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Novel C–H activation and C–S formation reactions on disulfide and diselenide ligands in dinuclear ruthenium complexes

Kazuko Matsumoto *, Hiroyasu Sugiyama

Department of Chemistry, School of Science and Engineering, and Advanced Research Institute for Science and Engineering Waseda University, 3-4-1 Ohkubo, Shinjuku, Tokyo 169-8555, Japan

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Abstract

The C–S bond formation reactions of the transition metal sulfides with organic molecules are collected and reviewed to understand the reactivity of the sulfide ligands supported by the transition metals. As an example of the role of the sulfide, the C–H bond activation is focused and discussed.

Keywords: C–S bond formation; C–H bond activation; Disulfide

1. Introduction

Inorganic sulfides on transition metals are usually not very reactive. Reactions with organic molecules to form C–S bonds with the disulfide ligands are limited to a few cases, which are shown in Scheme 1. Although C–S bond formation is the reverse reaction of C–S bond cleavage, which is an important key reaction in the industrial hydrodesulfurization (HDS) process [1–6], C–S bond formation has not been studied intensively. Recently, HDS [7–12] has been attracting increasing interest from chemists due to its close relation to certain environmental problems. As a basic approach to transition metal–sulfide chemistry, C–S bond formation is a convenient probe to understand more deeply the nature of sulfide ligands. Scheme 1 shows examples of previously reported C–S bond formation reactions [13–27]. These reactions are explained as bond formations between unsaturated carbon atoms and the sulfur ligands on the metal centers (Scheme 1).

The last example above, the reaction of Cr disulfide with diazomethane, can be considered as the addition of an unsaturated carbon atom, carbene, to the sulfur atom, and may be classified rather to the reaction type shown in Scheme 2 [28–30]. The second type of C–S bond formation includes C–X cleavage and addition of the carbon atom to the sulfide (Scheme 2). In most cases, the reactions are easily understood by considering the polar and activated C–halogen bonds [31–35]. However, C–S bond formation via C–H bond activation, such as in reactions (h) and (i) in Scheme 2, rarely occurs, and as such only a few reactions have been previously reported, none of which having complete systematic studies (Scheme 2) [36,37].

Through our studies of C–H activation by dichalcogenide bridged dinuclear Ru complexes, we will demonstrate the unique properties of the reactive bridging dichalcogen. The scope and limitation for the reaction of unsaturated hydrocarbons based on C–H activation will be summarized in the following chapters. Although C–H bond activation is mainly described in this review,

* Corresponding author. Tel.: +81 352 863 108; fax: +81 352 733 489.
E-mail address: kmatsu@waseda.jp (K. Matsumoto).

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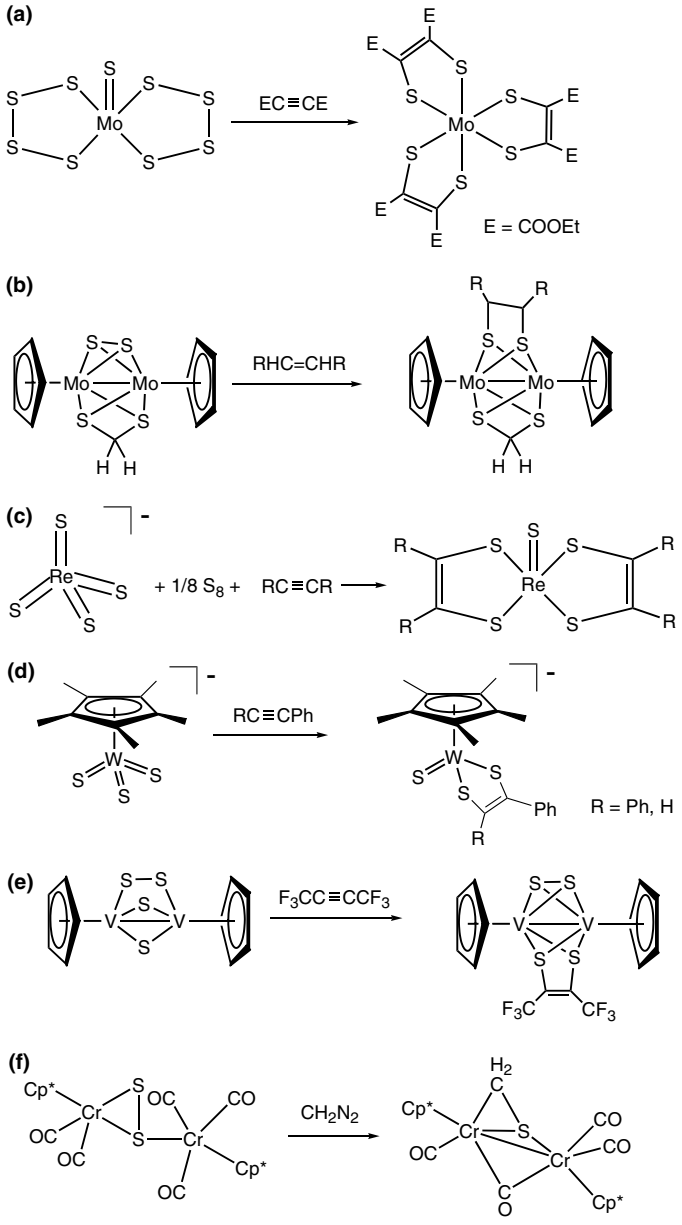
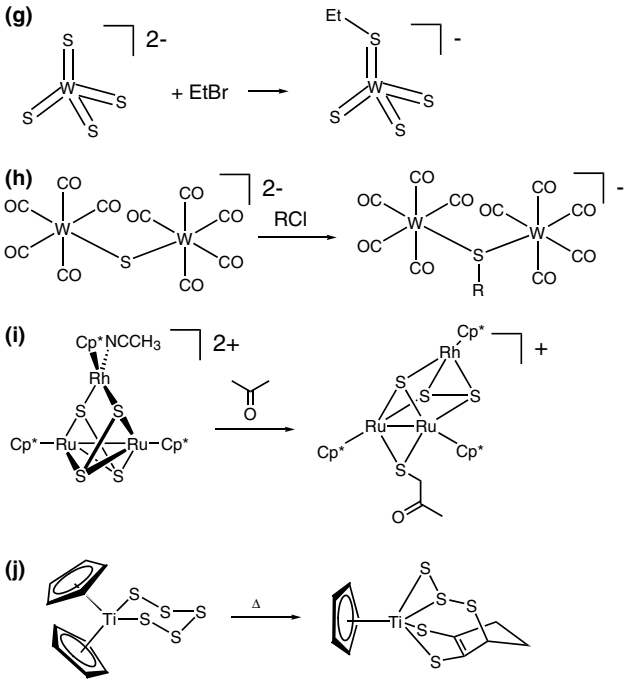


Scheme 1.

the present study is a milestone in our approach to the activation of small molecules.

2. Reactions of dichalcogenide-bridged dinuclear Ru^{III} complexes

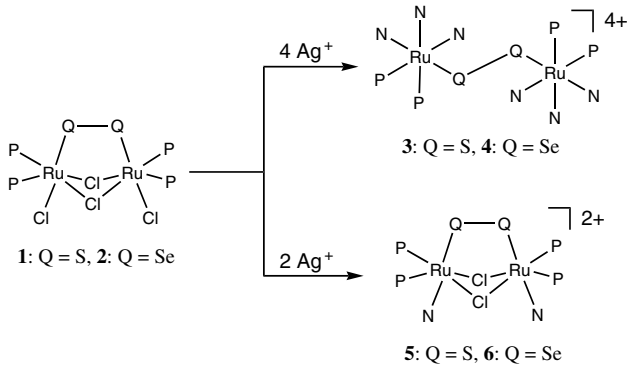
Among the many varieties of polychalcogenide ligands and their complexes [38–40], disulfide and its selenium analogue are especially noteworthy due to the fact that their strong π-coordination significantly alters the electronic properties and redox potential of the complexes significantly. The variety of coordination modes available for disulfide is another attractive point to be studied. The μ-η^1:η^1-disulfide [41–52] coordination mode in ruthenium complexes is the primary focus of this article. Due to the strong back-donation of Ru^{III} and Ru^{II} the disulfide exhibits novel properties. The $Ru^{III}SSRu^{III}$ core structure in $[\{Ru(NH_3)_5\}_2(\mu\text{-}S_2)]^{4+}$ and $[\{CpRu(PR_3)_2\}_2(\mu\text{-}S_2)]^{2+}$ consists of two $17e^-$ fragments with the two formally unpaired electrons of the two Ru^{III} centers being delocalized in the core. Three types of electronic configurations can be suggested for the core: contributions from: (i) two Ru^{III} and S_2^{2-}, (ii) Ru^{II}, Ru^{III} and S_2^- (supersulfide), and (iii) two Ru^{II} and neutral S_2. The contribution from (iii) was shown to be negligible through spectroscopy studies [41–46].



Scheme 2.

Since our first report of the disulfide-bridged Ru^{III} dinuclear complex, $[\{Ru(P(OCH_3)_3)_2Cl\}_2(\mu\text{-}S_2)(\mu\text{-}Cl)_2]$ (**1**) [53], we have developed various C–H cleavage and C–S formation reactions of unsaturated organic molecules on the disulfide ligand [54–63]. The selenium analogue, $[\{Ru(P(OCH_3)_3)_2Cl\}_2(\mu\text{-}Se_2)(\mu\text{-}Cl)_2]$ (**2**), has also been synthesized and similar reactions were performed [64]. Abstraction of the chloride from **1** and **2** in CH_3CN gives a series of cationic complexes (Scheme 3), which are more reactive than the parent compounds [65,66].

Spectroscopic and structural analyses have suggested a delocalized electronic structure for the $Ru^{III}SSRu^{III}$ unit in the complexes **1**, **3**, and **5**. This is the starting point for the exploration of the novel reactivity of the S–S bonds in our systems.



Scheme 3.

3. Reactions with dienes

Dienes react with the tetra- and di-cationic disulfide and diselenide complexes **3**–**6** to give C_4S_2 six-membered ring complexes (Scheme 4) [67,68].

Formally speaking, these reactions are [4 + 2] cycloadditions into the disulfide ligand. Such reactions are also known to expel disulfur, which is generated in situ from the pyrolysis of the appropriate precursors and used for organic disulfide compound syntheses (Scheme 5) [69–77]. Free disulfur is not stable, and therefore compounds **3**–**6** can be considered as dichalcogen stabilizers.

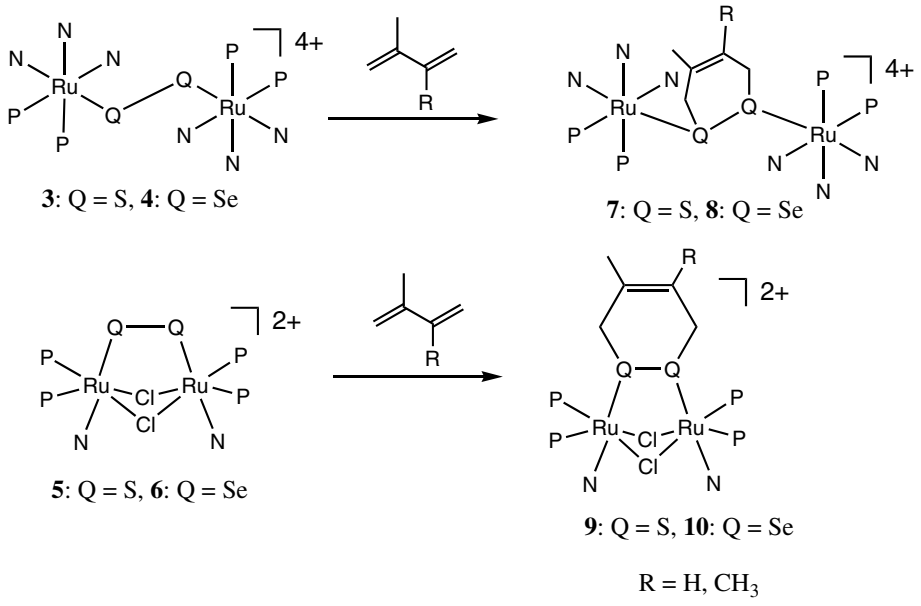
A similar type of cyclization reaction is also reported for disulfur oxide (Scheme 6) [78,79].

Unlike free disulfur, bridging disulfurs in **3** and **4** are stabilized by the two Ru^{III} atoms and yet maintain their high reactivity. Interestingly, reactivity of the disulfide is sensitive to the coordinating environment around the two Ru^{III} atoms. Substitution of the phosphite or other ligands on the Ru atoms has an unexpectedly large effect on the reactivity. For example, $[\{(C_5H_5)Ru(PPh_3)_2\}_2(\mu\text{-}S_2)]^{2+}$ did not appear to react with the dienes. The minor change from $P(OCH_3)_3$ to $P(CH_3)_3$ in **3** and **4** caused a complete loss in reactivity. Compared to reactions with other unsaturated organic molecules discussed in the next sections, dienes are most reactive towards the RuSSRu and RuSeSeRu compounds. Either a concerted or stepwise mechanism is involved in the reaction and, whichever is the case, both carbon atoms accept the additional bond to the sulfur with ease, contrary to the complicated bond metathesis involved. As described above, most previously known C–S bond formation reactions are found between sulfur and unsaturated carbon atoms. In addition, the C_4S_2 six-membered ring seems to be a structurally stable and favorable conformation and can sometimes be formed through quite a different reaction pathway, which will be mentioned later. Norbornadiene also reacts with complexes **3**–**6** to give the corresponding adducts (Scheme 7). The reactivity is expected based on the reactions of molecular disulfur (Scheme 7) Figs. 1 and 2 [69–77].

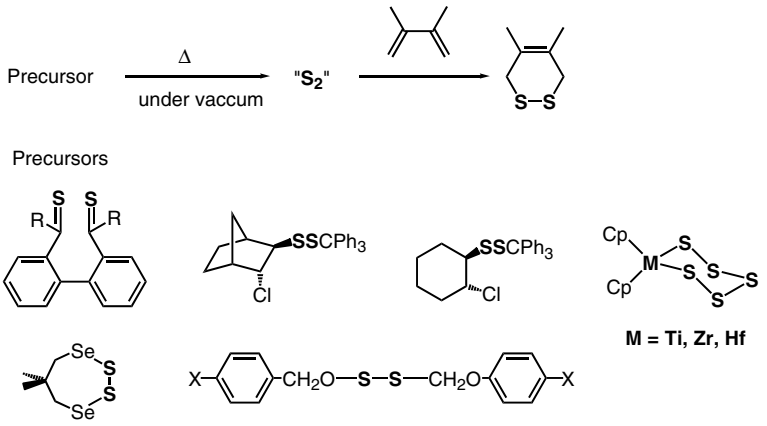
4. Reactions with ketones

Ketones react with tetra cationic complexes **3** and **4** to give the ketonated complexes via C–H/C–S bond metathesis at the α-position of the carbonyl group (Scheme 8) [80,81]. In the overall reaction, the cleaved hydrogen is released as a proton and is coupled to the counter-anion. Even though the reaction products may be considered as enolate adducts, the reaction does not undergo via preliminary generated enol from the ketone.

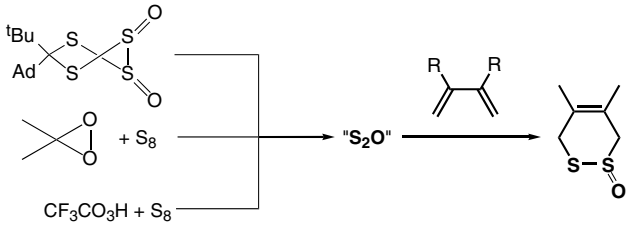
For example, acetylacetone, which is almost completely tautomerized to the enol form, is totally inert



Scheme 4.



Scheme 5.

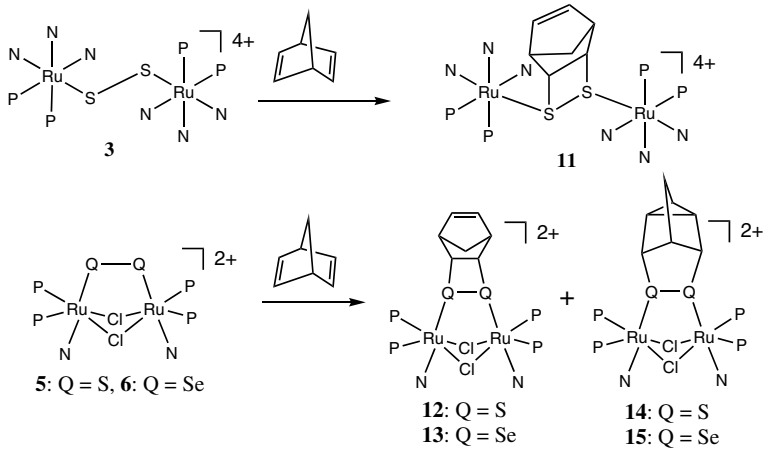


Scheme 6.

to both **3** and **4**. As shown in Scheme 8, in situ generated **3** or **4** from **1** or **2** also reacts with ketones to form the ketonated complexes. When the ketone has two possible α–C–H bonds to be activated, the selectivity depends on the reaction temperature. For example, the reaction of butanone gives two possible products arising from methylene and methyl C–H activations. The former is favored at low temperatures, whereas the latter is favored at high temperature. The C–H bond with the higher electron density seems to be favorably activated, however, at higher temperatures steric hindrance may also operate to change the selectivity. The C–S forming process proceeds in the reaction cavity of **3**, i.e., the bridging disulfide between the two Ru moieties. The cavity size is critical as it affects the reactivity for even the smallest unsymmetric ketone, butanone. Steric factors determine the activation site on the ketone, especially at higher temperatures as in most ketone reactions.

5. Reactions with alkenes and alkynes

Reaction of the tetra-cationic complexes **3** and **4** with terminal alkenes gives C_3Q_2 (Q = S, Se) five-membered



Scheme 7.

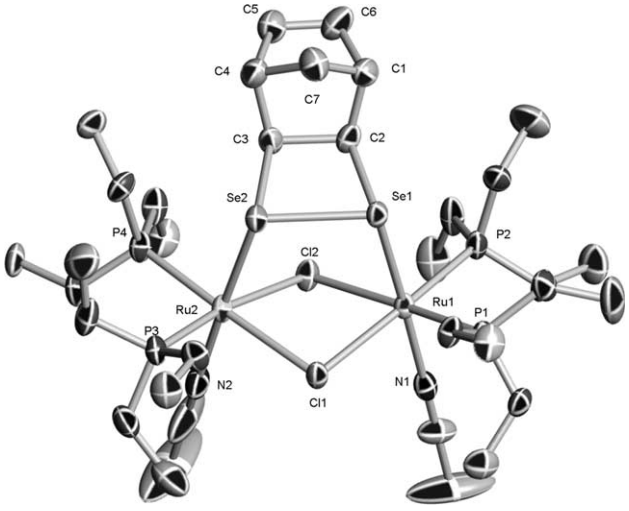


Fig. 1. Structure of complex **13** (drawn at 30% probability level).

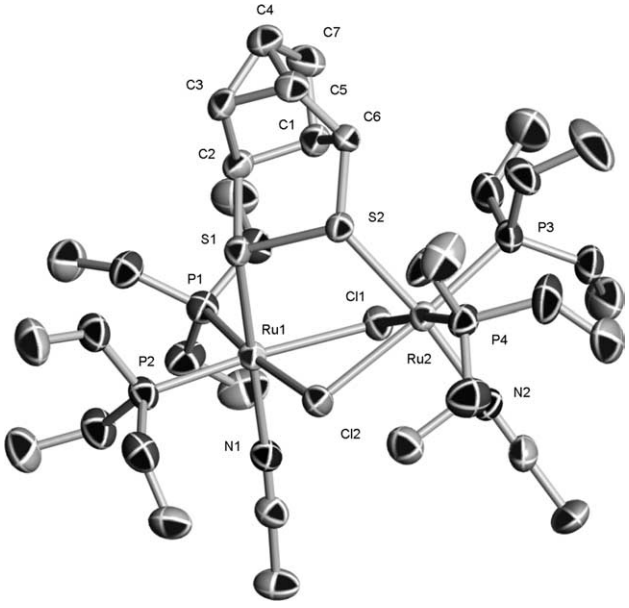
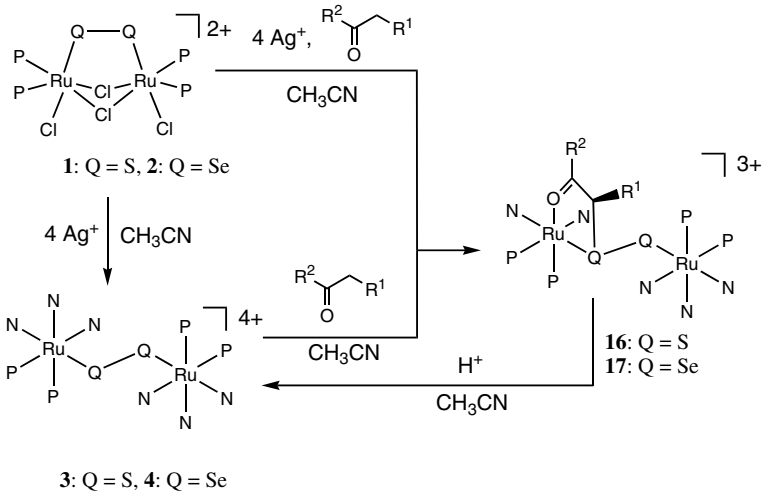


Fig. 2. Structure of complex **14** (drawn at 50% probability level).

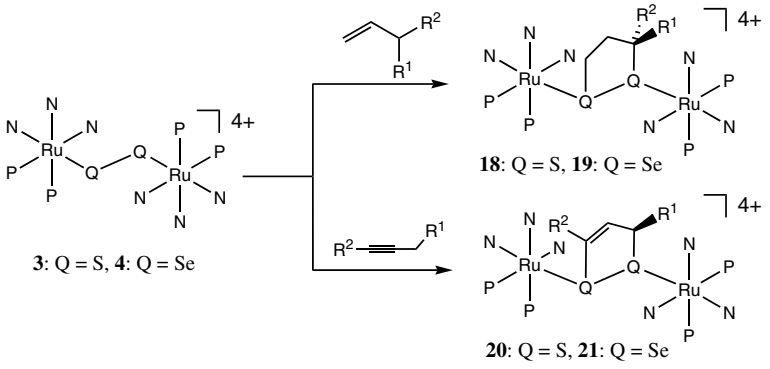
ring complexes, $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_3\}_2(\mu\text{-}QCH_2CH_2CR^1R^2Q)]^{4+}$ (Scheme 9) [82,83]. In the reaction, an allylic C–H bond is cleaved and replaced by a C–Q bond, shifting the released hydrogen to the neighboring carbon atom. Another C–Q bond is formed between the terminal carbon atom and the sulfur atom to cyclize a C_3Q_2 ring. The disulfide complex **3** does not react with internal alkenes, as opposed to the diselenide complex **4**. However, in the latter case a complicated reaction takes place to give a mixture of several complexes, including a rearrangement of the substrate alkene. In contrast, both terminal and internal alkynes react with **3** and **4** to give the corresponding unsaturated C_3Q_2 five-membered ring complexes, $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_3\}_2(\mu\text{-}QCR^1{=}CHCHR^2Q)]^{4+}$ (**20** and **21** in Scheme 9) via activation of the propargylic C–H bond [84].

The isolation of products **20** and **21**, from the internal alkyne reactions, is much easier than those from the terminal reactions, which contain unidentified side-reaction products in the reaction mixture. Recently, transition metal mediated [3 + 2] cycloadditions between allenyl-type alkyne and disulfur oxide or sulfur dioxide have been reported and seem to be similar to our reactions (Scheme 10) [85]. Another example of [3 + 2] cycloaddition is the reaction of zwitterionic 1,3-dipoles, having nitrogen and/or oxygen rather than carbon, with alkenes or alkynes (Scheme 11) [86].

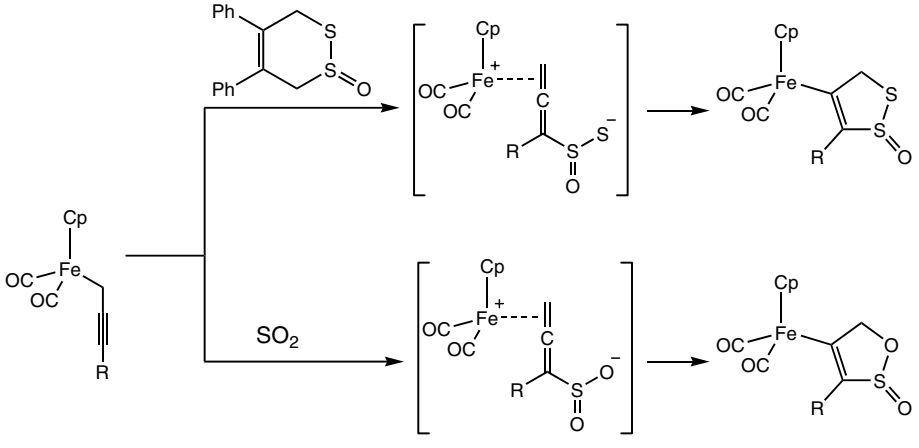
In the cyclizations found in our systems, C–H bond cleavage is the key step towards forming a new C–S bond. A significant primary isotope effect was observed ($k_H/k_D = 9$) in the reaction of **3** with 1-pen-



Scheme 8.



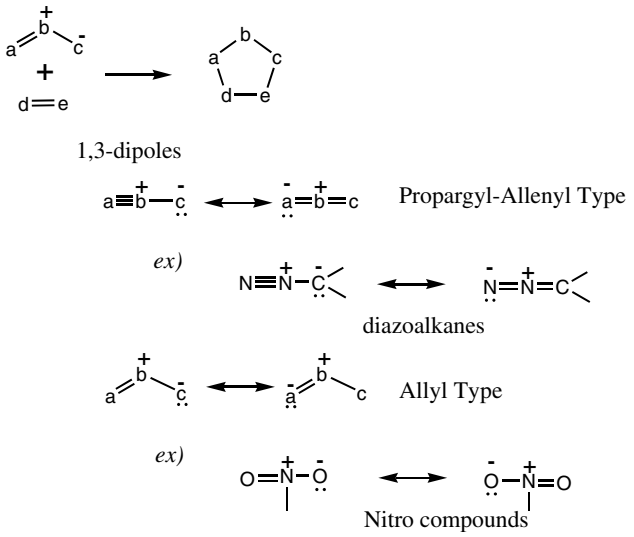
Scheme 9.



Scheme 10.

tene-3,3-d_2, which indicates that the C–H bond cleavage is the rate-determining step. Methylenecycloalkanes also react with **3** or **4**, but in this case various reaction patterns are observed, as summarized in Scheme 12, in which the ring size seems to control the reaction.

As shown in Scheme 12, the products are somewhat different from what is expected from the analogous

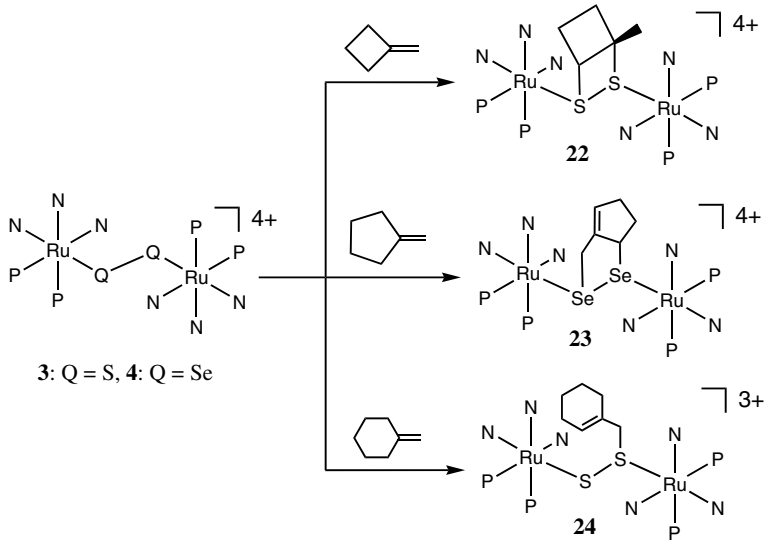


Scheme 11.

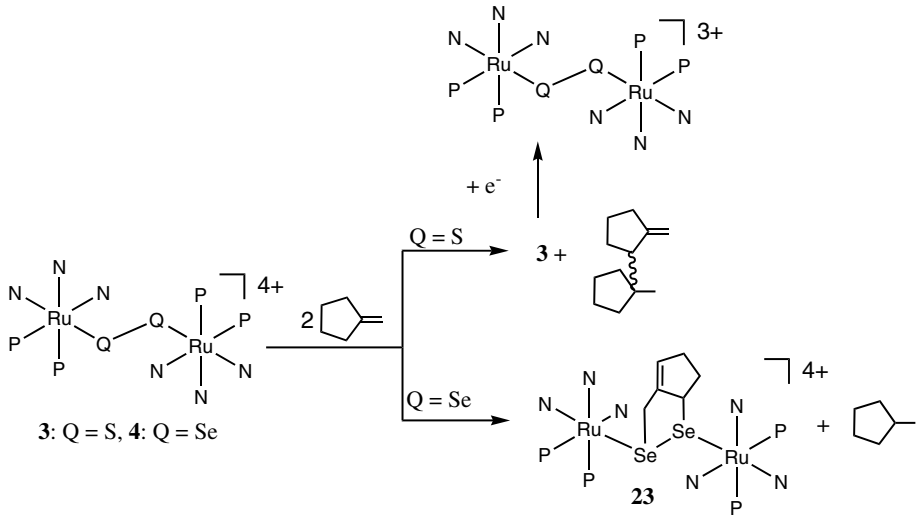
reactions of linear terminal alkenes in Scheme 9. Methylenecyclobutane gave a sterically strained C_2S_2 four-membered ring. The ring is further strained by the adjacent C_4 ring of the original substrate. The product from methylenecyclopentane appears virtually unchanged, however, two hydrogen atoms are eliminated during the reaction. A hydrogen atom is released as a proton in the reaction with methylenecyclohexane to give the tricationic complex **24**. In the reaction of **3** with methylenecyclopentane, dimerization products of the substrate were found in GC–MS analysis (Scheme 13). In the analogous reaction of **4** with methylenecyclopentane, two hydrogen atoms are lost to give complex **23** (Scheme 13). The two hydrogen atoms seem to be captured by another molecule of the substrate to give methylcyclopentane. Although both **3** and **4** react with 2 equivalents of methylenecyclopentane, the reaction cavity size of **4** allows the formation of the adduct on the diselenide ligand, whereas **3** cannot accept the substrate in the same way and releases the dimerization products (Scheme 13) Fig. 3.

6. Elimination reactions

When hydroxyl or halo substituted unsaturated substrates are used, various reaction products are obtained via elimination of H_2O or HX [87,88]. Almost all of these reactions proceed via activation of the allylic or propargylic C–H bonds. An example of H_2O elimination, is observed in the reaction of **3** or **4** with 3- buten-1-ol to give $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_3\}_2(\mu\text{-}QCH_2CH{=}CHCH_2Q)]^{4+}$, which is formed via the elimination of allylic hydrogen and the OH group on the adjacent carbon atom (Scheme 15). The same product is formed from the butadiene addition reaction. Similar to the hydroxyl group, halides are also good leaving groups and are eliminated as HX. As shown in Scheme 14, when the OH in 3-buten-1-ol is replaced by Cl, the "butadiene adduct" is obtained. In addition, the reaction of **3** with 3-chloro-1-butene gives the same product. The reaction of **3** with allyl halide gives the C_3S_2 ring compound **27**, demonstrating that the allyl halide acts like propyne. Actually, compound **27** is more easily obtained from the allyl halide rather than from propyne gas, since propyne gas or other terminal alkynes also give unidentified side-reaction products. This fact suggests



Scheme 12.



Scheme 13.

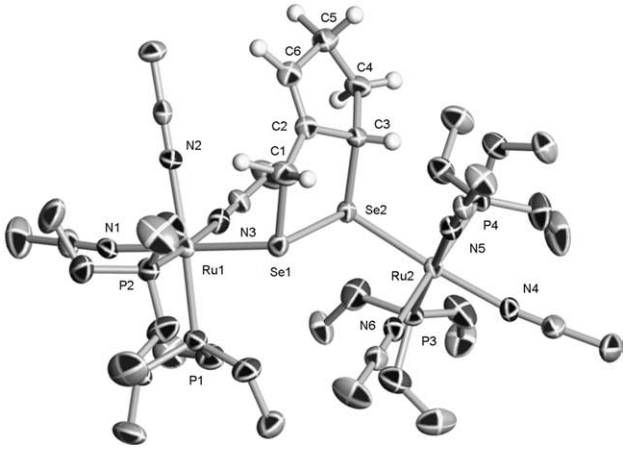
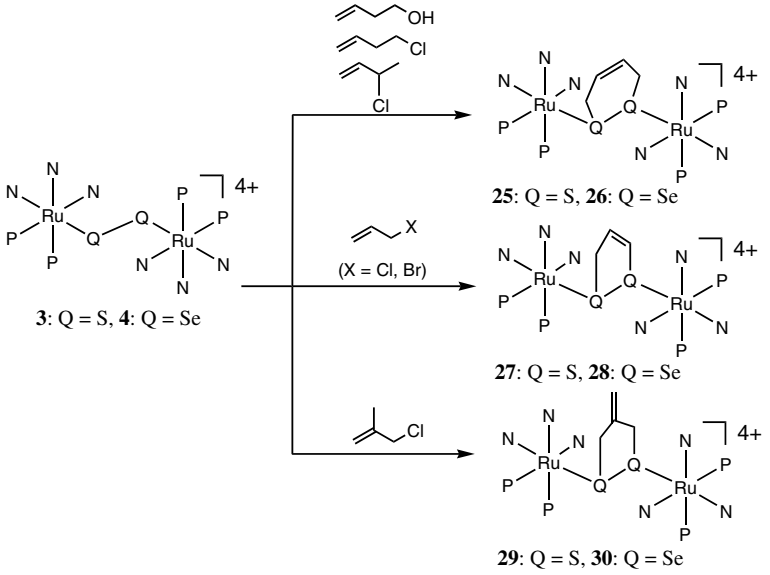


Fig. 3. Structure of complex **23** (drawn at 30% probability level).

that in the reactions with terminal alkynes, the unsaturated five-membered ring may further react with the substrate alkyne (Scheme 14) (Figs. 4 and 5). On the other hand, the unsaturated five-membered ring is also formed through the reaction with halo alkenes, and in this case the excess amount of the substrate does not seem to react further with the C_3S_2 complex. Even the equivalent amount of released HX does not interfere with the reaction. The reactions with halo-substituted substrates are significantly slower compared to the non-substituted ones. Interestingly, methally chloride reacts with **3** or **4** to give a methylene substituted C_3S_2 five-membered ring via activation of the methyl C–H bond. This reaction occurs visibly faster than the usual halo-alkene reactions.



Scheme 14.

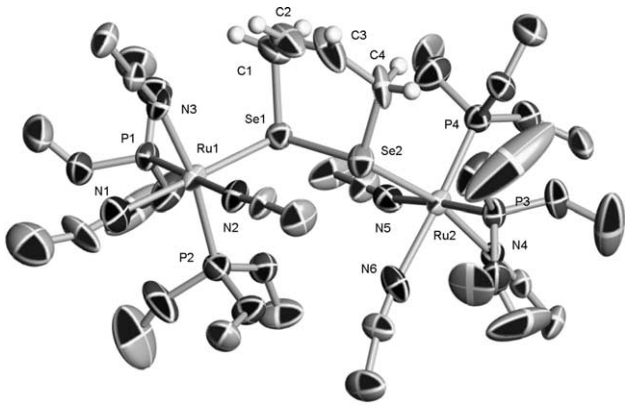


Fig. 4. Structure of complex **26** (drawn at 30% probability level).

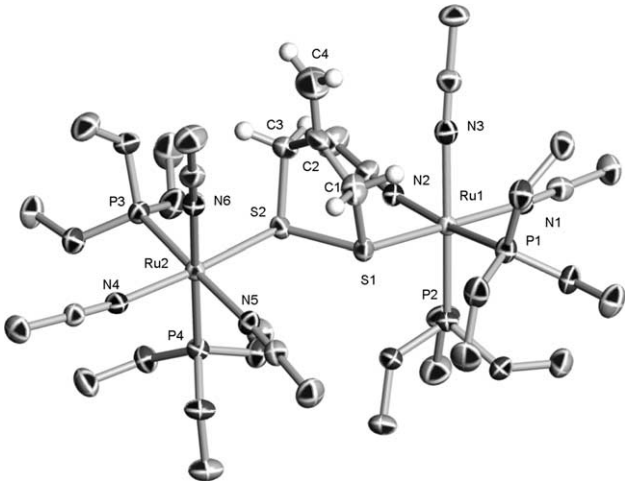


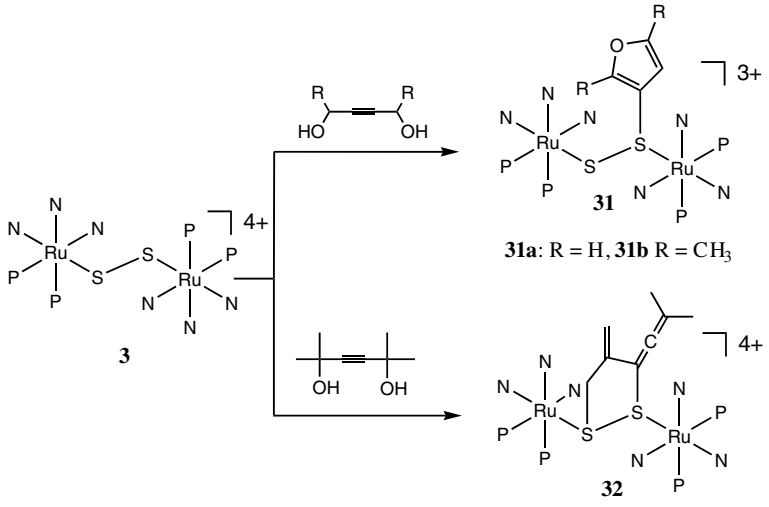
Fig. 5. Structure of complex **29** (drawn at 50% probability level).

Other intramolecular eliminations are also observed in propargyl diol reactions (Scheme 15). For example, HO(R)HCCCH(R)OH (R = H, CH_3) reacts with **3** to give furan adducts, $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_3\}_2\{\mu\text{-}SSC{=}RO(R){=}CH\}]^{3+}$ (**31**). In these reactions, both diols have propargyllic C–H bonds which can be activated. Surprisingly, 2,5-dimethyl-3-hexyn-2,5-diol, which has no propargyllic C–H bonds, also reacts with **3** to give an addition product via elimination of two H_2O molecules (Scheme 15).

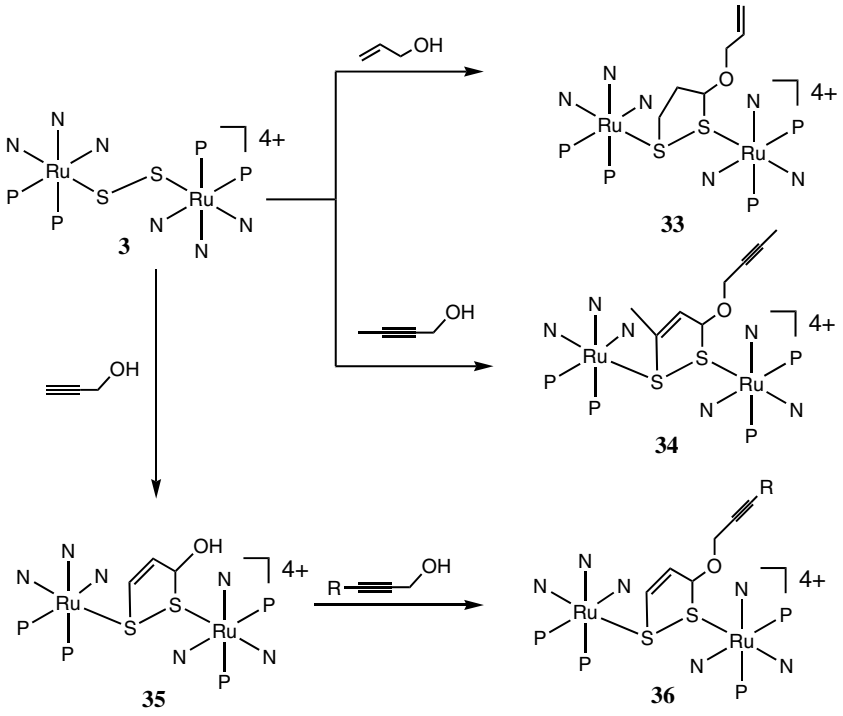
The formation of the methylidene-allenylidene complex **32** involves elimination of the two OH groups and two H atoms, one from each of the CH_3 groups attached to the same carbon. It is noteworthy that the C–H activation takes place at the non-propargyllic position in this reaction. No other example of such a reaction has been found. Our results are not limited to intramolecular eliminations, as intermolecular reactions were also observed. The reactions of allylalcohols or propargylalcohols show condensation coupling via intermolecular elimination of H_2O (Scheme 16) (Figs. 6 and 7). When the propargylalcohol is used, the hydroxyl intermediate **35** is isolable, and reacts further with another propargylalcohol to give the coupled products.

7. Concluding remarks

When a disulfide ligand is supported and activated in a suitable coordination environment, such as in compounds **3** and **4**, the dichalcogenide shows various reactivities with a wide range of organic substrates. Not only are these reactions noteworthy for their pure science insights, but also for the future application of these reactions towards the synthesis of organosulfur or organoselenium compounds. We have discussed the function of disulfide and diselenide as the reaction center rather than as the supporting ligands based on an analogy of the transition metal centers in metal complexes



Scheme 15.



Scheme 16.

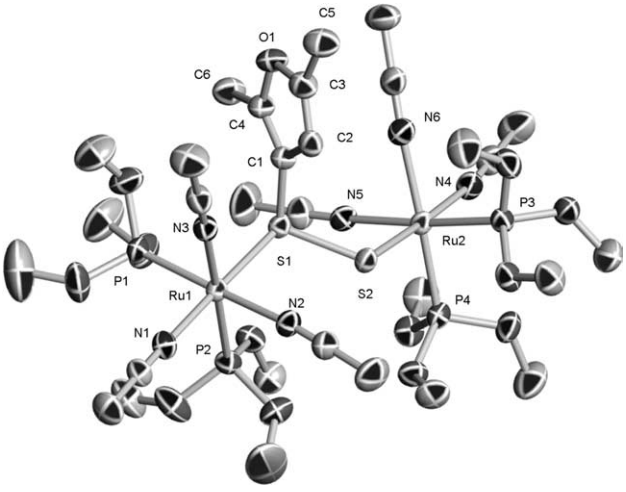


Fig. 6. Structure of complex **31b** (drawn at 50% probability level).

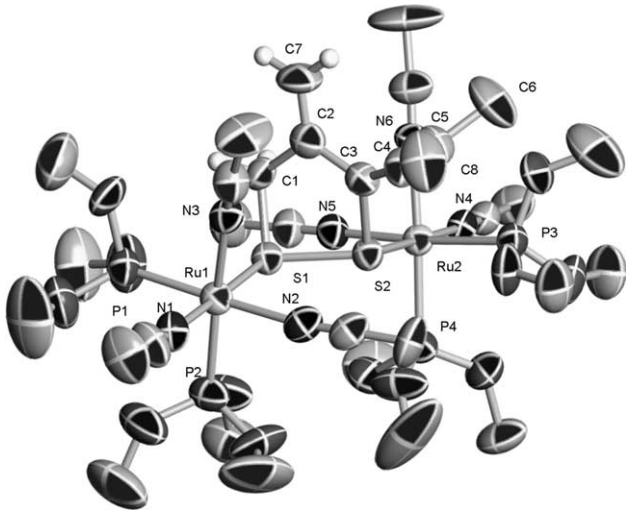


Fig. 7. Structure of complex **32** (drawn at 30% probability level).

[89]. Organic molecules are captured by the disulfide or diselenide bridge via C–S (or Se) bond formation, and then are transformed on the dichalcogenide cores to other molecules. The reaction of **3** with two molecules of methylenecyclopentane should be noted, since dimerization takes place in the reaction. Analogously, coupling reactions of allyl- and propargyl alcohols also involve a two-step reaction with two molecules substrate. We are still intensively studying the effect of the coligands on the Ru atoms in order to tune the reactivity and produce more practically useful systems. It is also noteworthy that the addition of organic molecules is accompanied with an unusual change in the oxidation state. Yielding two Ru^{II} and a neutral C_3S_2 ring (S^{-I} for each S), the final product of the alkene reaction is formed from the starting complex of two Ru^{III} and S_2^{2-} (S^{-I} for each

S). This "reductive addition" may be an important characteristic of our reaction system.

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