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Communication

Synthesis of a Vanadium(III) Tris(arylthiolato) Complex and Its Reactions with Azide and Azo Compounds: Formation of a Sulfenamide Complex via Cleavage of an Azo N═N Bond

Takashi Komuro,[†] Tsukasa Matsuo,[†] Hiroyuki Kawaguchi,*[,†] and Kazuyuki Tatsumi[‡]

Coordination Chemistry Laboratories, Institute for Molecular Science, Myodaiji,
Okazaki 444-8787, Japan, and Research Center for Materials Science and
Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho,
Chikusa-ku, Nagoya 464-8602, Japan

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The tris(arylthiolate) vanadium(III) complex (**1**) has been synthesized in good yield. This complex is found to undergo CH activation across a V–S bond in the presence of TMEDA to give a cyclometalated species along with free arylthiol. Complex **1** behaves as a two-electron reductant toward Ad–N_3, yielding an imide complex. Treatment of **1** with azobenzene produces an imide–sulfenamide compound, in which an azo N═N bond cleavage takes place concomitant with formation of a V═N and an S—N bond.

Thiolate complexes continue to attract considerable attention due to their unique chemical properties and structural diversity.[1] These complexes are also useful tools for understanding the active sites of metalloenzymes and the surfaces of metal sulfides.[2] Since thiolate groups meet the electronic and steric requirements necessary to stabilize a wide variety of metal complexes, they have been used as auxiliary ligands. On the other hand, thiolate complexes are known to undergo chemistry at the sulfur center, including oxidation/reduction and protonation/deprotonation, a complement to traditional chemistry for these complexes centered on the metal.[2,3] Recently, we have begun to investigate coordination chemistry of sterically hindered thiolate ligands, aiming to synthesize reactive low-coordination complexes in a sulfur-rich ligation environment.[4] In this Communication, we report the synthesis of a mononuclear vanadium(III) complex having the $[SC_6H_3\text{-}2,6\text{-}(SiMe_3)_2]^-$ ($=[SAr]^-$) ligands[5] and its reactivity studies with azide and azo compounds. Preliminary data suggest that the reaction proceeds through a cooperative activation sequence involving both vanadium and sulfur centers.

Treatment of $VCl_3(THF)_3$ with 3 equiv of LiSAr in toluene at 60 °C gave a dark orange solution. Solvent removal followed by hexamethyldisiloxane (HMDSO) extraction and crystallization produced $V(SAr)_3(THF)$ (**1**) as dark orange crystals in 80% yield (Scheme 1). The magnetic moment for **1** ($\mu_{\mathrm{eff}} = 2.8\ \mu_{\mathrm{B}}$) by the Evans method is consistent with a high-spin d^2 electronic configuration.

Formulation of **1** as a 4-coordinate monomer was confirmed by an X-ray crystal structure (Figure 1). Despite the expected steric preference for the 4-coordinate metal center to adopt a tetrahedral geometry, **1** has a trigonal monopyramidal structure.[6] The THF is at the vertex of the pyramid, and trigonal ligation to vanadium is provided by the three thiolate sulfurs with the mean deviation from the VS_3 plane less than 0.02 Å. The vacant site trans to the THF ligand is occupied by agostic C—H bonds from a SiMe group of the thiolate ligand [V—C(7)$_{\mathrm{agostic}}$, 2.611(3) Å].[7] The reality of the agostic interaction in **1** is supported by the V—S—C(ipso)

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[*] To whom correspondence should be addressed. E-mail: hkawa@ims.ac.jp.

[†] Institute for Molecular Science.

[‡] Nagoya University.

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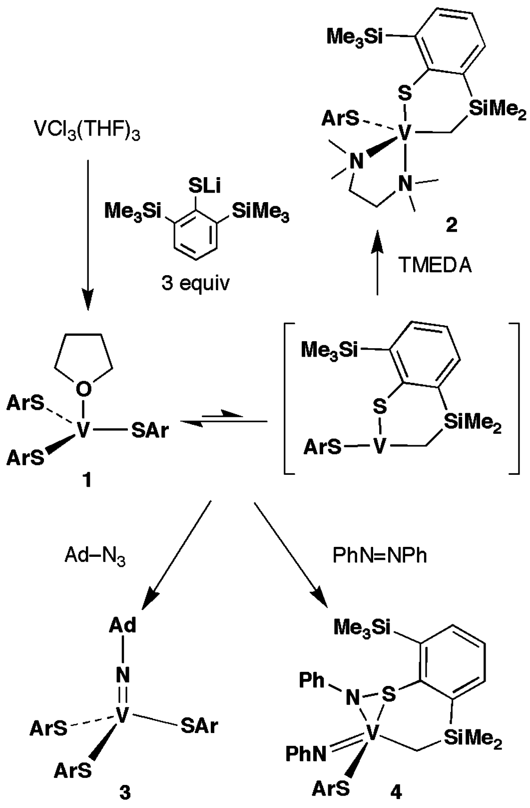
Scheme 1



angle being 15−20° larger than the corresponding angles of the nonagostic thiolate ligands. In addition, the V−S distance involving the agostic group is ca. 0.05 Å shorter than those to the ordinary thiolates. It was reported that two THF molecules could be accommodated by the V(III) center having three less sterically hindered arylthiolate ligands.[8]

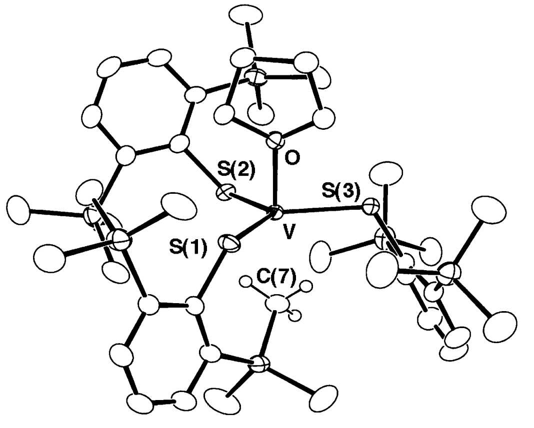


Figure 1. Structure of **1**. Selected interatomic distances (Å) and angles (deg): V−S(1) 2.277(1), V−S(2) 2.329(1), V−S(3) 2.328(1), V−O 2.111(2); S(1)−V−S(2) 119.98(3), S(1)−V−S(3) 123.79(3), S(2)−V−S(3) 116.10(3), S(1)−V−O 85.99(5), S(2)−V−O 99.81(6), S(3)−V−O 88.40(5).

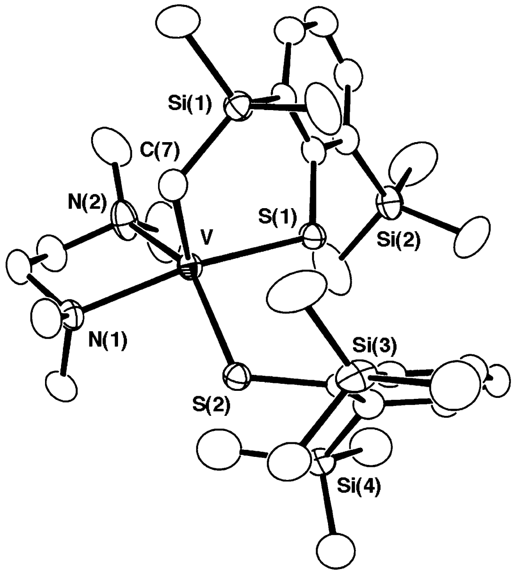


Figure 2. Structure of **2**. One set of the disordered trimethylsilyl group Si(4) is shown. Selected interatomic distances (Å) and angles (deg): V−S(1) 2.356(1), V−S(2) 2.380(1), V−N(1) 2.291(4), V−N(2) 2.249(5), V−C(7) 2.066(4); S(1)−V−S(2) 90.55(4), S(1)−V−N(1) 168.9(1), S(1)−V−C(7) 97.3(1), N(1)−V−N(2) 79.6(1).

Although some 3-coordinated V(III) fragments are known to be very reactive,[9] attempts to isolate the desolvated complex $[V(SAr)_3]$ have met with failure. The coordinated THF was not lost when **1** was recrystalized from HMDSO. Prolonged reflux of a toluene solution of **1** resulted in a complicated mixture. On the other hand, inspection of the ^{1}H NMR spectrum of paramagnetic **1** revealed the presence of a significant amount of free ArSH besides a set of poorly resolved broad resonances. Elimination of ArSH from **1** presumably occurs via CH activation across a V−S bond, in which a thiolate ligand undergoes cyclometalation with an agostic SiMe group to provide a bidentate *bit*-ArS ligand. This type of cyclometalation is quite commonplace for the relatively acidic SiMe groups.[10,11] Relief of the crowded coordination sphere about the metal center may be important as a driving force in the reaction.

Evidence for the presence of a cyclometalated species is provided by the observation that it may be trapped by TMEDA to afford paramagnetic V(*bit*-SAr)(SAr)(TMEDA) (**2**) ($\mu_{\mathrm{eff}} = 2.7\ \mu_{\mathrm{B}}$) as a reddish brown powder in 76% isolated yield. The solid-state structure (Figure 2) contains a 5-coordinate vanadium complex in an approximately trigonal bipyramidal environment with the *bit*-SAr sulfur [S(1)] and one of the TMEDA nitrogen donors [N(1)] occupying the axial sites. The cyclometalated V−C(7) distance of 2.066(4) Å is placed at the short end of the reported V(III)−alkyls.[11,12]

In complex **1**, THF is to be considered as a labile ligand for purposes of substituting with stronger and smaller donor ligands.[13] Furthermore, on the basis of the above results, we

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postulated that one of sterically demanding thiolates may potentially dissociate from the metal center during reactions to open up reversibly a larger reactive site. In order to prove the possibility of labile coordination of THF and/or $[ArS]^-$, we studied the reactions of **1** with 1-adamantyl azide ($Ad-N_3$) and azobenzene. Treatment of **1** with 1 equiv of $Ad-N_3$ in toluene at room temperature was found to produce the diamagnetic imide complex $V(SAr)_3(NAd)$ (**3**) in 73% yield with evolution of dinitrogen. The molecular structure of **3** shows the vanadium center to possess a pseudotetrahedral geometry, and the $V(SAr)_3$ fragment remains intact during the course of the reaction. The formation of **3** results in oxidation of V(III) to V(V). Accordingly, the average V−S distance decreases from 2.311 Å in **1** to 2.277 Å in **3**. The short V−N distance of 1.639(2) Å is clearly indicative of a $V-N_{imide}$ multiple bond.[14] In contrast to **1**, the imide complex **3** contains no agostic interaction.

Compound **1** reacted with 1 equiv of PhN═NPh in refluxing toluene, producing the sulfenamide V(V) complex V(NPh)(*bit*-PhNSAr)(SAr) (**4**) in 37% isolated yield.[15] The aliphatic region of the ^1H NMR spectrum of **4**, which contains three peaks assigned to $SiMe_3$ groups and two peaks assigned to a $SiMe_2$ group, is consistent with C_1 symmetry and indicates hindered rotation about the V−SAr bond. The methylene protons of the $V-CH_2-Si$ group appear as a pair of doublets at δ 3.81 and 2.22. A crystal structure determination of **4** revealed that the pseudotetrahedral coordination sphere about vanadium is composed of an imide group, a thiolate ligand, and a newly formed methylene−sulfenamide bidentate ligand (Figure 3). Within the sulfenamide moiety, both N(1) and S(1) are bound to the V atom [1.861(3) and 2.570(1) Å, respectively]. The S(1)−N(1) distance of 1.698(3) Å is typical of sulfenamide complexes.[16] The V−N(2) distance of 1.649(3) Å is similar to that of **3**.

The formation of the imide−sulfenamide complex **4** via scission of an N═N bond is noteworthy. Cleavage of azo substrates has been observed in low-valent transition-metal chemistry,[17] but this is the first documented example of an azo N═N cleavage coupled with formation of a sulfenamide ligand. Although the detailed mechanism of the reaction remains a matter of speculation, the cyclometalated V(III) species could be trapped by azobenzene instead of TMEDA to give an azo adduct intermediate that subsequently undergoes cleavage of an N−N bond by formation of an N−S bond, generating an imide and a sulfenamide group. Obviously, other mechanisms can be considered, including initial formation of an imide complex analogous to **3** via bimolecular activation of azobenzene.[18] However, no reaction of **3** with azobenzene was observed.

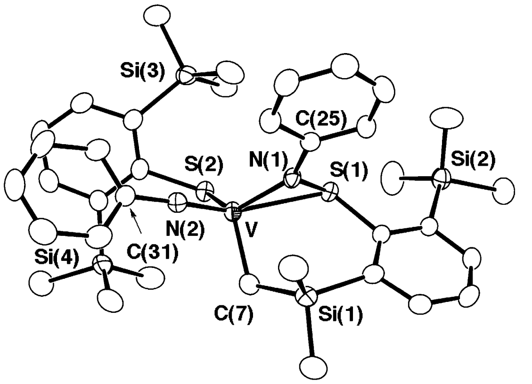

Figure 3. Structure of **4**. Selected interatomic distances (Å) and angles (deg): V−S(1) 2.570(1), V−S(2) 2.270(1), V−N(1) 1.861(3), V−N(2) 1.649(3), V−C(7) 2.029(3), S(1)−N(1) 1.698(3), S(1)−V−N(1) 41.32(8), N(1)−V−C(7) 105.4(1), S(1)−V−C(7) 93.2(1), V−N(2)−C(31) 173.2(2).

In conclusion, we have synthesized and characterized a tris(thiolato) complex of vanadium(III), **1**, which behaves as a two-electron reductant toward $Ad-N_3$ to give an imide complex **3**. In the reaction of **1** with azobenzenene, both V and thiolate S atoms are found to engage in cleavage of an azo N═N bond to produce an imide−sulfenamide complex **4** concomitant with cyclometalation of coordinated ArS^- and elimination of free ArSH. Further studies of this and related systems are in progress.

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Supporting Information Available: Crystallographic data, synthetic procedures, and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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