Allylic C−H Bond Activation on a Sulfur Center of a Disulfide-Bridged Diruthenium Complex with Concomitant Formation of C−S Bonds

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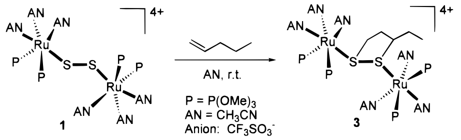
Much attention has been paid to sulfide-coordinated transition metal complexes, due to their chemistry relevant to the biological and catalytic processes.[1] Although there are several chemical reactivities in which the sulfur atom of the ligands usually acts as the reactive center,[2] C−H bond activation on the sulfur center has not been reported, except for our previous result and that of Rauchfuss et al. on C−H bond activation of acetone promoted by disulfide and monosulfide metal complexes.[3,4] Additionally, the reverse reaction of the olefin insertion into a S−H bridging ligand of a cationic cyclopentadienylmolybdenum complex can also be regarded as a C−H bond activation of a μ-alkanethiolate ligand.[5] This is in strong contrast to the extensive studies on C−H bond activation based upon transition metal centers in organometallic chemistry.[6] In this regard, exploitation of C−H bond activation on a sulfur center of ligands will be a new challenge in chemistry. So far the most widely reported reactions of sulfide, disulfide, hydrosulfide, and polysulfide ligands in the formation of C−S bond(s) are via (a) addition of sulfide, disulfide, and polysulfide ligands to acetylene and its derivatives[7,8] or alkenes;[8,9] (b) olefin insertion into coordinated S−H bonds;[5,10,11] and (c) attack of alkylating reagents on sulfide ligands.[12] Among the several C−S bond formations via inorganic sulfide ligands, chemical reactivities of disulfide ligand are less explored.[3,7e,8a] Here, we report the first sulfur-centered activation of an allylic C−H bond of monoolefin, such as 1-pentene and cyclohexene, on a disulfide-bridged dinuclear ruthenium complex, accompanied by formation of C−S bond(s).

Addition of an excess of 1-pentene to an acetonitrile solution of $[\{Ru(P(OMe)_3)_2(MeCN)_3\}_2(\mu\text{-}S_2)](CF_3SO_3)_4$ (**1**), prepared by treatment of $[\{RuCl(P(OMe)_3)_2\}_2(\mu\text{-}S_2)(\mu\text{-}Cl)_2]$ (**2**) with 4 equiv of $AgCF_3SO_3$ as previously reported,[13,14] at ambient temperature gave yellow crystals of $[\{Ru(P(OMe)_3)_2(MeCN)_3\}_2(\mu\text{-}S_2)(CH_2)_2CH(C_2H_5)](CF_3SO_3)_4$ (**3**) in a yield of 44% (eq 1).[15] The structure of **3** was confirmed based on the ^{31}P, ^{1}H, and ^{13}C NMR, CHN elemental analysis, and X-ray diffraction analysis.[15,16] Two doublets with an *ab* pattern (126.4 and 125.7 ppm, $^2J_{PP}$ = 81 Hz) and a singlet (125.0 ppm) were observed in the $^{31}P\{^1H\}$ NMR spectrum, indicating inequivalency of the two ruthenium atoms in **3**. The ^1H and ^{13}C NMR spectra of **3** also clearly show the pentyl moiety.[15] All of the three NMR spectra with sharp peak profiles show that **3** is diamagnetic, although it is a Ru(III) dinuclear compound.[17] X-ray analysis of **3** reveals that an allylic C−H bond of 1-pentene is cleaved and the two bridging sulfur atoms are bound to two carbon atoms at the 1 and 3 positions of 1-pentene to form a five-membered dithiolane moiety as shown in Figure 1. To our knowledge, this is the first example of allylic C−H bond activation on any sulfide center and two sulfur atoms of the disulfide bridging ligand are bonded to two alkyl carbon atoms. This double C−S bond formation is significant, since only one C−S bond is formed in our previous study on the activation of a C−H bond in acetone promoted by disulfide diruthenium complex, in which the second C−S bond cannot be formed by addition of excess acetone.[3] As a relevant reaction, the disulfide dinuclear rhenium complex reacts with acetylene and ethylene to give dithiolate complexes, in which the S−S bond is ruptured.[8a] All carbon−carbon bond lengths in the pentyl skeleton in **3** correspond to single bond character (Figure 1), which implies that one of the two allylic protons is transferred to the internal olefinic carbon. Hitherto there is no report on the formation of a C−S bond accompanied by a hydrogen atom transfer along the hydrocarbon chain. Hydrogen atom transfer from μ-S−H to the olefinic carbon has been proposed following the attack of the sulfido ligand on an olefin in the insertion reaction of unactivated



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[15] For the detailed preparation and NMR data of **3** and **4**, see the Supporting Information.

[16] Crystal data for **3**: $C_{33}H_{64}O_{24}N_6F_{12}S_6P_4Ru_2$, $T = 223$ K, $M_r = 1675.28$, yellow, triclinic, $P\bar{1}$, $a = 12.6240(5)$ Å, $b = 13.4087(5)$ Å, $c = 20.2605(7)$ Å, $\alpha = 104.679(1)°$, $\beta = 91.826(1)°$, $\gamma = 91.535(1)°$, $V = 3313.7$ (2) Å^3, $Z = 2$, $R = 0.0536$, $R_w = 0.1440$, GOF = 0.990.

[17] The oxidation state of the ruthenium atoms is considered to be 3+, based on the Ru−P bond lengths in **3** and **4** (see Supporting Information and ref 3).

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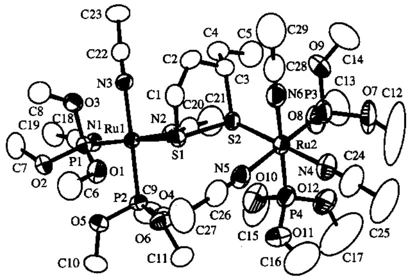


Figure 1. ORTEP drawing of complex **3**. Thermal ellipsoids are drawn at the 50% probability level.

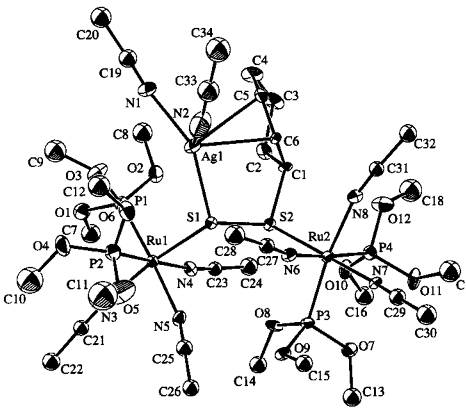
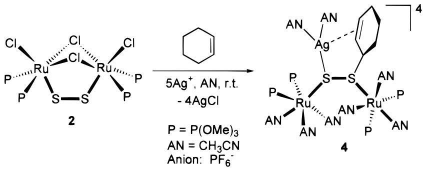


Figure 2. ORTEP drawing of complex **4**. Thermal ellipsoids are drawn at the 30% probability level.

olefins with the hydrosulfido ligand of a cationic cyclopentadienyl dimolybdenum complex.[5]

It is noteworthy that an internal linear or cyclic monoolefin, i.e., 2-hexene or cyclohexene, did not react with **1** under the same conditions as described above for the reaction with 1-pentene. However, treatment of **2** with 5 equiv of $AgPF_6$ in the presence of an excess of cyclohexene in MeCN leads to formation of a novel pale green complex, $[\{Ru(P(OMe)_3)_2(MeCN)_3\}_2(Ag(NCMe)_2)(\mu\text{-}S_2C_6H_9)](PF_6)_4$ (**4**), in 69% yield (eq 2).[15] Smaller amounts of silver salt result in the formation of the known paramagnetic $Ru^{II}SSRu^{III}$ complex $[\{Ru(P(OMe)_3)_2(MeCN)_3\}_2(\mu\text{-}S_2)]^{3+}$ (**5**)[14,18] as the major product. The ^1H NMR resonance of the cyclohexenyl group was observed in the ^1H NMR spectrum as broad signals.[15] ESR experiment confirmed that **4** is diamagnetic. A crystallographic analysis of **4** revealed that one of the bridging sulfur atoms is bonded to the allylic carbon atom of the cyclohexenyl group (Figure 2).[19,20] It is difficult to distinguish whether the double bond of the cyclohexenyl group is the one found in the original cyclohexene or is formed by a rearrangement during the reaction. However, the fact that a terminal olefin without the α-hydrogen atom, i.e., styrene, did not react with **2** under the same conditions suggests that the double bond of cyclohexene is retained in **4** and an allylic proton is essential for such a reaction.

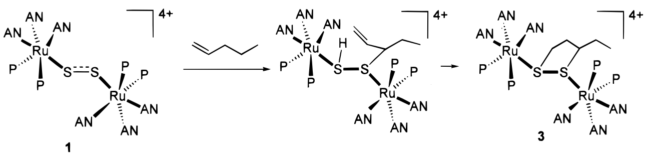


P = P(OMe)$_3$
AN = CH$_3$CN
Anion: PF$_6^-$

(2)

Addition of an excess of aqueous HCl solution to the acetonitrile solution of **4** at ambient temperature resulted immediately in the cleavage of the C−S bond to release cyclohexene together with complex **2** and $[\{RuCl(P(OMe)_3)_2\}(\mu\text{-}S_2)(\mu\text{-}Cl)_2\{Ru(NCMe)(P(OMe)_3)_2\}](PF_6)$ (**6**)[14] in a molar ratio of about 1 to 2 as confirmed by ^{31}P NMR. The facile protonation of the cyclohexenyl group in **4** can be regarded as a reversible process of the C−H bond activation. However, in contrast to **4**, the C−S bonds in **3** cannot be cleaved by acid.

Scheme 1



P = P(OMe)$_3$
AN = CH$_3$CN
Anion: CF$_3$SO$_3^-$

Formation of **4** indicates that the direct attack of the bridging sulfide on the double bond of cyclohexene does not take place, and rather a C−H bond in the allylic position is more easily activated to form a C−S bond. Therefore, in the reaction of eq 1, C−H bond activation would occur with concomitant formation of a C−S bond as the first step, prior to the addition of another bridging sulfur atom to the olefinic carbon, although we were not able to isolate or observe the corresponding intermediate analogous to **4** in the case of pentene by using 5 equiv of silver salt.[21] The double bond character of the S═S unit in the $Ru^{III}SSRu^{III}$ core has been reported.[14,22,23] Although both electrophilic and nucleophilic attacks of sulfido ligands on olefinic carbon have been assumed as the key step in the olefin insertion into a μ-S−H bond of hydrosulfide bridged dinuclear molybdenum complexes,[5,10] a C−H bond activation via addition of the allylic C−H bond to the S═S bridging ligand is considered to be more rational in the present system (Scheme 1),[24] which has been confirmed somehow by the reaction of complex **1** with conjugated dienes giving (2 + 4) addition products.[25] The fact that $Ru^{II}SSRu^{III}$ complex **5** did not react with ketones[3] or any olefins suggests that a $Ru^{III}SSRu^{III}$ core, i.e., higher electron deficiency on the bridging sulfide atoms, is essential for the C−H bond activation reactions. Addition of aromatic C−H bonds to olefins catalyzed by ruthenium(0) complexes has been reported.[6b,26] After the C−H bond activation, anti-Markownikov addition of the S−H bond thus formed to the terminal double bond of the pentenyl moiety follows to form **3** having a dithiolane moiety. As a whole, a hydrogen atom in the allylic position of 1-pentene is transferred to the internal olefinic carbon.

Supporting Information Available: Experimental procedures for the preparation, NMR data, and elemental analysis of **3** and **4** and X-ray data for **3** and **4** (PDF). This mateial is available free of charge via the Internet at http://pubs.acs.org.

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[19] Crystal data for **4**: $C_{34}H_{69}O_{12}N_8F_{24}S_2P_8AgRu_2$, $T = 293$ K, $M_r = 1859.85$, pale green, triclinic, $P\bar{1}$, $a = 19.430(6)$ Å, $b = 22.858(7)$ Å, $c = 16.741(4)$ Å, $\alpha = 99.99(2)°$, $\beta = 93.68(2)°$, $\gamma = 104.92(2)°$, $V = 7029(3)$ Å^3, $Z = 4$, $R = 0.087$, $R_w = 0.104$, GOF = 1.69.

[20] There are two independent molecules in one unit cell of crystal **4**, and there is not any basic difference in the RuSSRu core and the cyclohexenyl group between these two. However, in one molecule, the silver ion is coordinated by S, 2N of 2MeCN, and a double bond (Figure 2), whereas in the other molecule, the silver ion is surrounded by S, N of MeCN, O of $P(OMe)_3$, and a double bond (see the Supporting Information). A bridging sulfur atom coordinated to the silver ion causes a decrease of the torsion angle of Ru(1)−S(1)−S(2)−Ru(2) (130.3°) in **4** compared to that in **3** (−157.15°).

[21] The reaction of **2** with 1-pentene in the presence of 4 or 5 equiv of silver salt in MeCN gave a mixture of ruthenium dinuclear complexes, none of which contained a silver atom. The details of identification of the mixture will be submitted soon.

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[24] In this step, precoordination of the double bond of 1-pentene to the ruthenium atom by replacement of an MeCN ligand may be taking place to facilitate the C−H bond activation.

[25] The results of the reaction of **1** with dienes, such as isoprene and 2,3-dimethylbutadiene, will be submitted soon.

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