ORGANOMETALLICS

Synthesis of Rhodium–Primary Thioamide Complexes and Their Desulfurization Leading to Rhodium Sulfido Cubane-Type Clusters and Nitriles

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Supporting Information

ABSTRACT: Although molecular thioamide complexes of late-transition metals have been prepared since 1979, the chemistry of primary thioamide complexes remains relatively unexplored. To shed light on this area, we have investigated synthesis, structures, and reactivities of simple rhodium organometallic complexes with a primary arenecarbothioamide ligand [Cp*RhCl₂{S=C(Ar)NH₂- κ ¹S}] (Cp* = η ⁵-C₅Me₅). Intra- and intermolecular hydrogen bonding in the thioamide complexes is discussed on the basis of ¹H NMR spectroscopy



and X-ray analysis. When these rhodium complexes were treated with a large excess amount of Et₃N, desulfurization of the thioamide ligand took place to give arenecarbonitriles (ArCN) in high GC yield and the cubane-type cluster $[(Cp*Rh)_4(\mu_3-S)_4]$ (3) in good yield as the organometallic product. Use of a smaller amount (2.4 equiv) of Et₃N followed by treatment with NaBAr^F₄ (Ar^F = 3,5-(CF₃)₂C₆H₃) led to the isolation of the cationic clusters $[(Cp*Rh)_4(\mu_3-S)_4](BAr^F_4)$ or $[(Cp*Rh)_4(\mu_3-S)_4](BAr^F_4)_2$ in low yield. Reaction mechanisms of the desulfurization of the coordinated thioamides and the formation and oneor two-electron oxidation of 3 during the desulfurization are discussed.

INTRODUCTION

Thioamides, sulfur analogues of carboxamides, act as versatile and interesting ligands in coordination chemistry, because they and their deprotonated species, thioamidate anions, can take various coordination geometries such as *S*-bonded,^{1–8} *N*,*S*chelating,⁹ *N*,*S*-bridging,^{5a,10} and *S*,*S*-bridging (Chart 1).^{10a,11} Among those, thioamide-based pincer-type ligands have been received considerable attention in recent years.^{12,13} Some thioamide complexes of palladium and rhodium show catalytic performance in reactions such as cross-coupling^{13h,14,15} and asymmetric hydrogenation of carbonyl compounds.^{9e,16} Since the sulfur atoms in thioamides are less prone to be oxidized in comparison with commonly used organophosphorus ligand, thioamide-based palladium complexes can serve as a good catalyst even under aerobic conditions for Suzuki–Miyaura cross-coupling and Mizoroki–Heck reaction.^{15a,b}

Meanwhile, investigation into the coordination chemistry of thioamides may help to bring fundamental insight into the activation of carbon–sulfur bonds in organosulfur compounds.¹⁷ The carbon–sulfur double bond cleavage reaction of thioamides, i.e., desulfurization of thioamides, has also received attention. The desulfurization of thioamides has been achieved by using metals^{18,19} or some organic oxidants.^{20–22} In this process, primary thioamides are converted into the corresponding nitriles, providing one of the practical methods for preparation of organonitriles.^{18,19d,20}

Although molecular thioamide complexes have been known for more than 30 years $^{1-12}$ and have attracted considerable attention as described above, fundamental chemistry of primary thioamide complexes with late-transition metals remains unexplored; only one organometallic ruthenium complex^{7a} and very few coordination compounds of nickel^{1a,b} and cobalt^{4a,b} were crystallographically characterized. Now we have synthesized a series of simple rhodium complexes with a primary arenecarbothioamide ligand [Cp*RhCl₂{S=C(Ar)- $NH_2 - \kappa^1 S$]. Inspired by the formation of molecular sulfido complexes on desulfurization of thiophenes with late-transition metals,²³ we also envisioned that the desulfurization of the thioamide complexes produces nitriles and rhodium sulfido species, the latter of which can spontaneously be assembled into rhodium sulfido cubane-type clusters. The Rh₄S₄ clusters have been known in the literature, but their properties, particularly their solid-state structures, have not been described.²⁴ Only preparative methods and cyclic voltammetric analysis are mentioned very briefly^{23a,c,25a,b} in contrast to the well-documented iridium and ruthenium sulfido cubane-type complexes.^{25,26} Consequently, we also describe desulfurization of thioamide complexes obtained leading to arenecarbonitriles (ArCN) and the rhodium sulfido cubane-type cluster

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N,S-chelating9e S-bonded^{7a} BF₄ PPh₂ Ph_3 4ہ BocHN N.S-bridging^{10a} S.S-bridging¹¹ (cod)R el P $[Fe] = Fe(CO)_3$ pincer-type12j metallacycle14a CO οć simple neutral S-bonded thioamide ligands

This work

Phi

P٢

base-induced desulfurization leading to 'Cl [Rh₄S₄] clusters and ArCN

 $[(Cp*Rh)_4(\mu_3-S)_4]$ along with its mono- and dicationic derivatives $[(Cp*Rh)_4(\mu_3-S)_4]^{1+/2+}$, providing the first complete series of cuboidal species of rhodium with and without a metal-metal bonding interaction.

RESULTS AND DISCUSSION

C

 NH_2

Synthesis and Structures of Rhodium Complexes with a Primary Thioamide Ligand. When [Cp*RhCl₂], was allowed to react with thiobenzamide (1a) in CH_2Cl_2 at room temperature, a dark red solid started to precipitate in a few minutes. The solid was recrystallized from hot MeOH to give the rhodium complex $[Cp*RhCl{S=C(C_6H_5)NH_2-\kappa^1S}]$ (2a) in 82% yield as dark red crystals (Table 1, entry 1). Arenecarbothioamide complexes with electron-donating (2b and 2c) and -withdrawing groups (2d-2f) at the para position $[Cp*RhCl{S=C(Ar)NH_2-\kappa^1S}]$ were also prepared by a similar procedure (entries 2-6). In the ¹H NMR, the characteristic signals due to the N-H protons of 2 are observed at δ 10.23–10.48 and 7.63–8.96 (1H each), which were shifted downfield compared to the corresponding signals of the starting thioamides 1 (at around δ 7.7 and δ 7.2). The remarkable downfield shift and separation of the chemical shit in the ¹H NMR suggest the presence of hydrogen bonding in 2.

Molecular structures of 2 were confirmed by X-ray studies. Complex 2a was revealed to possess intra- and intermolecular NH…Cl hydrogen bondings between the two chlorido ligands and thioamide N-H groups, forming a dimeric 12-membered ring structure in the crystal (Figure 1). Unlike 2a, thioamide complexes 2d-f are helically linked through intra- and intermolecular NH…Cl hydrogen bonding in the crystal to form tubular structure (Figure 2). These results are in good accordance with the observation of two distinct downfield



^{*a*}Reaction conditions: a mixture of $[Cp*RhCl_2]_2$ (1 equiv) and 1 was stirred in CH_2Cl_2 at room temperature for 0.5 h. ^{*b*}Isolated yields.



Figure 1. Intermolecular interaction of 2a to form the dimeric structure (50% thermal probability). Carbon-bound hydrogen atoms are omitted for clarity.

signals in the ¹H NMR of 2. The C–S bond length in 2a is longer than that in 1a (2a, 1.702(3) Å; 1a, 1.68 Å (mean)), whereas the C-N bond distance in 2a is shorter than that in 1a (**2a**, 1.297(3) Å; **1a**, 1.32 Å (mean)).²⁷

Desulfurization of 2 Leading to Rhodium Sulfido Cubane-Type Complexes. Next, we undertook investigation into the base-promoted desulfurization of thioamide of 2. Formation of a stable rhodium sulfido covalent bond could be a driving force. When thiobenzamide complex 2a was treated with 20 equiv of NEt₃ for 1 h in benzene, the red color of the solution quickly changed to dark brown (Table 2). GLC analysis of the reaction mixture indicated that benzonitrile was formed in 76% GC yield, indicating that desulfurization of 2a smoothly took place as expected. From the reaction mixture, the neutral rhodium sulfido cubane-type cluster $[(Cp*Rh)_4(\mu_3-$ S)₄] (3), which shows a sharp singlet at δ 1.73 in the ¹H NMR, was isolated in 32% yield (entry 1). With longer reaction time the yield of 3 was improved to 93% (entry 2). Similar reactions of thioamide complexes 2 having various substituents afforded 3 and the corresponding ArCN (entries 3-6), though there



Figure 2. (a) Molecular structure of 2d (50% thermal probability). Carbon-bound hydrogen atoms and solvents are omitted for clarity. (b) Hydrogen-bonded infinite helical motif formed in 2d. (c) Perspective representation of 2d along the c axis.





^{*a*}Reaction conditions: a mixture of **2** (1 equiv) and Et₃N (20 equiv) was stirred in benzene at room temperature. ^{*b*}Isolated yields. ^{*c*}GLC yields. ^{*d*}Complex mixture. ^{*e*}1a was used instead of **2a** with 2.4 equiv of Et₃N.

was not observed a clear trend of electronic substituent effects. Unfortunately 3 was not observed in desulfurization of 2f with NO₂ group (entry 7). Since thioamide 1a is inert under weakly basic conditions and remains unchanged even after prolonged reaction time (entry 8), the coordination of sulfur to rhodium is considered to play a key role in the present base-induced desulfurization of thioamides.

In contrast, when 2.4 equiv of Et₃N was used, a complex mixture of organometallic species was formed, though PhCN was formed in 70–82% yields. When NaBAr^F₄ was added into the crude product, several new tetrarhodium clusters related to 3 were obtained (Scheme 1). Thus, the monocationic cubane-type cluster $[(Cp*Rh)_4(\mu_3-S)_4](BAr^F_4)$ (4(BAr^F₄)) was recovered from the reaction conducted in benzene, whereas the dicationic analogue $[(Cp*Rh)_4(\mu_3-S)_4](BAr^F_4)_2$ (5(BAr^F₄)₂)

and the cubane-like cluster with a thiobenzamidato ligand $[(Cp*Rh)_4(\mu_3-S)_3\{\mu_2-SC(Ph)NH-\kappa^2S:\kappa^1N\}](BAr^F_4)$ $(6(BAr^{F_4}))$ were isolated from the reaction in CH₂Cl₂, albeit in low yields. Complex $6(BAr_4^F)$ was characterized only by a preliminary X-ray study, which revealed that the thiobenzamidato ligand acts as a μ_3 -NHCS- $\kappa^1 N$, $\kappa^1 S$, $\kappa^1 S$ ligand, bridging two rhodium atoms through the sulfur atom and the third rhodium through the deprotonated nitrogen.²⁸ Obviously cluster $6(BAr^{F}_{4})$ is viewed as an incomplete desulfurization product of 2. As for the cationic cubane-type clusters, it has been known that related dicationic iridium and ruthenium sulfido clusters $[(Cp*M)_4(\mu_3-S)_4]^{2+}$ (M = Ir, Ru) are readily formed by oxidation of neutral cubane-type complexes $[(Cp^*M)_4(\mu_3-S)_4]$ with hydrogen chloride added or liberated in situ.^{25c,26c} These facts imply that the use of a large excess amine prohibits the oxidation of neutral cluster 3 by quenching proton in the reaction mixture. Indeed, treatment of 3 with an acid induced the formation of the mono- and dicationic clusters (vide infra).

Chemical Oxidation of Neutral Rhodium Sulfido Cluster 3. Rauchfuss and co-workers briefly noted the preparation of 3 and its mono- and dication clusters.^{23a} Hidai and co-workers described that such oxidized rhodium sulfido cubane-type clusters are observed in the electrochemical measurement of 3.^{25c} However, properties and structures of this series of cubane-type clusters remain unreported. To rationalize the formation of 4^+ and 5^{2+} , as well as to uncover their properties, we have examined the synthesis of these mono- and dicationic clusters by chemical oxidation of 3 (Table 3). Initially, when 3 was treated with 1 equiv of $[Cp_2Fe]$ - (BAr_{4}^{F}) in $CH_{2}Cl_{2}$, the monocationic cluster $4(BAr_{4}^{F})$ was obtained in 73% yield (entry 1). By using 2 equiv of [Cp₂Fe](BAr^F₄), the dicationic rhodium cluster $[(Cp^*Rh)_4(\mu_3-S)_4](BAr^F_4)_2$ ($5(BAr^F_4)_2$) was also synthesized in high yield (entry 2). Salts of S^{2+} with other counterions, $[(Cp*Rh)_4(\mu_3-S)_4](PF_6)_2$ (5(PF_6)_2) and $[(Cp*Rh)_4(\mu_3-S)_4]_ (BF_4)_2$ (5(BF_4)₂), were synthesized in high yields by similar two-electron oxidation of 3 (entries 3 and 4). A silver salt was also able to be used in the oxidation reaction; reaction of 3 and 2 equiv of AgOTf afforded the dicationic complex $[(Cp*Rh)_4(\mu_3-S)_4](OTf)_2$ (5(OTf)₂) in 36% yield (entry 5). As already mentioned, the iridium analogue cluster

As already mentioned, the iridium analogue cluster $[(Cp*Ir)_4(\mu_3-S)_4]$ is readily oxidized by HCl to give the dicationic complex $[(Cp*Ir)_4(\mu_3-S)_4]^{2+26c}$ However, use of

Scheme 1. Formation of Various [Rh₄S₄] Clusters and Molecular Structure of 6^{+a}



"PhCN was formed in 70–82% GLC yields in each reaction. Thermal ellipsoids are drawn at 50% probability. For clarity, carbon-bound hydrogen atoms and solvates are omitted, and Cp* ligands are shown in a capped-sticks style.

S—[[Rh] [Rh]- S—[Rh] 3	$\begin{array}{c c} Rh] & & \text{oxidant} \\ \hline CH_2CI_2 \\ rt, 1 \ h \\ [Rh] = Cp^*Rh \\ \hline & & [Rh] \\ & & & S \\ & & & [Rh] \\ & & & S \\ & & & Fh \\ & & & S \\ \end{array}$	-[Ŗh] X S / [Rh] S or 3h] S-	S-[Rh] X ₂ -S' [Rh]S [Rh] 5 x ₂
entry	oxidant (equiv)	product	yield ^{b} (%)
1	$[Cp_2Fe](BAr_4^F)$ (1)	$4(BAr_4^F)$	73
2	$[Cp_2Fe](BAr_4^F) (2)$	$5(BAr_{4}^{F})_{2}$	87
3	$[Cp_{2}Fe](PF_{6})$ (2)	$5(PF_6)_2$	90
4	$[Cp_{2}Fe](BF_{4})$ (2)	$5(BF_4)_2$	70
5	AgOTf (2)	5(OTf) ₂	36
6 ^{<i>c</i>}	HCl/Et ₂ O (5)	decomp	
7^d	TFA (5)	$5(CF_3CO_2)_2$	52
8 ^e	TFA (1)	$4(BAr_4^F)$	16
a			

Table 3. Chemical Oxidation of 3^a

^{*a*}Reaction conditions: a mixture of 3 and an oxidant was stirred in CH₂Cl₂ at room temperature for 1 h unless otherwise noted. ^{*b*}Isolated yield. ^{*c*}Reaction time was for 2 h. ^{*d*}Reaction time was for 8 h. ^{*e*}The reaction was carried out in the presence of NaBAr^F₄ (1 equiv).

HCl as the oxidant for 3 led to decomposition products (entry 6). Instead, reaction of 3 with CF₃COOH (TFA, 5 equiv) successfully afforded the two-electron oxidation product $[(Cp*Rh)_4(\mu_3-S)_4](CF_3CO_2)_2$ (5(CF₃CO₂)₂) in 52% yield (entry 7). Similar reaction of 3 with an equimolar amount of TFA in the presence of NaBAr^F₄ (1 equiv) gave the monocation 4(BAr^F₄), albeit in lower isolated yield (entry 8). These results indicate that neutral cluster 3 undergoes oxidation in the presence of an appropriate proton source.

Unfortunately, only a small amount (<1%) of hydrogen evolution was detected by GC analysis of these reaction mixtures, and the fate of proton is unclear. Alternatively, a part of 3 may be converted into a hydridorhodium or a hydrosulfido species during the reaction.²⁹

In the ¹H NMR at room temperature, monocation 4⁺ displays a very broad signal at δ 8.61 with $W_{1/2}$ = 857 Hz, whereas the dicationic cluster 5²⁺ shows one singlet signal at around δ 1.70.

Structural Elucidation of a Series of Rh₄**S**₄ **Clusters.** All of the cubane-type clusters obtained here have been unambiguously confirmed by X-ray studies (Table 4), providing the first structural characterization for the [Rh₄S₄] cubane-type cluster series. Neutral **3** has a typical 72e cubane-type cluster structure, in which six Rh…Rh distances are similar to each other (3.5302(6)-3.5617(3) Å), whereas in monocationic complex 4(BAr^F₄) inequivalent Rh–Rh distances (3.3824(4)-3.5783(4) Å) are observed, which reflects the 71e configuration of **4**⁺.

It should be mentioned that different molecular structures are observed with $\mathbf{5}^{2+}$ depending on the counterion. Judging from the 70e configuration of 5^{2+} , there is an expected Rh–Rh bonding interaction in the dications. In fact, a short Rh-Rh distance is found in $5(PF_6)_2$ (2.7541(5) Å) and $5(BAr_4^F)_2$ (3.0827(6) Å), respectively. In contrast, only relatively large Rh-Rh separations (3.3080(5) Å or longer) were found in $5(CF_3CO_2)_2$. To evaluate the difference of metal-metal bonding interactions variable-temperature NMR spectra of these salts in CD_2Cl_2 were measured in a range of -90 to 25 °C (Figure 3). In each case a sharp signal due to the Cp* protons finally broadened at around -80 °C, but there was observed a clear dependence on the anion. The signal for $5(CF_3CO_2)_2$ starts to split at -90 °C. These observations indicate that Rh-Rh bonding in 5^{2+} is mobile even at -80 °C, being in sharp contrast to the fact that the migration of the metal-metal bond in the iridium analogue $[(Cp*Ir)_4(\mu_3-S)_4](PF_6)_2$ is sufficiently



Table 4. Rh-Rh Bond Lengths Determined by X-ray Studies for 3, $4(BAr_4^F)$, $5(PF_6)_2$, $5(BAr_4^F)_2$, and $5(CF_3CO_2)_2^a$

^aThermal ellipsoids are drawn at 50% probability. For clarity, hydrogen atoms and solvates are omitted, and Cp* ligands are shown in a cappedsticks style.



Figure 3. Selected region of the variable-temperature 1 H NMR spectra of 5^{2+} in CD₂Cl₂.

slow at -40 °C in the ¹H NMR time scale.^{26c} Consequently, an expected metal-metal bonding in S^{2+} is considered to be delocalized over its rhodium sulfido framework, and the

differences between the solid-state structure of 5^{2+} is attributable mainly to the packing effects by the counterions.

Reaction Pathway for the Desulfurization of 2 Leading to a Series of Clusters 3, 4⁺, and 5²⁺. A plausible mechanism for the formation of the clusters is shown in Scheme 2. Initially, one molecule of HCl is eliminated by the action of the base to give the thioamidato complex [Cp*RhCl- $\{SC(Ph)=NH-\kappa^1S:\kappa^1N\}$ (7). This type of N,S-chelating thioamidato ligand has some precedents.9 Subsequent deprotonation of the N-H in 7 produces the corresponding nitrile along with the highly unsaturated terminal sulfido complex [Cp*Rh(=S)(NCPh)]. Repeated dimerization of the sulfidorhodium species leads to the neutral cubane-type cluster $3_{1}^{23c,25a,b}$ which can be oxidized to cationic cubane-type clusters 4^+ and 5^{2+} by proton as an oxidant. When an insufficient amount of the base was used as shown in Scheme 1, complex 7 is not consumed completely and provides another coordinatively unsaturated cationic species [Cp*Rh{SC(Ar)=NH- $\kappa^{1}S:\kappa^{1}N$ [(BAr^F₄) (8). Coupling of 8 with [Cp*Rh=S] gives rise to the dinuclear species $[(Cp*Rh)_2(\mu_2-S){\mu_2-SC(Ph)} =$ NH- $\kappa^1 S: \kappa^1 N$ [(BAr^F₄) (9), which further transformed to 6⁺ by coupling with 9 with $[(Cp*Rh)_2(\mu_2-S)_2]$.

Scheme 2. A Plausible Pathway for the Formation of 3, 4^+ , 5^{2+} , and 6^+



CONCLUSIONS

In this study, we have synthesized a series of rhodium complexes with a primary thioamide ligand and investigated their base-promoted desulfurization. The X-ray and the ¹H NMR analyses of the rhodium thioamide complexes revealed that there is intra- and intermolecular NH···Cl hydrogen bonding between the chlorido and thioamide N–H groups. The thioamide complexes undergo desulfurization with Et_3N at room temperature to give arenecarbonitriles in high yields. When the thioamide complexes are treated with a large excess amount of amine, the neutral rhodium sulfido cubane-type cluster $[(Cp*Rh)_4(\mu_3-S)_4]$ is obtained selectively. Use of a smaller amount of the base gave rise to the oxidation of the cubane cluster. Oxidation of the cuboidal cluster with $[Cp_2Fe]^{1+}$ or proton and the molecular structures of the cubane-type clusters have been established.

This study clearly demonstrated that activation of thioamides is accomplished by coordination to a late-transition metal center. In other words, arenecarbothioamides can be used in the synthesis of sulfur clusters as a molecular sulfur source. Further investigation into late-transition metal complexes with carboxamides and their sulfur and selenium analogues, thioamides and selenoamides, will be reported in due course.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under a dry nitrogen atmosphere by using standard Schlenk techniques unless otherwise specified. $[Cp*RhCl_2]_2^{30} p-MeOC_6H_4CSNH_2$ (**1b**),³¹ $p-NO_2C_6H_4CSNH_2$ (**1f**),³¹ NaBAr^F₄·2H₂O,³² $[Cp_2Fe](PF_6)$,³³ $[Cp_2Fe]-(BF_4)$,³³ and $[Cp_2Fe](BAr^F_4)^{34}$ were prepared according to the literature methods. CH_2Cl_2 (P₄O₁₀), acetone (CaSO₄), MeOH (Mg), EtOH (Mg), and Et₃N (KOH) were dried and distilled over appropriate drying reagents indicated. Trifluoroacetic acid was dried over activated MS4Å. CDCl₃ and C₆D₆ were degassed by freeze–pump–thaw cycles and stored over activated MS4Å. Dehydrated-grade solvents (benzene and ether) and other reagents were commercially obtained and used as received.

NMR spectra were recorded on a JEOL ECA-500 or a Bruker AV600 spectrometer. IR spectra were recorded on a JASCO FT/IR-4200 spectrometer by using KBr pellet. GLC analyses were performed on a Shimadzu GC-2014 instrument equipped with an FID detector and a capillary column (Agilent Technologies, DB-5, 30 m \times 0.25 mm). Elemental analyses were performed on a PerkinElmer 2400 series II CHN analyzer. Amounts of the solvent molecules in the crystals were determined not only by elemental analyses but also by ¹H NMR spectroscopy.

Synthesis of the Rhodium Thioamide Complexes $[Cp*RhCl_2[S=C(Ar)NH_2-\kappa^1S]]$ (2). A solution of $[Cp*RhCl_2]_2$ and $ArCSNH_2$ (2.0–2.3 equiv) in CH_2Cl_2 was stirred at room temperature for 0.5 h. The red solution quickly changed to a reddish suspension. The resulting suspension was dried in vacuo to give a reddish powder. This powder was dissolved in MeOH at 60 °C, and the resulting solution was cooled at –20 °C overnight to give the corresponding thioamide complexes 2.

[**Cp***RhCl₂(\hat{S} =C(C₆H₅)NH₂-κ¹S)] (2a). Following the general procedure, 2a was synthesized from [Cp*RhCl₂]₂ (566.7 mg, 0.917 mmol) and PhCSNH₂ (1a; 251.6 mg, 1.83 mmol) in CH₂Cl₂ (20 mL). 2a was isolated as dark red crystals (689.8 mg, 1.50 mmol, 82% yield). ¹H NMR (CDCl₃, 500 MHz): δ 10.36 (br s, 1H, NH), 7.80 (d, *J* = 7.5 Hz, 2H, *o*-Ph), 7.63 (br s, 1H, NH), 7.52 (t, *J* = 7.5 Hz, 1H, *p*-Ph), 7.42 (t, *J* = 7.5 Hz, 2H, *m*-Ph), 1.69 (s, 15H, Cp*). ¹³C{¹H} NMR (CDCl₃, 126 MHz): δ 196.6 (C=S), 137.4 (Ar), 132.9 (Ar), 128.9 (Ar), 127.1 (Ar), 96.2 (d, *J*_{RhC} = 8.4 Hz, Cp*), 9.0 (Cp*). IR (cm⁻¹): 3448 (ν_{NH}), 3220 (ν_{NH}), 1560 (ν_{SCN}). Anal. Calcd for C₁₇H₂₂Cl₂N₁Rh₁S₁: C, 45.76; H, 4.97; N, 3.14. Found: C, 45.66; H, 4.88; N, 3.05.

[Cp*RhCl₂{S=C(4-MeOC₆H₄)NH₂- κ^{1} S]·MeOH (2b·MeOH). Following the general procedure, 2b was synthesized from [Cp*RhCl₂]₂ (49.5 mg, 0.080 mmol) and 4-MeOC₆H₄CSNH₂ (1b; 29.0 mg, 0.173 mmol) in CH₂Cl₂ (4 mL). 2b·MeOH was isolated as dark red crystals (59.6 mg, 0.117 mmol, 73%). ¹H NMR (CDCl₃, 600 MHz): δ 10.23 (br, 1H, NH), 7.79 (d, *J* = 8.9 Hz, 2H, Ar), 7.50 (br, 1H, NH), 6.91 (d, *J* = 8.9 Hz, 2H, Ar), 3.86 (OMe), 3.49 (s, MeOH), 1.70 (s, 15H, Cp*). ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 194.3 (C= S), 163.6 (Ar), 129.6 (Ar), 129.1 (Ar), 114.1 (Ar), 96.1 (d, *J*_{RhC} = 7.7 Hz, Cp*), 55.7 (OMe), 9.0 (Cp*). IR (cm⁻¹): 3117 (ν _{NH}), 1256 (ν _{SCN}). Anal. Calcd for C₁₈H₂₄Cl₂N₁O₁Rh₁S₁·MeOH: C, 44.89; H, 5.55; N, 2.76. Found: C, 44.65; H, 5.46; N, 2.71. **[Cp*RhCl₂{S=C(4-MeC₆H₄)NH₂-κ¹5}]·MeOH (2c·MeOH).** Following the general procedure, **2c** was synthesized from $[Cp*RhCl₂]_2$ (133.5 mg, 0.216 mmol) and 4-MeC₆H₄CSNH₂ (73.9 mg, 0.489 mmol) in CH₂Cl₂ (8 mL). **2c**·MeOH was isolated as red needles (165.5 mg, 0.336 mmol, 78%). ¹H NMR (CDCl₃, 500 MHz): δ 10.25 (br, 1H, NH), 7.77 (br, 1H, NH), 7.71 (d, *J* = 8.0 Hz, 2H, Ar), 7.21 (d, *J* = 7.4 Hz, 2H,), 3.48 (s, MeOH), 2.38 (s, 3H, Me), 1.68 (s, 15H, Cp*). ¹³C{¹H} NMR (CDCl₃, 126 MHz): δ 195.4 (C=S), 143.8 (Ar), 134.4 (Ar), 129.5 (Ar), 127.7 (Ar), 96.1 (d, *J*_{RhC} = 8.4 Hz, Cp*), 21.7 (Me), 9.0 (Cp*). IR (cm⁻¹): 3073 (ν _{NH}), 1278 (ν _{SCN}). Anal. Calcd for C₁₈H₂₄Cl₂N₁Rh₁S₁·MeOH: C, 46.35; H, 5.73; N, 2.85. Found: C, 46.07; H, 5.66; N, 2.82.

[Cp*RhCl₂{S==C(4-ClC₆H₄)NH₂-κ¹S}]·MeOH (2d·0.5MeOH). Following the general procedure, 2d was synthesized from [Cp*RhCl₂]₂ (44.2 mg, 0.072 mmol) and 4-ClC₆H₄CSNH₂ (1d; 27.0 mg, 0.157 mmol) in CH₂Cl₂ (5 mL). 2d·0.5MeOH was isolated as reddish brown needles (53.3 mg, 0.111 mmol, 78%), which were suitable for an X-ray study. ¹H NMR (CDCl₃, 500 MHz): δ 10.36 (br, 1H, NH), 7.94 (br, 1H, NH), 7.77 (d, *J* = 8.6 Hz, 2H, Ar), 7.40 (d, *J* = 8.6 Hz, 2H, Ar), 3.49, MeOH), 1.69 (s, 15H, Cp*). ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 194.5 (C=S), 139.3 (Ar), 135.6 (Ar), 129.1 (Ar), 128.6 (Ar), 96.3 (d, *J*_{RhC} = 7.7 Hz, Cp*), 9.0 (Cp*). IR (cm⁻¹): 3054 (*ν*_{NH}), 1311 (*ν*_{SCN}). Anal. Calcd for C₁₇H₂₁Cl₃N₁Rh₁S₁. 0.5MeOH: C, 42.32; H, 4.67; N, 2.82. Found: C, 42.08; H, 4.77; N, 2.72.

[Cp*RhCl₂{S=C(4-CF₃C₆H₄)NH₂- κ^{1} S}]·0.5CH₂Cl₂ (2e· 0.5CH₂Cl₂). Following the general procedure, 2e was synthesized from [Cp*RhCl₂]₂ (132.3 mg, 0.214 mmol) and 4-CF₃C₆H₄CSNH₂ (1e; 97.1 mg, 0.473 mmol) in CH₂Cl₂ (6 mL). Recrystallization from CH₂Cl₂/hexanes gave 2e·0.5CH₂Cl₂ as red needles (213.1 mg, 0.383 mmol, 89%), which were suitable for an X-ray study. ¹H NMR (CDCl₃, 500 MHz): δ 10.36 (br, 1H, NH), 7.95 (br, 1H, NH), 7.78 (d, *J* = 8.6 Hz, 2H, Ar), 7.40 (d, *J* = 8.6 Hz, 2H, Ar), 5.32 (s, CH₂Cl₂), 1.69 (s, 15H, Cp*). ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 194.4 (C= S), 139.9 (Ar), 133.8 (q, *J*_{FC} = 32.9 Hz, Ar), 128.4 (Ar), 125.6 (q, *J*_{FC} = 3.3 Hz, Ar), 125.5 (q, *J*_{FC} = 272.3 Hz, CF₃), 96.3 (d, *J*_{RhC} = 7.7 Hz, Cp*), 9.0 (Cp*). IR (cm⁻¹): 3044 (ν_{NH}), 1322 (ν_{SCN}). Anal. Calcd for C₁₈H₂₁Cl₂F₃N₁Rh₁S₁·0.5CH₂Cl₂: C, 39.91; H, 3.98; N, 2.52. Found: C, 39.87; H, 3.89; N, 2.48.

[Cp*RhCl₂{S=C(4-NO₂C₆H₄)NH₂- κ^{1} S]·MeOH (2f·MeOH). Following the general procedure, 2f was synthesized from [Cp*RhCl₂]₂ (65.5 mg, 0.106 mmol) and 4-NO₂C₆H₄CSNH₂ (44.6 mg, 0.245 mmol) in CH₂Cl₂ (5 mL). 2f·MeOH was isolated as red needles (74.2 mg, 0.142 mmol, 67%). ¹H NMR (CDCl₃, 500 MHz): δ 10.48 (br, 1H, NH), 8.96 (br, 1H, NH), 8.25 (d, *J* = 8.8 Hz, 2H, Ar), 8.08 (d, *J* = 8.8 Hz, 2H, Ar), 3.48 (s, MeOH), 1.67 (s, 15H, Cp*). ¹³C{¹H} NMR (CDCl₃, 126 MHz): δ 193.6 (C=S), 150.0 (Ar), 142.3 (Ar), 129.0 (Ar), 123.8 (Ar), 96.6 (d, *J*_{RhC} = 7.2 Hz, Cp*), 9.0 (Cp*). IR (cm⁻¹): 3032 (ν _{NH}), 1346 (ν _{SCN}). Anal. Calcd for C₁₇H₂₁Cl₂N₂O₂Rh₁S₁· MeOH: C, 41.31; H, 4.82; N, 5.35. Found: C, 41.29; H, 4.53; N, 5.40.

Desulfurization of 2 and Isolation of [(Cp*Rh)₄(\mu_3-S)₄] (3). To a suspension of 2a (302.7 mg, 0.678 mmol) in benzene (37 mL) was added NEt₃ (1.90 mL, 13.7 mmol), and the mixture was stirred at room temperature for 4 h. The red-brown color of the suspension quickly changed to dark red. GLC analysis of the reaction mixture (internal standard, dodecane) indicated the generation of benzonitrile in 93% yield. The resulting suspension was filtered through a Celite pad, and the filtrate was dried in vacuo. The residue was washed with hexanes and ether to give 3 as a dark red powder (170.1 mg, 0.157 mmol, 93% yield). Single crystals of 3 suitable for X-ray diffraction study were prepared by recrystallization from CH₂Cl₂/EtOH. ¹H NMR (C₆D₆, 500 MHz): δ 1.73 (s, 60H, Cp*). Anal. Calcd for C₄₀H₆₀Rh₄S₄: C, 44.4S; H, 5.60. Found: C, 44.68; H, 5.51.

Synthesis of the Monocationic Complex $[(Cp*Rh)_4(\mu_3-S)_4]$ -(BAr^F₄) (4(BAr^F₄)). To a solution of 2a (29.1 mg, 26.9 μ mol) in CH₂Cl₂ (20 mL) was added a solution of $[Cp_2Fe](BAr^F_4)$ (26.3 mg, 25.1 μ mol) in CH₂Cl₂ (10 mL), and the mixture was stirred at room temperature for 1 h. The resulting dark brown solution was dried in vacuo. The residue was washed with hexanes and benzene to give 4(BAr^F₄) as a brown powder (35.7 mg, 18.4 μ mol, 73% yield). Single crystals of 4(BAr^F₄) suitable for X-ray diffraction study were prepared by recrystallization from CH₂Cl₂/THF/hexanes. ¹H NMR (CD₂Cl₂, 500 MHz): δ 8.61 (br, $W_{1/2}$ = 857 Hz Hz, Cp*), 7.72 (s, 8H, *o*-Ar^F), 7.56 (s, 4H, *p*-Ar^F). Anal. Calcd for C₇₂H₇₂B₁F₂₄Rh₄S₄: C, 44.48; H, 3.73. Found: C, 44.59; H, 3.61.

Synthesis of the Dicationic Complexes $[(Cp*Rh)_4(\mu_3-S)_4]X_2$ (5X₂). To a solution of 2a in CH₂Cl₂ was added a solution of $[Cp_2Fe]X$ (2 equiv) in CH₂Cl₂, and the mixture was stirred at room temperature for 1 h. The resulting solution was dried in vacuo. The residue was washed with hexanes and benzene to give the dicationic cubane-type complexes $5X_2$.

[(Cp*Rh)₄(μ_3 -S)₄](BAr^F₄)₂ (5(BAr^F₄)₂). Following the general procedure, S(BAr^F₄)₂ was synthesized from 2a (43.5 mg, 0.040 mmol) in CH₂Cl₂ (25 mL) and [Cp₂Fe](BAr^F₄) (79.3 mg, 0.0756 mmol) in CH₂Cl₂ (16 mL) and isolated as a brown powder (92.8 mg, 0.0331 mmol, 87%). Single crystals of 5(BAr^F₄)₂·0.5Shexane·0.4Sacetone suitable for X-ray diffraction study were prepared by recrystallization from acetone/hexanes. ¹H NMR (CD₂Cl₂, 500 MHz): δ 7.72 (s, 16H, *o*-Ar^F), 7.56 (s, 8H, *p*-Ar^F), 1.70 (s, 60H, Cp*). Anal. Calcd for C₁₀₄H₈₄B₂F₄₈Rh₄S₄: C, 44.50; H, 3.02. Found: C, 44.32; H, 2.94.

[(Cp*Rh)₄(μ_3 -S)₄](PF₆)₂ (5(PF₆)₂). Following the general procedure, S(PF₆)₂ was synthesized from 2a (80.2 mg, 0.074 mmol) in CH₂Cl₂ (85 mL) and [Cp₂Fe](PF₆) (48.7 mg, 0.147 mmol) in CH₂Cl₂ (30 mL) and isolated as a brown powder (92.0 mg, 67.1 μ mol, 91% yield). Single crystals of S(PF₆)₂·2CH₃COCH₃ suitable for X-ray diffraction study were prepared by recrystallization from acetone/hexanes. ¹H NMR (CD₂Cl₂, 500 MHz): δ 1.86 (br, 60H, Cp*). Anal. Calcd for C₄₀H₆₀F₁₂P₂Rh₄S₄: C, 35.05; H, 4.41. Found: C, 35.14; H, 4.33.

[(Cp*Rh)₄(μ_3 -S)₄](BF₄)₂ (5(BF₄)₂). Following the general procedure, $S(BF_4)_2$ was synthesized from 2a (36.9 mg, 0.034 mmol) in CH₂Cl₂ (40 mL) and [Cp₂Fe](BF₄) (18.6 mg, 0.0685 mmol) in CH₂Cl₂ (20 mL) and isolated as a brown powder (29.8 mg, 0.0238 mmol, 70% yield). ¹H NMR (CD₂Cl₂, 500 MHz): δ 1.80 (br, 60H, Cp*). Anal. Calcd for C₄₀H₆₀B₂F₈Rh₄S₄: C, 38.30; H, 4.82. Found: C, 38.11; H, 4.52. Molecular structure of $S(BF_4)_2$ was also confirmed by a preliminary X-ray study.

[(Cp*Rh)₄(μ_3 -S)₄](CF₃CO₂)₂ (5(CF₃CO₂)₂). To a solution of 2a (17.8 mg, 0.016 mmol) in CH₂Cl₂ (4 mL) was added CF₃COOH (6.5 μ L, 0.085 mmol, 5 equiv) at room temperature, and the mixture was stirred for 8 h. The color of the solution gradually changed from brown to dark brown. The resulting solution was dried in vacuo and washed with hexanes and benzene. The resulting brown powder was recrystallized from CH₂Cl₂/hexanes to afford 5(CF₃CO₂)₂ (11.1 mg, 8.5 μ mol, 52% yield) as dark red crystals, which were suitable for an X-ray study. ¹H NMR (CD₂Cl₂, 500 MHz): δ 1.76 (br, 60H, Cp*). Anal. Calcd for C₄₄H₆₀F₆O₄Rh₄S₄: C, 40.44; H, 4.63. Found: C, 40.27; H, 4.50.

[(Cp*Rh)₄(μ₃-S)₄](OTf)₂ (5(OTf)₂). To a solution of 2a (12.3 mg, 0.011 mmol) in CH₂Cl₂ (2 mL) was added AgOTf (8.8 mg, 0.0342 mmol, 3 equiv) at room temperature, and the mixture was stirred for 1 h. The brown solution gradually changed to a dark brown suspension. The resulting suspension was filtered through a plug of Celite. The filtrate was dried in vacuo, and the residue was recrystallized from CH₂Cl₂/ether to afford 5(OTf)₂ (5.6 mg, 4.06 µmol, 36% yield) as dark red plates. ¹H NMR (CD₂Cl₂, 500 MHz): δ 1.77 (s, 60H, Cp*). Anal. Calcd for C₄₂H₆₀F₆O₆Rh₄S₆: C, 36.58; H, 4.39. Found: C, 36.56; H, 4.18.

X-ray Diffraction Studies. All diffraction data except for 1a were collected on a Rigaku Mercury CCD area detector with graphite-monochromated Mo K α radiation ($\lambda = 0.71070$ Å) at -150 °C for the 2θ range of $6-55^\circ$. Intensity data were corrected for Lorenz-polarization effects and for empirical absorptions (REQAB).³⁵ The structure solution and refinements were carried out by using the CrystalStructure³⁶ crystallographic software package and Yadokari-XG 2009.³⁷ For 1a, diffraction data were collected on a Bruker Apex II Ultra at -173 °C, and intensity data were processed using Apex2 software suit. The position of the non-hydrogen atoms were determined by direct methods (SHELXS-97³⁸ for 1a, 3, and

 $5(PF_6)_2$ ·2(acetone); SIR2008³⁹ for **2a**, **2d**, **2e**, **2f**, $4(BArF_4)$, $5(BArF_4)_2$ · 0.55hexane-0.45acetone, $5(CF_3CO_2)_2$, and $6(BArF^4)$ ·0.5hexane) and subsequent Fourier syntheses (DIRDIF-99).⁴⁰ All non-hydrogen atoms were refined on F^2 by full-matrix least-squares techniques (SHELXL-97 and SHELXL-2014³⁸) with anisotropic thermal parameters except for the several carbon and fluorine atoms with nonpositive definite anisotropic displacement parameters, which are refined with isotropic thermal parameters. All hydrogen atoms were placed using AFIX instructions. Severely disordered solvent molecules were treated with PLATON/SQUEEZE⁴¹ for **2d**, **2e**, and **2f**. Although there are some alerts of type A and B due to the disorder of some of the Cp* and CF₃ groups, they do not affect the results of the structural determination. Details of the X-ray diffraction study are summarized in Supplementary Tables S1–S3.

ASSOCIATED CONTENT

S Supporting Information

Figures, tables, and CIF files giving NMR charts and crystallographic data. 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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(28) Although the R1 value was somewhat high, the C-S and C-N bond lengths in 2a and 6^+ as well as 'parent' thiobenzamide (1a) have

been compared to reveal considerable contribution of the iminothiolate form (S–C=NH) to the thiobenzamidato ligand in 6^+ in the solid state; the C–S bond distances are elongated in the order of **1a** (1.68 Å (mean)) < **2a** (1.702(3) Å) < 6^+ (1.756(12) Å), while C–N bond lengths are shortened in the order of **1a** (1.32 Å (mean)) > **2a** (1.297(3) Å) > 6^+ (1.276(15) Å). Similar structural parameters are observed in related iminothiolato complexes with μ_2 -SCN- κ^2S coordination mode [Rh{ μ_2 -SC(Ph)=NCHMePh- κ^2S } (cod)]₂, (C–S, 1.83 Å (mean); C–N, 1.26 Å (mean))¹¹ and [Fe{ μ_2 -SC(Ph)=NPh- κ^2S }{ μ_2 -C(Ph)=NPh- η^1 C: κ^1N }(CO)₃]₂ (C–S, 1.819(4) Å; C–N, 1.267(S) Å).

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