Articles

Syntheses of Ketonated Disulfide-Bridged Diruthenium Complexes via C−H Bond Activation and C−S Bond Formation

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The α-C−H bonds of 3-methyl-2-butanone, 3-pentanone, and 2-methyl-3-pentanone were activated on the sulfur center of the disulfide-bridged ruthenium dinuclear complex $[\{RuCl(P(OCH_3)_3)_2\}_2(\mu\text{-}S_2)(\mu\text{-}Cl)_2]$ (**1**) in the presence of AgX (X = PF_6, SbF_6) with concomitant formation of C−S bonds to give the corresponding ketonated complexes $[\{Ru(CH_3CN)_2(P(OCH_3)_3)_2\}(\mu\text{-}SSCHR^1COR^2)\{Ru(CH_3CN)_3(P(OCH_3)_3)_2\}]X_3$ ([**5**]$(PF_6)_3$, R^1 = H, R^2 = $CH(CH_3)_2$, X = PF_6; [**6**]$(PF_6)_3$, R^1 = CH_3, R^2 = CH_2CH_3, X = PF_6; [**7**]$(SbF_6)_3$, R^1 = CH_3, R^2 = $CH(CH_3)_2$, X = SbF_6). For unsymmetric ketones, the primary or the secondary carbon of the α-C−H bond, rather than the tertiary carbon, is preferentially bound to one of the two bridging sulfur atoms. The α-C−H bond of the cyclic ketone cyclohexanone was cleaved to give the complex $[\{Ru(CH_3CN)_2(P(OCH_3)_3)_2\}(\mu\text{-SS-1-cyclohexanon-2-yl})\{Ru(CH_3CN)_3(P(OCH_3)_3)_2\}](SbF_6)_3$ ([**8**]$(SbF_6)_3$). And the reactions of acetophenone and *p*-methoxyacetophenone, respectively, with the chloride-free complex $[\{Ru(CH_3CN)_3(P(OCH_3)_3)_2\}_2(\mu\text{-}S_2)]^{4+}$ (**3**) gave $[\{Ru(CH_3CN)_2(P(OCH_3)_3)_2\}(\mu\text{-}SSCH_2COAr)\{Ru(CH_3CN)_3(P(OCH_3)_3)_2\}](CF_3SO_3)_3$ ([**9**]$(CF_3SO_3)_3$, Ar = Ph; [**10**]$(CF_3SO_3)_3$, Ar = *p*-$CH_3OC_6H_4$). The relative reactivities of a primary and a secondary C−H bond were clearly observed in the reaction of butanone with complex **3**, which gave a mixture of two complexes, i.e., $[\{Ru(CH_3CN)_2(P(OCH_3)_3)_2\}(\mu\text{-}SSCH_2COCH_2CH_3)\{Ru(CH_3CN)_3(P(OCH_3)_3)_2\}](CF_3SO_3)_3$ ([**11**]$(CF_3SO_3)_3$) and $[\{Ru(CH_3CN)_2(P(OCH_3)_3)_2\}(\mu\text{-}SSCHCH_3COCH_3)\{Ru(CH_3CN)_3(P(OCH_3)_3)_2\}](CF_3SO_3)_3$ ([**12**]$(CF_3SO_3)_3$), in a molar ratio of 1:1.8. Complex **12** was converted to **11** at room temperature if the reaction time was prolonged. The relative reactivities of the α-C−H bonds of the ketones were deduced to be in the order 2° > 1° > 3°, on the basis of the consideration of contributions from both electronic and steric effects. Additionally, the C−S bonds in the ketonated complexes were found to be cleaved easily by protonation at room temperature. The mechanism for the formation of the ketonated disulfide-bridged ruthenium dinuclear complexes is as follows: initial coordination of the oxygen atom of the carbonyl group to the ruthenium center, followed by addition of an α-C−H bond to the disulfide bridging ligand, having S═S double-bond character, to form a C−S−S−H moiety, and finally completion of the reaction by deprotonation of the S−H bond.

Introduction

Studies of transition metal sulfide and polysulfide complexes have been recognized as an important field of basic and applied inorganic chemistry.[1−6] Although the reactivity of sulfide ligands in metal sulfides has been explored to some extent,[4−6] the reactions are mostly additions of coordinated sulfides, disulfides, and polysulfides either to C≡C bonds[7−14] or to C═C bonds[12−18] and there are few examples of C−H bond activations on sulfur centers. Activation of the C−H bond of acetone on the disulfide complex $[\{RuCl(P(OCH_3)_3)_2\}_2(\mu\text{-}S_2)(\mu\text{-}Cl)_2]$ (**1**) in the presence of 4 equiv of a silver salt has been reported to give [{Ru(CH_3-

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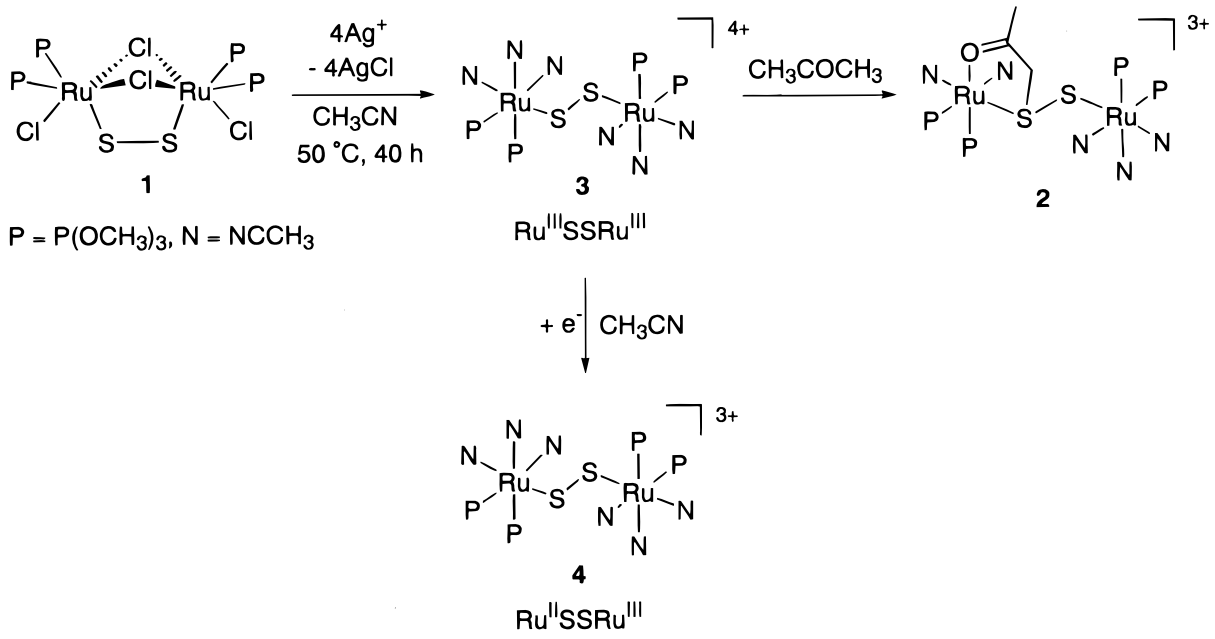
Scheme 1



$CN)_2(P(OCH_3)_3)_2\}(\mu\text{-}SSCH_2COCH_3)\{Ru(CH_3CN)_3(P(OCH_3)_3)_2\}](CF_3SO_3)_3$ ([**2**]$(CF_3SO_3)_3$) through formation of the chloride-free complex $[\{Ru(CH_3CN)_3(P(OCH_3)_3)_2\}(\mu\text{-}S_2)]^{4+}$ (**3**) (Scheme 1).[19] Activation of the C−H bond of acetone has also been achieved on a monosulfide metal complex to produce $(C_5Me_5)_3RhRu_2S_3(SCH_2COMe)^+$.[20] Very recently, activation of an allylic C−H bond of an alkene on a disulfide bridging ligand in a diruthenium complex accompanied by the formation of one or two C−S bonds has been realized in our group.[21] These C−H bond activation reactions on sulfur centers contrast markedly with the extensively studied organometallic chemistry on transition metal centers.[22−24] The chemical reactivities of disulfide ligands in transition metal complexes have been little studied and may open a new field not only of sulfur chemistry but also of organometallic-like chemistry on sulfur centers.[9,12,25−29]

Disulfide diruthenium complexes such as **1** and others having an $Ru^{III}SSRu^{III}$ core have been reported to exhibit electron-deficient, double-bond character on the two bridging sulfur atoms.[30−35] Previously, we reported that the reactions of the disulfide-bridged diruthenium complex $[\{RuCl(P(OCH_3)_3)_2\}_2(\mu\text{-}S_2)(\mu\text{-}Cl)_2]$ (**1**) with 1, 2, and 4 equiv of a silver salt in acetonitrile resulted in successive substitutions of the terminal and bridge chloride ions with acetonitrile.[36,37] With 4 equiv of the silver salt, **3**, with an $Ru^{III}SSRu^{III}$ core, was obtained as the initial product, which was, however, easily reduced in CH_3CN to the more stable paramagnetic complex $[\{Ru(CH_3CN)_3(P(OCH_3)_3)_2\}(\mu\text{-}S_2)]^{3+}$ (**4**), with an $Ru^{II}SSRu^{III}$ core (Scheme 1).[36,37]

After a series of studies on the properties of S_2-bridged dinuclear ruthenium complexes with and without chloride bridging ligands,[19,21,36−43] it has become clear that the sulfur center in the $Ru^{III}SSRu^{III}$ unit has, like many other transition metal centers, a variety of reactivities toward many organic substrates. In the present study, to explore the true mechanism and the driving force operating in C−H bond activation on the sulfur center of a disulfide-bridged complex, we have synthesized various ketonated disulfide-bridged diruthenium complexes via activation of the α-C−H bonds of the starting ketones. The

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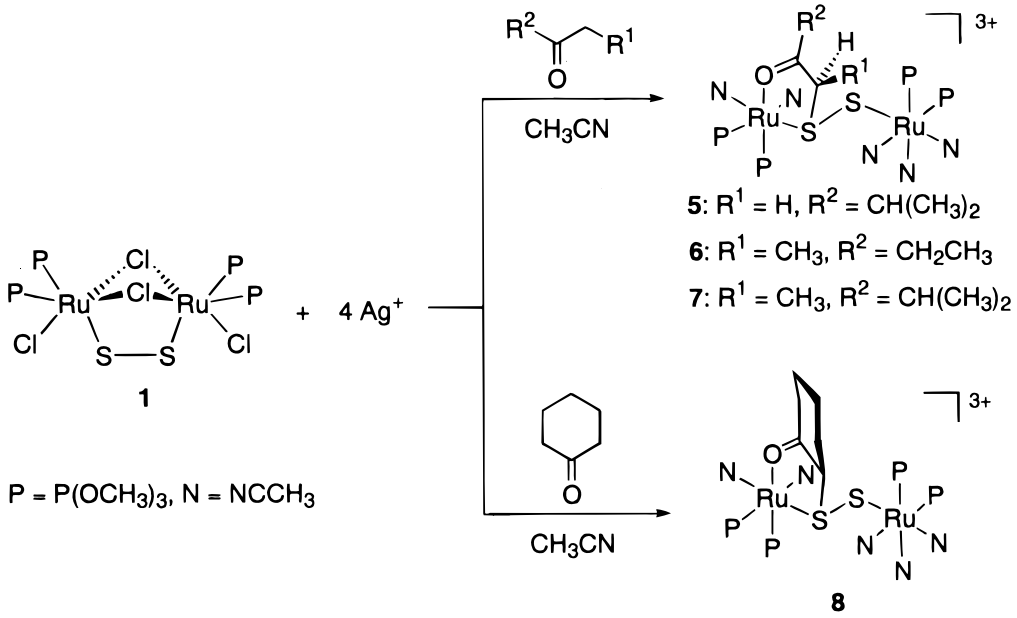
Scheme 2



mechanism is considered on the basis of these reactions carried out under different conditions.

Results and Discussion

Syntheses of the Ketonated Complexes. In contrast to the previous synthesis of the ketonated disufide-bridged diruthenium complex **2**,[19] a more simplified method has been developed for the syntheses of ketonated complexes from various symmetric and unsymmetric ketones via activation of the α-C−H bonds on the sulfur center of a disulfide-bridged diruthenium complex. This is a modification of the previous method used for the preparation of complex **2**.[19] Treatment of **1** with 4 equiv of a silver salt and large excesses of the linear ketones 3-methyl-2-butanone, 3-pentanone, and 2-methyl-3-pentanone, respectively, in CH_3CN at room temperature resulted in the formation of the pale green ketonated complexes $[\{Ru(CH_3CN)_2(P(OCH_3)_3)_2\}(\mu\text{-}SSCHR^1COR^2)\{Ru(CH_3CN)_3(P(OCH_3)_3)_2\}]X_3$ ([**5**]$(PF_6)_3$, R^1 = H, $R^2 = CH(CH_3)_2$, X = PF_6; [**6**]$(PF_6)_3$, $R^1 = CH_3$, $R^2 = CH_2CH_3$, X = PF_6; [**7**]$(SbF_6)_3$, $R^1 = CH_3$, $R^2 = CH(CH_3)_2$, X = SbF_6) in 61−66% yields (Scheme 2). Analogously, the cyclic ketone cyclohexanone with $AgSbF_6$ as the silver salt gave the corresponding complex $[\{Ru(CH_3CN)_2(P(OCH_3)_3)_2\}(\mu\text{-SS-1-cyclohexanon-2-yl})\{Ru(CH_3CN)_3(P(OCH_3)_3)_2\}](SbF_6)_3$ ([**8**]$(SbF_6)_3$) in a 69% yield (Scheme 2).

All complexes obtained were identified by ^{1}H NMR spectroscopy and elemental analyses (see Experimental Section). The structures of **7** and **8** were confirmed by X-ray analyses (vide infra).

In contrast to the preceding ketones, $(CH_3)_3CCOC(CH_3)_3$ (no α-hydrogen) failed to react under conditions similar to those described above. Furthermore, we carried out the reactions with CH_3COOCH_3 and acetylacetone, which have higher contributions of their enol forms, but no product with a C−S bond was obtained. Only the Ru^{II}/Ru^{III} complex **4** was recovered after workup, indicating failure of the C−S bond to form.

Protonation of the Ketonated Complexes. The newly formed C−S bonds in the ketonated disulfide complexes are relatively susceptible to protonation. Addition of an excess amount of acid, for example, $HClO_4$ or CF_3SO_3H, to a CD_3CN solution of a ketonated complex at room temperature immediately leads to the cleavage of the C−S bond with quantitative recovery of the ketone along with generation of the chloride-free complex **3**. The reaction was confirmed by ^{1}H and ^{31}P NMR analysis. When HCl is used, the ruthenium complexes $[\{RuCl(P(OCH_3)_3)_2\}(\mu\text{-}S_2)(\mu\text{-}Cl)_2\{Ru(CH_3CN)(P(OCH_3)_3)_2\}]^+$ and **1** are formed by the replacement of the coordinated CH_3CN with chloride ions.[36] The former complex is further totally converted to the **1** if the reaction time is extended to several days in the presence of excess HCl.

The easy protonation of the ketonated complexes accompanied by the scission of the C−S bond can be regarded as the reverse of the C−H bond activation of ketones by ruthenium complex **3**. Similar reversible formation of covalent C−S bonds on a high-valent molybdenum monosulfide complex was previously reported.[16,18,44,45] It is well-known that desulfurization of organic sulfides, especially thiophene and its derivatives, is a very important process in the petroleum industry.[46] The fact that the C−S bonds in ketonated disulfide complexes can be readily cleaved by simple protonation at room temperature provides useful information for studies of desulfurization reactions in which dinuclear transition metals that sandwich sulfide ligands may play a key role in the C−S bond cleavage process.

A Modified Method for the Preparation of Complex 3 and Formation of Ketonated Complexes Directly from 3. (a) Preparation of Complex 3. Complex **3** is considered to be a reactive intermediate in the C−H bond activation reactions for the ketonated complexes. Formerly, **3** was prepared by adding 4 equiv of a silver salt to **1**, but this procedure often gives a mixture of **3** and **4**. As a more convenient synthesis of **3**, the acetonated complex **2** was treated with CF_3SO_3H to give **3** in high yield. Complex **3** can be isolated and stored as the staring material for further reactions (Scheme 3).

(b) Reactions of 3 with Ketones. The aromatic ketonated complexes $[\{Ru(CH_3CN)_2(P(OCH_3)_3)_2\}(\mu\text{-}SSCH_2COAr)\{Ru(CH_3CN)_3(P(OCH_3)_3)_2\}](CF_3SO_3)_3$ ([**9**]$(CF_3SO_3)_3$, Ar = Ph; [**10**]$(CF_3SO_3)_3$, Ar = *p*-$CH_3OC_6H_4$) can be prepared from the reactions of complex **3** with acetophenone and *p*-methoxy-

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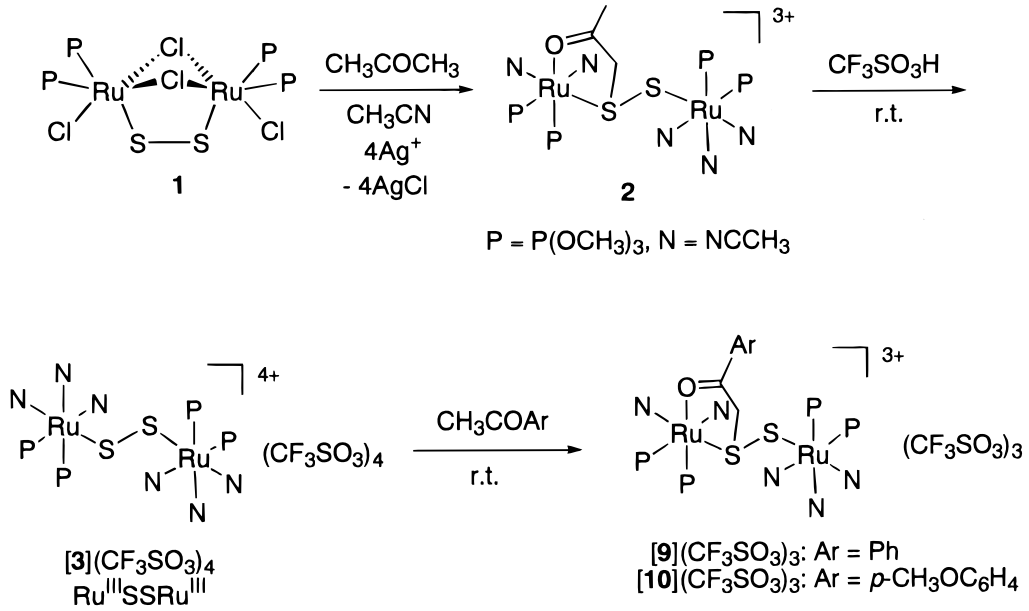
Scheme 3

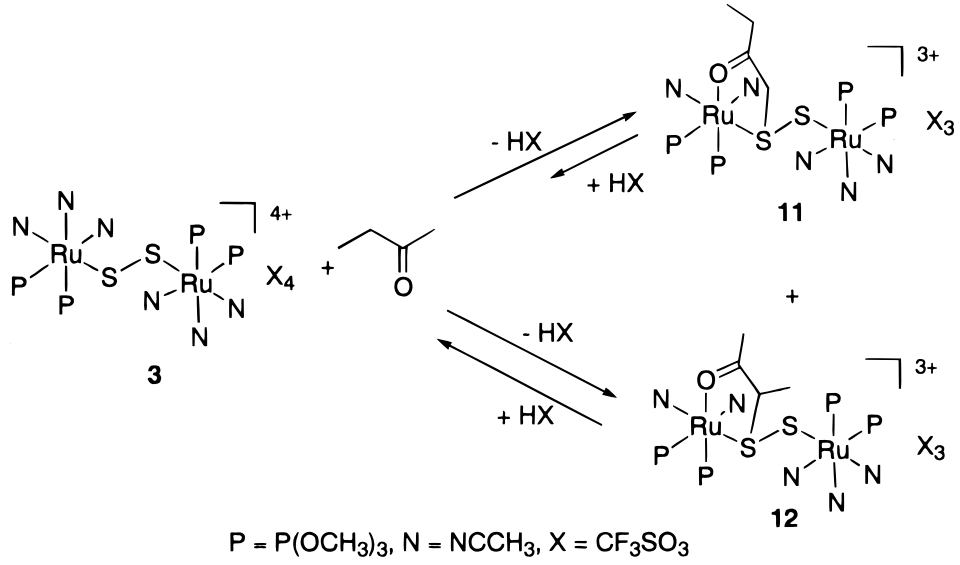


acetophenone, respectively (Scheme 3). [**9**]$(CF_3SO_3)_3$ can also be obtained from the reaction of **1** with acetophenone in the presence of 4 equiv of $AgCF_3SO_3$. However, preparations of the ketonated complexes from complex **3** provide cleaner results with higher yields. Derivatives bearing electron-withdrawing groups such as NO_2 or $CH_3C(O)$ in the para positions did not react, nor did the C−H bonds in the aromatic rings of the substrates.

NMR Spectroscopy. The $^{31}P\{^1H\}$ NMR spectra of the ketonated complexes consist of two well-separated doublets ($\Delta\delta = 3.7-5.3$ ppm) and two less separated doublets or a broad singlet corresponding to an AB pattern. The former can be assigned to the two phosphorus nuclei on the carbonyl-coordinated ruthenium center, and the latter can be assigned to the two phosphorus nuclei on the other ruthenium center, surrounded by two P donors, three N donors, and one S donor. In the ^1H NMR spectra of **5**−**8**, the sulfide-bound methylene or methine proton signals lie in the range δ 4.22−3.98 as a broad singlet (**5**), a quadruplet (**6**, **7**), or a multiplet (**8**), which is similar to that of complex **2**, whereas the signals of the diastereotopic methylene protons bound to the sulfur atoms in complexes **9** and **10** appear as two doublets with AB patterns at δ 4.95 and 4.53 ($J_{gem} = 19$ Hz) for **9** and at δ 4.91 and 4.36 ($J_{gem} = 18$ Hz) for **10**. The protons of the methyl groups attached to the chelating rings in complexes **6** and **7** exhibit doublets around δ 1.6−1.5 in the ^1H NMR spectra.

Reaction with Butanone. The reactions of complex **1** with 3-methyl-2-butanone and 2-methyl-3-pentanone, both having asymmetric α-protons, exclusively afford complexes **5** and **7** in the presence of a silver salt by the activation of the α-C−H bonds of the α-methyl and α-methylene groups, respectively, indicating that the preferred orders for the α-C−H bonds are respectively as follows: 1° > 3°; 2° > 3°. To compare the relative reactivities of the α-C−H bonds of a primary versus a secondary carbon atom, butanone was treated with **3** in CD_3CN in an NMR tube and the reaction was monitored with ^1H NMR spectroscopy, which revealed a mixture of the following complexes: [{$Ru(CH_3CN)_2(P(OCH_3)_3)_2$}($\mu$-$SSCH_2COCH_2CH_3$){$Ru(CH_3CN)_3(P(OCH_3)_3)_2$}]$(CF_3SO_3)_3$ ([**11**]$(CF_3SO_3)_3$) and [{$Ru(CH_3CN)_2(P(OCH_3)_3)_2$}($\mu$-$SSCHCH_3COCH_3$){$Ru(CH_3CN)_3(P(OCH_3)_3)_2$}]$(CF_3SO_3)_3$ ([**12**]$(CF_3SO_3)_3$). The distinct signals of complexes **11** and **12** were clearly observed in the ^1H NMR spectrum of the reaction mixture. A doublet at δ 1.62 is assigned to the methyl protons in the β-position with respect to the carbonyl group in **12**. A multiplet around δ 4.2 is due to the overlapping resonances of the methylene and the methine protons bound to one of the two sulfur atoms in **11** and **12**, respectively (see Experimental Section). The relative molar ratio of **11** to **12** and the total yield of the mixture of **11** and **12** were determined from an integration of the ^1H NMR signals using benzene as an internal reference. The molar ratio of **11** to **12** was 1:1.8 with a total yield of 74% when the reaction was carried out for 60 min at 5 °C, whereas the ratio increased to 1:1.1 after the reaction mixture was warmed to 20 °C for 20 min (82%) and further changed to 1:0.5 with a yield of 95% after the mixture was maintained for 2 h at the same temperature. The amount of **12** dropped considerably, nearing zero after 20 h, and that of **11** rose to 92% based on the analysis of the ^1H NMR spectrum. These results demonstrate that complex **12**, formed from the activation of the secondary C−H bond of butanone, is the predominant product in the early stage and then begins to decompose at ambient temperature in the presence of protons released from butanone to regenerate the $Ru^{III}SSRu^{III}$ complex **3**, which again activates the primary and secondary C−H bonds of butanone to give complexes **11** and **12**. Upon repetition of this process, the relative ratio of the two products inclines more toward **11**. The fact that the isolated complex **12** is sufficiently stable in solution indicates that **12** is decomposed by protonation to recover butanone and complex **3** under the reaction conditions, where a small amount of acid is generated from the reaction. A broad signal appearing around δ 10 in the ^1H NMR spectrum of the reaction mixture confirms the release of H^+ ions. A representation of the conversion is shown in Scheme 4. One can regard **12** as a kinetic product and **11** as a thermodynamic one. Thus, the α-C−H bond on the secondary carbon is more easily cleaved than that on the primary carbon. In summary, the order of the relative reactivities of the C−H bonds can be expressed as 2° > 1° > 3°. The lowest reactivity of the tertiary C−H bond may reflect the greatest steric hindrance of the branched groups. Reversible olefin binding to the sulfur center of a sulfide-bridged dinulcear molybdenum

Scheme 4



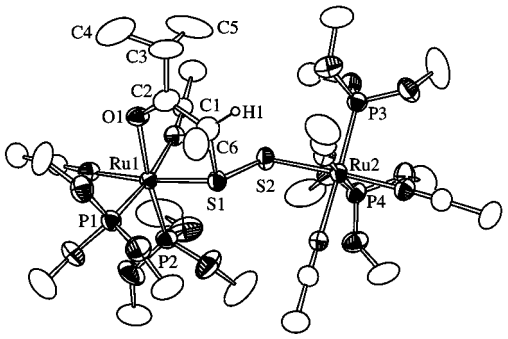


Figure 1. ORTEP drawing of cation **7**. Thermal ellipsoids are drawn at the 30% probability level.

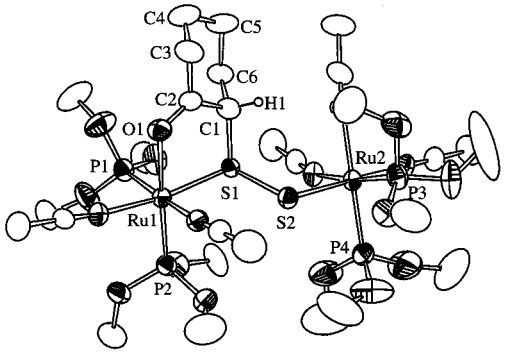


Figure 2. ORTEP drawing of cation **8**. Thermal ellipsoids are drawn at the 30% probability level.

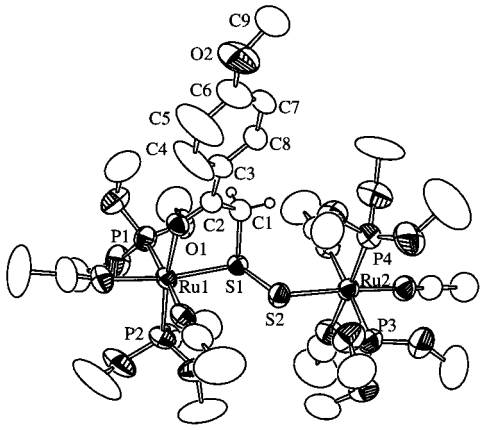


Figure 3. ORTEP drawing of cation **10**. Thermal ellipsoids are drawn at the 30% probability level.

complex, another very rare reversible C−S bond reaction, was observed previously.[16,18,44,45]

On the basis of the above experiment, one can expect to obtain complex **11** as the main product by prolonging the reaction time or raising the reaction temperature, whereas, for complex **12**, the reaction should be carried out at a lower temperature for a short period. Indeed, complex **11** was obtained as the sole product when the CH_3CN solution of **1** containing 4 equiv of the silver salt was stirred overnight at room temperature in the presence of butanone. Unfortunately, the attempt to isolate pure **12** or to obtain single crystals suitable for X-ray analysis was not successful. The fact that the secondary α-C−H bond is more reactive than the primary one implies that a radical pathway might be involved in the reaction. However, addition of a radical-trapping agent, $^tBu_3C_6H_2OH$ (10 equiv to Ru_2S_2 complex **1** or [**3**]$(CF_3SO_3)_4$), or irradiation of the reaction mixture by a mercury lamp did not significantly change the relative molar ratio of **11** to **12** or the total yield, indicating that a radical mechanism can be excluded for the present C−H bond activation and C−S bond formation reaction.

Crystallographic Analyses of the Ketonated Complexes. The structures of [**7**]$(PF_6)_3$, [**8**]$(SbF_6)_3$, [**10**]$(CF_3SO_3)_3$, and [**11**]$(PF_6)_3$ were determined by X-ray crystallography, and the ORTEP diagrams of their complex cations are shown in Figures 1−4, respectively. These four structures possess the same coordination mode as the acetonated complex reported previously,[19] in which one ruthenium atom is coordinated by two P atoms of $P(OCH_3)_3$, two N atoms of CH_3CN, one S atom of μ-S_2^{2-}, and one O atom of the ketonated moiety and the other is surrounded by two P atoms, three N atoms and one S atom. One of the two bridging sulfur atoms is bonded to the α-C atom, forming a five-membered chelate system. The S−S bond distances of these complexes range from 2.040(7) to 2.069(4) Å, which are comparable to that of **2** (2.067(6) Å)[19] and are similar to or slightly longer than those found in other nonalkylated disulfide complexes (2.01−2.05 Å).[36,39−43] The oxidation states of the two ruthenium atoms in complexes **7**, **8**, **10**, and **11** are considered to be 3+ on the basis of the Ru−P distances (2.21−2.25 Å), as discussed previously.[19] Selected bond lengths, bond angles, and torsion angles for these complexes are

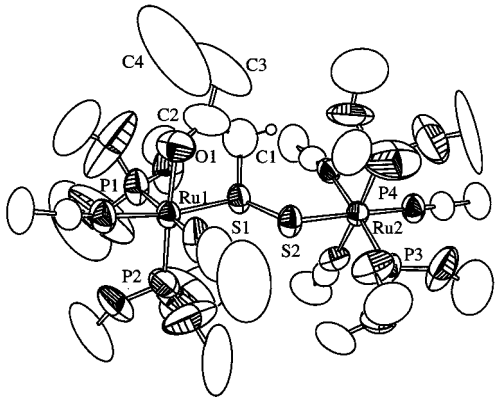


Figure 4. ORTEP drawing of cation **11**. Thermal ellipsoids are drawn at the 30% probability level.

Table 1. Selected Bond Distances (Å)

	[**7**]$(PF_6)_3$	[**8**]$(SbF_6)_3$	[**10**]$(CF_3SO_3)_3$	[**11**]$(PF_6)^3$
Ru1−S1	2.348(2)	2.342(3)	2.340(1)	2.320(6)
Ru2−S2	2.367(2)	2.373(3)	2.373(2)	2.354(6)
Ru1−P1	2.243(3)	2.241(3)	2.252(2)	2.234(7)
Ru1−P2	2.218(3)	2.225(3)	2.231(2)	2.207(8)
Ru2−P3	2.231(3)	2.225(4)	2.231(2)	2.217(6)
Ru2−P4	2.227(3)	2.237(4)	2.231(2)	2.234(7)
Ru1−O1	2.157(5)	2.179(7)	2.148(4)	2.14(2)
S1−S2	2.049(3)	2.069(4)	2.060(2)	2.040(7)
S1−C1	1.853(9)	1.86(1)	1.815(5)	1.86(3)
C1−C2	1.54(1)	1.50(2)	1.512(8)	1.58(4)
C2−O1	1.21(1)	1.20(1)	1.228(7)	1.22(3)

Table 2. Selected Bond Angles and Torsion Angles (deg)

	[**7**]-$(PF_6)_3$	[**8**]-$(SbF_6)_3$	[**10**]-$(CF_3SO_3)_3$	[**11**]-$(PF_6)_3$
		Bond Angles		
Ru1−S1−S2	106.6(1)	109.2(1)	109.83(7)	108.5(3)
Ru2−S2−S1	107.9(1)	109.2(1)	107.05(7)	108.3(3)
Ru1−O1−C2	121.8(6)	120.1(7)	121.6(4)	124(2)
Ru1−S1−C1	99.9(3)	97.8(4)	97.2(2)	97.1(10)
S1−C1−C2	110.7(6)	114.5(8)	111.3(4)	115(2)
S2−S1−C1	103.0(3)	103.4(4)	101.5(2)	101.7(9)
		Torsion Angles		
Ru1−S1−S2−Ru2	−167.91(9)	−168.2(1)	170.55(6)	172.9(3)
Ru1−S1−C1−C2	−15.5(8)	−8.8(8)	31.9(4)	19(2)
Ru1−O1−C2−C1	−14(1)	−2(1)	8.5(7)	0(4)
Ru2−S2−S1−C1	87.4(3)	88.5(4)	87.37(19)	−85(1)

compared in Tables 1 and 2. The torsion angles Ru1−S1−C1−C2 and Ru1−O1−C2−C1 in the ketonated complexes are clearly different, as shown in Table 2. This may reflect the difference in bulk for the ketonated moieties.

It is noteworthy that high diastereoselectivity is obtained in the formation of the ketonated complexes, in which a larger group on the carbon atom bonded to one of the two bridging sulfide atoms always occupies a position farther away from the sulfur atom that is not bound to the ketonate group to avoid the steric congestion. This situation is seen clearly in the Newman-type projections of **7**, **8**, **10**, and **11** shown in Figure 5.

Proposed Mechanism for the Formation of Ketonated Complexes. A plausible mechanism for the reaction of **3** with ketones to give the corresponding ketonated complexes is shown in Scheme 5. Although the relative reactivities of the C−H bonds found in this study are in the order 2° > 1° > 3°, the fact that a radical-trapping agent or irradiation does not affect the reaction indicates that a radical process is not involved in the formation of the ketonated complexes. An electron-withdrawing substituent at the para position of acetophenone retards the reaction, which implies that an increase in the acidity

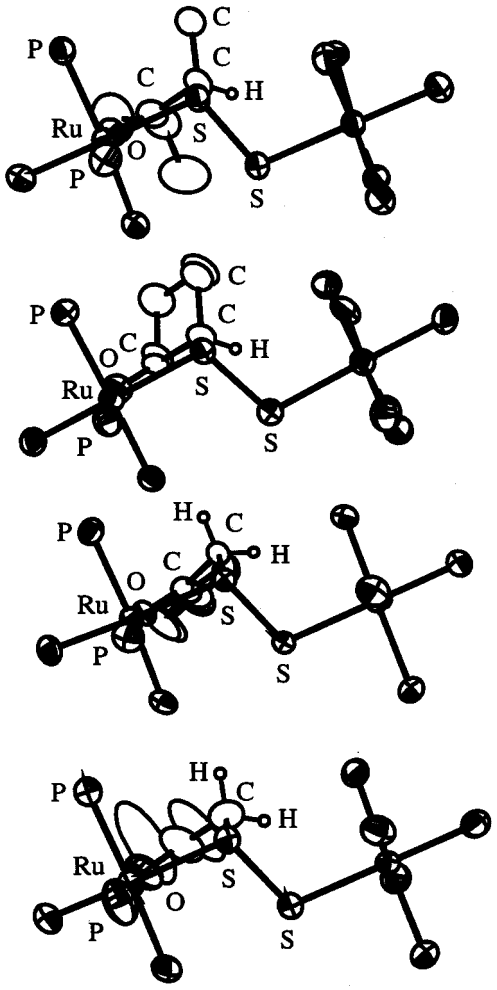
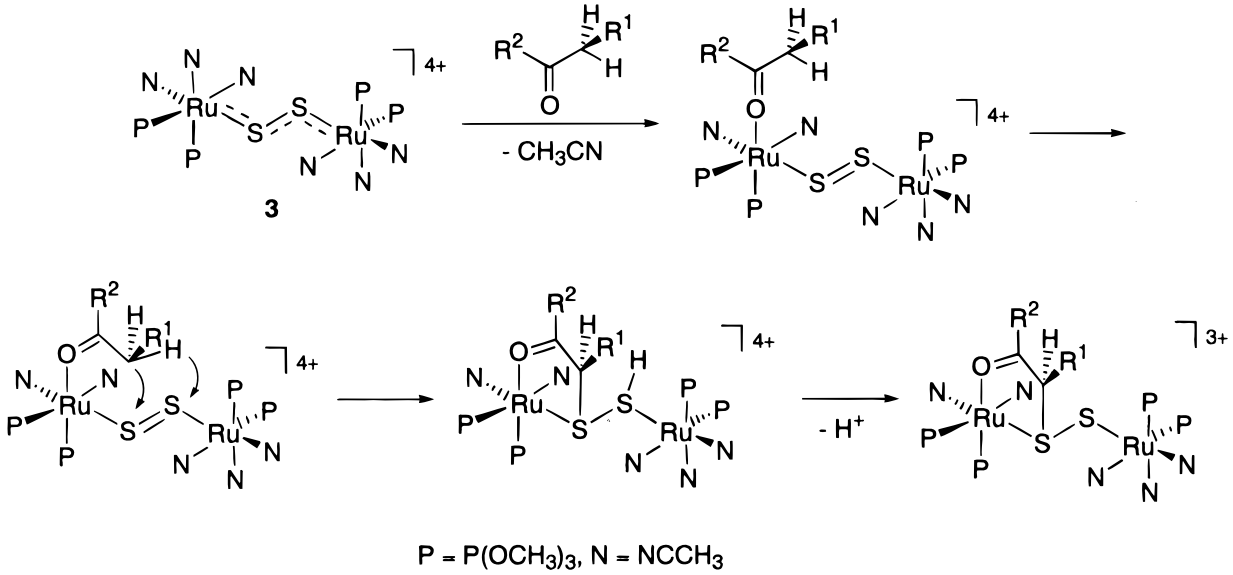


Figure 5. Newman-type projections of **7**, **8**, **10**, and **11** (from top to bottom).

of the aceotophenone derivative suppresses the reaction and is apparently contradictory to a mechanism in which simple deprotonation of the ketone initiates the nucleophilic attack on the sulfur atom. In our recent studies, allylic C−H bonds were found to be cleaved in the $Ru^{III}SSRu^{III}$ complexes **3** and **1**.[21] To explain the remarkable reactivity of the $Ru^{III}SSRu^{III}$ core toward various olefins, double-bond character for the disulfide unit was suggested.[21] The present reactions of various ketones with the same ruthenium complex further support the S═S double-bond character and the mechanism of C−H addition to the S═S bond (Scheme 5). A ketone approaches the Ru center with the carbonyl group to replace one of the three coordinated CH_3CN molecules that is trans to one of the two $P(OCH_3)_3$ ligands. When the α-C−H bond of a ketone is directed parallel to the S_2 moiety, addition of the C−H σ bond to the S═S π bond occurs to form a C−S and an S−H bond (Scheme 5). The nucleophilic addition is facilitated by the strong electron-withdrawing ability of the two Ru^{III} atoms. Complex **4**, with the same structure as **3** but with an $Ru^{II}SSRu^{III}$ core, did not react with either ketones or olefins, which supports the nucleophilic addition process. The reaction is completed by deprotonation of the S−H bond. The double-bond character of a coordinated S═S unit has been reported previously.[30−36] Addition of a C−H bond to a double C═C bond promoted by other ruthenium complexes was recently reported.[47,48] Although

(47) Kakiuchi, F.; Sato, T.; Yamauchi, M.; Chatani, N.; Murai, S. *Chem. Lett.* **1999**, 19 and references therein.

Scheme 5



we could not detect the S−H bond by ^{1}H NMR spectroscopy, the olefin reactions support the presence of such bonds.[21]

Conclusions

The α-C−H bonds of various ketones have been activated on the sulfur center of a disulfide ruthenium dinuclear complex to form the corresponding ketonated complexes having C−S bonds. Although the Ru atoms are not directly involved in the C−H splitting process, they play an important role in modifying the nature of the disulfide bridge. Nucleophilic addition of the α-C−H bonds of ketones to S═S bonds is proposed as the key step in the activation of the C−H bonds and formation of the C−S bonds.

Experimental Section

All experiments were carried out under nitrogen, by using standard Schlenk tube techniques or a glovebox. The solvent CD_3CN was dried over CaH_2 and then purified by trap-to-trap distillation prior to use. Other solvents that were purchased dry were used without further purification. Complex **1** was prepared as described in the literature.[49] The NMR spectra were recorded on a JEOL Lambda 270 spectrometer, operating at 270 MHz for ^{1}H and 109 MHz for ^{31}P, or on a JEOL Lambda 500, spectrometer operating at 500 MHz for ^{1}H. The chemical shifts are reported in δ units (ppm) downfield from Me_4Si for ^{1}H and H_3PO_4 (85%, external reference) for ^{31}P. Carbon, hydrogen, and nitrogen analyses were carried out on a Perkin-Elmer PE 2400II elemental analyzer.

A Modified Method for the Preparation of [{Ru(CH$_3$CN)$_3$(P(OCH$_3$)$_3$)$_2$}$_2$(μ-S$_2$)](CF$_3$SO$_3$)$_4$ ([3](CF$_3$SO$_3$)$_4$). The modified method is based on the reported one[36] for the preparation of [**3**]$(CF_3SO_3)_4$. A mixture of **1** (90.4 mg, 0.10 mmol), $AgCF_3SO_3$ (103.9 mg, 0.40 mmol), CH_3CN (0.5 mL), and acetone (1.5 mL) was stirred for 2 h at room temperature. The resulting mixture was centrifuged to remove AgCl, and the pale green supernate was evaporated to dryness in vacuo. The residue was washed with Et_2O (3 × 2 mL) to give the acetonated complex **2**. This crude product of **2** was dissolved in CH_3CN (1.0 mL), the solution was treated with CF_3SO_3H (0.06 mL), and the mixture was stirred for 30 min at room temperature. After removal of the volatiles under reduced pressure, the residue was washed with Et_2O (3 × 2 mL) to give [{Ru(CH$_3$CN)$_3$(P(OCH$_3$)$_3$)$_2$}$_2$(μ-S$_2$)](CF$_3$SO$_3$)$_4$ ([**3**](CF$_3$SO$_3$)$_4$) as a dark blue powder (140.5 mg, 88%). ^{1}H NMR (CD_3CN, δ, 270 MHz, 293 K): 3.86 (vt, $^3J_{PH}$ = 6 Hz, 36H, 4P(OCH_3)$_3$), 2.71 (s, 6H, 2CH_3CN trans to S), 1.95 (s, 12H, 4CH_3CN, overlapped with the signals of CD_2HCN).

Syntheses of [{Ru(CH$_3$CN)$_2$(P(OCH$_3$)$_3$)$_2$}(μ-SSCHR^{1}COR^2){Ru(CH$_3$CN)$_3$(P(OCH$_3$)$_3$)$_2$}]X$_3$ ([5](PF$_6$)$_3$, R^1 = H, R^2 = CH(CH$_3$)$_2$, X = PF$_6$; [6](PF$_6$)$_3$, R^1 = CH$_3$, R^2 = CH$_3$CH$_2$, X = PF$_6$; [7](SbF$_6$)$_3$, R^1 = CH$_3$, R^2 = CH(CH$_3$)$_2$, X = SbF$_6$). General procedure: To a mixture of **1** (100.0 mg, 0.11 mmol) and $AgPF_6$ (170.0 mg, 0.49 mmol) in CH_3CN (10 mL) was added an excess amount of 3-methyl-2-butanone (3 mL). After being stirred for 7 h at room temperature, the reaction mixture was filtered to remove AgCl. The pale green filtrate was evaporated to dryness, and the residue was dissolved in a mixture of CH_3CN and CH_2Cl_2. This solution was filtered, and the filtrate was kept under ether diffusion to give the complex [{Ru(CH$_3$CN)$_2$(P(OCH$_3$)$_3$)$_2$}(μ-SSCH$_2$COCH(CH$_3$)$_2$){Ru(CH$_3$CN)$_3$(P(OCH$_3$)$_3$)$_2$}](PF$_6$)$_3$ ([**5**](PF$_6$)$_3$) as pale green crystals (61% yield). ^{1}H NMR (CD_3CN, δ, 270 MHz, 293 K): 4.17 (br s, 2H, SCH_2), 3.8−3.6 (m, 36H, 4P(OCH_3)$_3$), 3.12 (sept, J = 7.0 Hz, 1H, CH(CH$_3$)$_2$), 2.46 (s, 3H, CH_3CN), 2.35 (s, 3H, CH_3CN), 1.97 (s, 9H, 3CH_3CN, overlapped with the signals of CD_2HCN), 1.23 (d, J = 7.0 Hz, 3H, CH(CH_3)CH$_3$), 1.20 (d, J = 7.0 Hz, 3H, CH(CH$_3$)CH_3). ^{31}P{^{1}H} NMR (CD_3CN, δ, 109.4 MHz, 293 K): 135.3 (d, $^2J_{PP}$ = 86 Hz), 133.8 (d, $^2J_{PP}$ = 87 Hz), 133.4 (d, $^2J_{PP}$ = 87 Hz), 130.0 (d, $^2J_{PP}$ = 86 Hz), −145.6 (sept, $^1J_{PF}$ = 106 Hz, PF$_6$). Anal. Calcd for $C_{27}H_{60}F_{18}N_5O_{13}P_7S_2Ru_2$: C, 21.80; H, 4.06; N, 4.71. Found: C, 21.62; H, 4.06; N, 4.44. The same procedure as described above was used for the syntheses of complexes **6** and **7**, but with $AgSbF_6$ as the anion source in the preparation of **7**.

[**6**](PF$_6$)$_3$: pale green crystals, 66% yield. ^{1}H NMR (CD_3CN, δ, 270 MHz, 293 K): 4.14 (q, J = 8.1 Hz, 1H, SCHCH$_3$), 3.8−3.6 (m, 36H, 4P(OCH_3)$_3$), 2.86 (q, J = 7.0 Hz, 2H, CH_2CH$_3$), 2.46 (s, 3H, CH_3CN), 2.34 (s, 3H, CH_3CN), 1.97 (s, 9H, 3CH_3CN, overlapped with the signals of CD_2HCN), 1.57 (d, J = 8.1 Hz, 3H, SCHCH_3), 1.14 (t, J = 7.0 Hz, 3H, CH$_2$CH_3). ^{31}P{^{1}H} NMR (CD_3CN, δ, 109.4 MHz, 293 K): 133.6 (d, $^2J_{PP}$ = 87 Hz), 132.7 (br s, 2P(OCH$_3$)$_3$), 129.3 (d, $^2J_{PP}$ = 87 Hz), −144.8 (sept, $^1J_{PF}$ = 106 Hz, PF$_6$). Anal. Calcd for $C_{27}H_{60}F_{18}N_5O_{13}P_7S_2Ru_2$: C, 21.80; H, 4.06; N, 4.71. Found: C, 21.48; H, 3.99; N, 4.47.

[**7**](SbF$_6$)$_3$: pale green crystals, 62% yield. ^{1}H NMR (CD_3CN, δ, 270 MHz, 293 K): 4.22 (q, 1H, J = 7.9 Hz, SCHCH$_3$), 3.8−3.6 (m, 36H, 4P(OCH_3)$_3$), 3.24 (sept, J = 7.0 Hz, 1H, CH(CH$_3$)$_2$), 2.45 (s, 3H, CH_3CN), 2.34 (s, 3H, CH_3CN), 1.97 (s, 9H, 3CH_3CN, overlapped with the signals of CD_2HCN), 1.49 (d, J = 7.9 Hz, 3H, SCHCH_3), 1.21 (d, J = 6.6 Hz, 3H, CH(CH_3)CH$_3$), 1.18 (d, J = 6.9 Hz, 3H, CH(CH$_3$)CH_3). ^{31}P{^{1}H} NMR (CD_3CN, δ, 109.4 MHz, 293 K): 133.2 (d, $^2J_{PP}$ = 88 Hz), 132.7 (br s, 2P(OCH$_3$)$_3$), 129.5 (d, $^2J_{PP}$ = 88 Hz). Anal. Calcd for $C_{28}H_{62}F_{18}N_5O_{13}P_4S_2Sb_3Ru_2$: C, 18.96; H, 3.52; N, 3.95. Found: C,

(48) Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Nature* **1993**, *366*, 529.
(49) Matsumoto, T.; Matsumoto, K. *Chem. Lett.* **1992**, 559.

Table 3. Summary of Crystallographic Data

	[**7**](PF$_6$)$_3$	[**8**](SbF$_6$)$_3$	[**10**](CF$_3$SO$_3$)$_3$	[**11**](PF$_6$)$_3$
empirical formula	$C_{28}H_{63}O_{13}N_5F_{18}P_7S_2Ru_2$	$C_{28}H_{61}O_{13}N_5F_{18}P_4S_2Ru_2Sb_3$	$C_{34}H_{60}O_{23}N_5F_9P_4S_5Ru_2$	$C_{26}H_{59}O_{13}N_5F_{18}P_7S_2Ru_2$
fw	1502.88	1773.19	1564.19	1474.83
a (Å)	25.000(5)	20.993(3)	15.7178(7)	12.471(3)
b (Å)	12.535(4)	13.919(4)	24.4198(11)	21.72(1)
c (Å)	12.341(3)	21.258(3)	16.8492(8)	12.206(3)
α (deg)	119.15(2)			101.96(3)
β (deg)	92.61(1)	94.95(1)	90.8310(10)	110.46(2)
γ (deg)	88.54(2)			84.28(3)
V (Å^3)	3103(1)	6188(1)	6466.5(5)	3029(1)
Z	2	4	4	2
space group (No.)	$P\bar{1}$ (2)	$P2_1/n$ (14)	$P2_1/c$ (14)	$P\bar{1}$ (2)
d_{calcd} (g cm^{-3})	1.608	1.903	1.557	1.617
μ (cm^{-1})	8.39	20.44	8.24	8.58
diffractometer	AFC-7R	AFC-7R	SMART 1000	AFC-7R
radiation, λ (Å)	Mo Kα, 0.710 69	Mo Kα, 0.710 69	Mo Kα, 0.710 69	Mo Kα, 0.710 69
$2\theta_{max}$ (deg)	55	55	55	50
abs cor	ψ scan	ψ scan	SADABS	ψ scan
no. of reflns measd	11 630	10 971	12 765	8143
no of reflns obsd	6042 ($I > 3\sigma(I)$)	5261 ($I > 2\sigma(I)$)	8450 ($I > 2\sigma(I)$)	4021 ($I > 2\sigma(I)$)
no. of params	745	708	763	568
R1[a]	0.058	0.062	0.066	0.098
wR2[b]	0.072	0.201	0.195	0.108
residuals (e/Å^3)	+0.75, −0.34	+0.77, −0.63	+1.01, −0.93	+1.40, −0.95

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for observed data. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]]^{1/2}$.

18.37; H, 3.44; N, 3.73. The pale green crystals of [**7**](PF$_6$)$_3$ suitable for the X-ray analysis were obtained by using AgPF$_6$ as the anion source.

Synthesis of [{Ru(CH$_3$CN)$_2$(P(OCH$_3$)$_3$)$_2$}(μ-SS-1-cyclohexanon-2-yl){Ru(CH$_3$CN)$_3$(P(OCH$_3$)$_3$)$_2$}](SbF$_6$)$_3$ ([8](SbF$_6$)$_3$). The same procedure as described above for the synthesis of **5** was used in the preparation of [**8**](SbF$_6$)$_3$, but with AgSbF$_6$ as the anion source. Pale green crystals were obtained in a yield of 69%. ^{1}H NMR (CD$_3$CN, δ, 270 MHz, 293 K): 3.98 (m, 1H, SC*H*), 3.8−3.6 (m, 36H, 4P(OC*H*$_3$)$_3$), 2.88 (m, 1H, COC*H*H′), 2.66 (m, 2H, COCH*H*′ and SCHC*H*H′), 2.12 (m, 1H, COCH$_2$C*H*H′), 1.98 (m, 1H, SCHCH$_2$C*H*H′), 1.73 (m, 2H, SCHCH*H*′CH*H*′), 1.54 (m, 1H, COCH$_2$CH*H*′), 2.45 (s, 3H, C*H*$_3$CN), 2.34 (s, 3H, C*H*$_3$CN), 1.97 (s, 9H, 3C*H*$_3$CN, overlapped with the signals of CD$_2$HCN). ^{31}P{^{1}H} NMR (CD$_3$CN, δ, 109.4 MHz, 293 K): 132.8 (d, $^2J_{PP}$ = 87 Hz), 131.7 (br s, 2P(OCH$_3$)$_3$), 127.4 (d, $^2J_{PP}$ = 87 Hz). Anal. Calcd for $C_{28}H_{60}F_{18}N_5O_{13}P_4S_2Sb_3Ru_2$: C, 18.98; H, 3.41; N, 3.95. Found: C, 19.02; H, 3.51; N, 4.01.

Protonation of the Ketonated Complexes 2 and 5−7. General procedure: To a CD$_3$CN (0.6 mL) solution of acetonated complex **2** (0.100 g, 0.068 mmol) was added HCl (37 wt % in water, 0.113 mL, 1.36 mmol) at room temperature. The reaction mixture was analyzed after 10 min by ^{1}H and ^{31}P NMR spectroscopy, which revealed the formation of **1** and [RuCl{P(OCH$_3$)$_3$}$_2$](μ-S$_2$)(μ-Cl)$_2$[Ru(CH$_3$CN){P(OCH$_3$)$_3$}$_2$]$^+$ in a molar ratio of 1:2, along with the released acetone. The same procedure as described for the protonation of **2** was used in the reactions of complexes **5**−**7** with various acids.

Syntheses of [{Ru(CH$_3$CN)$_2$(P(OCH$_3$)$_3$)$_2$}(μ-SSCH$_2$COAr){Ru(CH$_3$CN)$_3$(P(OCH$_3$)$_3$)$_2$}](CF$_3$SO$_3$)$_3$ ([9](CF$_3$SO$_3$)$_3$, Ar = Ph; [10](CF$_3$SO$_3$)$_3$, Ar = *p*-CH$_3$OC$_6$H$_4$). To a CH$_3$CN (1 mL) solution of **3** (80.7 mg, 0.050 mmol) was added acetophenone, and the mixture was stirred for 1 h at room temperature. The reaction solution became pale green, whereupon Et$_2$O (6 mL) was added to give a precipitate. The supernate was removed via a syringe, and the residue was washed with THF (6 mL) and dried under reduced pressure to give [{Ru(CH$_3$CN)$_2$(P(OCH$_3$)$_3$)$_2$}(μ-SSCH$_2$COPh){Ru(CH$_3$CN)$_3$(P(OCH$_3$)$_3$)$_2$}](CF$_3$SO$_3$)$_3$ ([**9**](CF$_3$SO$_3$)$_3$) as a pale green powder (64.4 mg, 81%). ^{1}H NMR (CD$_3$CN, δ, 270 MHz, 293 K): 8.18 (d, J_{om} = 8 Hz, 2H, *o*-C$_6$H$_5$), 7.88 (t, J_{mp} = 8 Hz, 1H, *p*-C$_6$H$_5$), 7.69 (t, 2H, *m*-C$_6$H$_5$), 4.95 (d, $^2J_{HH'}$ = 19 Hz, 1H, SC*H*H′), 4.53 (d, $^2J_{HH'}$ = 19 Hz, 1H, SCH*H*′), 3.82 (d, $^3J_{PH}$ = 11 Hz, 9H, P(OCH$_3$)$_3$), 3.6−3.7 (m, 27H, 3P(OCH$_3$)$_3$), 2.54 (s, 3H, C*H*$_3$CN), 2.39 (s, 3H, C*H*$_3$CN), 1.95 (s, 9H, 3C*H*$_3$CN, overlapped with the signals of CD$_2$HCN). ^{31}P{^{1}H} NMR (CD$_3$CN, δ, 109.4 MHz, 293 K): 135.9 (d, $^2J_{PP}$ = 84 Hz), 134.3 (d, $^2J_{PP}$ = 88 Hz), 133.9 (d, $^2J_{PP}$ = 88 Hz), 130.1 (d, $^2J_{PP}$ = 84 Hz). Anal. Calcd for $C_{33}H_{58}F_9N_5O_{22}P_4S_5Ru_2$: C, 25.84; H, 3.81; N, 4.56. Found: C, 25.29; H, 3.64; N, 4.26.

[**10**](CF$_3$SO$_3$)$_3$ was synthesized and purified in the same procedure as described for **9** by using *p*-CH$_3$OC$_6$H$_4$C(O)CH$_3$ instead of acetophenone (yield: 94%). The single crystals of [**10**](CF$_3$SO$_3$)$_3$ suitable for X-ray analysis were obtained by recrystallization from CH$_3$CN and THF at room temperature. ^{1}H NMR (CD$_3$CN, δ, 270 MHz, 293 K): 8.16 (d, J_{om} = 9 Hz, 2H, *o*-C$_6$H$_4$OCH$_3$), 7.17 (d, 2H, *m*-C$_6$H$_4$OCH$_3$), 4.91 (d, $^2J_{HH'}$ = 18 Hz, 1H, SC*H*H′), 4.36 (d, $^2J_{HH'}$ = 18 Hz, 1H, SCH*H*′), 3.95 (s, 3H, C$_6$H$_4$OC*H*$_3$), 3.81 (d, $^3J_{PH}$ = 11 Hz, 9H, P(OCH$_3$)$_3$), 3.6−3.7 (m, 27H, 3P(OCH$_3$)$_3$), 2.52 (s, 3H, C*H*$_3$CN), 2.39 (s, 3H, C*H*$_3$CN), 1.95 (s, 9H, 3C*H*$_3$CN, overlapped with the signals of CD$_2$HCN). ^{31}P{^{1}H} NMR (CD$_3$CN, δ, 109.4 MHz, 293 K): 137.9 (d, $^2J_{PP}$ = 84 Hz), 135.9 (d, $^2J_{PP}$ = 87 Hz), 135.5 (d, $^2J_{PP}$ = 87 Hz), 132.3 (d, $^2J_{PP}$ = 84 Hz). Anal. Calcd for $C_{34}H_{60}F_9N_5O_{23}P_4S_5Ru_2$: C, 26.10; H, 3.87; N, 4.48. Found: C, 25.73; H, 3.68; N, 4.20.

Reaction of [{Ru(CH$_3$CN)$_3$(P(OCH$_3$)$_3$)$_2$}$_2$(μ-S$_2$)](CF$_3$SO$_3$)$_4$ ([3](CF$_3$SO$_3$)$_4$) with Butanone. To a solution of **3** (32 mg, 0.02 mmol) in CD$_3$CN (0.54 mL) were added butanone (0.089 mL, 1 mmol) and benzene (0.009 mL, 0.1 mmol, as an internal reference) at 5 °C, and the reaction was monitored by ^{1}H NMR spectroscopy. A mixture of [{Ru(CH$_3$CN)$_2$(P(OCH$_3$)$_3$)$_2$}(μ-SSCH$_2$COCH$_2$CH$_3$){Ru(CH$_3$CN)$_3$(P(OCH$_3$)$_3$)$_2$}](CF$_3$SO$_3$)$_3$ ([**11**](CF$_3$SO$_3$)$_3$) and [{Ru(CH$_3$CN)$_2$(P(OCH$_3$)$_3$)$_2$}(μ-SSCHCH$_3$COCH$_3$){Ru(CH$_3$CN)$_3$(P(OCH$_3$)$_3$)$_2$}](CF$_3$SO$_3$)$_3$ ([**12**](CF$_3$SO$_3$)$_3$) in a molar ratio of 1:1.8 was detected after 60 min at 5 °C in a total yield of 78%. The reaction mixture was then warmed to 20 °C, and the relative molar ratio of **11** to **12** and the total yield of **11** and **12** were determined by the analysis of ^{1}H NMR spectrum as described under Results and Discussion.

^{1}H NMR for [**11**](CF$_3$SO$_3$)$_3$ (CD$_3$CN, δ, 500 MHz, 293 K): 4.23 (d, J = 19.0 Hz, 1H, SC*H*H′), 4.18 (d, J = 19.0 Hz, 1H, SCH*H*′), 3.8−3.6 (m, 36H, 4P(OC*H*$_3$)$_3$), 3.00 (dq, J = 18.9, 7.2 Hz, 1H, C*H*H′CH$_3$), 2.83 (dq, J = 18.9, 7.2 Hz, 1H, CH*H*′CH$_3$), 2.49 (s, 3H, C*H*$_3$CN), 2.38 (s, 3H, C*H*$_3$CN), 1.97 (s, 9H, 3C*H*$_3$CN, overlapped with the signals of CD$_2$HCN), 1.19 (t, J = 7.2 Hz, 3H, CHH′C*H*$_3$).

^{1}NMR for [**12**](CF$_3$SO$_3$)$_3$ (CD$_3$CN, δ, 500 MHz, 293 K): 4.17 (q, J = 8.2 Hz, 1H, SC*H*CH$_3$), 3.8−3.6 (m, 36H, 4P(OC*H*$_3$)$_3$), 2.56 (s, 3H, C*H*$_3$CO), 2.49 (s, 3H, C*H*$_3$CN), 2.38 (s, 3H, C*H*$_3$CN), 1.97 (s, 9H, 3C*H*$_3$CN, overlapped with the signals of CD$_2$HCN), 1.62 (d, J = 8.2 Hz, 3H, SCHC*H*$_3$).

Isolation and Crystallization of [11](SbF$_6$)$_3$. This complex could be isolated as a pure solid from the **1**−butanone reaction solution after standing at room temperature overnight in the presence of AgSbF$_6$. Yield: 63%. Anal. Calcd for $C_{26}H_{58}F_{18}N_5O_{13}P_4S_2Sb_3Ru_2$: C, 17.88; H, 3.35; N, 4.01. Found: C, 17.78; H, 3.44; N, 3.95.

The pale green crystals of [**11**](PF$_6$)$_3$ suitable for the X-ray analysis

were obtained by using $AgPF_6$ as the anion source in CH_3CN with Et_2O diffusion.

X-ray Crystallographic Studies. Diffraction data for [**7**]$(PF_6)_3$, [**8**]$(SbF_6)_3$, and [**11**]$(PF_6)_3$ were collected on a Rigaku AFC 7R four-circle diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å). The unit cell parameters of **7**, **8**, and **11** were obtained by least-squares refinements of 25 reflections ($25° < 2\theta < 30°$). Three standard reflections were recorded every 150 reflections and used for the decay corrections. The diffraction data were corrected for Lorentz and polarization effects, and absorption corrections based on ψ scans were applied. Structure solutions were performed with the TEXSAN program package. Some atoms were treated isotropically to maintain reasonable reflection:parameter ratios, and some rigid-group constraints were applied for the highly disordered PF_6 counteranions. Diffraction data for [**10**]$(CF_3SO_3)_3$ were collected on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation. All intensity data were processed by the SAINT-Plus program package, and the structure solution was performed with the SHELXTL software package. Details of all four crystallographic analyses are summarized in Table 3.

Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of [**7**]$(PF_6)_3$, [**8**]$(SbF_6)_3$, [**10**]$(CF_3SO_3)_3$, and [**11**]$(PF_6)_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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