Pure Appl. Chem., Vol. 80, No. 5, pp. 993–1003, 2008.
doi:10.1351/pac200880050993

Transition-metal-catalyzed synthesis of organosulfur compounds*

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Abstract: Rhodium complexes are efficient catalysts for the synthesis of organosulfur compounds. They catalyze the addition reaction of organosulfur groups to unsaturated compounds, the substitution of C–H with organosulfur groups, and single-bond metathesis reactions. They cleave S–S bonds and transfer the organosulfur groups to various organic and inorganic molecules, including alkynes, allenes, disulfides, sulfur, isonitriles, imines, diphosphines, thiophosphinites, hydrogen, 1-alkylthio-1-alkynes, thioesters, and allyl sulfides.

Keywords: organosulfur; transition metals; catalysis; addition; C–H substitution; metathesis.

INTRODUCTION

The compounds of heteroatoms in the third row of the periodic table, particularly sulfur and phosphorous, are widely used for drugs and materials, and it is necessary that efficient methods of synthesizing organoheteroatom compounds with sulfur and phosphorous be developed. Compared with oxygen and nitrogen, the second-row heteroatoms, sulfur, and phosphorous are larger, polarizable, and oxidizable, and the synthesis of these organoheteroatom compounds requires different procedures [1].

The synthesis of organoheteroatom compounds involves the process of bond formation between carbon and a heteroatom, and conventional methods in general employ substitution reactions of organohalogen or organosulfonate compounds with heteroatom nucleophiles (Scheme 1). The use of highly reactive leaving groups is essential for this synthesis. A leaving group is introduced in an organic molecule typically by the activation of an alcohol. This method, however, has a serious drawback from the standpoint of efficiency. The introduction of leaving groups requires multistep transformations, and such groups are eventually wasted because they are not incorporated in the product. We considered that the addition of heteroatom reagents to C–C multiple bonds (method 1) and the substitution of C–H bonds by heteroatom reagents (method 2) are preferable, because the substrates are inexpensive and readily available compared with organohalogen compounds, and the processes do not waste leaving groups. The use of elemental heteroatoms for the heteroatom reagent is also considered attractive. The elements are inexpensive and available in large quantities, and in general, the smell of heteroatom elements is weaker than that of other heteroatom reagents often used, such as thiols and phosphines. In studies of new synthetic methods, single-bond metathesis reactions were very important (method 3), and a variety of such reactions involving cleavage of heteroatom bonds were developed. In this article,

*Paper based on a presentation at the 14th International Symposium on Organometallic Chemistry Directed Towards Organic Synthesis (OMCOS-14), 2–6 August 2007, Nara, Japan. Other presentations are published in this issue, pp. 807–1194.
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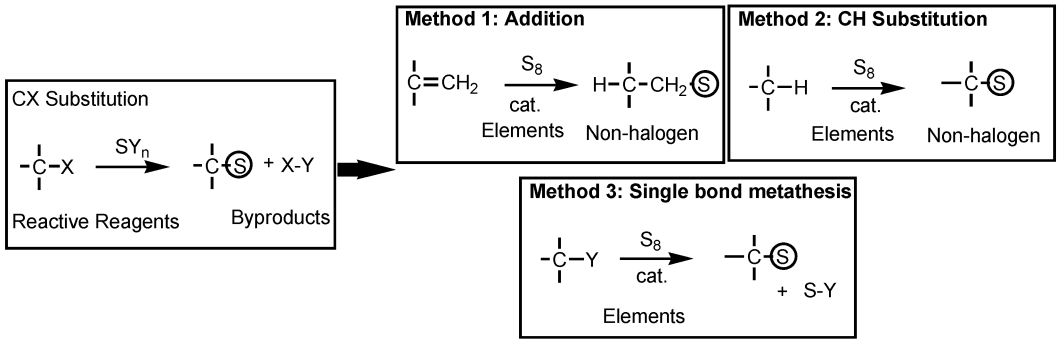
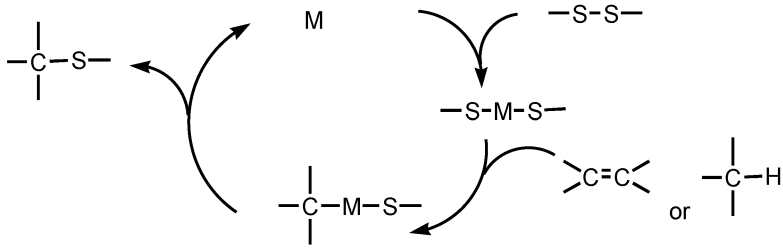


Scheme 1 New synthetic method for organosulfur compounds.

we summarize our results on the synthesis of organoheteroatom compounds by these methods with emphasis on organosulfur chemistry.

Sulfur is not reactive with unsaturated C–C bonds and C–H bonds, and we employ transition-metal catalysis in the transformations. It has been thought however, that transition metals form strong complexes with sulfur reagents and cannot be used to catalyze organosulfur transformations. We show here that rhodium complexes are effective for reactions involving sulfur reagents.

Our study started with the consideration of a possible mechanism for the transition-metal-catalyzed synthesis of organosulfur compounds (Scheme 2). The first step of the synthesis using sulfur should be the cleavage of a S–S bond, for example, by oxidative addition to a low-valent metal complex. The resultant compounds with M–S bonds then activate organic molecules either at the unsaturated bonds or C–H bonds to form organometallic compounds with the C–M–S structure. The C–S bond forms and the active metal species is regenerated. All the processes need to proceed effectively in this cycle. In particular, it is very important to understand the chemical properties of C–M–S intermediates. That sulfur reagents are serious catalyst poisons for transition-metal catalysis may be due to the formation of very strong and inactive M–S bonds, and some methods are required to activate the S–M–S or C–M–S intermediates.



Scheme 2 A putative mechanism cycle for organosulfur synthesis.

One of our approaches in this area is to compare the reactivity of elements in the same region of the periodic table (Fig. 1). Previously, we developed synthetic reactions of organogallium and organotin reagents [2]. These are diagonal elements in the periodic table and exhibit similar reactivity in carbometallation reactions with acetylenes. Comparative studies led to the development of vinylation and alkynylation reactions of enolates, phenols, and anilines [2]. In this study, organometallic complexes of rhodium and palladium were compared as catalysts; they are adjacent elements of groups 9 and 10. Comparative studies of sulfur and phosphorous reagents were also conducted; these are adjacent elements of groups 15 and 16.

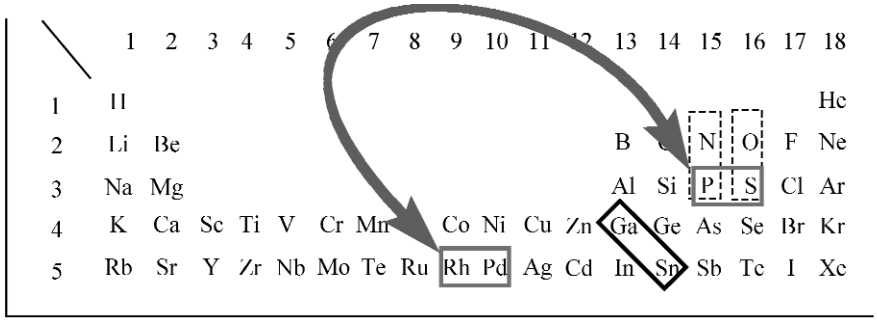
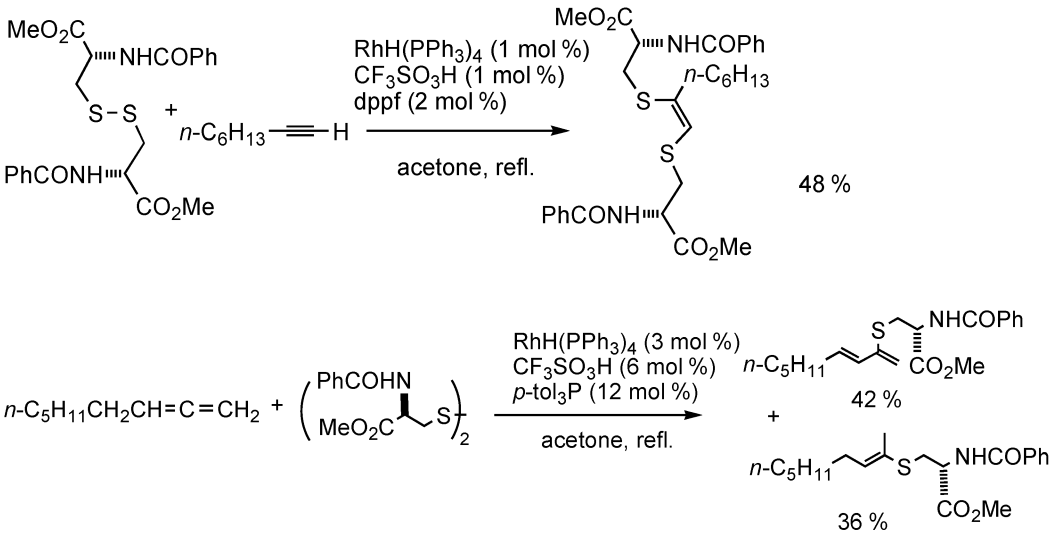


Fig. 1 Use of adjacent metal reagents and catalysts for the development of new synthetic methods.

ADDITION REACTION

We developed an addition reaction of tertiary phosphines to unsaturated compounds, which is catalyzed by rhodium and palladium complexes [3]. The method was applied first to alkynes [4], then to reactive alkenes, allenes [5], and 1,3-dienes [6], and finally to unactivated alkenes including ethylene and propylene [7]. Such a step-up methodology turned out to be effective in this study. We then compared the reactivity of organophosphorous compounds with organosulfur compounds in transition-metal-catalyzed addition reactions.

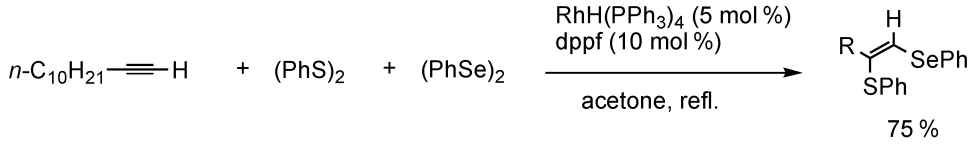
In the presence of a catalytic amount of a rhodium complex $RhH(PPh_3)_4$ (1 mol %), tri(*p*-tolyl)phosphine (2 mol %), and trifluoromethanesulfonic acid (1 mol %), dialkyl disulfides react with terminal alkynes giving (*Z*)-1,2-di(alkylthio)alkenes (Scheme 3) [8]. The reaction proceeds in the *cis*-addition mode. The presence of trifluoromethanesulfonic acid is essential [9]. It is likely that a $Rh–OSO_3CF_3$ species is formed, and the strong electron-withdrawing group accelerates the reductive elimination of C–Rh–S species to form the C–S bonds. A palladium complex was reported to catalyze the *cis*-addition of diaryl disulfides [10], and the rhodium-catalyzed method has the advantage of being applicable to dialkyl disulfides. The reaction of allenes with dialkyl disulfides gives equimolar amounts of 2-alkylthio-1,3-alkadienes and 2-alkylthio-2-alkenes with concomitant hydride transfer [11]. The dif-



Scheme 3 Reactions of disulfides and unsaturated compounds.

ference in the product derived from alkynes and allenes may be ascribed to the nature of the organorhodium compounds: vinylrhodium in the former and π-allylrhodium in the latter.

Phenylthio and phenylseleno exchange reactions proceed between diphenyl disulfide and diphenyl diselenide, and the rhodium-catalyzed addition to 1-alkynes using this equilibrium mixture gives predominantly 1-phenylseleno-2-phenylthio-1-alkenes (Scheme 4) [12]. This novel method constructs C–S and C–Se bonds regioselectively in an organic molecule in one step.

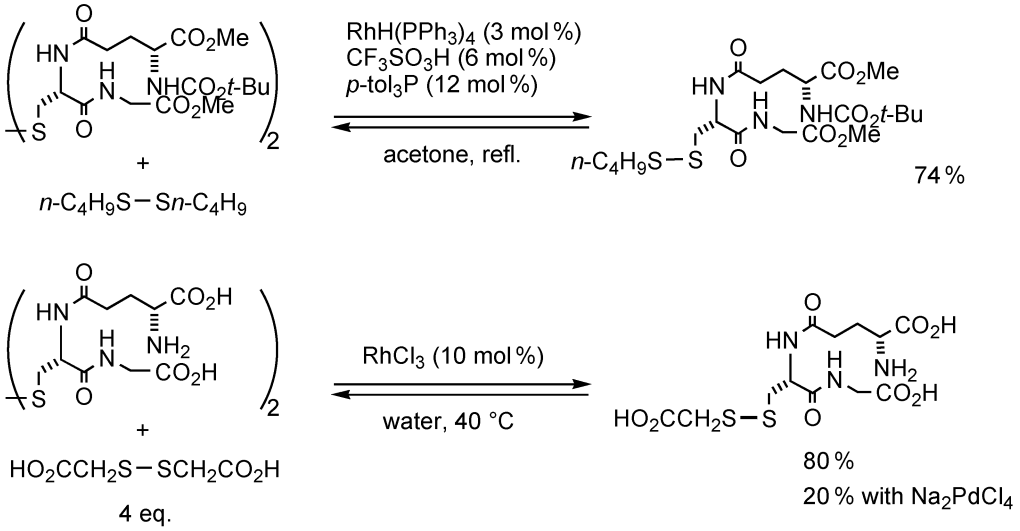


Scheme 4 Selenothiolation reaction of alkynes.

A rhodium complex can cleave S–S bonds of organic disulfides and transfer the organosulfur groups to unsaturated compounds, alkynes, and allenes.

DISULFIDE EXCHANGE REACTION: SINGLE-BOND METATHESIS OF S–S BONDS

The disulfide exchange reaction cleaves the RS–SR bond and transfer the RS group to another disulfide. It proceeds by heating, photoirradiation, and treatment with acid or base [13]. Then an equimolar amount of two disulfides RS–SR and R'S–SR' are reacted, an equilibrium mixture containing R'S–SR, RS–SR, and R'S–SR' in a ratio of 2:1:1 forms if the bond energies of the S–S bonds are identical. The exchange of diaryl disulfides readily takes place by these methods, whereas the reaction of dialkyl disulfides is relatively sluggish. The transition-metal-catalyzed method is effective for the latter reaction [14]. The rhodium complex derived from $RhH(PPh_3)_4$ (3 mol %), tri(*p*-tolyl)phosphine (12 mol %), and trifluoromethanesulfonic acid (6 mol %) catalyzes the disulfide exchange in refluxing acetone, and equilibrium is reached within 15 min (Scheme 5). The reaction is insensitive to various functional groups and is applicable to protected glutathione. The addition of trifluoromethanesulfonic acid is es-



Scheme 5 Disulfide exchange reaction.

sential, and it is believed to accelerate reductive elimination of the S–M–S complex. The exchange of dialkyl disulfides and dialkyl diselenides proceeds with the rhodium complex and yields dialkyl selenosulfides.

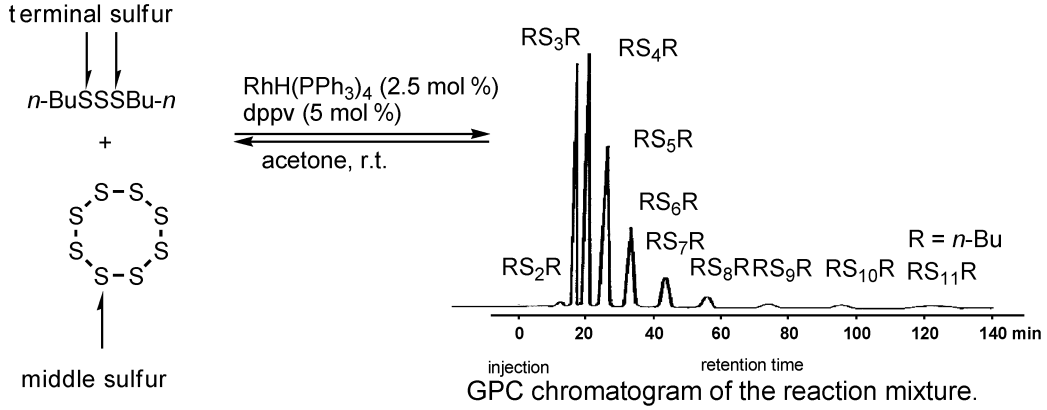
Disulfides are an important functional group for the construction of the tertiary structures of peptides and proteins, and their derivatization is an interesting way to modify their biological activities. $RhCl_3$ is effective at carrying out this transformation in water (Scheme 5) [15]. When unprotected glutathione disulfide and di(carboxymethyl) disulfide are treated in water in the presence of $RhCl_3$ (10 mol %) at 40 °C for 6 h, carboxymethyl *N*-(*N*-γ-glutamylcysteinyl)glycyl disulfide is obtained in 80 % yield.

Other water-soluble, transition-metal chlorides, namely, $CoCl_2$, $IrCl_3$, $NiCl_2{\cdot}6H_2O$, K_2PtCl_4, $FeCl_3$, $RuCl_3$, $OsCl_2$, $MnCl_2$, $YbCl_3$, $EuCl_3$, $CuCl_2$, and $ZnCl_2$, are not at all effective. The only exception is $PdCl_2{\cdot}2NaCl$, which exhibits modest catalytic activity. This behavior is in accordance with our observations of transformations of organophosphorous compounds using rhodium complexes and palladium complexes [4–7]. Certain characteristic features of the Rh–S and Pd–S bonds may be reflected in the activity of these metal complexes.

REACTIONS OF ELEMENTAL SULFUR

Elemental sulfur exhibits reactivity different from those of disulfides in the exchange reaction. The sulfur atom of organic disulfides contains a C–S bond and a S–S bond (terminal sulfur atom), whereas the sulfur atom in higher organic polysulfides and elemental sulfur contains two S–S bonds (middle sulfur atom). The reactivities of the terminal and middle sulfurs are different in principle. For example, an activated intermediate derived from sulfur and a rhodium complex has a Rh–S–S moiety, and that derived from an organic disulfide has a Rh–S–C moiety. These compounds may exhibit different reactivities toward the formation of Rh=S by α-scission, and the reaction may be facile for the Rh–S–S compound. It is, therefore, important to know whether the disulfide reaction can be applied to sulfur.

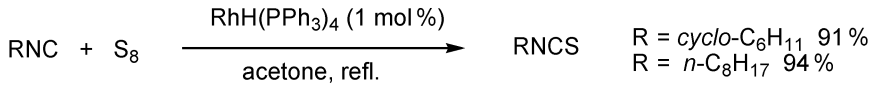
When sulfur and dibutyl trisulfide in acetone are treated with $RhH(PPh_3)_4$ (2.5 mol %) and 1,2-bis(diphenylphosphino)ethylene (dppv) (5 mol %) at room temperature for 5 min, solid sulfur rapidly disappears. High-performance liquid chromatography (HPLC) analysis of the reaction mixture revealed the formation of tetrasulfide, pentasulfide, hexasulfide, and heptasulfide, which were isolated and characterized (Scheme 6) [16]. Higher polysulfides were also detected by HPLC. The use of dppv is essential in this reaction, which may be due to the higher stability of the corresponding rhodium complex. Because the thermal exchange reaction of sulfur and organic polysulfides is generally conducted



Scheme 6 Sulfur atom exchange reaction.

at temperatures higher than 100 °C [17], this result indicates high catalytic activity of the rhodium complex on this reaction.

The rhodium complex can be used for C–S bond formation with sulfur, and the treatment of isonitriles and sulfur in refluxing acetone in the presence of $RhH(PPh_3)_4$ (1 mol %) gives isothionitriles (Scheme 7) [18]. The rhodium catalysis can be applied to the reactions of sulfur.

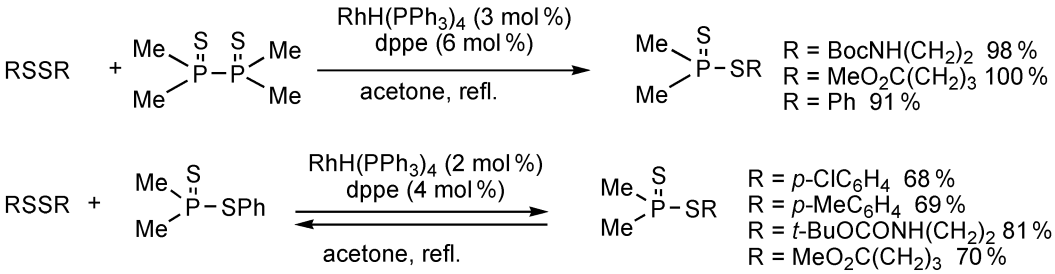


Scheme 7 Sulfurization reaction of isonitriles.

SINGLE-BOND METATHESIS OF S–S AND P-HETEROATOM BONDS

The disulfide exchange reaction can be regarded as single bond metathesis of S–S and S–S bonds, and the rhodium-catalyzed method is extended to the metathesis of S–S bonds with heteroatom bonds containing phosphorous, P–P, and P–S bonds. Dithiophosphinates and thiophosphinates are esters derived from phosphinic acids and thiols, and their synthesis may be carried out by rhodium-catalyzed metathesis.

When an equimolar mixture of tetramethylbiphosphine disulfide and diphenyl disulfide in acetone was heated at reflux for 0.5 h in the presence of $RhH(PPh_3)_4$ (1.5 mol %) and 1,2-bis(diphenylphosphino)ethane (dppe) (3 mol %), phenyl dimethyldithiophosphinate was obtained in 91 % yield (Scheme 8) [19]. The catalyzed reaction of biphosphine disulfides with organic disulfides proceeded at temperatures much lower than that of the reported thermal method, which is between 210–230 °C [20].



Scheme 8 Alkylthiolation reactions of organophosphorous compounds.

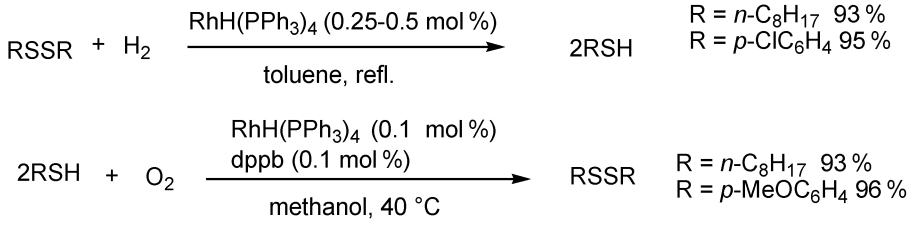
Dithiophosphinates undergo the alkylthio exchange reaction with disulfides under equilibrium conditions, which results in the single-bond metathesis of P–S and S–S bonds. The treatment of phenyl dimethyldithiophosphinate and di(*p*-chlorophenyl) disulfide in the presence of $RhH(PPh_3)_4$ (2 mol %) and dppe (4 mol %) in refluxing acetone for 0.5 h gives *p*-chlorophenyl dimethyldithiophosphinate in 68 % yield (Scheme 8). The rhodium-catalyzed method can be used for the synthesis of compounds possessing multiple sulfur and phosphorous atoms.

DISULFIDE/THIOL INTERCONVERSION

The interconversion of disulfides and thiols is a fundamental transformation in organosulfur chemistry, and such switching plays an important role in biological systems. Among various oxidants and reductants, oxygen and hydrogen are apparently the most convenient. Autoxidation of thiols to disulfides in the presence of a metal complex, typically copper phthalocyanine under alkaline conditions, is well

known [21]. The reaction is considered to involve coupling of sulfur radicals formed from thiolate anions by one-electron oxidation with the metal complex. Hydrogen reduction of a disulfide to a thiol catalyzed by a metal complex was not known, with the exception of the reaction of a cyclic disulfide in the presence of 10 equiv of Pd black [22]. Our study showed that thiol oxidation to disulfide with oxygen and disulfide reduction to thiol with hydrogen are both catalyzed by a rhodium complex.

When 1-octanethiol was reacted under oxygen atmosphere in methanol at 0 °C for 1 h in the presence of $RhH(PPh_3)_4$ (0.1 mol %) and 1,4-bis(diphenylphosphino)butane (dppb) (0.2 mol %), dioctyl disulfide was obtained in 93 % yield (Scheme 9) [23]. No base is required for this reaction. The phosphine is essential in the oxidation reaction, and a trace of disulfide was formed in its absence. Hydrogen peroxide was not detected in the reaction mixture, and the fate of oxygen in this reaction may be conversion to water. The oxidation reaction involves O–O bond cleavages. The same rhodium complex is capable of catalyzing the reduction of disulfides to thiols in the presence of hydrogen. Treatment of dioctyl disulfide with atmospheric hydrogen in refluxing toluene in the presence of $RhH(PPh_3)_4$ (0.25–0.5 mol %) gave octanethiol in 93 % yield. Addition of phosphine inhibited this reaction.



Scheme 9 Disulfide/thiol interconversion reaction.

The thiol oxidation forms S–S and H_2O from S–H, S–H, and 1/2 O_2; the disulfide reduction is a single-bond metathesis reaction of S–S and H–H bonds to S–H and S–H bonds. $RhH(PPh_3)_4$ catalyzes both oxidation and reduction. The structure of the active catalyst, however, appears to be different in the two reactions, because the reduction does not require phosphine, while the oxidation requires dppb. The development of a single catalyst system, which interconverts disulfides and thiols, may be an interesting subject, because such a system is potentially useful as a molecular switch.

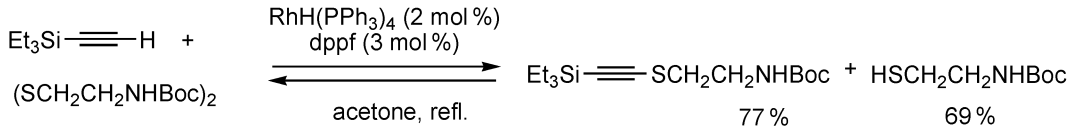
SINGLE-BOND METATHESIS OF C–H AND S–S BONDS

As noted in the introduction, the conversion of a C–H bond to a C–S bond is considered the ideal for the synthesis of organosulfur compounds. During our studies on the rhodium-catalyzed reactions of disulfide, a reaction to convert 1-alkynes to 1-alkylthio-1-alkynes was developed as a rhodium-catalyzed single-bond metathesis of C–H and S–S bonds to C–S and S–H bonds [24]. 1-Alkylthio-1-alkynes are versatile intermediates in organic synthesis, and the conventional methods employ stoichiometric amounts of base. Our rhodium-catalyzed method does not require base.

This reaction was developed during the studies of the addition reaction of dibutyl disulfide and trimethylsilylacetylene to form 1,1,2-trialkylthioethylene (Scheme 10) [25]. Mechanistic studies revealed the formation of 1-trimethylsilyl-2-butylthioacetylene, which indicated the involvement of 1-alkylthiolation of the acetylene C–H.

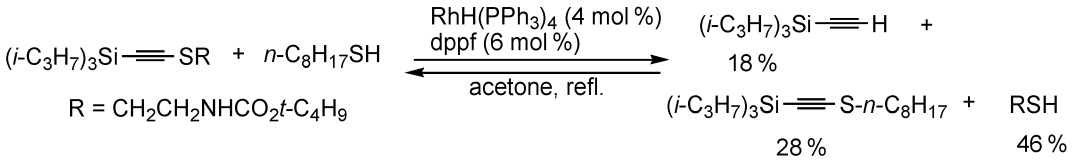
Scheme 10 Trialkylthiolation reaction of silylacetylene.

The treatment of triethylsilylacetylene and bis(*t*-butoxycarbonylaminoethyl) disulfide in the presence of a catalytic amount of $RhH(PPh_3)_4$ (2 mol %) and dppf (3 mol %) in refluxing acetone for 1 h gave the corresponding 1-alkylthioacetylene in 77 % yield along with 2-(*t*-butoxycarbonylamino)ethanethiol in 69 % yield (Scheme 11) [24]. Because the rhodium complex is an active catalyst for the oxidation of thiols to disulfides with oxygen, careful deactivation of the rhodium catalyst is required before workup. The thiol does not interfere with the alkylthiolation reaction, and therefore base is not required in this reaction. Another notable aspect of this reaction is the competition between addition and C–H substitution in the reaction of 1-alkynes and disulfides; using the same system of a rhodium complex and a phosphine, addition takes place in the presence of trifluoromethanesulfonic acid (see Scheme 3), and C–H substitution occurs in its absence.



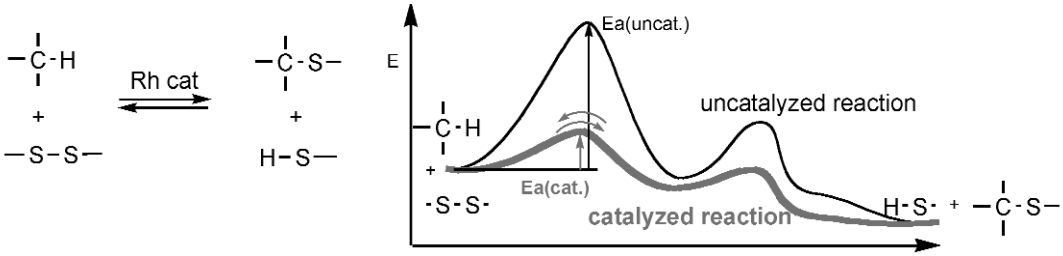
Scheme 11 Alkylthiolation reaction of 1-alkynes.

It has also become clear that this alkylthiolation is an equilibrium. The treatment of a 1-alkylthio-1-alkyne with a thiol in the presence of rhodium catalyst gives the parent 1-alkyne and the alkylthio exchanged 1-alkylthio-1-alkyne, which indicates reversibility of the alkylthiolation reaction (Scheme 12). As is noted in the following, 1-alkylthio-1-alkynes undergo reversible alkylthio exchange via C–S bond cleavage (Scheme 14).



Scheme 12 Equilibrium reaction of a thioacetylene and a 1-alkyne.

The results suggest that a C–S bond can be formed from a C–H bond under equilibrium conditions using transition-metal catalysis, and whether this concept can be applied to other C–H bonds is an interesting question (Scheme 13). Because equilibrium reactions have low activation energies, this methodology avoids the use of excessive energy. Suitable methods to shift equilibrium control the yields of the products and convert the products in starting materials. Such approaches can be interesting in terms of directing organometallic chemistry to organic synthesis.

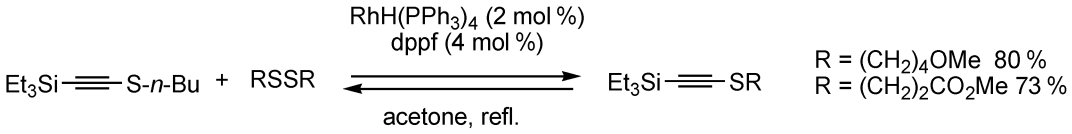


Scheme 13 Catalyzed equilibrium between C–H bond and C–S bonds.

SINGLE-BOND METATHESIS OF C–S AND S–S BONDS

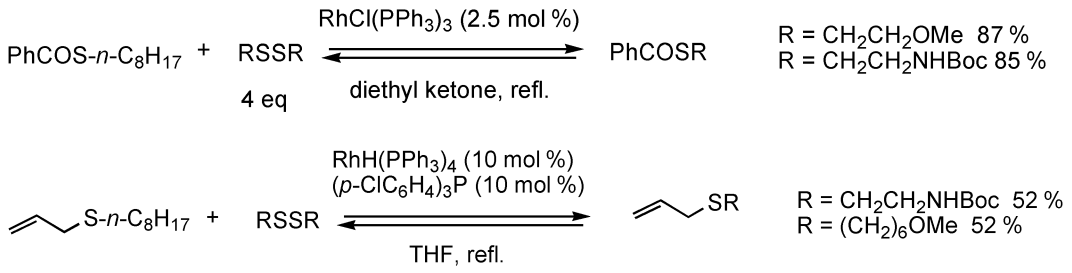
The formation of an alkylthio-exchanged product in the reaction of a 1-alkylthio-1-alkyne and a thiol indicates that the C–S bond is cleaved with the rhodium complex, and a sulfide and a disulfide are expected to undergo alkylthio exchange. Because the cleavage reaction proceeds via organorhodium intermediates possessing the S–Rh–C moiety, studies of such reactions provide information on the reactivity of the S–M–C compounds shown in Scheme 2.

The reaction of 1-butylthio-2-triethylsilylacetylene and dialkyl disulfide in the presence of $RhH(PPh_3)_4$ (2 mol %) and dppf (4 mol %) in refluxing acetone gives an equilibrium mixture of the alkylthio-exchanged product and the starting material (Scheme 14) [24]. This single-bond methathesis reaction of C–S and S–S bonds can be a tool to detect C–S bond cleavage by the metal complex. It is likely that the C–S bond cleavage involves oxidative addition to a low-valent rhodium complex, and by analogy, such processes may be involved in many single-bond metathesis reactions in this work. Rhodium catalysis can be utilized in organosulfur chemistry for both the formation and cleavage of C–S bonds.



Scheme 14 Alkylthio exchange reaction of thioacetylenes.

The rhodium complex cleaves other C–S bonds of organosulfur compounds. In the presence of $RhCl(PPh_3)_3$ (2.5 mol %), thioesters exchange alkylthio groups with disulfides under equilibrium conditions (Scheme 15) [26]. The ester exchange reaction is catalyzed by acid, base, or metal complex, whereas the thioester exchange reaction is not known. An acylrhodium intermediate should be involved, and any other reactivity of the intermediate would be interesting.

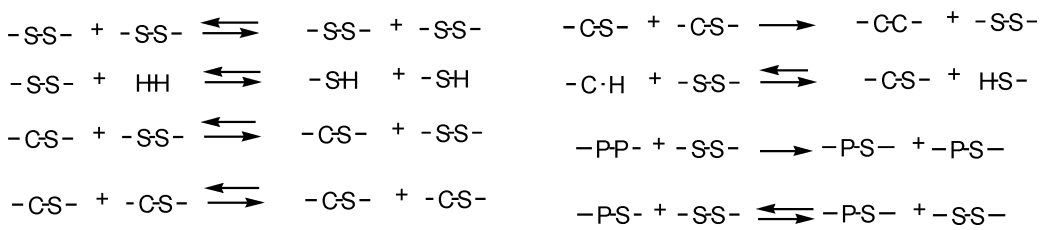


Scheme 15 Alkylthio exchange reactions of organosulfur compounds.

Allyl sulfides also undergo alkylthio exchange with disulfides in the presence of $RhH(PPh_3)_4$ (10 mol %) and tri(*p*-chlorophenyl)phosphine (10 mol %) (Scheme 15) [27]. A π-allylrhodium species should be formed in this reaction. The alkylthio exchange reaction can be conducted with organosulfur compounds, and the use of the organorhodium intermediates formed in these reactions may be a subject of interest.

CONCLUSIONS

Transition-metal-catalyzed methods can be used for the synthesis and transformation of organosulfur compounds and may be applicable to a broad range of compounds. Addition to unsaturated compounds, C–H substitution, and single-bond metathesis reactions (Scheme 16) are very important transformations associated with this methodology.



Scheme 16 Rh-catalyzed single-bond metathesis reactions.

ACKNOWLEDGMENTS

This work was supported by JSPS (Nos. 16109001 and 17689001). M. A. expresses her thanks to the Grant-in-Aid for Scientific Research on Priority Areas, "Advanced Molecular Transformation of Carbon Resources" from MEXT (Nos. 18037005 and 19020008).

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