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Organometallic-like C–H Bond Activation and C–S Bond Formation on the Disulfide Bridge in the RuSSRu Core Complexes

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ABSTRACT

C–S bond formations on the disulfide bridge in the dinuclear Ru^{III} complexes have been found in the reaction with unsaturated organic molecules, such as alkenes and ketones. The reactions are initiated by the organometallic-like C–H bond activation. Through the mechanistic study of these novel reactions, the specific nature of the disulfide bridging ligand has been unveiled: (i) the double bond character of the sulfur–sulfur bond, which allows the Diels–Alder-type [4 + 2] cycloaddition reaction with butadiene to form a C₄S₂ ring, (ii) the C–H bond activation on the S–S bond forming a C–S bond. All of the C–H activation reactions and the ensuing C–S bond formation reactions suggest that the disulfide ligand can act in a manner similar to the transition metal centers of the organometallic complexes.

Introduction

Monosulfide and disulfide ligands in transition metal complexes are noteworthy¹ for their strong donating ability, and in this regard, they are different from the higher polysulfide ligands. Actually, disulfide ligands have

recently attracted the increasing interest of researchers in the field of HDS (hydrodesulfurization) reactions, in which the presence of the terminal and bridging disulfide on the catalyst edge has been revealed by surface analysis² to be the active site. The role of the disulfur in the catalytic reaction has also been explained by theoretical approaches.³ Compared to the transition metal monosulfide complexes, transition metal disulfide complexes have not been studied very much. In this Account, recently found very novel reactions of ketones and alkenes with the disulfide bridging ligand in a dinuclear ruthenium complex are described. These reactions are noted, since they include C–H bond activation of the substrate and the C–S bond formation on the disulfide ligand, suggesting that although the disulfide ligand had previously been believed to be rather inert, disulfide in certain complexes easily reacts with a wide variety of unsaturated molecules.

The HDS reaction targets the cleavage of the C–S bonds of thiophenes and other sulfur-containing aromatic compounds. In the reverse reaction, C–S bond formations are observed in the reactions of transition metal–sulfur complexes with various organic molecules and are classified into two types: the first class is addition reactions between the coordinated sulfur atoms and unsaturated sp or sp² hybridized carbon atoms (eqs 1–5).^{4–9} Diazo-methane is also known to react with the bridging sulfide and selenide in the dinuclear Cr^{II} complexes (eq 6).¹⁰

The second group includes the reactions between the coordinated sulfur atoms and sp³ hybridized carbon atoms. In most cases of this type of reaction, alkyl halides are used.^{6,11,12}

In some very rare cases, the C–H bond activation takes place as shown below, and C–S bonds are formed.^{13,14}

The C–H bond activation is one of the most challenging themes in organometallic chemistry to functionalize

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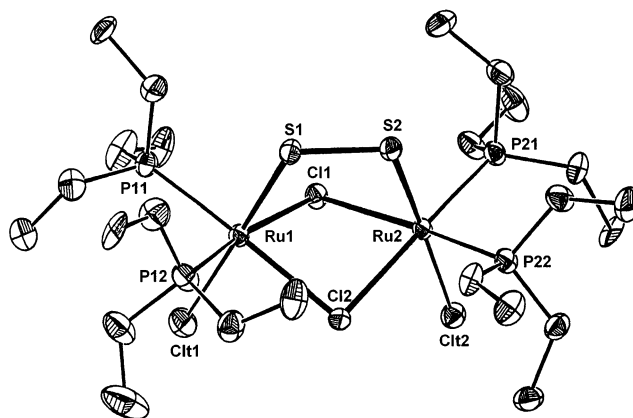
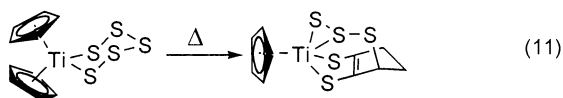
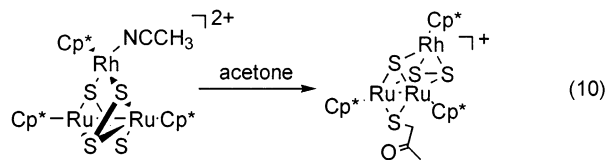
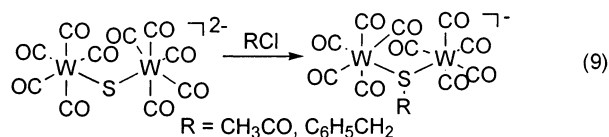
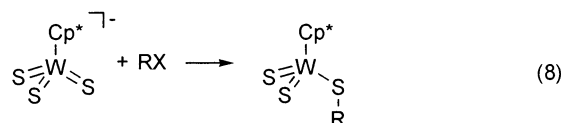
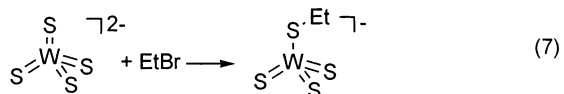
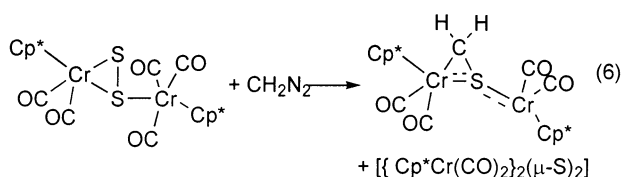
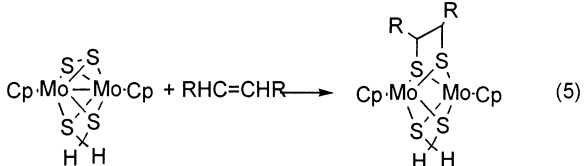
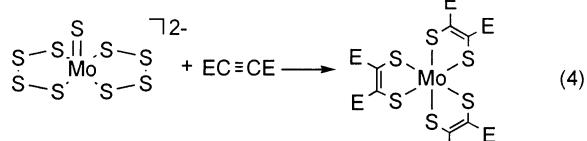
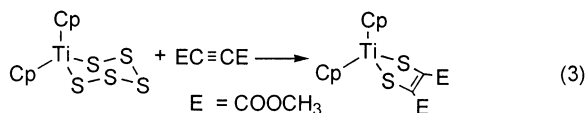
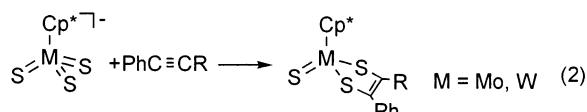
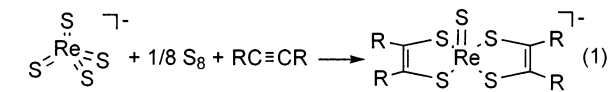


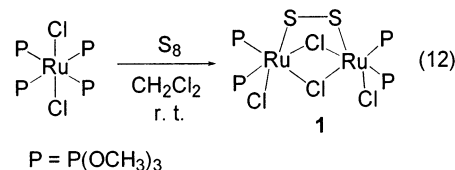
FIGURE 1. Structure of $[\{\text{RuCl}(\text{P}(\text{OCH}_3)_3)_2\}_2(\mu\text{-S}_2)(\mu\text{-Cl})_2]$ (**1**).

unreactive molecules with much lower energy than that of other reaction paths.

Synthesis of the RuSSRu Core Complexes Having Bridging and Terminal Chloride Ligands

The disulfide ligand, S_2^{2-} , has been noted for its strong electron-donating nature, which is exemplified as the remarkably low $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ redox potentials and the unusual absorption maximum in the visible region in $[\{\text{CpRu}(\text{PPh}_3)_2\}_2(\mu\text{-S}_2)](\text{BF}_4)_2$ ¹⁵ and $1,4\text{-}[\{\text{MeCpRu}(\text{PPh}_3)_2\}_2(\mu\text{-S}_2)]^{2+}$ ¹⁶ (Cp = cyclopentadienyl, MeCp = methylcyclopentadienyl). Several other earlier workers also noticed the distinct properties of the $\text{Ru}^{\text{III}}\text{SSRu}^{\text{III}}$ core, such as the intense blue-green color, strong Raman bands observable to higher progression, and unusually low redox ($\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$) potentials.^{17–19} However, compounds with a RuSSRu core or a similar MSSM core of any transition metal are rare, and the electronic state was not fully understood.

The first $\text{Ru}^{\text{III}}\text{SSRu}^{\text{III}}$ core complex prepared in our group is $[\{\text{RuCl}(\text{P}(\text{OCH}_3)_3)_2\}_2(\mu\text{-Cl})_2(\mu\text{-S}_2)]$ (**1**) (Figure 1), which was synthesized from *trans*- $\text{RuCl}_2(\text{P}(\text{OCH}_3)_3)_4$ and sulfur powder in CH_2Cl_2 under anaerobic conditions, as shown in eq 12.^{20,21} The two $\text{RuCl}(\text{P}(\text{OCH}_3)_3)_2$ moieties in **1** are bridged by a disulfide and two chloride ions, and each of the two Ru atoms has one terminal chloride. This structure, together with the spectroscopic and electrochemical properties, tempted us to explore more deeply the chemical nature of the complex. The structure of **1** is especially attractive, since the two Ru atoms are close to each other and held together by the stable disulfide bridge. The two bridging and two terminal chloride ions can be removed by Ag^+ to give an interesting reactive space between the two Ru atoms.



The stepwise removal of the terminal and bridging chloride ligands of **1** with Ag^+ gives $[\{\text{RuCl}(\text{P}(\text{OCH}_3)_3)_2\}_2(\mu\text{-S}_2)(\mu\text{-Cl})_2\{\text{Ru}(\text{P}(\text{OCH}_3)_3)_2\}(\text{CH}_3\text{CN})]^+$ (**2**), $[\{\text{Ru}(\text{CH}_3\text{CN})-$

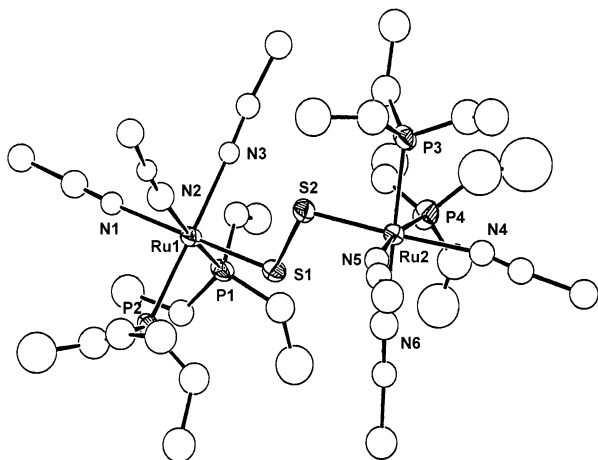
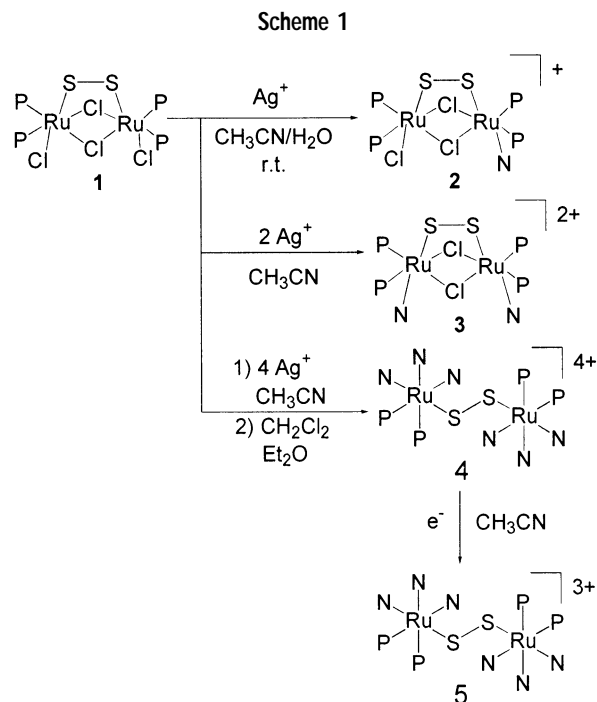


FIGURE 2. Structure of $[\{\text{Ru}(\text{CH}_3\text{CN})_3(\text{P}(\text{OCH}_3)_3)_2\}_2(\mu\text{-S}_2)]^{4+}$ (**4**) $^{4+}$.

$(\text{P}(\text{OCH}_3)_3)_2\}_2(\mu\text{-S}_2)(\mu\text{-Cl})_2]^{2+}$ (**3**), and $[\{\text{Ru}(\text{P}(\text{OCH}_3)_3)_2(\text{CH}_3\text{CN})_3\}_2(\mu\text{-S}_2)]^{4+}$ (**4**). Synthesis of **2** requires trace of water, as shown in Scheme 1, and the reaction is accelerated by increasing the water amount. On addition of 4 equiv of Ag^+ in CH_3CN , all four chloride ligands are removed, and **4** is obtained after recrystallization in CH_2Cl_2 . However, recrystallization in CH_3CN gives an isostructural paramagnetic compound, $[\{\text{Ru}(\text{P}(\text{OCH}_3)_3)_2(\text{CH}_3\text{CN})_3\}_2(\mu\text{-S}_2)]^{3+}$ (**5**), in which one of the Ru atoms is reduced to Ru^{II} , and the compound has a paramagnetic $\text{Ru}^{\text{II}}\text{SSRu}^{\text{III}}$ core. The X-ray structure of **4** is shown in Figure 2. In complexes **2**–**5**, the S–S distances are in the range of 1.971(4) to 1.995(3) Å. The cis or trans geometry around the disulfide bridge does not affect significantly the S–S distance, but reduction of **4** to **5** apparently elongates the distance from 1.933(11) to 1.995(3) Å.

UV–Vis Spectra. The UV–vis spectra of compounds **1**, **2**(PF_6), and **5**(PF_6) $_3$ are shown in Figure 3; those of **3**(CF_3SO_3) $_2$ and **4**(CF_3SO_3) $_4$ are shown in Figure 4. None



of the compounds has near-IR absorption up to 2000 nm. The spectral change in Figure 4 corresponds to the reduction of **4** to **5** by CH_3CN . In CH_2Cl_2 , **4** is not reduced, and the compound is stable.

To obtain a clear image of the electronic state and to explain the ESR (see the later section) spectra, the π -MO scheme for the RuSSRu core is given in Figure 5.²¹ The strong visible absorptions of **1**, **2**(PF_6), **5**(PF_6) $_3$, **3**(CF_3SO_3) $_2$, and **4**(CF_3SO_3) $_4$ are the transitions from π_3 to π_4 , and are LMCT. Compounds **1**, **2**, **3**, and **4** are diamagnetic, since the unpaired electrons of the two low-spin Ru^{III} ions are paired, as shown in Figure 5. Compound **5** with the

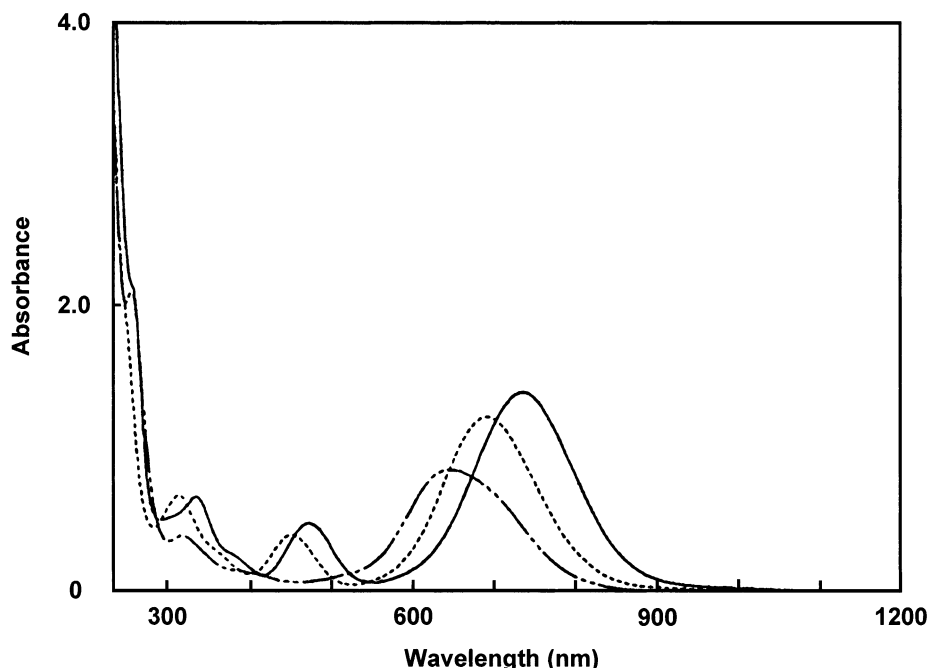


FIGURE 3. UV–vis spectra of **1** (—, 1.44×10^{-4} M), **2**(PF_6) (---, 1.40×10^{-4} M), and **5**(PF_6) $_3$ (— · —, 1.33×10^{-4} M) in CH_3CN .

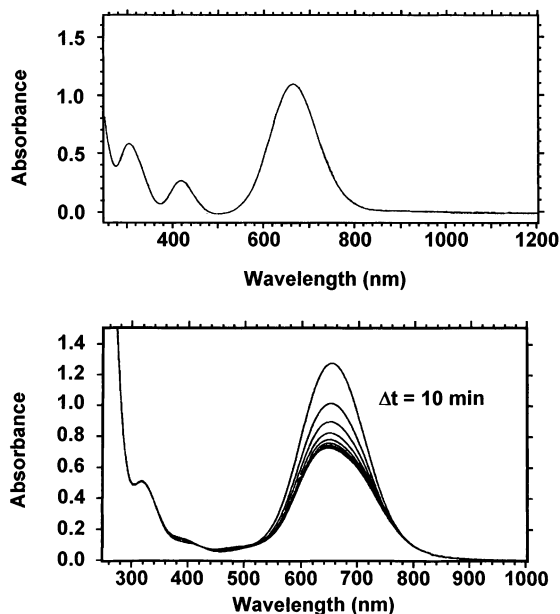


FIGURE 4. UV-vis spectra of **3** (upper, 1.47×10^{-4} M), and **4** (lower, 1.81×10^{-4} M) in CH_3CN . The uppermost curve in the lower figure corresponds to **4**, and the lowest curve to **5**.

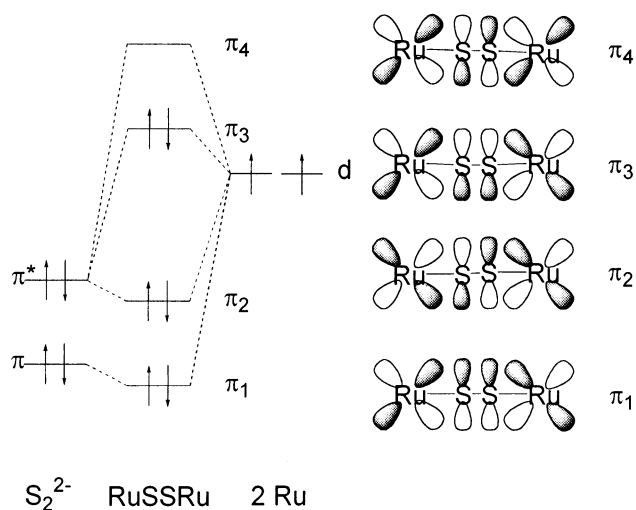


FIGURE 5. π -MO scheme for the $\text{Ru}^{\text{III}}\text{SSRu}^{\text{III}}$ core.

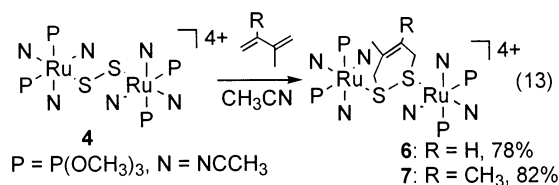
$\text{Ru}^{\text{II}}\text{SSRu}^{\text{III}}$ core is paramagnetic, since its one unpaired electron is in the π_4 orbital.

Cyclic Voltammetry and ESR Spectroscopy. Compound **1** exhibits a quasireversible wave corresponding to the one-electron $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ reaction at -0.20 V (vs Ag/AgCl) in the cyclic voltammogram.²¹ The potential is ~ 0.61 V cathodically shifted, as compared to the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ potential of 0.41 V for the starting compound *trans*- $\text{RuCl}_2\text{-(P(OCH}_3)_3)_4$. Similarly, large cathodic shifts are reported with other disulfide-bridged compounds, which shows the strong π donation of the disulfide ligand. The $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ wave of **2** is observed at $+0.08$ V (vs Ag/AgCl). Compound **5**(PF_6)₃ exhibits the $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}\text{Ru}^{\text{II}}$ irreversible wave at -0.30 V (vs Ag/AgCl) and quasireversible wave of $\text{Ru}^{\text{III}}\text{-Ru}^{\text{III}}/\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$ at $+0.74$ V.

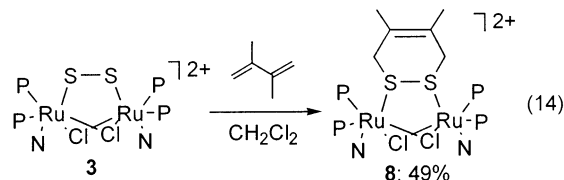
Compound **5** is the first well-characterized mixed-valent complex with a *trans*- $\text{Ru}^{\text{II}}\text{SSRu}^{\text{III}}$ core and is ESR-

active owing to the Ru^{III} atom. The intervalence interaction between the two Ru atoms through the distinct S_2^{2-} ligand is elucidated by the ESR spectroscopy. The powder and solution ESR spectra of **5**(PF_6)₃ at 288 K shows a rhombic signal with $g_1 = 2.12$, $g_2 = 2.05$, and $g_3 = 1.995$. This small anisotropy is a remarkable contrast to the highly anisotropic axial or rhombic symmetry of usual monomeric low-spin Ru^{III} species and suggests that the unpaired electron of **5** is delocalized over the two metals and the bridging disulfide ligand.²¹

Reactions of the RuSSRu Core with Conjugated Dienes. The reactions of the disulfide ligand in the dinuclear Ru^{III} complexes with dienes give a clue to the long-standing discussion about the electronic structure of the RuSSRu^{4+} core,¹⁷⁻¹⁹ namely, whether it should be formulated as (i) two Ru^{III} centers bridged by a disulfide S_2^{2-} , (ii) two Ru^{II} centers bridged by a singlet disulfur S_2^0 , or (iii) an Ru^{II} center and an Ru^{III} center bridged by a supersulfide $\text{S}_2^{\cdot-}$. The character of the S_2 ligand can be examined with spectroscopy^{22,23} and also by the reaction of the S_2 ligand with conjugated dienes. Complex **4**(CF_3SO_3)₄ reacts with conjugated dienes, such as isoprene or 2,3-dimethylbutadiene, in CH_3CN at room temperature to give the complexes carrying a C_4S_2 six-membered ring, [$\{\text{Ru}(\text{P}(\text{OCH}_3)_3)_2(\text{CH}_3\text{CN})_2\}_2\{\mu\text{-SCH}_2\text{C}(\text{R})=\text{C}(\text{CH}_3)\text{CH}_2\text{S}\}$]-(CF_3SO_3)₄ (**6**)(CF_3SO_3)₄, R = H, **7**)(CF_3SO_3)₄, R = CH₃) (eq 13).²⁴ Having methyl groups at both ends, 2,4-hexadiene



did not react with **4**(CF_3SO_3)₄ because of the steric hindrance. Analogously, the reaction of the dicationic complex [$\{\text{Ru}(\text{P}(\text{OCH}_3)_3)_2(\text{CH}_3\text{CN})_2\}_2(\mu\text{-S}_2)(\mu\text{-Cl})_2$](CF_3SO_3)₂ (**3**)(CF_3SO_3)₂ with 2,3-dimethylbutadiene gave [$\{\text{Ru}(\text{P}(\text{OCH}_3)_3)_2(\text{CH}_3\text{CN})_2\}_2\{\mu\text{-SCH}_2\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{CH}_2\text{S}\}(\mu\text{-Cl})_2$](CF_3SO_3)₂ (**8**)(CF_3SO_3)₂ (eq 14). These cycloaddition



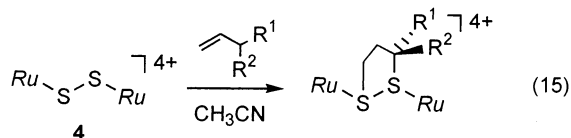
reactions suggest that the contribution of type ii is significantly large. In contrast, such clear contribution of type ii was not found in the previous RuSSRu cores of [$(\text{H}_3\text{N})_5\text{RuSSRu}(\text{NH}_3)_5$]⁴⁺^{17,18} and [$\text{Cp}(\text{R}_3\text{P})\text{RuSSRu}(\text{PR}_3)\text{-Cp}$]²⁺.¹⁵ The reactions of 2,3-dimethylbutadiene with [$\text{Cp}(\text{Ph}_3\text{P})\text{RuSSRu}(\text{PPh}_3)\text{Cp}$]²⁺ or the $\text{P}(\text{CH}_3)_3$ analogue of **4** and **3** did not proceed under similar conditions.²⁵ Several organic disulfides are known as the precursor of unstable free neutral inorganic disulfur, and the neutral disulfur gives the [4 + 2] cycloadducts in the reaction with conjugated dienes.²⁶ Compared to the unstable free dis-

ulfur in situ prepared, the disulfide ligands in the RuSS-Ru⁴⁺ cores are stabilized by coordination to the Ru atoms and yet maintain the reactivity to dienes.

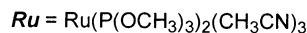
The ¹³C{¹H} NMR spectrum of **6** shows two sp² carbon resonances at δ 117.5 and 130.3 ppm, which are assigned to the C=C double bond in the C₄S₂ moiety. Similar sp² carbon resonance is also observed at δ 128.6 for **7**. In the ¹H NMR spectrum of **6**, the olefinic proton resonance appears at δ 5.99.

In the reaction of **4** with dienes, it is conceivable that the C=C double bond replaces the CH₃CN ligand and acts as an anchor to facilitate the ensuing reaction. In the subsequent steps, the diene molecule approaches the S₂ center to form the C-S bonds. This mechanism is possible for **4**; however, it is impossible for **3**, since even if similar substitution of CH₃CN with a diene occurs in the reaction of **3**, the diene molecule is anchored away from the S₂, and the subsequent reaction is impossible. These facts suggest that the reaction is explained rather simply as a Diels-Alder-type addition of the dienes to the disulfide ligand of **3** and **4**. These reactions clearly show that the disulfide ligand has a double bond character.

Reactions of the RuSSRu Core with Alkenes. Compound [**4**](CF₃SO₃)₄ reacts with terminal alkenes, such as 1-pentene, allylethyl ether, allylphenyl ether, 1,4-hexadiene, and 3-methyl-1-butene in CH₃CN at room temperature to give the complexes carrying a C₃S₂ ring: [**9**](P(OCH₃)₃)₂(CH₃CN)₃{μ-SCH₂CH₂CR¹R²S}(CF₃SO₃)₄, (**9**)-(CF₃SO₃)₄, R¹ = CH₂CH₃, R² = H; [**10**](CF₃SO₃)₄, R¹ = OCH₂CH₃, R² = H; [**11**](CF₃SO₃)₄, R¹ = OC₆H₅, R² = H; [**12**](CF₃SO₃)₄, R¹ = CH=CHCH₃, R² = H; [**13**](CF₃SO₃)₄, R¹ = R² = CH₃) via activation of the allylic C-H bond (eq 15).^{27a} Having no C-H bond at the allylic position, 3,3-dimethyl-1-butene does not react with [**4**](CF₃SO₃)₄.



- 9**: R¹ = CH₂CH₃, R² = H, 44%
10: R¹ = OCH₂CH₃, R² = H, 60%
11: R¹ = OC₆H₅, R² = H, 73%
12: R¹ = CH=CHCH₃, R² = H, 48%
13: R¹ = R² = CH₃, 40%



In every case, the C₃S₂ five-membered ring is saturated, which was confirmed by the ¹H NMR spectra of the isolated complexes. The complexes **9**, **11**, **12**, and **13** have been fully characterized by X-ray crystallography.

Although cyclization reaction is observed in the reaction of [**4**](CF₃SO₃)₄ with terminal alkenes, internal alkenes do not react with **4**. The C-S bond formation between the bridging disulfide and an internal alkene is found only in the reaction of **1** with cyclohexene in the presence of 5 equiv of AgPF₆, giving [**14**](PF₆)₄, x = 1 or 2).^{27b} The X-ray structure (Figure 6) of **14**

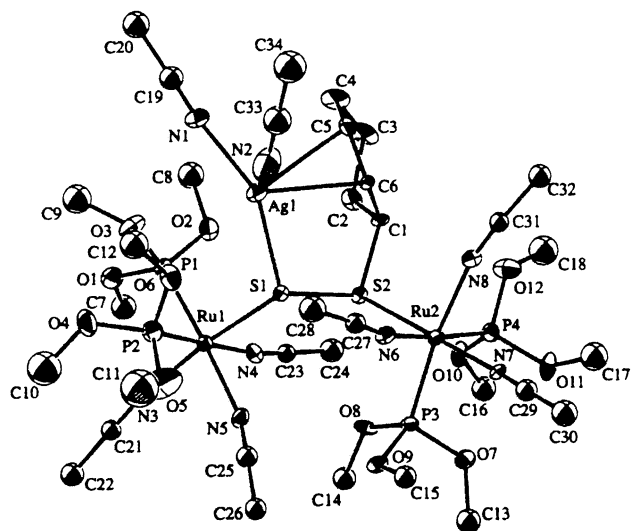
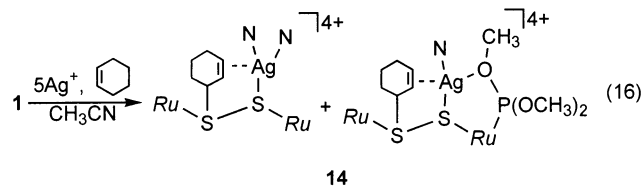


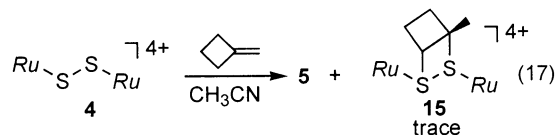
FIGURE 6. Structure of [**14**]⁴⁺ (one of the two crystallographically independent molecules).

suggests that the allylic C-H of cyclohexene is cleaved. Compound **14** was prepared, however, in the presence of Ag⁺, and the reaction may involve a somewhat different reaction path from that for **9**–**13**. The reaction might be a very rare exception (eq 16).

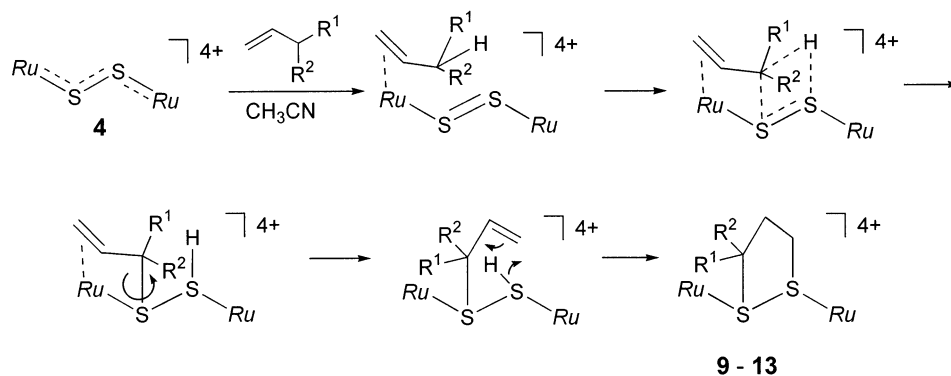


Although it is difficult to judge whether the C=C double bond in the cyclohexenyl moiety is retained or rearranged through the reaction, the reaction apparently needs the existence of a C=C double bond and the allylic C-H bond. Alkenes without the allylic C-H bond do not react at all, and the activation of the allylic C-H bond must be the initial step in the formation of **9**–**13** and **14**. Compound **14** can be regarded as the intermediate-like product of the allylic C-H bond activation.

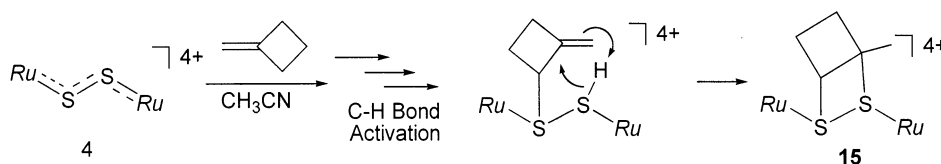
Compound [**4**](CF₃SO₃)₄ reacts with various methylenecycloalkanes.^{27a} The reaction of [**4**](CF₃SO₃)₄ with methylenecyclobutane gave a complex mixture, whose major component was dark blue crystalline [**5**](CF₃SO₃)₃, with a trace of [**15**](CF₃SO₃)₄ (eq 17). Compound **15** has a C₂S₂ four-membered ring. Formation of [**15**](CF₃SO₃)₄ seems to be through a route different from that for the C₃S₂ five-membered rings in **9**–**13**. The possible route to **15** will be discussed later.



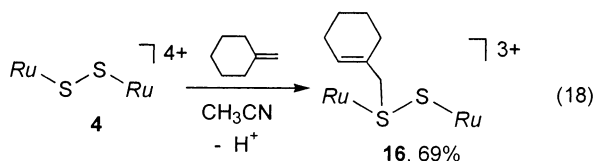
Scheme 2



Scheme 3



The reaction of **[4]**(CF₃SO₃)₄ with methylenecyclopentane did not give any noticeable product. Only the Ru^{II}-Ru^{III} complex **[5]**(CF₃SO₃)₃ was recovered. The reaction of **[4]**(CF₃SO₃)₄ with methylenecyclohexane resulted in the formation of $\{[\text{Ru}(\text{P}(\text{OCH}_3)_3)_2(\text{CH}_3\text{CN})_3]_2\{\mu\text{-S}(\text{CH}_2(\text{C}=\text{CH}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)\text{S})\}(\text{CF}_3\text{SO}_3)_3\}$ (**[16]**(CF₃SO₃)₃) (eq 18). Compound **16** has only one C–S bond, and a proton is lost from the methylenecyclohexane.



The liberated proton is lost as CF₃SO₃H, and the charge of the complex cation is changed from +4 to +3, as in the previously reported ketonated complexes (see the last section in this Account).^{28,29}

The above reactions show three types of alkene addition to the bridging disulfide ligand in the RuSSRu core. The mechanism for the formation of the C₃S₂ five-membered ring in **9–13** is suggested in Scheme 2. The mechanism involves the metathesis between the allylic C–H bond and the S–S bond to form the C–S and S–H bonds. This is the initial essential key step common to all of the three types of addition reactions. The subsequent anti-Markovnikov's addition of the S–H to the C=C double bond gives the five-membered ring of the product. The deuterium label experiment was carried out by using **[4-*d*₁₈]**(CF₃SO₃)₄ and 1-pentene-3,3-*d*₂ (91.5% atom D), which confirmed the mechanism shown in Scheme 2. The ¹H NMR spectrum of the deuterated product was consistent with the proposed mechanism.^{27a} It should be noted that significant primary kinetic isotope effect (*k*_H/*k*_D = 9.1) was observed, and therefore, the C–H bond (or C–D bond) cleavage is the rate-determining step of the reaction.

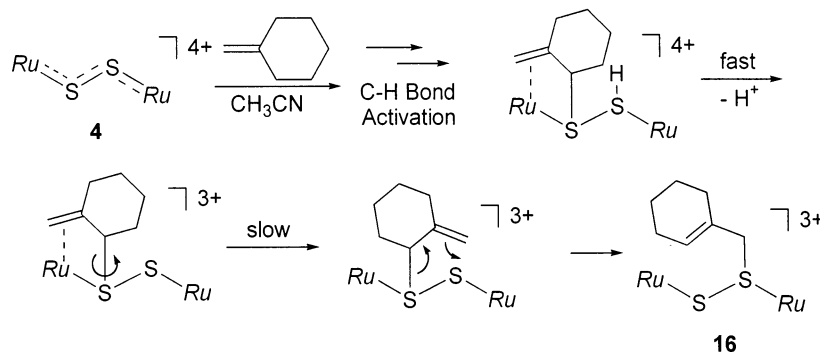
In contrast, the C₂S₂ four-membered ring in **15** was formed via Markovnikov's addition of the S–H to the C=C double bond (Scheme 3). In contrast to the present RuSSRu core system, Markovnikov's addition occurs exclusively in the addition reaction of the S–H to the C=C double bond in the dinuclear molybdenum complex.^{9d} The latter is the only one precedent of this kind of reactions.

On the other hand, the six-membered ring in methylenecyclohexane is too bulky to rotate smoothly around the C–S bond like in Schemes 2 and 3. The liberation of a proton on the sulfur atom occurs before the rotation, and **16** is produced as shown in Scheme 4.

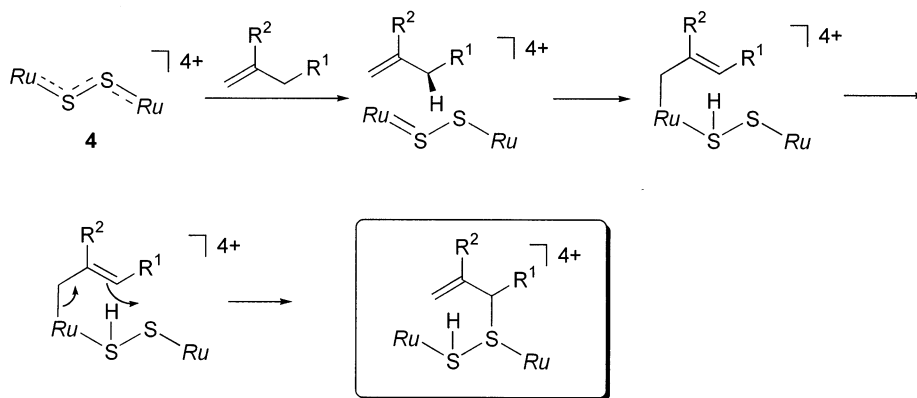
Although a variety of reactions were found in the reaction with alkenes, the C–H bond cleavage is the common key step, and the intermediate having the C–S bond in Scheme 2 explains the three reaction patterns reasonably. As a possible route to the intermediate, a metathesis reaction is suggested between the allylic C–H bond and the S–S bond with a double bond character. It should be noted that similar C–H bond cleavage is known on a phosphorus atom of $\{(\text{H}_3\text{C})_5\text{C}_5\}\text{P}\{\text{C}(\text{CH}_3)_3\}$ and $\{(\text{H}_3\text{C})_5\text{C}_5\}\text{Fe}(\text{CO})_2\{\text{PN}\{\text{CH}(\text{CH}_3)_2\}_2\}$.³⁰ As another possible mechanism for the C–S bond formation, ene-reaction of the C=C double bond with the S=S double bond is conceivable.³¹ However, this mechanism cannot explain the formation of **15**. It is also conceivable that since the conjugate RuSSRu core has the contribution of the Ru=S double bond character, ene-reaction takes place between the C=C double bond and the Ru=S double bond. This mechanism gives the same intermediate having the C–S bond in Scheme 2 (Scheme 5).

The C–H bond activation may also be possible on the Ru center, and in the following step, the alkyl moiety and a hydrogen atom may be transferred to the S₂ moiety. However, the formal oxidation state of the Ru atom in **4** (Ru^{III}) is higher than the usual Ru oxidation states of 0

Scheme 4

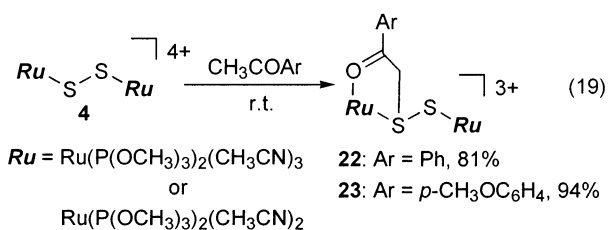


Scheme 5



and II in usual organometallic reactions, and therefore, the last mechanism seems improbable.

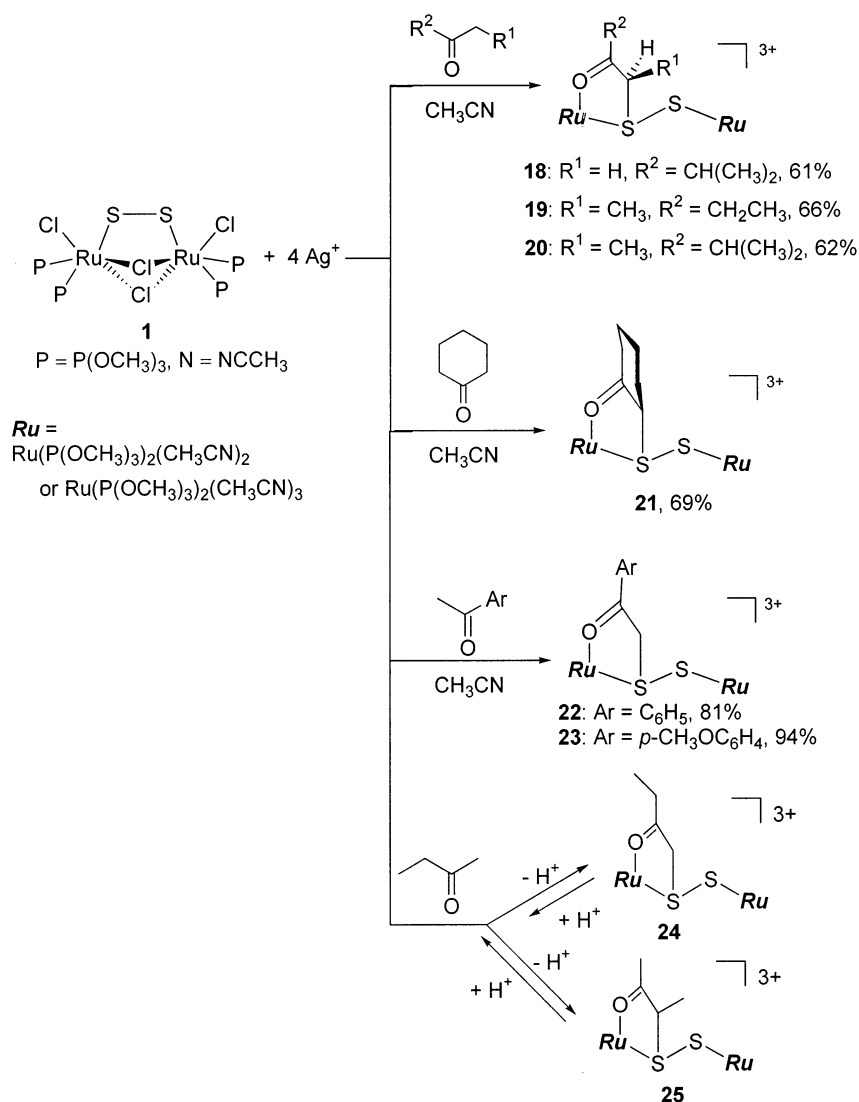
Reactions of the RuSSRu Core with Ketones. Compound **[4](CF₃SO₃)₄** was found by chance to react with acetone to give the acetonated complex $[\{\text{Ru}(\text{CH}_3\text{CN})_2(\text{P}(\text{OCH}_3)_3)_2(\mu\text{-SSCH}_2\text{COCH}_3)\{\text{Ru}(\text{CH}_3\text{CN})_3(\text{P}(\text{OCH}_3)_3)_2\}\}(\text{CF}_3\text{SO}_3)_3]$ (**[17](CF₃SO₃)₃**).²⁸ Further experiment with a variety of ketones gave the corresponding ketonated complexes.²⁹ Both the isolated compound **4** and in situ-generated **4** can be used for the reaction. Treatment of **1** with 4 equiv of silver salt and ketones in CH₃CN gave the ketonated complexes **18–25** (Scheme 6). The aromatic ketonated complexes $[\{\text{Ru}(\text{CH}_3\text{CN})_2(\text{P}(\text{OCH}_3)_3)_2(\mu\text{-SSCH}_2\text{COAr})\{\text{Ru}(\text{CH}_3\text{CN})_3(\text{P}(\text{OCH}_3)_3)_2\}\}(\text{CF}_3\text{SO}_3)_3]$ (**[22](CF₃SO₃)₃**, Ar = C₆H₅; **[23](CF₃SO₃)₃**, Ar = *p*-CH₃OC₆H₄) were obtained from the reactions of **[4](CF₃SO₃)₄** with *p*-substituted acetophenones. The reaction did not proceed with the acetophenone derivatives bearing an electron withdrawing group, such as NO₂ or CH₃C(O) in the *p* position (eq 19). The C–H bond in the aromatic ring of the substrates did not react, either. In the reaction with ketones, one C–S bond is formed via the C–H bond activation, and a proton is liberated.



As expected, (CH₃)₃CCOC(CH₃)₃ (without an α hydrogen) did not react at all, since the substrate does not have an α-C–H bond. Furthermore, the reaction with acetylacetone was examined to see the effect of the conjugated ketones. Acetylacetone has substantial contribution of the enol form, and the reaction gave only the Ru^{II}Ru^{III} complex $[\{\text{Ru}(\text{P}(\text{OCH}_3)_3)_2(\text{CH}_3\text{CN})_3(\mu\text{-S}_2)\}^{3+}]$ (**5**).

It is important to know which C–H bond is preferably activated in unsymmetric ketones.²⁹ The reactions of **1** in the presence of 4 equiv of AgCF₃SO₃ with 3-methyl-2-butanone and 2-methyl-3-pentanone exclusively afforded complexes **18** and **20**, respectively. This shows that the activation of the α-C–H bond occurs to the α-methyl and α-methylene groups, respectively, indicating that the preferred α-C–H bond is in the following order: 1° > 3° and 2° > 3°. On the other hand, butanone, having primary and secondary C–H bonds, reacted with **[4](CF₃SO₃)₄** to give a mixture of complexes $[\{\text{Ru}(\text{CH}_3\text{CN})_2(\text{P}(\text{OCH}_3)_3)_2(\mu\text{-SSCH}_2\text{COCH}_2\text{CH}_3)\{\text{Ru}(\text{CH}_3\text{CN})_3(\text{P}(\text{OCH}_3)_3)_2\}\}(\text{CF}_3\text{SO}_3)_3]$ (**[24](CF₃SO₃)₃**) and $[\{\text{Ru}(\text{CH}_3\text{CN})_2(\text{P}(\text{OCH}_3)_3)_2(\mu\text{-SSCH}_2\text{COCH}_2\text{CH}_3)\{\text{Ru}(\text{CH}_3\text{CN})_3(\text{P}(\text{OCH}_3)_3)_2\}\}(\text{CF}_3\text{SO}_3)_3]$ (**[25](CF₃SO₃)₃**). These compounds result from the activations of the primary and secondary C–H bonds, respectively. The distribution of **24** and **25** depends on the reaction temperature; i.e., **25** increases at lower temperatures, whereas **24** increases at higher temperatures (Table 1). Complex **25** is preferably formed throughout all the reaction temperatures for the initial short period. This shows that, essentially, activation of secondary C–H bond is preferred. However, after prolonged reaction, **24** becomes the major product. This fact suggests that **24** and **25** are the

Scheme 6

Table 1. Distributions of **24** and **25**

method ^a	temp, °C	radical trap ^b	yield, %	24/25	$\text{CH}_3/\text{CH}_2^c$
A	40	–	>99	0.66	0.44
A	40	+	96	0.46	0.30
A	6	–	>99	0.24	0.16
A	6	+	>99	0.23	0.15
B	40	–	83	2.9	1.9
B	40	+	80	2.6	1.7
B	6	–	87	0.74	0.49
B	6	+	83	0.63	0.42

^a Method A: the reaction of **4** with butanone, method B: the reaction of **1** with butanone under the presence of 4 equiv of AgCF_3SO_3 . ^b 2,4,6-tri-*tert*-butyl-phenol (10 equiv to Ru complex **1** or **4**). ^c **24/25** ratio per number of the C–H bonds to be activated.

thermodynamic and the kinetic product, respectively. Actually, the ^1H NMR monitoring of the reaction of [**4**]- $(\text{CF}_3\text{SO}_3)_3$ with butanone in CD_3CN showed that **25** was formed at the early stage; however, after a while, **25** began to decrease at ambient temperature, and **24** gradually became the dominant species. The schematic representation of the conversion reaction is shown in Scheme 6. The ketonyl group can be released from the disulfide as the

original ketone on addition of protic acid. The reversible olefin binding to the sulfur center of the sulfide-bridged dinuclear molybdenum complex was observed previously, which is another very rare reversible C–S bond reaction.^{9d}

A plausible reaction mechanism is shown in Scheme 7 for the reaction of **4** with ketones. The relative reactivity of the C–H bonds found in the present study is in the order $2^\circ > 1^\circ > 3^\circ$. To check the possible involvement of the free radical process in the formation of the ketonated complexes, a radical trapping agent or irradiation of a Hg lamp was attempted, but neither affected the reaction. An electron-withdrawing substituent at the *p* position of acetophenone retards the reaction, which implies that an increase in the acidity of the acetophenone derivative suppresses the reaction. This fact apparently denies the mechanism that simple deprotonation of the ketone initiates the nucleophilic attack of the sulfur atom. Rather, the reaction can be understood as the addition of a C–H bond to the S=S double bond or as the metathesis reaction between the S=S double bond and the α -C–H bond. When a ketone molecule approaches the Ru center

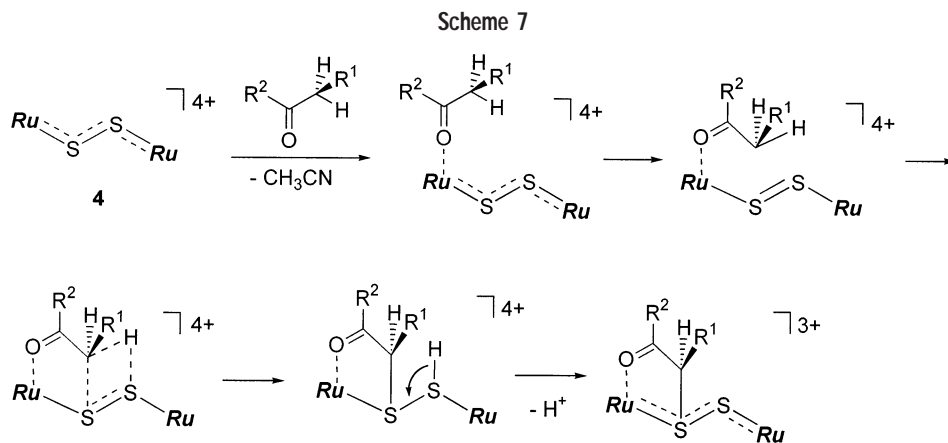
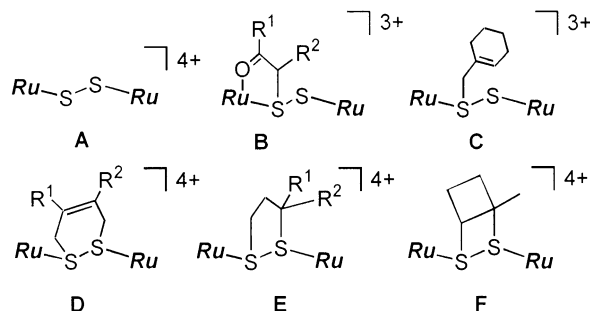


Table 2. Summary of the S–S Distances and Ru–S–S–Ru Angles of the Ru₂S₂ Cores

		S–S distances, Å	Ru–S–S–Ru, deg
A	complex 4	1.933(11)	168.0(3)
B	ketonated complexes ^a	2.040(7)–2.069(4)	167.91(9)–172.9(3)
C	complex 16	2.083(2)	170.23(6)
D	C ₄ S ₂ complexes ^b	2.093(5)–2.099(3)	167.87(13)–169.79(7)
E	C ₃ S ₂ complexes ^c	2.1102(15)–2.164(5)	142.22(16)–59.15(8)
F	complex 15	2.159(4)	143.25(13)

^a Complexes **17**, **20**, **21**, **23**, and **24**. ^b Complexes **6** and **7** and R¹ = R² = H. ^c Complexes **9**, **11**, **12**, and **13**.



with the carbonyl group to replace one of the coordinated CH₃CN molecules trans to one of the two P(OCH₃)₃ ligands and the α-C–H bond of the ketone is oriented parallel to the S₂ moiety, metathesis would occur between the C–H σ bond and the S=S π bond to form the C–S and S–H bonds (Scheme 7). This type of metathesis is analogous to the reaction with alkenes described above. The complex [{Ru(P(OCH₃)₃)₂(CH₃CN)₃]₂(μ-S₂)³⁺ (**5**), having the same core structure with **4** but with the reduced Ru^{II}SSRu^{III} oxidation state, did not react with either ketones or olefins. The reaction is completed by deprotonation of the S–H bond. In the above reactions, the S=S double-bond nature is essential to achieve the addition of the α-C–H bond to the disulfide bond. This reminds the authors that the addition of a C–H bond to a C=C double bond has only recently been realized by also using ruthenium complexes.³²

The four-centered reaction explains the activations of the allylic and keto C–H bonds. However, it is difficult to distinguish whether the activation is either heterolytic or homolytic cleavage. These two processes correspond to the radical process and the ionic one. The former seems more reasonably acceptable for the present reactions if the nature of the Ru^{III}SSRu^{III} core in **4** is considered.

However, since the radical trapping reagent and irradiation with a mercury lamp did not give significant change in the reactions, the free radical process seems unacceptable. Even so, the radical process cannot be denied, since if the free radical is not liberated in the solution to react with the trapping reagent or to receive photoreaction, the reaction is not affected. The conjugated RuSSRu core may accommodate and stabilize two radical centers produced from the C–H bond, and this could explain such a mild C–H activation on the disulfide bridge. It is noteworthy that the C(sp³)–H bond activation reaction induced by the two radical centers of a Rh^{II}-porphyrine complex has been reported.³³

The Bond Multiplicity of the Disulfide in the RuSSRu Core. The complexes formed from the reactions of **4** with the unsaturated organic molecules are either tricationic or tetracationic complexes, depending on whether they have one or two C–S bonds, respectively. The tricationic complexes (ketonated complexes and **16**) are formed via the C–H bond activation and the elimination of a proton on the sulfur atom. When a proton is liberated, the lone pair electrons must be left to form the conjugated RuSSRu core. Such a feature appears in the structural parameters of the S–S distances and the Ru–S–S–Ru torsion angles

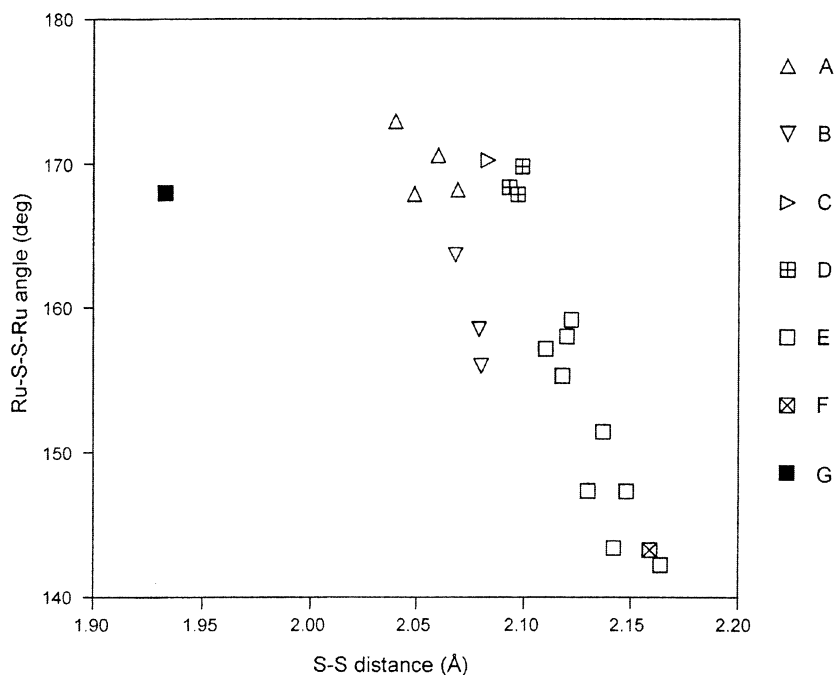


FIGURE 7. Plots of the S–S distance (Å) vs Ru–S–S–Ru angle (deg).

summarized in Table 2. A good correlation is found in the plot of the S–S distances vs Ru–S–S–Ru torsion angles (Figure 7). The structural parameters of the starting complex **4** are also added in the plot.

As expected, **4** has the shortest S–S distance in the complexes; however, the Ru₂S₂ core is slightly distorted from the ideal conjugated system. This is presumably due to the steric hindrance between the two Ru(P(OCH₃)₃)₂-(CH₃CN)₃ moieties. By comparison with the reported typical single and double S–S bond distances (2.05 and 1.89 Å),³⁴ the bond order of the S–S in **4** is assigned close to two, whereas the tricationic complexes having one C–S bond such as the ketonated complexes and **16**, have the single S–S bonds. On the other hand, almost all of the tetracationic complexes have significantly long S–S bonds in the C₃S₂ and C₂S₂ ring structures, and these S–S bonds are longer than a typical single bond. However, the S–S bonds in the C₄S₂ rings are close to the typical single S–S bond, like in the tricationic complexes.

Conclusion

The disulfide bridge in the Ru^{III}SSRu^{III} core is found to have unusual physical and chemical properties. Contribution of a variety of delocalized and localized modes in the RuSSRu core causes various C–S bond formations with dienes, alkenes, and ketones. Especially in the reaction with alkenes and ketones, the C–H bond activation is always involved as the important key step, and this C–H activation under such mild conditions is made possible by the double bond character of the S₂ ligand. The conjugated and delocalized RuSSRu core structure also contributes to such novel reactions. It is known that free neutral disulfur prepared in situ reacts with dienes to give [4 + 2] cycloaddition products. However, free disulfide is too reactive and is not easy to handle. In contrast, the

disulfide ligand in the present system is substantially stable, yet reacts with various unsaturated organic reagents. This is the advantage of the present system. If the C=C double bond of the alkenes and the C=O bond of the ketones act as the anchoring group to fix the substrate and situate the C–H bond in a suitable orientation to the S=S bond, a more advanced system may be constructed by changing the ligands surrounding the RuSSRu core in which the substrate molecule is confined close to the core by the surrounding ligands, and less reactive molecules, such as alkanes, can be activated via C–H cleavage.

As the reactive centers related to the present RuSSRu system, several transition metal–dioxygen complexes of the MOOM core come to mind. Most of these cores are regarded as peroxo or superoxo cores, and C–H bond activation reactions are reported.³⁵ For instance, [Cu(triisopropyltriazacyclononane)]₂(μ-η²-O₂)²⁺ reacts with 2 equiv of 2,4-di(*tert*-butyl)phenol to give diphenol.³⁶ During the reaction, the O₂ ligand is changed to two μ-hydroxo ligands by reduction, and the O–O bond is cleaved. In another dinuclear copper complex, benzylic C–H bond activation results in the hydroxylation of the benzylic position by dioxygen.³⁷ Kitajima et al. reported that the thermal decomposition of [Co(HB(3,5-*t*Pr₂pz)₃)₂-(O₂)] gave a μ-alkoxo-μ-hydroxo complex, Co₂(μ-OH)[HB(μ-3-OCMe₂-5-*t*Prpz)(3,5-*t*Pr₂pz)₂][HB(3,5-*t*Pr₂pz)₃] via activation of methine C–H bond of the *t*Pr group in the ligand.³⁸ The C–H bond activation of the isopropyl group in the pyrazolylborate ligand is also reported in the Co complex.³⁹ For these C–H activation reactions by M₂O₂ complexes, both concerted and nonconcerted mechanisms are suggested.

Although several addition reactions of alkenes and alkynes to terminal monosulfides or a disulfide have been known previously, as shown in eqs 1–6, and several

electrophilic additions to terminal or bridging monosulfides are known (eqs 7–9), the present reactions show for the first time that the disulfide ligand can cleave a C–H bond. But in order to cleave a C–H bond, it must be situated in a suitable position relative to the disulfide. In this respect, the present compound **4** has advantages; i.e., the complex has wide-open space above the disulfide to accommodate the substrate molecule with the C–H bond parallel to the S=S bond. It is also important that **4** has a replaceable ligand CH₃CN, which is easily substituted by the substrate molecule. These structural features must be fulfilled to synthesize a reactive disulfide system. The electronic effect of the co-ligands on the Ru is also important. We observed that the reactivity was almost nil when P(OCH₃)₃ was substituted by P(CH₃)₃. Presumably, these are the reasons that despite that many metal mono- and disulfide complexes are known, C–H activation was not discovered until recently. Theoretical calculation of the C–S bonds in the novel complexes and of the reaction pathways will be a great help in understanding this novel reaction system.

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