775(3),Y1–S5 2.675(4), Y1–S2 2.952(4), Y1–S4 3.269(5), S1–S2 1.998(5), S2–S3 2.099(6), S3–S4 1.996(7), S4–S5 1.987(9), Y1–O1 2.400(5); S2–S1–Y1 74.42(14), S4–S5–Y1 87.8(2), S5–S4–S3 111.1(3), S1–S2–S3 105.3(3), S4–S3–S2 102.2(3).

The ¹H and ¹³C NMR spectra of **1** showed that only the signals attributable to the resonances of the Tp^{Me2} ligand and the coordinated THF molecule were observed, indicating that no benzyl group exists in **1**. In accordance with this observation, the molecular structure of **1** (Figure 1) displayed that the center metal ion Y³⁺ bonded with a κ_3 -Tp^{Me2} ligand, a κ_4 -S₅ moiety, and one coordination THF molecule. The twist-boat YS₅ ring conformation in **1** is significantly different from those observed in late transition-metal pentasulfides.¹² The later exhibited a chair MS₅ conformation, in which two terminal S atoms are coordinated to the center metal.¹³ This conformation in **1** is similar to that in the known compounds Sm (Tp^{iPr2})(κ -3,5-ⁱPr₂Hpz)(S₅) and Cp*₂ThS₅.¹⁰ Four Y–S distances are 2.775(3) (Y1–S1), 2.952(4) (Y1–S2), 3.269(5) (Y1–S4), and

2.675(4) Å (Y1–S5), and are comparable to the corresponding values found in Sm $(Tp^{iPr2})(\kappa-3,5^{-i}Pr_2Hpz)(S_5)$ (Sm–S1 2.755(1); Sm–S2 2.952(1); Sm–S4 3.090(1); Sm–S5 2.792(1) Å),^{10a} and revealed two kinds of Y–S bonds, *viz*, two Y–S σ bonds (Y1–S1 and Y1–S5) and two Y–S donor bonds (Y1–S2 and Y1–S4). The S–S distances are also slight different.

To gain more insight into the mechanism for the formation of 1, the stepwise reactions of Tp^{Me2}Y(CH₂Ph)₂(THF) with S₈ in different stoichiometric ratios were investigated as shown in Scheme 2. Reaction of Tp^{Me2}Y(CH₂Ph)₂(THF) with S₈ in a 1:0.25 molar ratio in THF at room temperature afforded a tetranuclear yttrium thiolate cluster $[Tp^{Me2}Y]_4(\mu$ -SCH₂Ph)₆- $(\mu_4$ -S) (2) in 94% yield. The equimolar reaction of Tp^{Me2}Y- $(CH_2Ph)_2$ THF and 1/8 S₈ under the same conditions also gave $\mathbf 2$ in low yield, and the partial starting materials $\mathrm{Tp}^{\mathrm{Me2}}\mathrm{Y}$ - $(CH_2Ph)_2$ THF were recovered. Treatment of 2 with 1/8 equiv of S₈ in THF at room temperature produced a tetranuclear cubane-like Y_4S_4 cluster $[Tp^{Me2}Y(\mu_3-S)]_4$ (3) (31%, a known compound),⁸ accompanied by small amount of yttrium disulfide $[Tp^{Me2}Y]_2(\mu \cdot \eta^2 \cdot \eta^2 \cdot S_2)_2$ (4). Complex 4 can also be synthesized by the reaction of $Tp^{Me2}YCH_2Ph)_2(THF)$ and S_8 in a 1:0.5 molar ratio or 2 with S_8 in a 1:1 molar ratio in 83% and 90% isolated yields, respectively. 3 further reacted with 0.25 equiv of S_8 also led to the formation of 4 (87%). Moreover, 4 continuously reacted with 3/8 equiv or excess of S_8 in THF at room temperature to produce the vttrium pentasulfide 1 in 92% isolated yield. From these stepwise reactions, we found that only 7/8 equiv of S_8 were consumed to form the final product 1 from the starting materials. So we also investigated the reaction of $Tp^{Me2}Y(CH_2Ph)_2(THF)$ with elemental S in a 1:7/8 molar ratio and found 1 was obtained in almost quantitative yield (97%). Complexes 2 and 4 were characterized by spectroscopic and analytical techniques, and their molecular structures were unequivocally confirmed by single-crystal X-ray diffraction analysis, and are shown in Figure 2 (2) and Figure 3 (4). In the ¹H NMR spectrum of **2**, three single peaks at δ = 5.63, 2.35, and 2.56 ppm are attributed to 4-H- Tp^{Me2} and Me- Tp^{Me2} respectively, and there are three multiple peaks at $\delta = 5.80-$ 6.90 ppm, which are attributed to the phenyl ring protons of the PhCH₂S groups, and one single peak at δ = 3.33 ppm is attributable to the CH₂ protons of the PhCH₂S groups. The integral area ratio of the 4-H-Tp^{Me2} signals of the Tp^{Me2} ligands and the CH_2 signals of the PhCH₂S groups is not 3/4 but 1/1,

Scheme 2. Synthesis of Yttrium Polysulfido Complexes 2, 3, and 4





Figure 2. Molecular structure of 2 with ellipsoids set at 30% probability. All hydrogen atoms and Tp^{Me2} ligand are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Y1–S2 2.788(3), Y1–S1 2.856(5), Y3–S1 2.924(2), Y3–S3 2.781(3); Y3–S2A 2.830(3), Y3–S3A 2.814(3).



Figure 3. Molecular structure of **4** with ellipsoids set at 30% probability. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Y1–O1 2.455(4), Y1–S1 2.715 (2), Y1–S3 2.754(2), Y1–S2 2.840(2), Y1–S4 2.855(2), Y2–O2 2.430(4), Y2–S4 2.722(2), Y2–S2 2.741(2), Y2–S1 2.860(2), Y2–S3 2.884(2), S1–S2 2.101(2), S3–S4 2.111(2); Y1–S1–Y2 84.52(5), Y2–S2–Y1 84.45(5), Y1–S3–Y2 83.40(5), Y2–S4–Y1 84.50(5).

indicating that some benzyl or PhCH₂S group was eliminated during the formation of **2**. This result was further confirmed by its molecular structure. Figure 2 displays that **2** adopts a pseudo-tetrahedral symmetry. Four Y³⁺ centers occupy the vertices of tetrahedron, while the six SCH₂Ph groups contact the edges of the tetrahedron. Each of the Y³⁺ centers carries one κ_3 -Tp^{Me2} ligand, three μ_2 -SCH₂Ph groups, and one μ_4 -S atom. The Y–SCH₂R (Y1–S2 2.788(3), Y3–S3 2.781(3); Y3–S2A 2.830(3), Y3–S3A 2.814(3) Y1–S2 2.788(3)Å) and Y–S²⁻ (Y1–S1 2.856(5), Y3–S1 2.924(2) Å) bond distances are in the normal range of the bridged Y–S σ -bonds.⁷

Complex 4 crystallizes from the THF solvent in the monoclinic system, space group $P2_1$. Structure determination results show that **2** is a dimer with the two Y atoms bonded to two S_2 groups in a classic μ - η^2 : η^2 -bonding mode. The four Y–S distances (Y1–S1, Y1–S2, Y2–S1, and Y2–S2) are 2.715(2), 2.840(2), 2.754(2), and 2.855(5) Å, respectively, and are between those expected Y–S single and donor bonds. These bond data are comparable to the values found in $[Cp_2Yb](\mu-\eta^2:\eta^2-S_2)$ (Yb– S_{av} 2.759(8) Å), when the differences in the

metal ionic radii are considered.^{7b} The S–S bond lengths are 2.101(2) Å (S1–S2) and 2.111(2) Å (S3–S4) and are also comparable to those observed in complex {[(SiMe₃)₂NC-(NCy)₂]₂Er}₂(μ - η^2 : η^2 -S₂) (S–S 2.120(6) Å).^{7a}

On the basis of the observations described above, we proposed a possible process for the formation of 1, displayed in Scheme 3. The S atoms first inserted into the Y–C σ -bonds of the yttrium dialkyl complex Tp^{Me2}Y(CH₂Ph)₂(THF) to produce the thiolate intermediate I. Further another S atom inserted into one of the Y–S σ -bonds of I to form an alkylperthio intermediate II. Then the nucleophilic attack of the residual PhCH₂ group to the alkylperthio group in II led to the formation of **2**, following a BnSBn-elimination process.^{7b} The S atom further inserted into one of the Y–S σ -bonds of **2** to form an alkylperthio intermediate III. Then the intramolecular elimination of organic disulfide BnSSBn or thioether BnSBn occurred in III to give the cublane-like Y_4S_4 cluster 3.¹³ The S atoms continuously inserted into the Y-S bonds of 3 to afford 4, following the collapse of the cubic skeleton of 3. The final product 1 was formed through a continuously insertion of S atoms into the Y–S (S_2) bonds of 4.

To explore the reactivity and transformation of the rare-earth metal pentasulfide 1, we have investigated the reactions of 1 with a series of electrophilic reagents such as Me₃SiCl, Me₂SiCl₂, o-C₆H₄(CH₂Br)₂, NHC, etc. As presented in Scheme 4, the reaction of 1 with 2 equiv of Me₃SiCl in THF at room temperature gave the yttrium dichloride TpMe2YCl2(THF)2 (73%), organic product Me₃SiSSiMe₃, and S₈ determined by the GC/MS method. The equimolar reaction of 1 with Me₂SiCl under the same conditions also afforded these products and the residual 1. A cyclo-silylthione 5 has been determined by GC/MS when 1 reacted with Me₂SiCl₂.¹⁴ The reaction of 1 with $o-C_6H_4(CH_2Br)_2$ in THF at room temperature produced yttrium dibromide Tp^{Me2}YBr₂(THF)₂ (6), and an organic disulfide $C_6H_4C_2H_4S_2$ (7) in 87% and 66% isolated yields, respectively. When 1 reacted with N,N'-di(2,6diisoproporylphenyl)NHC, 4 and NHCS (8) was observed.

We also investigated the reactivity of the yttrium monoalkyl complex Tp^{Me2}CpYCH₂Ph(THF) toward elemental S and found that Tp^{Me2}CpYCH₂Ph(THF) reacted elemental S in a 1:1 molar ratio under the same conditions to give the expected yttrium thiolate complex Tp^{Me2}CpYSCH₂Ph(THF) (9) in high yield, as shown in Scheme 5. However, when the molar ratio between elemental S and the monoalkyl complex exceeded the value of 1, the reactions became complicated, and might be attributable to the occurrence of ligand rearrangement. For example, when Tp^{Me2}CpYCH₂Ph(THF) reacted with 2 equiv of elemental S or 9 reacted with another equivalent of elemental S under the same conditions, a lot of insoluble white precipitates appeared in solution, and 4 was isolated from the solution phase in about 30% yield. Interestingly, if 1 equiv or an excess of elemental S was added into the above reaction system. the white precipitates slowly disappeared, and the solution became clear. After workup, another yttrium pentasufide $[(Tp^{Me2})_2Y]^+[Cp_2Y(\kappa_4-S_5)]^-$ (10) was obtained in 35% isolated yield. This result indicated that the ligand rearrangement might be reversible in the system. X-ray diffraction results (Figure 4) show that 10 is an ionic-type complex, in which the cation is $[(Tp^{Me2})_2Y]^+$ and the anion is $[Cp_2Y(\kappa_4-S_5)]^-$. The total structure of the anion $[Cp_2Y(\kappa_4-S_5)]^-$ is very similar to the known actinide complex $Cp*_2ThS_5$, and the Y^{3+} ion is coordinated with two η^5 -Cp rings and one κ_4 -S₅²⁻ ligand to form distorted octahedron geometry. The Y-S distances (Y2-



Scheme 4. Reactions of 1 with Some Electrophilic Reagents



Scheme 5. Reactions of Tp^{Me2}CpYCH₂Ph(THF) with S₈



S1 2.737(2), Y2–S2 3.092(6), Y2–S4 3.117(7), and Y2–S5 2.706(2) Å) are comparable to those values found in $Cp_2^{+}ThS_5$ (Th–S1 2.768(4) and Th–S2 3.036(3) Å).^{10b} The S1–Y2–S5 angle of 122.05(7)° is slightly larger than the S1–Th–S1′ angle reported in $Cp_2^{+}ThS_5$ (113.3(1)°).

CONCLUSION

In summary, two rare-earth metal pentasulfides have been synthesized through the reactions of the rare earth mono- and dialkyl precursors with S_8 . The rare-earth metal thiolate (2), sulfide (3), and disulfide (4) as the key intermediates have been



Figure 4. Molecular structure of the anion $[Cp_2Y(\kappa_4-S_5)]^-$ of **10** with ellipsoids set at 30% probability. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Y2–S1 2.737(2), Y2–S2 3.092(6), Y2–S4 3.117(7), Y2–S5 2.706(2), S1–S2 1.998(4), S2–S3 2.068(5), S3–S4 2.076(6), S4–S5 2.107(4); S5–Y2–S1 112.05(7), S2–S1–Y2 79.88(10), S1–S2–S3 111.8(2), S2–S3–S(4) 100.6(2), S3–S4–S5 105.5(2), S4–S5–Y2 79.69(11).

obtained by the step reactions or controlling the reaction stoichiometric ratio, which powerfully proved the proposed mechanism for the formation of the pentasulfide anion (S_5^{2-}) . Preliminary studies on the reactivity of 1 showed that the S_5^{2-} anion can not only facilely turn into the corresponding thioether and organic disulfide, but also degrade to form the S_2^{2-} anion. Further investigations regarding the reactivity and potential applications of these rare-earth metal polysulfides are currently in progress.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out under a dry and oxygen-free nitrogen atmosphere in an MBRAUN glovebox. The nitrogen gas in the glovebox was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox were monitored by an O_2/H_2O

Combi-Analyzer (MBRAUN) to ensure that both concentrations stayed below 1 ppm. Toluene, THF, and hexane were distilled from sodium strip/benzophenone ketyl, degassed, dried over fresh Na chips, and stored in the glovebox. (Tp^{Me2})CpYBn(THF) and (Tp^{Me2})YBn₂-(THF) were prepared according to literature procedure.^{11a,15} TMSCl and Me2SiCl2 were purchased from J&K and dried with 4 Å sieves. C_6D_6 and THF- d_8 was obtained from Cambridge Isotope and dried by sodium chips. N,N-Diisopropylphenyl-NHC (8a) was prepared according to literature procedure.¹⁶ Other commercially available reagents were purchased and used without purification. ¹H NMR and ¹³C NMR spectra were recorded on a JEOL ECA-400 NMR spectrometer (FT, 400 MHz for ¹H; 100 MHz for ¹³C) in C_6D_6 or THF- d_8 at room temperature. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. The resonances of B-H bond in the Tp^{Me2} ligand are too broad to be observed in their ¹H NMR spectra.

Synthesis of $Tp^{Me2}Y(\kappa_4$ -S₅) (THF) (1). Method A. Solid sulfur S (128 mg, 4.0 mmol) was added to a solution of Tp^{Me2}YBn₂(THF) (320 mg, 0.5 mmol) in THF (20 mL) at room temperature. After being stirred overnight, the transparent solution was evaporated to dryness under a vacuum. The residue was washed by *n*-hexane two times $(15 \text{ mL} \times 2)$ to give the yellow powders 1. The powders were dissolved in THF, and yellow crystalline samples of 1 were obtained in 93% isolated yield (288 mg) by the solvent evaporation method. ¹H NMR (400 MHz, THF- d_{8} , rt): δ 1.77 (m, 4H, O(CH₂CH₂)₂), 2.37–2.40 (two overlapped single peaks, 18H, CH3-Tp^{Me2}), 3.62 (m, 4H, O- $(CH_2CH_2)_2$, 5.79 (s, 3H, 4-H-Tp^{Me2}); ¹H NMR (400 MHz, C₆H₆ d_{6} , rt): δ 1.10 (m, 4H, O(CH₂CH₂)₂), 2.10–18 (two overlapped single peaks, 18H, CH₃-Tp^{Me2}), 3.58 (m, 4H, O(CH₂CH₂)₂), 5.47 (s, 3H, Tp^{Me2}); ¹³C NMR (100 MHz, THF- d_{8} , rt): δ 12.94, 15.12, 26.15, 68.02, 107.06, 145.85, 151.52; elemental analysis calcd (%) for C₁₉H₃₀BN₆OS₅Y (618.5232): C 36.90, H 4.89, N 13.59; found: C 36.77, H 4.81, N 13.74.

Method B. Solid sulfur S (48 mg, 1.5 mmol) was added to a solution of 4 (261 mg, 0.25 mmol) in THF (30 mL) at room temperature. After being stirred overnight, the transparent solution was evaporated to dryness under a vacuum. The residue was washed by *n*-hexane two times (15 mL \times 2) to give the yellow powders 1 in 92% isolated yield (285 mg).

Method C. Solid sulfur S (112 mg, 3.5 mmol) was added to a solution of $Tp^{Me2}YBn_2$ (thf) (320 mg, 0.5 mmol) in THF (20 mL) at room temperature. After being stirred overnight, the transparent solution was evaporated to dryness under a vacuum. The residue was washed by *n*-hexane two times (15 mL × 2) to give the yellow powders 1 in 97% isolated yield (300 mg).

Synthesis of $[Tp^{Me2}Y]_4(\mu$ -SCH₂Ph)₆(μ_4 -S) (2). Solid sulfur S (32 mg, 1.0 mmol) was added to a solution of $Tp^{Me2}YBn_2$ (thf) (320 mg, 0.5 mmol) in THF (20 mL) at room temperature. After being stirred overnight, the transparent solution was evaporated to dryness under a vacuum. The residue was washed by *n*-hexane two times (15 mL × 2) to give the yellow powders 2. The powders were dissolved in THF, and colorless crystalline samples of 2 were obtained in 94% isolated yield (272 mg) by solvent evaporation method. ¹H NMR (400 MHz, C_6H_6 - d_6 , rt): δ 2.35 (s, 36H, CH₃-Tp^{Me2}), 2.56 (s, 36H, CH₃-Tp^{Me2}), 3.33 (s, 12H, CH₂Ph), 5.63 (s, 12H, 4-H-Tp^{Me2}), 5.92 (d, J = 8.0 Hz, 12H, CH₂C₆H₅), 6.71 (t, J = 8.0 Hz, 12H, CH₂C₆H₅), 6.87 (t, J = 8.0 Hz, 6H, CH₂C₆H₅); ¹³C NMR (100 MHz, d_6 - C_6H_6 , rt): δ 13.47, 19.38, 37.40, 105.59, 124.91, 127.43, 129.14, 142.39, 144.13, 152.30; elemental analysis calcd for C₁₀₂H₁₃₀B₄N₂₄S₇Y₄ (2315.6078): C 52.91, H 5.66, N 14.52; found: C 52.72, H 5.57, N 14.75.

Synthesis of $[Tp^{Me2}Y(\mu_3-5)]_4$ (3). Solid sulfur S (8 mg, 0.25 mmol) was added to a solution of 2 (579 mg, 0.25 mmol) in THF (20 mL) at room temperature. After being stirred overnight, the transparent solution was evaporated to dryness under a vacuum. The residue was washed by *n*-hexane two times (15 mL × 2) to give the pale yellow powders 3. The powders were dissolved in THF, and colorless crystalline samples of 3 were obtained in 31% isolated yield (152 mg) by solvent evaporation method. The ¹H and ¹³C NMR spectra data and crystallographic analysis data of 3 are identified as that of the known compound $[Tp^{Me2}Y(\mu_3-S)]_4^{-11a}$

Synthesis of $[Tp^{Me2}Y]_2(\mu-\eta^2:\eta^2-S_2)_2$ (THF)₂ (4). Method A. Solid sulfur S (64 mg, 2.0 mmol) was added to a solution of Tp^{Me2}YBn₂(THF) (320 mg, 0.5 mmol) in THF (20 mL) at room temperature. After being stirred overnight, the transparent solution was evaporated to dryness under a vacuum. The residue was washed by *n*-hexane two times $(15 \text{ mL} \times 2)$ to give the yellow powders 4. The powders were dissolved in THF, and yellow crystalline samples of 4 were obtained in 83% isolated yield (210 mg) by solvent evaporation method. ¹H NMR (400 MHz, C₆H₆-d₆, rt): δ 1.41 (m, 4H, O(CH₂CH₂)₂), 2.21 (s, 9H, CH₃-Tp^{Me2}), 2.82 (s, 9H, CH₃-Tp^{Me2}), 3.57 (m, 4H, O(CH₂CH₂)₂), 5.56 (s, 3H, 4-H-Tp^{Me2}); ¹H NMR (400 MHz, THF-d₈, rt): δ 1.77 (m, 4H, O(CH₂CH₂)₂), 2.40-2.59 (two overlapped single peaks, 18H, CH3-Tp^{Me2}) 3.62 (m, 4H, O- $(CH_2CH_2)_2$, 5.68 (s, 3H, Tp^{Me2}); ¹³C NMR (100 MHz, THF- d_8 , rt): δ 13.24, 15.69, 26.19, 68.03, 106.49, 145.14, 151.49; elemental analysis calcd for C38H60B2N12O2S4Y2 (1044.6564): C 43.69, H 5.79, N 16.09; found: C 43.83, H 5.86, N 15.86.

Method B. Solid sulfur S (64 mg, 2.00 mmol) was added to a solution of 2 (579 mg, 0.25 mmol) in THF (20 mL) at room temperature. After being stirred overnight, the transparent solution was evaporated to dryness under a vacuum. The residue was washed by *n*-hexane two times (15 mL \times 2) to give the pale yellow powder 4. Yield: 90%, 470 mg.

Method C. Solid sulfur S (32 mg, 1.00 mmol) was added to a solution of 3 (490 mg, 0.25 mmol) in THF (20 mL) at room temperature. After being stirred overnight, the transparent solution was evaporated to dryness under a vacuum. The residue was washed by *n*-hexane two times (15 mL × 2) to give the pale yellow powder 4. Yield: 87%, 454 mg. Reactivity of $Tp^{Me2}Y(\kappa_4$ -S₅) (THF) (1) toward Some Electrophilic

Reactivity of $Tp^{Me2}Y(\kappa_4$ -S₅) (THF) (1) toward Some Electrophilic Reagents. Reaction of 1 with Me_3SiCl . A 5 mL THF solution of Me_3SiCl (mg, 0.5 mmol) was added dropwise into a solution of 1 (309 mg, 0.5 mmol) in THF (15 mL) at room temperature. After being stirred overnight, the solution was divided into two parts: one part was hydrolyzed by H_2O and extracted by petroleum ether. The organic phase ($Me_3SiSSiMe_3$ and S_8) was determined by GC/MS. The other part was concentrated to dry, and the solid residues were washed by *n*hexane two times (10 mL × 2) to give the white powder $Tp^{Me2}YCl_2(THF)_2$, a known compound.¹⁷ Yield: 219 mg, 73%.

*Reaction of 1 with Me*₂SiCl₂. A 5 mL THF solution of Me₂SiCl₂ (mg, 0.5 mmol) was added dropwise into a solution of 1 (309 mg, 0.5 mmol) in THF (15 mL) at room temperature. After being stirred overnight, the solution was divided into two parts: one part was hydrolyzed by H₂O and extracted by petroleum ether. The organic phase (*cyclo*-(Me₂SiS)₂ (**5**) and S₈) was determined by GC/MS. The other part was concentrated to dry, and the solid residues were washed by *n*-hexane two times (10 mL × 2) to give the white powders Tp^{Me2}YCl₂(THF) yet. Yield: 244 mg, 81%.

Reaction of 1 with o- $C_6H_4(CH_2Br)_2$. A 5 mL THF solution of *o*- $C_6H_4(CH_2Br)_2$ (mg, 0.5 mmol) was added dropwise into a solution of 1 (309 mg, 0.5 mmol) in THF (15 mL) at room temperature. After being stirred for overnight, the reaction mixture gradually transforms from yellow settled solution to light yellow solution. All volatiles were evaporated under reduced pressure. The residue was extracted with *n*-hexane (25 mL), and the turbid solution was filtrated. The filter cake was redissolved in THF, and recrystallized from THF to afford the colorless crystals of Tp^{Me2}YBr₂(THF) (**6**) in 85% yield (262 mg). ¹H NMR (400 MHz, C_6H_6 - d_6 , rt): δ 1.18 (m, 4H, O(CH₂CH₂)₂), 2.09 (s, 9H, CH₃-Tp^{Me2}), 2.61 (s, 9H, CH₃-Tp^{Me2}), 3.82 (m, 4H, O-(CH₂CH₂)₂), 5.45 (s, 3H, 4-H-Tp^{Me2}); ¹³C NMR (100 MHz, C_6H_6 - d_6 , rt): δ 12.91, 15.17, 25.33, 71.93, 106.69, 145.76, 151.24; elemental analysis calcd for C₁₉H₃₀BN₆OBr₂Y (618.0062): C 36.93, H 4.89, N 13.60; found: C 36.68, H 4.77, N 13.88. Because of the poor crystal quantity, no satisfactory crystal data of **6** was obtained.

The filtrate was concentrated, and pure product 7^{18} was obtained by column chromatography (silica gel, with a mixture of ethyl acetate/ petroleum ether). Yield: mg, 66%. ¹H NMR (400 MHz, d_1 -CHCl₃, rt): δ 1.56 (s, 4H, CH₂S-), 7.33 (d, J = 2.4 Hz, 4H, C₆H₄-); ¹³C NMR (100 MHz, CHCl₃-d₁, rt): δ 38.94, 129.09, 131.77, 135.49.

Table 1. Crystallographic Data for Complexes 1, 2, 4, and 10

	1	2	4	10
formula	C ₁₉ H ₃₀ BN ₆ OS ₅ Y	$C_{102}H_{130}B_4N_{24}S_7Y_4$	$C_{38}H_{60}B_2N_{12}O_2S_4Y_2$	$C_{40} H_{54} B_2 N_{12} S_5 Y_2$
formula weight (g/mol)	618.50	2315.60	1044.64	1062.69
temp (K)	173(2)	296(2)	298(2)	173(2)
crystal color	pale-yellow	colorless	colorless	pale-yellow
radiation ($\lambda = 0.710730$ Å)	$Mo-K_{\alpha}$	$Mo-K_{\alpha}$	Mo-K _a	Mo-K $_{\alpha}$
scan type	ω -2 θ	ω -2 θ	ω -2 θ	ω -2 θ
crystal system, space group	monoclinic, $P2(1)/c$	cubic, $Pa\overline{3}$	monoclinic, $P2(1)/c$	triclinic, P1
unit cell dimens (Å, deg)	a = 18.497(8)	a = 28.859(2)	a = 18.240(4)	a = 8.5206(12)
	b = 8.129(4)	b = 28.859(2)	b = 16.970(3)	b = 16.896(2)
	c = 19.778(9)	c = 28.859(2)	c = 19.830(4)	c = 20.087(3)
	$\alpha = 90$	$\alpha = 90$	$\alpha = 90$	$\alpha = 81.705(2)$
	$\beta = 114.392(7)$	$\beta = 90$	$\beta = 110.00(3)$	$\beta = 87.565(2)$
	$\gamma = 90$	$\gamma = 90$	$\gamma = 90$	$\gamma = 86.122(2)$
volume $(Å^3)/Z$	2709(2) /4	24034(3) /8	5768(2) /4	2853.5(7) /2
density (calculated) (Mg/m ³)	1.514	1.280	1.201	1.237
abs coeff (mm ^{-1}), $F(000)$	2.563,1268	2.086, 9584	2.186, 2152	2.243, 1092
crystal size (mm ³)	$0.30 \times 0.10 \times 0.05$	$0.18 \times 0.16 \times 0.10$	$0.18 \times 0.12 \times 0.06$	$0.200 \times 0.100 \times 0.05$
θ range for data collection (deg)	2.08-26.10	1.41-25.07	1.19-25.10	1.025-27.00
limiting indices	$-22 \le h \le 22$	$-34 \le h \le 34$	$-21 \le h \le 21$	$-10 \le h \le 10$
	$-10 \le k \le 10$	$-32 \le k \le 34$	$-19 \le k \le 20$	$-21 \le k \le 16$
	$-24 \le l \le 24$	$-32 \le l \le 34$	$-17 \leq l \leq 23$	$-25 \le l \le 25$
reflns collected/unique	17177/5337	137403/7126	28585/10240	20208/12266
	[R(int) = 0.0551]	[R(int) = 0.4991]	[R(int) = 0.0756]	[R(int) = 0.0527]
completeness to θ = 25.10 (%)	99.3	100.0	99.8	98.4
max and min transmission	0.8826 and 0.5136	0.8185 and 0.7052	0.8800 and 0.6944	0.746 and 0.663
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
data/restraints/param	5337/60/344	7126/0/437	10240/53/553	12266/49/584
foodness-of-fit on F^2	1.099	1.173	1.043	0.924
final <i>R</i> indices ^b $[I > 2\sigma(I)]$	$R_1 = 0.0722$	$R_1 = 0.0805$	$R_1 = 0.0539$	$R_1 = 0.0713$
	$wR_2 = 0.2071$	$wR_2 = 0.2015$	$wR_2 = 0.1223$	$wR_2 = 0.1995$
R indices ^b (all data)	$R_1 = 0.1134$	$R_1 = 0.2306$	$R_1 = 0.0981$	$R_1 = 0.1239$
	$wR_2 = 0.2516$	$wR_2 = 0.2810$	$wR_2 = 0.1274$	$wR_2 = 0.2284$
largest diff peak and hole (e/Å $^{3})$	3.035 and -1.004	0.983 and -1.037	1.051 and -0.631	1.086 and -0.673

Reaction of 1 with NHC (8a). A 5 mL THF solution of o- $C_6H_4(CH_2Br)_2$ (mg, 0.5 mmol) was added dropwise into a solution of 1 (309 mg, 0.5 mmol) in THF (15 mL) at room temperature. After being stirred overnight, the reaction mixture gradually transformed from yellow settled solution to light yellow solution. All volatiles were evaporated under reduced pressure. The residue was washed by nhexane two times (10 mL \times 2) and recrystallized from the mixed solvent of THF and n-hexane. The yellow block crystals of organic compound 8 (NHCS) were obtained in 47% isolated yield (99 mg). If the residue was purified through column chromatography, 8 can be obtained in 87% isolated yield. ¹H NMR (400 MHz, C_6H_6 - d_6 , rt): δ 1.16 (d, J = 4.0 Hz, 12H, CH₃-), 1.44 (d, J = 4.0 Hz, 12H, CH₃-), 2.92 (m, 4H, CH-), 6.19 (s, 2H, CH=CH), 7.16 (m, 4H,C₆H₃-), 7.26 (m, 2H, $C_6H_{3^-}$); ¹³C NMR (100 MHz, $C_6H_6-d_{60}$ rt): δ 23.88, 24.20, 29.26, 118.70, 124.30, 130.17, 134.72, 146.98, 168.39. To know the metalcontaining components, the in situ ¹H NMR spectrum of the residue was obtained, and the metal-containing component was found to be 4. See SFigure 1.

Synthesis of $CpTp^{Me2}YSBn(THF)$ (9). Solid sulfur S (16 mg, 0.5 mmol) was added to a solution of $CpTp^{Me2}YBn(THF)$ (307 mg, 0.5 mmol) in THF (20 mL) at room temperature. After being stirred overnight, the transparent solution was evaporated to dryness under a vacuum. The residue was washed by *n*-hexane two times (15 mL × 2) to give the pale yellow powder 9. The powders were dissolved in THF, and colorless crystalline samples of 9 were obtained in 96% isolated yield (310 mg) by the solvent evaporation method. ¹H NMR (400 MHz, $C_6H_6-d_6$, rt): δ 1.21 (m, 4H, O(CH₂CH₂)₂), 2.13 (s, 10H, CH₃-Tp^{Me2}), 2.57 (s, 8H, CH₃-Tp^{Me2}), 3.53 (m, 4H, O(CH₂CH₂)₂), 3.75 (s, 2H, CH₂C₆H₅), 5.65 (s, 3H, 4-H-Tp^{Me2}), 6.47 (s, 5H, Cp), 7.02 (t,

 $J = 8.0 \text{ Hz}, 1\text{H}, \text{CH}_2\text{C}_6\text{H}_5), 7.16 \text{ (t, } J = 8.0 \text{ Hz}, 2\text{H}, \text{CH}_2\text{C}_6\text{H}_5), 7.49 \text{ (d, } J = 8.0 \text{ Hz}, 2\text{H}, \text{CH}_2\text{C}_6\text{H}_5); {}^{13}\text{C} \text{ NMR} (100 \text{ MHz}, \text{C}_6\text{H}_6\text{-}d_6, \text{rt}): \delta 13.30, 14.88, 25.36, 35.31, 70.77, 106.91, 112.06, 125.10, 127.85, 129.10, 144.90, 147.42, 151.23; elemental analysis calcd for C_{31}\text{H}_{42}\text{BN}_6\text{SOY} (646.4869): C 57.59, H 6.55, N 13.00; found: C 57.42, H 6.49, N 13.10.$

Synthesis of $[(Tp^{Me2})_2Y]^+[Cp_2Y(\kappa_4-S_5)]^-$ (10). Method A. Solid sulfur S (64 mg, 2.0 mmol) was added to a solution of CpTp^{Me2}YBn(THF) (307 mg, 0.5 mmol) in THF (20 mL) at room temperature. After being stirred overnight, the transparent solution was evaporated to dryness under a vacuum. The residue was washed by *n*-hexane two times (15 mL × 2) to give the pale yellow powders 10. The powders were dissolved in THF, and colorless crystalline samples of 10 were obtained in 35% isolated yield (186 mg) by the solvent evaporation method. ¹H NMR (400 MHz, THF-*d*₈, rt): δ 1.86 (s, 18H, CH₃-Tp^{Me2}), 2.53 (s, 18H, CH₃-Tp^{Me2}), 5.81 (s, 4H, 4-H-Tp^{Me2}), 6.00 (s, 10H, Cp), 6.29 (s, 2H, 4-H-Tp^{Me2}); ¹³C NMR (100 MHz, THF-*d*₈, rt): δ 12.50, 12.99, 107.26, 108.22, 149.65, 151.46; elemental analysis calcd (%) for C₄₀H₅₄B₂N₁₂S₅Y₂ (1062.6963): C 45.21, H 5.12, N 15.82; found: C 45.34, H 5.19, N 15.66.

Method B. Solid sulfur S (16 mg, 0.5 mmol) was added to a solution of 9 (323 mg, 0.5 mmol) in THF (30 mL) at room temperature. After being stirred for 0.5 h, the transparent solution became slowly turbid. Then another solid sulfur S (32 mg, 1.0 mmol) was continuously added to the turbid solution, and it was stirred for 12 h. The solution slowly turned clear. All volatiles were removed under a vacuum. The residue was washed by *n*-hexane two times (15 mL \times 2) and recrystallized from the mixed solvents of THF and *n*-hexane to give the crystals 10 in 27% isolated yield (143 mg).

X-ray Crystallographic Analysis Method. Suitable crystals were sealed in the thin-wall glass capillaries under a microscope in the glovebox. Data collections were performed on a Bruker SMART APEX (at 293 K) or Bruker SMART APEX (II) (at 173 K, or 293 K) diffractometer with CCD area detector using graphite-monochromated Mo K α radiation (λ = 0.71073 Å). The determination of crystal class and unit cell was carried out by SMART program package. The raw frame data were processed using $\rm SAINT^{19a}$ and $\rm SADABS^{19b}$ to yield the reflection data file. The structure was solved by using the SHELXTL program.^{19c} Refinement was performed on F2 anisotropically by the full-matrix least-squares method for all the non-hydrogen atoms. The analytical scattering factors for neutral atoms were used throughout the analysis. All hydrogen atoms were placed at the calculated positions and included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance. A summary of the crystallographic data and selected experimental information is given in Table 1.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b02747.

SFigure 2. In situ ¹H NMR spectrum of the reaction of **1** with NHC; SFigure 3. Molecular structure of **8**; SFigure 4. Molecular structure of **9**; STable 1. Crystal data and structure refinement for **8**; STable 2. Crystal data and structure refinement for **9**; scanned ¹H, ¹³C NMR, of all new compounds (PDF)

Crystallographic information file (CIF)

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Notes

The authors declare no competing financial interest.

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