Metal-Catalyzed Carbon–Sulfur Bond Formation

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Contents

I. Introduction

In organic synthetic reactions, the scope and application of organosulfur chemistry have increased tremendously since sulfur-containing groups serve an important auxiliary function in synthetic sequences.[1] Illustrative examples are the reversal of polarity (Umpolung), the enhancement of the acidity of C–H bonds, and the transfer of chirality from sulfur to carbon.[2] On the other hand, transition metal complex-catalyzed reactions have made a great contribution to the recent growth of organic synthesis,[3] and a wide variety of synthetic transformations with combination of mainly group 8–10 transition metal catalysts with heteroatom-containing compounds such as silicone,[4] tin,[5] and boron[6] compounds is well established. Considerable attention has also been focused on sulfur-containing transition metal complexes as model compounds of both active sites of natural enzymes[7] and catalytic metal surfaces.[8] However, transition metal complex-catalyzed synthetic reactions using sulfur-containing compounds remain open to study, since sulfur-containing compounds have long been known to act as catalyst poisons because of their strong coordinating and adsorptive properties and often rendered the catalytic reactions totally ineffective.[9] In the past decade, the progress in organometallic chemistry has been to overcome the problems such as mismatched combination of transition metal catalysts with sulfur-containing compounds, and several useful transformations of sulfur-containing compounds using transition metal catalysts have been developed.[10]

In this article, transition metal complex-catalyzed organosulfur chemistry leading to selective formation of carbon–sulfur bonds is reviewed with an emphasis on recent progress.[11] Although numerous carbon–sulfur bond forming reactions on the transition metal complexes as a stoichiometric reaction have been reported, the present article surveys only the novel transition metal complex-catalyzed reactions which will open up new opportunities in organosulfur chemistry.

II. Substitution and Related Reactions

A. Reaction of Halides with Sulfur-Containing Compounds

The difficulty of nucleophilic substitution at an sp^2-carbon atom by conventional organic techniques is overcome by using transition metal complexes.[12] As carbon–carbon bond formation by cross-coupling of alkenyl halides with either Grignard reagents or organolithium compounds is an attractive and important pathway for the synthesis of the substituted alkenes, the efficiency of the palladium-catalyzed reaction will be enhanced by stereoselective synthesis of alkenyl sulfides upon treatment of thiolate anions. Since alkenyl sulfides are valuable synthetic precursors of carbonyl compounds[13] and alkynes,[14] various methods for their syntheses have been explored. The major methods, which include Wittig-type reactions,[15] dehydration of β-hydroxy thioacetals,[16] and dehydrochlorination of β-chloro sulfides,[17] use carbonyl compounds as a starting material. Posner et al. reported a two-step synthesis of alkenyl sulfides from alkenyl halides.[18] The first palladium-catalyzed nucleophilic substitution of aryl halides by thiolate anions has been reported by Migita and co-workers. Aryl bromide and iodides were found to react with both aliphatic and aromatic thiols in the presence of sodium *tert*-butoxide and a catalytic amount of Pd-$(PPh_3)_4$ at 100 °C for 18 h to give the corresponding sulfides in high yields (eq 1). The reaction was thought to proceed through a path different from that of the $S_{RN}1$ reaction because it was not inhibited by
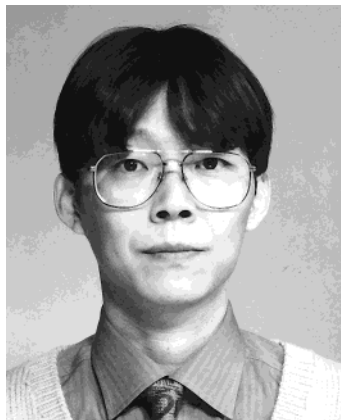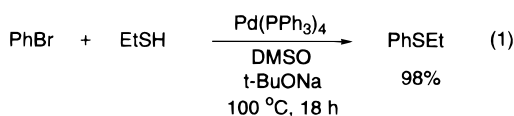
Teruyuki Kondo received his bachelor's degree in 1984, master's degree in 1986, and Ph.D. degree in 1989 from Kyoto University. His Ph.D. studies on the new methodologies for carbon–carbon bond forming reactions using group VII and VIII metal complex catalysts were carried out under the direction of Professor Yoshihisa Watanabe. He joined Kyoto University, Faculty of Engineering, as Research Associate in 1989 and was promoted to Associate Professor of Graduate School of Engineering at the same university in 1996. From 1994 to 1995, he did postdoctoral work with Professor K. Barry Sharpless at the Scripps Research Institute. He received the Progress Award in Japan Petroleum Institute in 1994 and the Progress Award in Synthetic Organic Chemistry, Japan, in 1999. His current research concerns studies on new catalytic performance of organotransition metal complexes toward carbon–carbon and carbon–heteroatom bond forming reactions as well as carbon–carbon bond cleaving reactions.
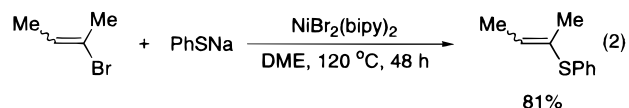
Take-aki Mitsudo received his bachelor's degree in 1967, master's degree in 1969, and Ph.D. degree in 1973 from Kyoto University. He was immediately appointed as Research Associate in the laboratory of Professor Yoshinobu Takegami at the same university. From 1982 to 1983, he carried out postdoctoral research with Professor Richard F. Heck at the University of Delaware. He was promoted to Lecturer in 1989, Associate Professor in 1990, and Full Professor in 1993. His research interests started from the chemistry of η^3-vinylcarbene complexes and have been mainly in exploitation of new synthetic methodology with emphasis in fundamental and industrially important organic reactions, particularly by the application of organometallic chemistry. His recent research interests include design and understanding structural and electronic relationship of novel organometallic complexes bearing catalytic activities for various modes of carbon–carbon bond forming and cleaving reactions.

the presence of p-dinitrobenzene, which is known to be a good inhibitor of the $S_{RN}1$ reaction.[19]

$$\text{PhBr} + \text{EtSH} \xrightarrow[\substack{\text{DMSO} \\ t\text{-BuONa} \\ 100\ ^\circ\text{C, 18 h}}]{\text{Pd(PPh}_3)_4} \text{PhSEt} \quad (1) \quad 98\%$$
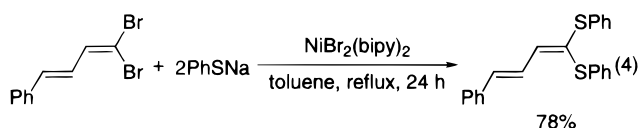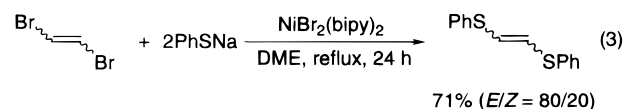
A one-step synthesis of alkenyl sulfides by transition metal complex-catalyzed cross-coupling reaction was also reported by Murahashi and co-workers in 1979.[20] The sulfenylation of (Z)- and (E)-β-bromostyrene with lithium or sodium benzenethiolates in the presence of a Pd(PPh$_3$)$_4$ catalyst at 80 °C gave (Z)- and (E)-(2-phenylethenylthio)benzene in 95% yields in a stereospecific manner, respectively. In the absence of the palladium catalyst, the sulfenylation does not occur with thiolates and only occurs upon treatment with copper methanethiolate at 200 °C.[21] The isomeric purity of each product was over 99.5%.

Synthesis of diaryl sulfides by nickel(II)-catalyzed arylation of arenethiolates was then reported. The catalyst is a newly prepared o-phenylene-bis(diphenylphosphino)nickel(II) bromide complex.[22] A similar synthesis of both alkenyl sulfides and ketene thioacetals by nickel(II)-catalyzed reaction of alkenyl halides with sodium benzenethiolate has been reported (eq 2).[23] In an aprotic solvent such as 1,2-

$$\text{Me} \overset{\text{Me}}{\underset{\text{Br}}{\diagdown}} + \text{PhSNa} \xrightarrow[\text{DME, 120 }^\circ\text{C, 48 h}]{\text{NiBr}_2\text{(bipy)}_2} \text{Me} \overset{\text{Me}}{\underset{\text{SPh}}{\diagdown}} \quad (2) \quad 81\%$$
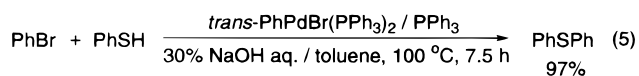
dimethoxyethane and toluene, the desired alkenyl sulfides were obtained in generally good yields. Analogous conditions allow for the disubstitution of either 1,2-dibromoethylene or 1,1-dibromoethylenic compounds (eqs 3 and 4). For the latter, and contrary
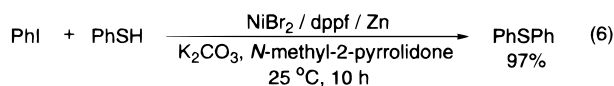
$$\text{Br} \overset{}{\underset{\text{Br}}{\diagdown}} + 2\text{PhSNa} \xrightarrow[\text{DME, reflux, 24 h}]{\text{NiBr}_2\text{(bipy)}_2} \text{PhS} \overset{}{\underset{\text{SPh}}{\diagdown}} \quad (3) \quad 71\% \ (E/Z = 80/20)$$

$$\text{Ph} \overset{\text{Br}}{\underset{\text{Br}}{\diagdown}} + 2\text{PhSNa} \xrightarrow[\text{toluene, reflux, 24 h}]{\text{NiBr}_2\text{(bipy)}_2} \text{Ph} \overset{\text{SPh}}{\underset{\text{SPh}}{\diagdown}} \quad (4) \quad 78\%$$

to palladium(0),[20] nickel(II) catalyzes the regiospecific disubstitution of bromine atoms by thiolate to give the corresponding ketene thioacetals in good yields.

Aryl and alkenyl sulfides can be conveniently prepared in high yields by the nickel- or palladium-catalyzed reactions of halides with thiols under phase-transfer conditions (in a mixture of toluene, 30% NaOH$_{aq}$, and/or hexadecyltributylphosphonium bromide) at 100 °C for 7.5 h (eq 5).[24]
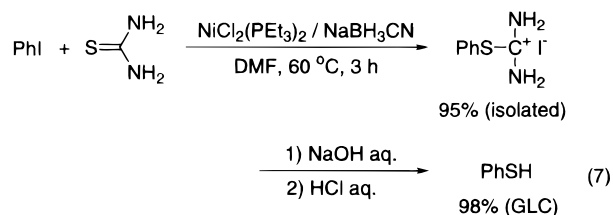
$$\text{PhBr} + \text{PhSH} \xrightarrow[\text{30\% NaOH aq. / toluene, 100 }^\circ\text{C, 7.5 h}]{\textit{trans}\text{-PhPdBr(PPh}_3)_2 \text{ / PPh}_3} \text{PhSPh} \quad (5) \quad 97\%$$

In the presence of both a base, such as K$_2$CO$_3$, and an in situ generated nickel(0) catalyst combined with dppf [dppf = 1,1′-bis(diphenylphosphino)ferrocene], thiophenol reacted with an equimolar amount of iodobenzene at 25 °C or bromobenzene at 60 °C to give phenyl sulfide in an excellent yield.[25] Unsymmetrical sulfides were also prepared by the same procedure; for example, the reaction of thiophenol with iodobenzene at 25 °C for 10 h gave phenyl sulfide in 97% yield (eq 6).

$$\text{PhI} + \text{PhSH} \xrightarrow[\substack{\text{K}_2\text{CO}_3, \ N\text{-methyl-2-pyrrolidone} \\ 25\ ^\circ\text{C}, 10\ \text{h}}]{\text{NiBr}_2 / \text{dppf} / \text{Zn}} \underset{97\%}{\text{PhSPh}} \quad (6)$$

Page and co-workers also reported that thiols smoothly reacted with alkyl iodides in the presence of Na_2CO_3 and a catalytic amount of (dppm)PtCl$_2$ [dppm = 1,2-bis(diphenylphosphino)methane] to give the corresponding sulfides.[26] Of interest is the successful application to thioacetal formation using 1,1-diiodides, which does not require the use of strong bases or the intermediacy of a thiolate anion. In addition, palladium(0)-catalyzed reactions of halides with thiols can be applied to the synthesis of S-aryl derivatives of cysteine[27] and sulfur-containing phenylalanine derivatives.[28]

The coupling reaction of thiols with aromatic halides was investigated for the elaboration of combinatorial libraries, realizing a large number of commercially available thioethers and the rich chemistry of sulfur-containing compounds.[29] Various thiols coupled with resin-bound aromatic iodides in excellent yields under optimized reaction conditions (Pd$_2$(dba)$_3$dppf catalyst, (*i*-Pr)$_2$NEt, in DMA at 60 °C for 24 h).

Nucleophilic displacement of aryl iodides with thiourea to S-aryl-isothiuronium iodides catalyzed by nickel(0) catalyst has been reported.[30] Subsequent alkaline hydrolysis of S-aryl-isothiuronium iodides gave the corresponding aromatic thiols in quantitative yields (eq 7). 2-Benzothiazolamines were easily

$$\text{PhI} + \text{S}{=}\text{C}{\bigg\langle}\substack{\text{NH}_2 \\ \text{NH}_2} \xrightarrow[\text{DMF}, 60\ ^\circ\text{C}, 3\ \text{h}]{\text{NiCl}_2(\text{PEt}_3)_2 / \text{NaBH}_3\text{CN}} \text{PhS}{-}\overset{\text{NH}_2}{\underset{\text{NH}_2}{\text{C}^+}}\ \text{I}^-$$

$$95\%\ \text{(isolated)}$$

$$\xrightarrow[\substack{\text{2) HCl aq.}}]{\substack{\text{1) NaOH aq.}}} \underset{98\%\ \text{(GLC)}}{\text{PhSH}} \quad (7)$$

prepared by this method using 1,2-aminoiodoarenes and thiols (eq 8).[30b]

$$(8)$$
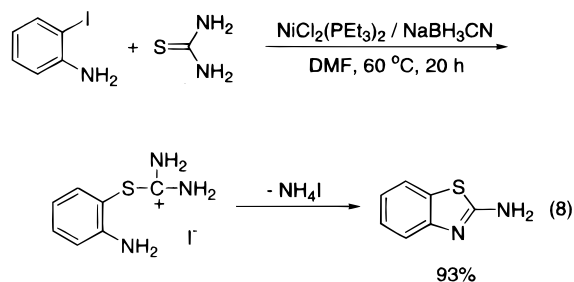
First, transition metal complex-catalyzed conversion of benzylic alcohols to the corresponding benzylic thiols can be realized by Co$_2$(CO)$_8$-catalyzed reaction

$$(9)$$
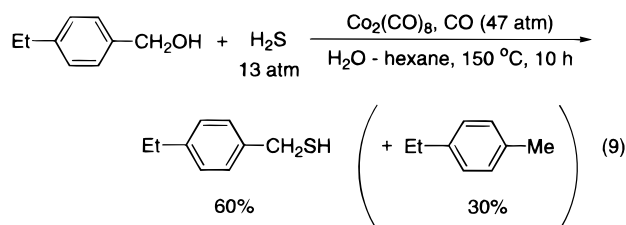
using H$_2$S under carbon monoxide pressure (H$_2$S, 13 atm; CO, 47 atm) at 150 °C for 10 h (eq 9).[31]

B. Synthesis of Allylic Sulfides

The transition metal complex-catalyzed substitution reaction of allylic alcohol derivatives with nucleophilic reagents is now a well-established methodology in organic synthesis and is widely used to construct complex organic molecules.[32,33] However, even though a wide range of nucleophiles such as carbon, nitrogen, and oxygen nucleophiles and transition metal catalysts, especially those involving palladium,[33] have been studied,[34] the sulfur nucleophiles are not very popular in such reactions. Effectively, under the classical alkylation conditions, sulfur nucleophiles could poison the catalyst system by precipitating the metals from the solution or tying up the complex in solution in an unreactive form.[9] Since allylic sulfides are important reagents and/or quite useful intermediates in organic synthesis,[35] general, selective, and highly efficient methods for preparation of allylic sulfides catalyzed by transition metal complexes have been desired. An initial solution avoiding the precipitation or complexation of the catalyst was palladium-catalyzed thiono–thiolo allylic rearrangement of O-allyl phosphoro- and phosphonothionates (eq 10).[36] The rearrangement of

$$(10)$$
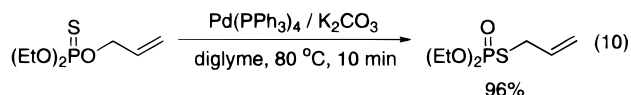
organophosphorus thiono esters to thiolo esters (thiono–thiolo rearrangement) is known to be effected thermally as well as by the catalysis of alkyl halides,[37] Lewis acids,[38] and protic acids.[39] In addition to these, a palladium(0) complex also catalyzes this rearrangement very efficiently. Noteworthy is the regioselectivity,[40] which was found to give mainly the products in which the sulfur atom was bonded to the least substituted carbon atom, regardless of the substitution pattern of the allylic groups. The reaction was generally applied to a wide variety of substrates with substituents both on the phosphorus atom and the allylic moiety.

O-Allyl or S-allyl dithiocarbonates can be converted into the corresponding allylic sulfides under mild reaction conditions in one step in the presence of a catalytic amount of a palladium complex (eq 11).[41] In

$$(11)$$

$$50 - 86\%$$
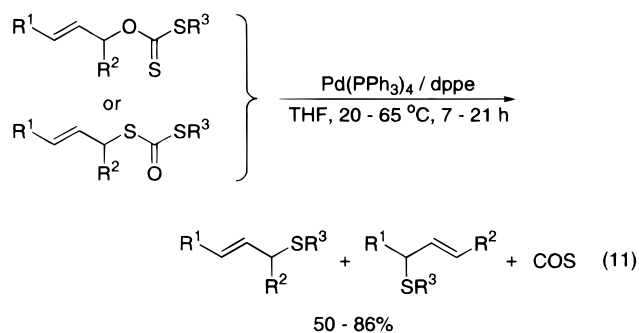
some cases, addition of a dppe ligand [dppe = 1,2-bis-(diphenylphosphino)ethane] to the catalyst was required to avoid the formation of a catalytically unre-

active palladium−dithiocarbonate complex.[41b] It should be noted that the *O*-allyl *S*-alkyl dithiocarbonates undergo relatively facile Claisen rearrangements[42] which may compete if the allylation is slow. However, this does not appear to be a problem because the present allylation is generally much faster. The reaction proceeds with net retention of configuration, and the formation of carbon oxide sulfide (COS) was detected by IR spectroscopy.[41a] In addition, benzylic sulfides as well as allylic sulfides were also prepared from *O*-benzyl dithiocarbonates by the same method.

A mild chemo-, regio-, and diastereoselective substitution of allylic carbonates and vinyl epoxides by silylated thiols catalyzed by a palladium complex can overcome difficulties in conventional displacement of allylic halides or allyloxyphosphonium salts with thiols (eqs 12 and 13).[43] The reaction also proceeded with

$$(12)$$

$$(13)$$
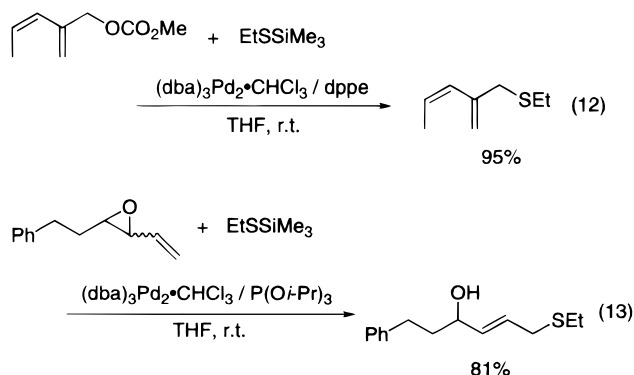
net retention of configuration and with excellent geometrical control with trisubstituted alkenes. Michael-type processes do not compete with this substitution.

Palladium-catalyzed allylation of five-[44] and six-membered[45] heterocyclic ambident sulfur nucleophiles has been studied. For example, the reaction of thiobenzoxazolone with cinnamyl ethyl carbonate gave an *S*-cinnamylated compound as a major product (eq 14). Thiobenzothiazolone and thiobenzimid-

$$(14)$$
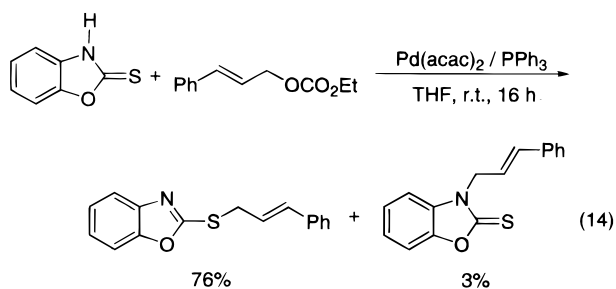
azolone, which have both nucleophilic nitrogen and sulfur atoms, reacted with cinnamyl ethyl carbonate to give only *S*-cinnamylated compounds in each case. With no exception, the regioselective rule is S > N.

$$(15)$$
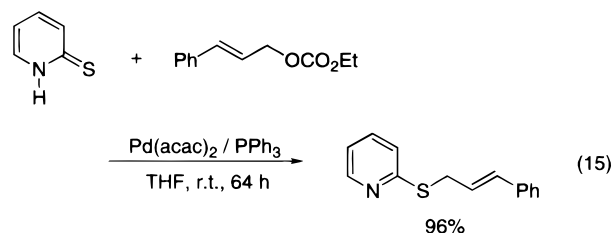
Similarly, six-membered heterocyclic compounds such as 2-thiopyridone exclusively gave *S*-allylated products (eq 15).

Highly regio- and diastereoselective palladium-catalyzed substitution of allylic and dienylic cyclic carbonates with sodium benzenesulfinate (NaSO₂-Ph)[46] and sodium thiophenoxide has been developed.[47] The optically active cyclic allyl carbonate (**1**) reacted with sodium benzenesulfinate in refluxing THF for 1 h in the presence of a catalytic amount of Pd(PPh₃)₄ to give (*E*)-allylic alcohol (**2**) as the sole product, while sodium thiophenoxide attacked 'proximal' to the oxygen atom with inversion to afford the threo-β-hydroxy sulfide (**3**) (eq 16). Pd(0)-catalyzed

$$(16)$$
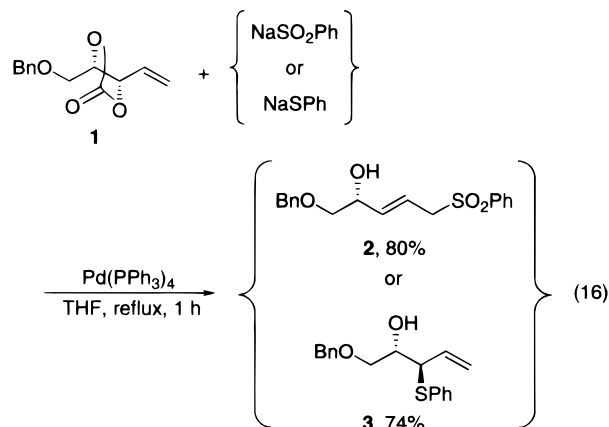
substitution of (*E*)-dienylic cyclic carbonate (**4**) with NaSO₂Ph effected complete regioselective introduction of a nucleophile to the ϵ-position to give the (*E,E*)-dienyl alcohol (**5**) (eq 17).

$$(17)$$
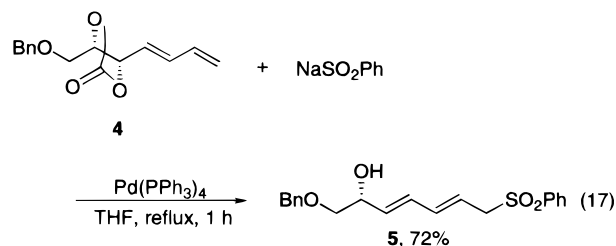
Although several methods for preparation of allylic sulfides without poisoning the catalysts have been developed and described above,[36,43] some of these methodologies have a serious drawback with regard to substrate preparation. The most convenient preparation of allylic sulfides seems to be *S*-allylation of thiols with allylic compounds. Recently, palladium-catalyzed *S*-allylation of aromatic and heteroaromatic thiols with allylic carbonates has been reported (eq 18).[48] Allylic rearrangements consistent with a π-al-

$$(18)$$
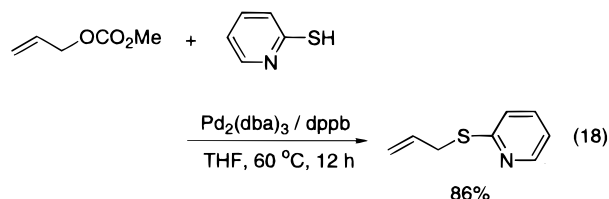
lylpalladium intermediate are observed. Regioisomeric allylic carbonates gave identical mixtures of

regio- and steroisomeric sulfides in which the substitution occurred at the less hindered allylic terminus of the π-allyl system. (Z)-Allylic carbonate gave a 90/10 mixture of E/Z allylic sulfides.

Palladium-catalyzed S-allylation of sulfur nucleophiles such as thiols can be used for deprotection of allyl carbamate such as N-allyloxycarbonyl proline ethyl ester (eq 19).[49] Interestingly, thiobenzoic acid

$$(19)$$
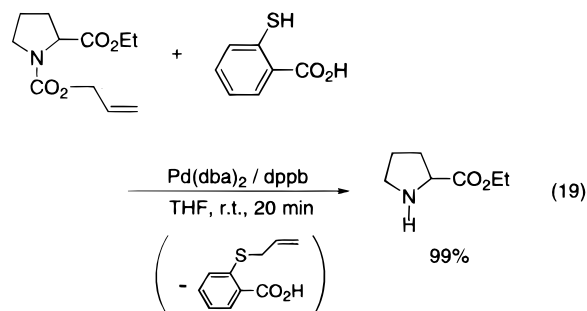
is superior to thiophenol for the removal of the N-allyloxycarbonyl group of carbamates to give the corresponding secondary amines. The thioallyl ether byproduct formed in this deprotection procedure is easily eliminated by simple base treatment. In all cases, the deprotection proceeded with retention of optical purity.

Quite recently, ruthenium-catalyzed S-allylation of thiols with allylic carbonates enabling the general synthesis of allylic sulfides has been reported (eq 20).[50] In contrast to the palladium-catalyzed reac-

$$(20)$$
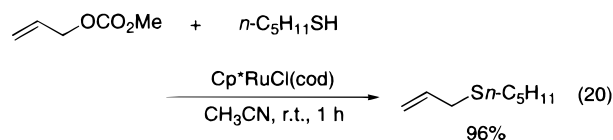
tions, aliphatic thiols as well as aromatic and heteroaromatic thiols were smoothly allylated under mild reaction conditions to give both allylic alkyl and allylic aryl sulfides in high yields.

III. Addition of Thiols to Unsaturated Compounds
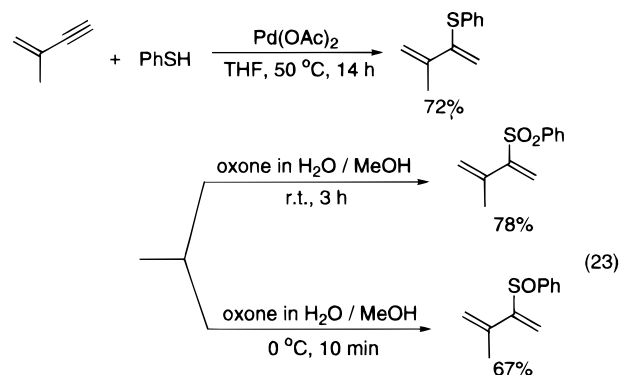
A. Addition of Thiols to Alkynes

Although thiols have been widely employed as the source of ligands for various transition metals,[10] the transition metal complex-catalyzed reactions using them as substrates have been scarcely developed.[51] The addition of thiols to alkynes is one of the most straightforward methods of obtaining vinyl sulfides, which are important synthetic intermediates.[52] The first example of transition metal complex-catalyzed addition of thiols to alkynes was developed by using molybdenum and iridium catalysts, in which thiols could function as both the electron and proton donor in the catalytic system.[53] Although the addition of thiophenol to dimethyl acetylenedicarboxylate proceeded in the presence of a catalytic amount of Et$_3$N or PPh$_3$, molybdenum catalysts such as oxomolybdenum complexes, O=MoL$_2$ or MoO$_2$L$_2$ (L = dithiocarbamate), were much more stereospecific producing trans adduct in 25% yield (E > 90%) (eq 21).

$$(21)$$

25% (E/Z = > 9/1)
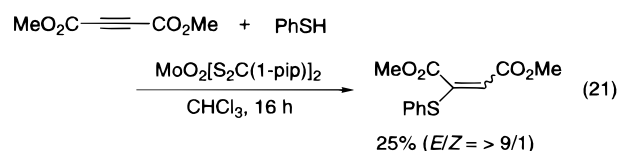
It is also well-known that thiols add to alkynes under radical conditions to afford anti-Markovnikov-type vinylic sulfides with excellent regioselectivity, usually as a stereoisomeric mixture.[54] In contrast to this, Pd(OAc)$_2$- and PdCl$_2$(PhCN)$_2$-catalyzed hydrothiolation of aromatic alkynes occurs to give the corresponding Markovnikov adducts with excellent regioselectivity, probably via thiopalladation of alkynes by a palladium sulfide species, which may be formed by ligand-exchange reaction. In the case of alkynes having propargylic protons, a sequential addition/isomerization reaction occurs to give the internal vinylic sulfides regioselectively. In addition, RhCl-(PPh$_3$)$_3$ exhibits excellent catalytic activity toward the regio- and stereoselective anti-Markovnikov addition of thiols to alkynes, which may proceed by the formation of a (hydrido)rhodium sulfide species and probably via the subsequent hydrorhodation of alkynes to afford (vinyl)rhodium intermediates. From the same starting materials (alkyne and thiol), therefore, the regioselectivity of hydrothiolation can be attained simply by changing the catalysts (eq 22).[55]

$$(22)$$
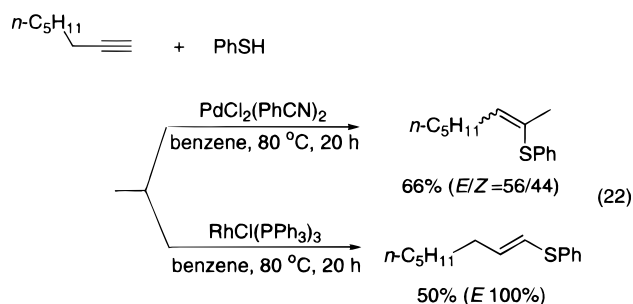
Palladium-catalyzed addition of thiophenol to conjugated enynes with a terminal triple bond occurs in a regioselective manner to give 2-(phenylthio)-1,3-dienes, which were selectively oxidized to either 2-(phenylsulfinyl) or 2-(phenylsulfonyl)-1,3-dienes by proper choice of the reaction conditions and oxidant (eq 23).[56]

$$(23)$$

Dinuclear ruthenium complexes Cp*Ru(μ-SR)$_2$-RuCp* [Cp* = pentamethylcyclopentadienyl; R = Et, i-Pr, t-Bu] and the related Cp*Ru(η^1-C$_6$F$_5$)(μ-S)(μ-

SC$_6$F$_5$)RuCp* are active catalysts for the addition of thiols to polar alkynes such as methyl propiolate and dimethyl acetylenedicarboxylate at room temperature (eq 24).[57] Many catalytically active ruthenium inter-

$$(24)$$

78% ($E/Z = 1/2$)
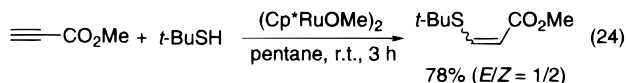
mediates and stop complexes for the catalytic cycles have been isolated and fully characterized.

B. Addition of Thiols to Alkenes and Allenes

The Markovnikov addition of thiols to alkenes is a well-known reaction,[58] but few examples of transition metal complex-catalyzed addition of thiols to *unactivated alkenes* have been reported. There is also lack of literature precedent when it comes to styrene substrates, probably because they polymerize so easily under acidic conditions. Examples are limited to those using a stoichiometric amount of a metal complex.[59] In 1973, Mukaiyama and co-workers used TiCl$_4$ as a promoter in the addition of ethanethiol to styrene and α-methylstyrene in cyclohexane solvent (eq 25).[60] Belley and Zamboni also found AlCl$_3$- and

$$(25)$$

99%
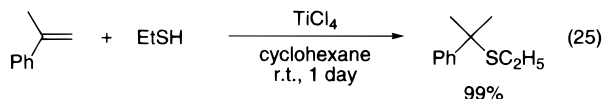
TiCl$_4$-mediated addition of thiols to styrenes during their program to find new LTD$_4$ antagonists.[61]

The first example using manganese(III) acetate in the reaction of 1,1-diarylethenes with α-mecaptoketones has been reported (eq 26). A mixture of the


$$(26)$$

46%   26%
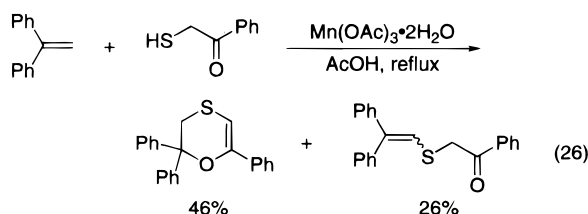
ethenes and α-mercaptoketones was treated with manganese(III) acetate in acetic acid, affording cycloaddition products in moderate yields, together with substituted products. Thiyl radicals easily formed by manganese(III) oxidation with ethanethiol or thiophenol reacted with alkynes to give preferentially (*E*)-vinyl sulfides in quantative yields.[62]

Thiols have been studied as nucleophiles in the conjugate addition reactions with 3-(2-alkenyl)-2-oxazolidinones. Stereoselective thiol conjugate additions catalyzed by a Lewis acid are interesting not only from the standpoint of biological and synthetic importance, but also from the difficulty encountered in the catalyzed reactions using thiols in industry.[63] Quite a number of asymmetric thiol conjugate addition reactions are known,[64] but previous examples of enantioselective thiol conjugate additions have all been based on the activation of thiol nucleophiles by use of chiral base catalysts, such as amino alcohols[65] and the lithium thiolate complex of amino bisether.[66]

Shibasaki and co-workers also reported the lanthanoid tris(binaphthoxide)-catalyzed asymmetric Michael addition of thiols to α,β-unsaturated carbonyl compounds [LSB = LaNa$_3$tris(binaphthoxide)] (eq 27).[67]

$$(27)$$

86% (90% ee)
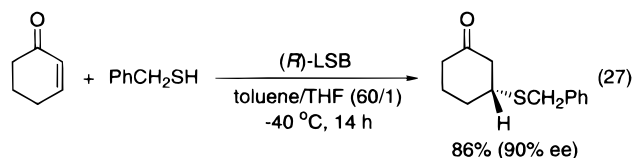
Quite recently, Kanemasa and co-workers reported the first examples of enantioselective thiol conjugate additions catalyzed by a chiral Lewis acid, the DBFOX/Ph aqua complex of nickel(II) perchlorate [DBFOX = 4,6-dibenzofurandiyl-2,2′-bis(4-phenyloxazoline], (eq 28).[68]


$$(28)$$

100% (80% ee)
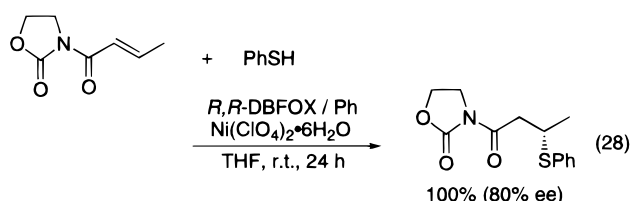
Palladium-catalyzed hydrosulfination of alkenes has been reported by Keim and co-workers. *S*-Alkyl alkanethiosulfonates and sufonic acid can easily be synthesized from sulfur dioxide, alkenes, hydrogen, and a cationic palladium(II)-diphosphine complex like [Pd(dppp)(MeCN)$_2$][BF$_4$]$_2$ [dppp = 1,3-bis(diphenylphosphino)propane] at temperatures above the ceiling temperature of the SO$_2$−alkene copolymer (eq 29).[69]

$$n\text{-}C_3H_7SO_2SC_3H_7\text{-}n \; + \; n\text{-}C_3H_7SO_3H \; + \; H_2O \quad (29)$$
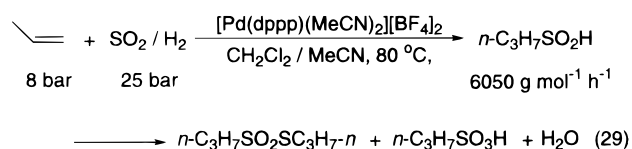
The addition reaction of thiols to allenes is one of the most straightforward routes to vinylic sulfides, which are well-known to be important synthetic intermediates.[52] It has been reported that thiols add to allenes by a free-radical mechanism.[70] However, thiyl radicals, as the key species in the radical addition, usually attack at both the center and terminal carbons of allenes, so the radical reaction results in the formation of a regioisomeric mixture of thiol adducts. These features make the radical reaction synthetically less useful. Contrary to this, Ogawa and Sonoda et al. reported that palladium-(II) acetate exhibits excellent catalytic activity toward the highly regioselective addition of thiophenol to allenes, in which a phenylthio group is introduced at the center carbon of the allenes.[71] The radical addition of 1,1-dimethylallene proceeded very rapidly to give the thermodynamically more stable adduct, exclusively,[70c,d] while the Pd(OAc)$_2$-catalyzed addition to 1,1-dimethylallene provided its regioisomer as the sole product. Accordingly, both methods are complementary to each other for the regioselective synthesis

of vinylic sulfides from 1,1-disubstituted allenes (eq 30).

(30)
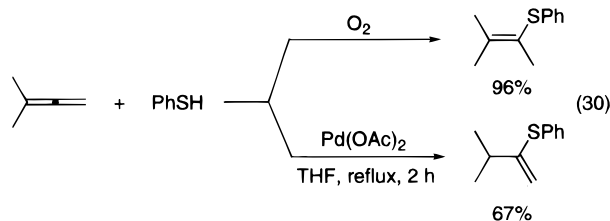
## IV. Insertion of Unsaturated Compounds into Sulfur–Sulfur and Sulfur–Heteroatom Bonds

A. Insertion of Alkynes into Sulfur–Sulfur Bonds

The transition metal complex-catalyzed addition of disulfides to alkynes in one step opens a versatile synthetic route to functionalized alkenes. The replacement of the new carbon–sulfur bonds by C–M, C–X, or C–C bonds constitutes a convenient method for preparation of tri- or tetrasubstituted alkenes. A particular feature of the addition of disulfides to alkynes is its regio- and stereoselectivity. The reactions proceed in a syn fashion, resulting in products with configurations opposite to those formed by radical processes. The reaction can be explained by the following mechanism: (1) oxidative addition of disulfides to transition metal catalysts leading to M–S bond formation; (2) *cis*-insertion of alkynes into an M–S bond; (3) reductive elimination to give the adducts with regeneration of an active catalyst species.

Many examples for the first oxidative addition step of organic disulfides to transition metal complexes have been reported. Most of the reactions gave the thiolato-bridged di- or polynuclear complexes. The thiolato-bridged complexes, [CpFe(CO)SR]$_2$ [Cp = cyclopentadienyl],[72,73] [CpCoSMe]$_2$,[72] and [CpV(S-Me)$_2$]$_2$[74] were prepared by the reaction of dimethyl disulfide with [CpFe(CO)$_2$]$_2$, CpCo(CO)$_2$, and CpV-(CO)$_4$, respectively (eqs 31–33).

(31)

$(R = CH_3, C_2H_5, i\text{-}C_3H_7, t\text{-}C_4H_9, CH_2Ph)$

(32)

(33)
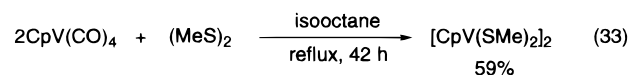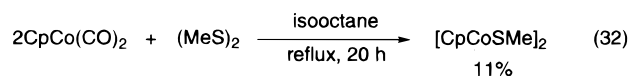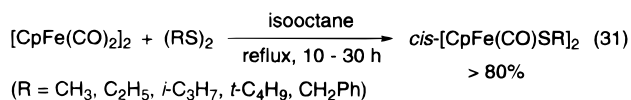
Treatment of Ru$_3$(CO)$_{12}$ with (EtS)$_2$ and (PhS)$_2$ also leads to polymeric products formulated as [Ru(CO)$_2$-(SR)$_2$]$_n$ (R = Et or Ph).[75] Oxidative addition of (RS)$_2$ [R = Ph, *o*- and *m*-O$_2$NC$_6$H$_4$, *t*-Bu, CN] to Pd(PPh$_3$)$_4$ was shown to lead to complexes containing S–Pd–S linkages (eq 34).[76] These complexes could be dimeric (R = Ph) or monomeric (R = *o*- or *m*-O$_2$NC$_6$H$_4$) depending on the nature of the organic group. How-

(34)
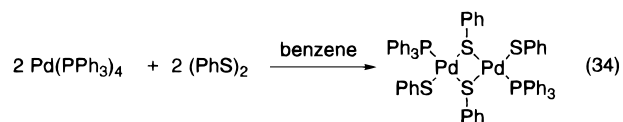
ever, all of the corresponding platinum complexes were monomeric, e.g., Pt(PPh$_3$)$_2$(SR)$_2$ (eq 35). The

(35)
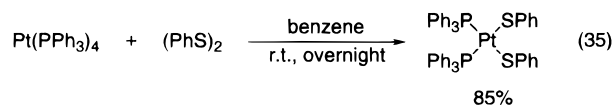
complex, Pt(PPh$_3$)$_2$(SR)$_2$, further reacts with transition metal complexes having labile groups such as norbornadiene or CH$_3$CN to give the thiolato-bridged heterodinuclear complexes (eq 36).

(36)
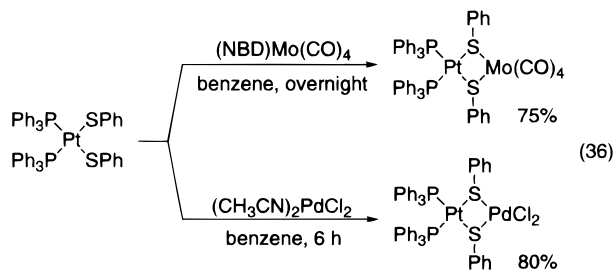
Oxidative addition of cyclic disulfides, such as hexachloronaphthalene-1,8-disulfide (S$_2$C$_{10}$Cl$_6$), to Pt-(PPh$_3$)$_4$ and RhCl(PPh$_3$)$_3$ has also been reported to give the corresponding monomeric *cis*-Pt(S$_2$C$_{10}$Cl$_6$)-(PPh$_3$)$_2$ and *trans*-RhCl(S$_2$C$_{10}$Cl$_6$)(PPh$_3$)$_2$ via cleavage of an S–S bond in disulfides, respectively (eq 37).[77]

(37)
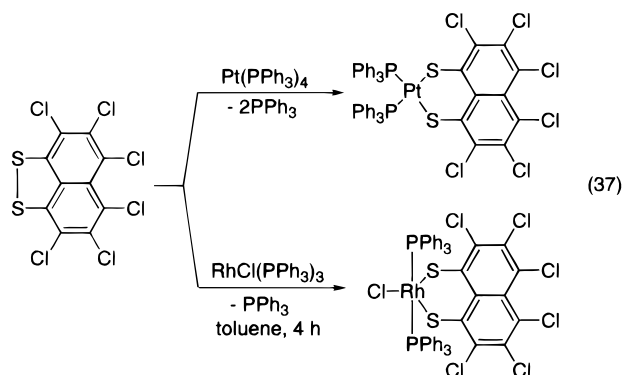
Reactions of Ni(cod)$_2$ [cod = 1,5-cyclooctadiene] with diaryl disulfides in the presence of basic ligands gave oxidative addition products formulated as Ni-(SAr)$_2$L$_2$ [Ar = Ph, *p*-ClC$_6$H$_4$, *p*-MeC$_6$H$_4$, and *p*-O$_2$-NC$_6$H$_4$; L = bpy and PEt$_3$] (eq 38).[78] Ni(SPh)$_2$(bpy)$_2$

(38)
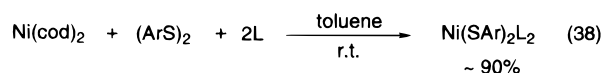
showed paramagnetism with μ_{eff} of 3.05 μ_B in the solid state and electric conductivity in solution. It also served as a good catalyst for coupling reactions between sodium thiophenoxide and aryl halides to give the corresponding sulfides.

Oxidative addition of disulfides to Mo$_2$ and W$_2$ quadruple bonds has also been reported.[79] Reaction of [Cp*Ru(μ_3-Cl)]$_4$ with 2 equiv of diferrocenyl disul-

fide gave the corresponding ferrocenylthiolato-bridged diruthenium complex, [Cp*RuCl(μ-SR)]₂ [R = ferrocenyl] (eq 39).[80] The crystal structure and some reactivities of the complex have also been reported.

(39)

63%
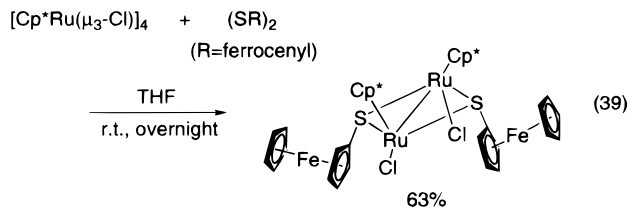
As for the insertion of alkynes into M−S bonds, relatively few examples have been known so far. Addition of 2 equiv of dimethyl acetylenedicarboxylate to a concentrated CH₃CN solution of [Et₄N]₂-[Mo₂O₂(μ-S)₂(S₂)₂] at room temperature quickly precipitated an air-stable canary-yellow microcrystalline product which contains an ordered Mo₂O₂(μ-S)₂[S₂C₂-(CO₂CH₃)₂]₂²⁻ dianion confirmed by spectroscopic data and a single-crystal X-ray diffraction study.[81]

Insertion of alkynes into Mo−S and W−S bonds has been reported.[82] For example, the reaction of the bis(hexafluorobut-2-yne) complex, [CpMoCl(CF₃-CCCF₃)₂], with TlSR gives η²-C,C-vinyl complexes [CpMo[η³-C(CF₃)C(CF₃)SR](CF₃CCCF₃)] [R = i-Pr or t-Bu] (eq 40).

(40)

65%
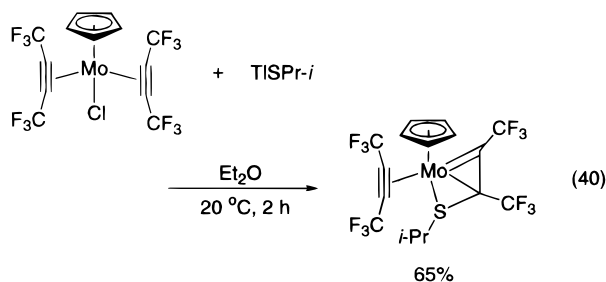
The reactions between the thiolates, such as [Mn-(CO)₄(SR)]₂, CpFe(CO)₂(SR), [Fe(CO)₃(SR)]₂, [CpCo-(SCF₃)]₂, CpCo(SC₆F₅)₂, and [Co(CO)₃(SC₆F₅)]₂ [R = CF₃ or C₆F₅], with the alkynes, CF₃CCCF₃ or CF₃-CCH, gave metallothiacyclobutenes, metalated alkenes, dimetalated alkenes, and so on.[83] Reactions of iron and ruthenium thiolate complexes such as CpM(CO)₂(SCH₃) with trifluoropropyne gave a number of products, which included the sulfur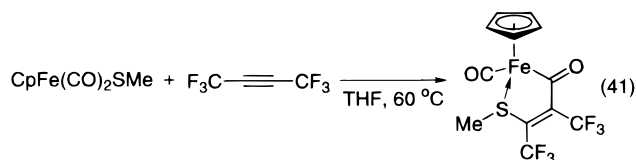-coordinated CpM(CO)COC(CF₃)=CHSMe complexes [M = Fe, Ru].[84] Both alkynes and carbon monoxide readily inserted into M−SCH₃ bonds, and the resultant sulfur-coordinated M−COC=CSCH₃ groups can undergo further insertion by alkynes (eq 41).

(41)

Photochemical activation of Fe₃(CO)₉(μ₂-H)(μ₃-StBu) in the presence of PhCCPh gave Fe₃(CO)₈(η²-μ₂-HPhCCPh)(μ₃-StBu) with loss of CO, while thermal reaction of Fe₃(CO)₉(μ₂-Cl)(μ₃-StBu) with PhCCH

(42)

17%   23%
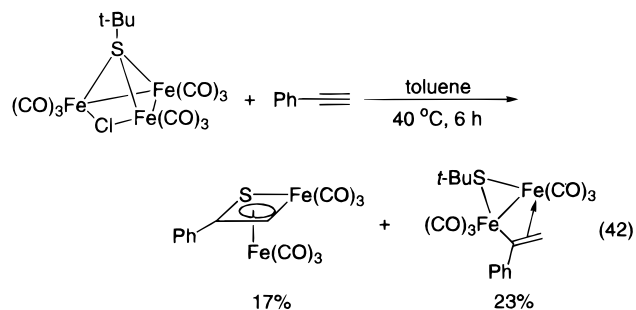
resulted in fragmentation, yielding the dinuclear products Fe(CO)₃[Fe(CO)₃−S−CPh−CH] and Fe₂-(CO)₆(η²-μ₂-H₂CCPh)(μ₂-StBu) (eq 42).[85]

Reaction of Cp or Cp*Co^{III}(1-phenylmethanimine-N,1-dithiolato) with dimethyl acetylenedicarboxylate leading to preferential insertion of alkyne into a sulfur adjacent to the nitrogen atom−cobalt bond gave the adducts in which Co and S of the 1,2,5,3-cobaltadithiazole ring in the cobalt complex are bridged by the 1,2-dimethoxycarbonylethylene-1,2-diyl group (eq 43).[86]

(43)

99%
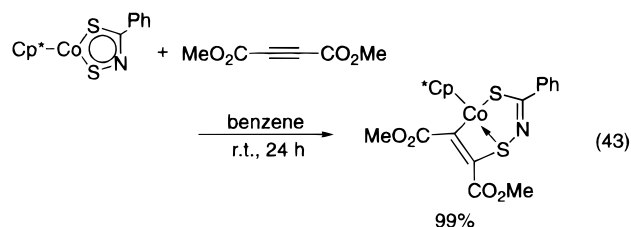
Cp*Ru(μ-SR){μ:η²:η¹:η¹-C(Ph)=CHR}RuCp* was obtained by the reaction of [Cp*Ru(SR)]₂ with phenylacetylene as an intermediate of ruthenium-catalyzed formation of vinylthioethers from thiols and alkynes (eq 44).[57]

(44)

80%
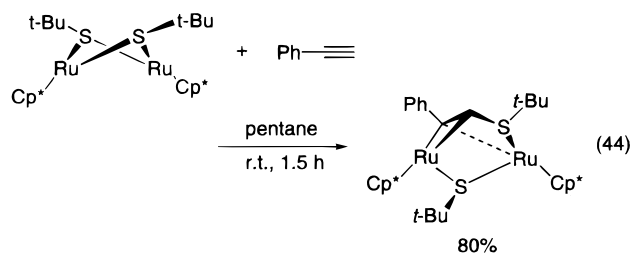
Final reductive elimination is perhaps the most fundamental reaction in organometallic chemistry and provides the key bond forming step in catalytic transformations.[3a,87] While reductive eliminations that form carbon−carbon and carbon−hydrogen bonds are now common,[87] analogous reactions that from carbon−heteroatom bonds are rare.[88] To our knowledge, only one example of carbon−sulfur bond forming reductive elimination has been reported. Warming a benzene solution of (dppe)Pd(SR)(Ar) at 50 °C in the presence of triphenylphosphine formed the corresponding alkyl aryl sulfide in quantative yield and two Pd(0) phosphine compounds (eq 45).[89]

(45)

(+ Pd(dppe)₂ + Pd(PPh₃)₄)
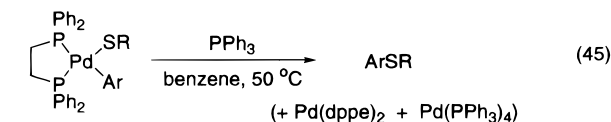
In contrast to C–C bond forming eliminations, a trapping reagent for [(dppe)Pd] is necessary for high yields of products. Moreover, it is clear that the intimate mechanism for these C–S bond forming processes differs markedly and the rate acceleration by electron-withdrawing substituents on the aryl group points to a transition state that contains some character analogous to nucleophilic aromatic substitution.

By combination of these three fundamental processes, e.g., (1) oxidative addition of disulfides, (2) insertion of alkynes into M–S bonds, and (3) C–S bond forming reductive elimination, a new addition reaction of disulfides to alkynes catalyzed by transition metal complexes has been constructed. Aromatic disulfides stereoselectively added to terminal alkynes to give (Z)-1,2-bis(arylthio)-1-alkenes in high yields (eq 46), while the reaction did not proceed with internal alkynes.[90] The noncatalytic reaction could

$$n\text{-}C_6H_{13} \!\!-\!\!\!=\!\!\!- + (PhS)_2 \xrightarrow[\text{benzene, 80 °C, 12 h}]{Pd(PPh_3)_4} \begin{array}{c} n\text{-}C_6H_{13} \\ PhS \quad SPh \end{array} \quad (46)$$

100%
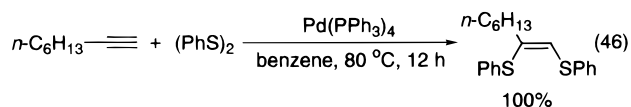
be performed under photoirradiation, yielding either the E-isomer alone or a mixture of the E- and Z-isomers. In addition, with substrates containing both double and triple bonds, only addition to the triple bond took place. The mechanism suggested was shown to be in accordance with the observation that the palladium complex obtained by Graziani[76] reacted with 1-octyne to give the same product as that formed in the catalytic reaction.

In the presence of carbon monoxide, the carbonylative addition of disulfides to alkynes proceeded (eq 47). Furthermore, bis(triisopropylsilyl)disulfide was

$$n\text{-}C_6H_{13} \!\!-\!\!\!=\!\!\!- + (PhS)_2 + \begin{array}{c} CO \\ 60 \text{ kgcm}^{-2} \end{array}$$

$$\xrightarrow[\text{benzene, 80 °C, 39 h}]{Pd(PPh_3)_4} \begin{array}{c} n\text{-}C_6H_{13} \quad SPh \\ SPh \quad O \end{array} \quad (47)$$

shown to undergo Pd(PPh_3)_4-catalyzed *syn*-addition to alkynes in benzene at 80 °C to give the corresponding insertion products in moderate to excellent yields (eq 48).[91]

$$n\text{-}C_8H_{17} \!\!-\!\!\!=\!\!\!- + (i\text{-}Pr_3SiS)_2 \xrightarrow[\text{benzene, reflux, 15 h}]{Pd(PPh_3)_4}$$

$$\begin{bmatrix} & S^{SiPr\text{-}i} \\ n\text{-}C_8H_{17} & S_{SiPr\text{-}i} \end{bmatrix} \xrightarrow[\text{0 °C, 1 h}]{CH_3I} \begin{array}{c} SMe \\ n\text{-}C_8H_{17} \quad SMe \end{array} \quad (48)$$

90%

B. Insertion of Alkynes into Sulfur–Heteroatom Bonds

Transition metal complex-catalyzed insertion of a carbon–carbon unsaturated linkage into sulfur–heteroatom bonds is particularly attractive from the synthetic viewpoint. Particularly interesting and challenging reactions in this category are those involving the regio- and stereoselective simultaneous introduction of two different heteroatoms as exempli-

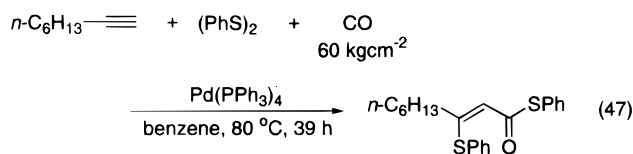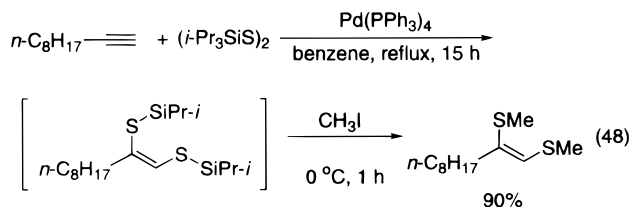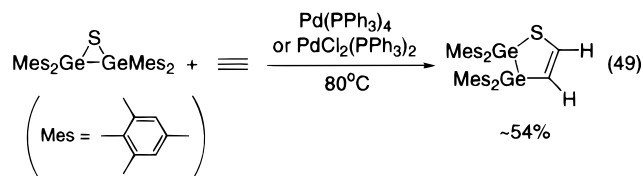fied by S–Ge, S–B, S–Si, and S–P and related bond additions, which enables more versatile and elegant synthetic elaboration of the adducts. For example, thiadigermirane reacted with alkynes in the presence of a catalytic amount of Pd(PPh_3)_4 or PdCl_2(PPh_3)_2 at 80 °C cleanly to produce the adduct in moderate yield (eq 49).[92] In contrast to digermirane, the adduct

$$\begin{array}{c} S \\ Mes_2Ge\!-\!GeMes_2 \end{array} + \equiv \xrightarrow[\text{80°C}]{\substack{Pd(PPh_3)_4 \\ \text{or } PdCl_2(PPh_3)_2}} \begin{array}{c} S \\ Mes_2Ge \quad H \\ Mes_2Ge \quad H \end{array} \quad (49)$$

$$\left(Mes = \underset{}{\text{–}} \right)$$

~54%

obtained is the insertion product of alkynes into the S–Ge bond. No product of the insertion into the Ge–Ge bond was obtained.

First, thioboration of terminal alkynes with 9-(alkylthio)-9-borabicyclo[3.3.1]nonane derivatives catalyzed by palladium complexes has been reported by Suzuki and co-workers (eq 50).[93] The reaction is highly regio-

$$n\text{-}C_6H_{13} \!\!-\!\!\!=\!\!\!- + PhS\!-\!B \xrightarrow[\text{THF, 50 °C, 3 h}]{Pd(PPh_3)_4}$$

$$\begin{array}{c} n\text{-}C_6H_{13} \\ B \\ SPh \end{array} \xrightarrow[\text{r.t., 1 h}]{MeOH} \begin{array}{c} n\text{-}C_6H_{13} \\ SPh \end{array} \quad (50)$$

72%
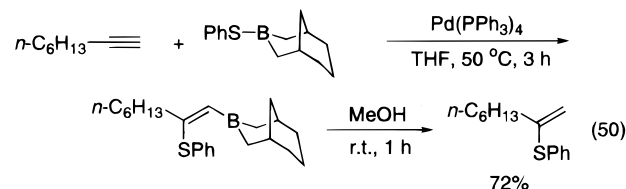
and stereoselective, and the synthetic utility of the reaction was demonstrated by the regio- and stereoselective one-pot synthesis of alkenyl sulfides via the palladium-catalyzed thioboration–cross-coupling sequence.

The hybrid density functional (B3LYP) calculations have also been carried out to study the mechanism of thioboration of alkynes catalyzed by Pd(0) and Pt(0) complexes.[94]

Tanaka and co-worker recently showed that heating a mixture of disulfides, disilanes, and terminal alkynes in the presence of a platinum catalyst realized regio- and stereoselective thiosilylation of alkynes to afford (Z)-1-silyl-2-thio-1-alkenes in good yields (eq 51).[95] The products with the sulfur atom at the

$$n\text{-}C_6H_{13} \!\!-\!\!\!=\!\!\!- + (4\text{-}Cl\text{-}C_6H_4S)_2 + (SiCl_3)_2$$

$$\xrightarrow[\text{toluene, 110 °C, 6 h}]{Pt(C_2H_4)(PPh_3)_2} \begin{array}{c} n\text{-}C_6H_{13} \\ 4\text{-}Cl\text{-}C_6H_4S \quad SiCl_3 \end{array} \quad (51)$$

95%
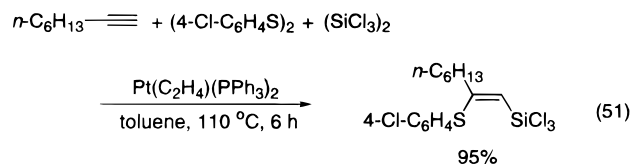
internal position were obtained selectively. Mechanistic investigations revealed that a novel platinum-catalyzed disproportionation reaction of a disulfide (ArS)_2 with (SiCl_3)_2 forming ArSSiCl_3 took place rapidly at the early stage of the reaction, which could be easily monitored by ^{13}C NMR spectroscopy. In addition, as confirmed by ^{31}P NMR spectroscopy, oxidative addition of PhSSiCl_3 to Pt(PEt_3)_3 readily occurred at room temperature to afford *trans*-Pt-(PhS)(SiCl_3)(PEt_3)_2. Actually, thiosilylation reaction took place when PhSSiCl_3 was employed to give the corresponding adduct in good yield. They tentatively propose that the catalyst involves insertion of an

alkyne into the S–Pt (but not Si–Pt) bond, which is consistent with (a) the strong trans influence of the silyl ligand, (b) enhanced bond strength of the Si–Pt bond by introduction of electronegative groups (Cl) to Si, (c) the regioselectivity of the catalysis that suggests terminal attachment of the bulkier platinum moiety at the insertion step.

Palladium complexes efficiently catalyze the addition of O,O,S-triphenyl phosphorothioate (PhSP(O)-(OPh)$_2$) to terminal alkynes to produce (Z)-1-(diphenoxyphosphinyl)-2-(phenylthio)alkenes in high yields with high regio- and stereoselectivity (eq 52).[96] The

$$n\text{-}C_6H_{13}\text{---}\equiv \quad + \quad (\text{PhO})_2\text{P(O)SPh}$$

$$\xrightarrow[\text{toluene, 100 °C, 5 h}]{\text{Pd(PPh}_3)_4} \quad \overset{n\text{-}C_6H_{13}}{\underset{\text{PhS}}{\diagdown}}\text{---}\overset{\text{P(OPh)}_2}{\underset{\text{O}}{|}} \quad (52)$$

$$92\%$$
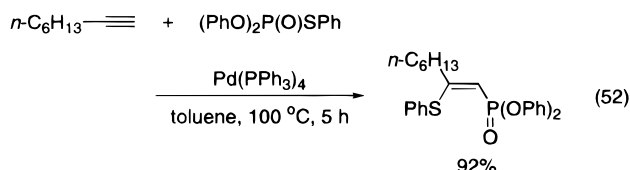
adducts are potentially versatile in organic synthesis and find applications in the preparation of bidentate ligands having phosphorus and sulfur atoms for transition metal complexes.

C. Insertion of Alkenes into Sulfur–Sulfur Bonds

Addition of sulfenyl compounds RSX to carbon–carbon unsaturated bonds is well documented for reagents such as sulfenyl halides and thiosulfonium salts in which the X atom or group is electron withdrawing (X = Cl, $^{+}$SR$_2$).[97] Less polar reagents such as disulfides and sulfenamides normally do not add to alkenes. There are scattered reports in the literature relating to the electrophilic addition of disulfides to alkenes in the presence of a catalytic amount of iodine,[98] hydrogen fluoride,[99] bo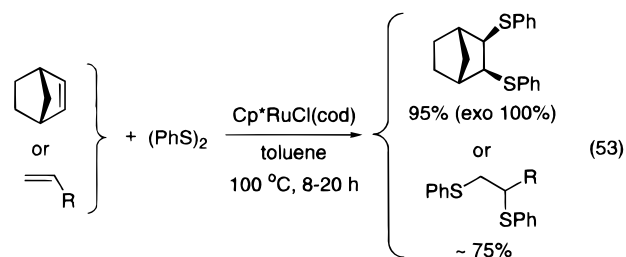ron trifluoride etherate,[100] and iodosylbenzene.[101] In addition, hydroxysulfenylation of alkenes with disulfides and trifluoroacetic acid promoted by Pb(OAc)$_4$[102] and Cu(OAc)$_2$[103] have also been reported. However, the stereochemical course of all reactions mentioned above was reported to proceed via an anti mechanism, since the reactions proceed via an ionic mechanism.[100–103] No formation of syn-addition products of disulfides to alkenes has been reported so far. If the transition metal complex-catalyzed addition of disulfides to alkenes occurs via the same mechanism of addition to alkynes, syn-addition products of disulfides to alkenes should be obtained in high yields with high stereoselectivity. As expected, the authors recently developed the first transition metal complex-catalyzed addition of disulfides to alkenes which is characteristic of the ruthenium catalyst.[104] For example, Cp*RuCl(cod)-catalyzed addition of disulfides to 2-norbornene smoothly proceeded to give the corresponding vicinal-dithioethers in high yields with high stereoselectivity (exo 100%), which means that stereoselective cis-thioruthenation of alkenes, followed by reductive elimination with retention of the stereochemistry, gave the products (eq 53). Ethylene and a variety of terminal alkenes bearing several functional groups can be used in this reaction. Stoichiometric reaction of (PhS)$_2$ with Cp*RuCl(cod) afforded a novel thiolato-bridged Ru(III) dimer,
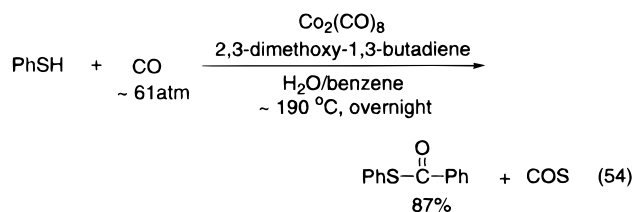
$$\left.\begin{array}{c} \square\!\!\!\!\square \\ \text{or} \\ \equiv\!\!\!\text{---R} \end{array}\right\} + \text{(PhS)}_2 \xrightarrow[\substack{\text{toluene} \\ 100\ °C,\ 8\text{-}20\ h}]{\text{Cp*RuCl(cod)}} \begin{array}{c} \text{SPh} \\ \text{SPh} \\ 95\%\ (\text{exo } 100\%) \\ \text{or} \\ \text{PhS}\diagdown\!\!\!\!\diagup\overset{R}{\underset{\text{SPh}}{}} \\ \sim 75\% \end{array} \quad (53)$$

[Cp*RuCl(μ-SPh)]$_2$, which gave the corresponding adducts by the stoichiometric reaction with 2-norbornene, and also showed high catalytic activity for the addition of (PhS)$_2$ to 2-norbornene.

In addition, hydrosulfenylation of alkenes catalyzed by hemin/NaBH$_4$[105] and Co(eobe)/PhSiH$_3$[106] [eobe = N,N'-bis(2-ethoxycarbonyl-3-oxobutylidene)ethylenediaminato] with disulfides to give Markovnikov-type adducts has been reported.

V. Thiocarbonylation and Related Carbonylation Reactions

A. Thiocarbonylation

Carbonylation chemistry is widely used in organic synthesis in both academia and industry. Among the numerous methods for the introduction of a carbonyl moiety into an organic molecule, the direct functionalization of a substrate using carbon monoxide has received great deal of attention.[107] The development of transition metal complex-catalyzed carbonylation involving the formation of a thiocarbonyl unit and employing chalcogen compounds as a substrate represents a challenging goal in carbonylative organic synthesis, because the strong thiophilicity of transition metals[10] may render catalytic reactions ineffective even in the presence of carbon monoxide.[9] Transition metal complex-catalyzed reactions of thiols with carbon monoxide were first investigated by Alper and co-workers.[108] As for the carbon–sulfur bond forming reactions with thiols and carbon monoxide, thioesters were obtained in high yields by the Co$_2$(CO)$_8$-catalyzed carbonylation of thiols in the presence of 1,3-dienes such as 2,3-dimethoxy-1,3-butadiene, in which (diene)cobalt carbonyl complexes, i.e., [(diene)Co(CO)$_2$]$_2$, are the key catalytic species (eq 54).[109] The carbonylation is applicable to a variety

$$\text{PhSH} \quad + \quad \underset{\sim 61\text{atm}}{\text{CO}} \xrightarrow[\substack{\text{H}_2\text{O/benzene} \\ \sim 190\ °C,\ \text{overnight}}]{\substack{\text{Co}_2\text{(CO)}_8 \\ \text{2,3-dimethoxy-1,3-butadiene}}} \overset{O}{\underset{}{\text{PhS}-\overset{\|}{\text{C}}-\text{Ph}}} + \text{COS} \quad (54)$$

$$87\%$$

of thiophenols and benzylic thiols, but alkanethiols are inert under these reaction conditions. The formation of COS as a byproduct was confirmed by mass spectrometric analysis of the evolved gases (intense signal at m/z 60).

The first transition metal complex-catalyzed thioformylation of alkynes with aromatic thiols and carbon monoxide which permits simultaneous introduction of a formyl and a sulfide unit into carbon–

carbon multiple bonds has been revealed by Sonoda and Ogawa et al.[110] The reaction of 1-octyne with thiophenol and carbon monoxide (30 atm) in the presence of 3 mol % of RhH(CO)(PPh$_3$)$_3$ at 120 °C for 5 h led to high-yield formation of the corresponding thioformylation product, in which carbon monoxide was incorporated predominantly at the terminal carbon of the alkyne (eq 55). Palladium complexes
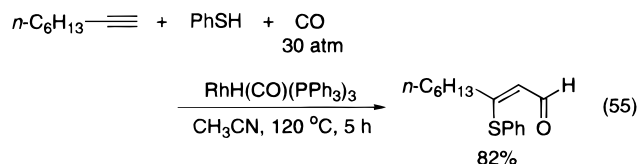
involving Pd(OAc)$_2$, Pd(PPh$_3$)$_4$, and PdCl$_2$(PPh$_3$)$_2$, which is effective for the Markovnikov-type addition of thiols to alkynes,[55,56] exerted no effect on the carbonylation or resulted in the formation of a complex mixture. Aromatic thiols can be employed successfully for the thioformylation of alkynes, whereas the thioformylation with alkanethiols such as dodecanethiol required prolonged reaction time and was accompanied with formation of a considerable amount of thioesters. A possible mechanism may include the regioselective thiorhodation of alkynes by the rhodium sulfide complex ([Rh(SR)(CO)(PPh$_3$)$_2$]$_n$)[111] formed in situ.

In transition metal complex-catalyzed addition and related reaction and control of the regiochemistry as well as the stereochemistry is always of great importance. As mentioned previously, the RhH(CO)-(PPh$_3$)$_3$-catalyzed thioformylation of alkynes with thiols and CO exhibits excellent regioselectivity where carbon monoxide and the alkylthio group are introduced selectively into the terminal and internal positions of alkynes, respectively.[110] Interestingly, switching the catalyst simply from RhH(CO)(PPh$_3$)$_3$ to Pt(PPh$_3$)$_4$ leads to a sharp reversal of the regioselectivity of the CO introduction. Namely, in the reaction of alkynes with thiols and carbon monoxide in the presence of platinum(0) catalysts, a dramatic changeover of the regioselectivity of the CO introduction was observed and a novel "hydrothiocarboxylation" of alkynes (that is, a hydride and a thiocarboxyl group are introduced into the terminal and internal positions of alkynes, respectively) was found to take place successfully (eq 56).[112] The use of excess alkyne
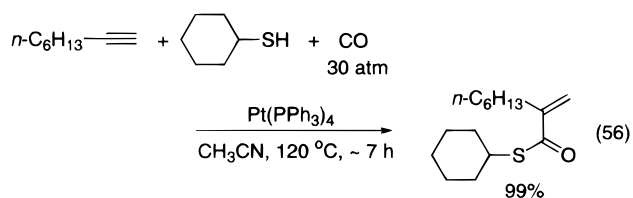
afforded the hydrothiocarboxylation product predominantly, while the reaction using excess thiol gave rise to the other product, which was obtained by further conjugate addition of thiol to the hydrothiocarboxylation product, exclusively. The procedure for this hydrothiocarboxylation can be employed with a variety of aromatic and aliphatic thiols, giving the corresponding α,β-unsaturated thioesters regioselec-

tively in excellent yields. Although elucidation of the precise mechanism requires further detailed investigation, a possible reaction pathway may include CO insertion into the Pt–S bond of an intermediate complex such as *trans*-PtH(SR)(PPh$_3$)$_2$,[113] followed by regioselective acylplatination of alkyne and reductive elimination of the product.

The search for new methods for the preparation of thiol esters and sulfur-containing γ-lactones is a topic of current interest.[114] Not only do these compounds constitute a group of natural products, but they are also attractive building blocks in the synthesis of complex organic molecules.[1,115] Palladium(0) complexes were found to exhibit excellent catalytic activity toward the thiocarbonylation of propargylic alcohols, affording thiofuranones, thioesters, or dithioesters as the principal product, depending on the reaction conditions (eq 57),[116] which represents one of the most straightforward routes to these compounds.
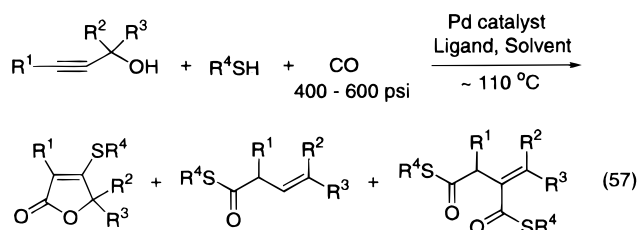
Palladium-catalyzed carbonylative lactonization of propargylic alcohols with organic disulfides and CO has also been reported.[117] For example, the reaction of 2-propyn-1-ol with diphenyl disulfide and CO in the presence of a catalytic amount of Pd(PPh$_3$)$_4$ at 100 °C for 50 h gave 43% of 3-(phenylthio)-2-buten-4-olide with the formation of (Z)-1,2-bis(phenylthio)-3-hydroxy-1-propene in 35% yield (eq 58). 1,3-Bis-
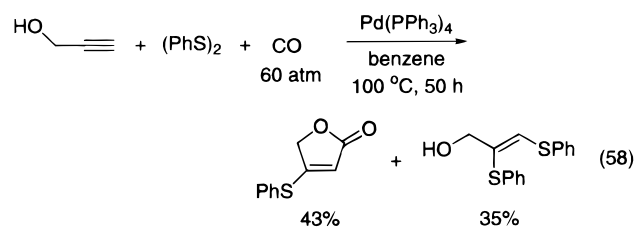
(phenylthio)-4-hydroxy-2-buten-1-one was not detected at all under these reaction conditions. Diphenyl diselenide can be used in place of diphenyl disulfide to give a similar 3-(phenylseleno)-2-buten-4-olide. The present one-pot lactonization was then applied to a homopropargyl alcohol, which provided the corresponding δ-lactones in good yields.

Allenes are also thiocarbonylated using thiols and carbon monoxide with a palladium catalyst to give the corresponding β,γ-unsaturated thioesters, regioselectively (eq 59).[118]
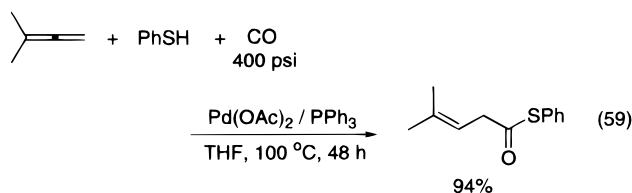
Palladium complexes can also catalyze regioselective thiocarbonylation of allylic alcohols with thiols and CO to give β,γ-unsaturated thioesters.[119] Among the catalytic systems examined, Pd(OAc)$_2$ with PPh$_3$ and p-toluenesulfonic acid (p-TsOH) exhibited excellent catalytic activity to give the thiocarbonylation products in high yields (eq 60). The function of

$$\text{CH=CH-CH(CH}_3\text{)OH} + \text{PhSH} + \text{CO at 400 psi} \xrightarrow[\text{CH}_2\text{Cl}_2, 100\ ^\circ\text{C, 48 h}]{\underset{p\text{-TsOH}}{\text{Pd(OAc)}_2 / \text{PPh}_3}} \text{PhS-CO-CH}_2\text{-CH=CH-CH}_3 \quad (60)$$
$$94\%(E/Z = 5/1)$$
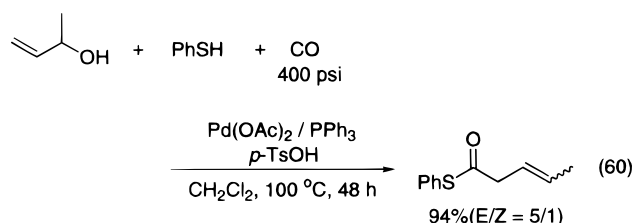
p-TsOH is presumably to protonate the hydroxyl group of the substrate so as to eliminate H$_2$O to form a π-allyl palladium complex. Thiocarbonylation of allylic carbonates and phosphonates can be carried out without p-TsOH, which also demonstrates that the function of the acid is to assist the elimination of the hydroxyl group. All reactions with acyclic and cyclic allylic alcohols occur in a highly regioselective manner, at the less-hindered allylic terminal carbon of the substrate, to give the corresponding thioesters.

The carbonylative cyclization of acetylenic alcohols with carbon monoxide is one of the most straightforward methods of obtaining α-methylenelactones.[120] In particular, the preparation of five-membered (γ) lactones by the carbony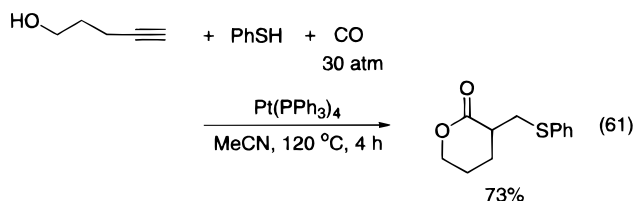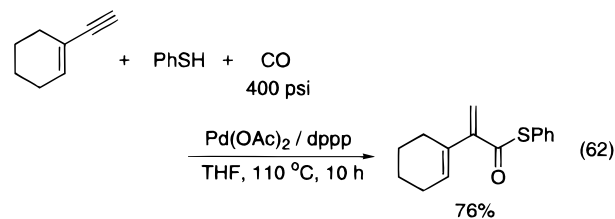lation of acetylenic alcohols has been studied intensively; however, only very limited data are available for the carbonylative routes to six-membered (δ) lactone rings.[121] The previously described method of Pt(PPh$_3$)$_4$-catalyzed carbonylation of alkynes with thiols and CO can be applied to the carbonylative cyclization of acetylenic alcohols to δ-lactones.[122] When the carbonylation of 5-hydroxy-1-pentyne with thiophenol was carried out in the presence of 3 mol % Pt(PPh$_3$)$_4$ catalyst under CO (30 atm) at 120 °C for 4 h, α-((phenylthio)methyl)-δ-lactone was obtained selectively in good yield (eq 61).

$$\text{HO-CH}_2\text{CH}_2\text{CH}_2\text{-C}\equiv\text{CH} + \text{PhSH} + \text{CO at 30 atm} \xrightarrow[\text{MeCN, 120 }^\circ\text{C, 4 h}]{\text{Pt(PPh}_3)_4} \quad (61)$$
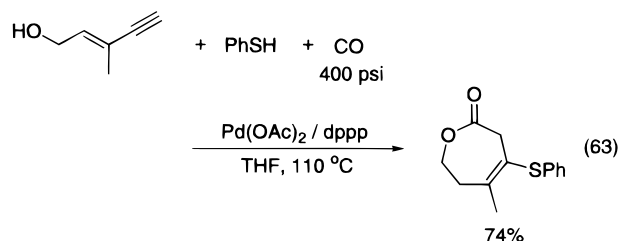$$73\%$$

Since the product would be obtained by Michael addition of thiophenol to α-methylene-δ-lactone, cyclocarbonylation was examined in the absence of thiophenol to give the desired α-methylene-δ-lactone in only 39% yield along with a few byproducts. Consequently, the use of 10 mol % thiophenol in the present cyclocarbonylation reaction resulted in the selective formation of α-methylene-δ-lactone in 67% yield.

The sulfur-substituted dienes have been widely used in Diels–Alder and other reactions.[123] The sulfur-containing group not only increases the reactivity of the diene, but also acts as a handle for further functional group transformations.[124] On the

basis of the publication by Bäckvall and co-workers on the palladium-catalyzed addition of thiophenol to conjugated enynes,[56] highly chemo- and regioselective thiocarbonylation of conjugated enynes with thiols and CO catalyzed by a palladium complex has been developed (eq 62).[125] It was shown that Pd(OAc)$_2$ with

$$+ \text{PhSH} + \text{CO at 400 psi} \xrightarrow[\text{THF, 110 }^\circ\text{C, 10 h}]{\text{Pd(OAc)}_2 / \text{dppp}} \quad (62)$$
$$76\%$$

dppp was the best catalyst system, and the reaction proceeded efficiently in THF as the solvent. The thiocarbonylation of enynes was highly chemoselective, and only the triple bond was attacked by the sulfur nucleophile. Importantly, only one regioisomer was formed in these reactions, by selective attack of the phenylthiocarbonyl group at carbon-2 of the 1,3-conjugated enynes. Both cyclic and acyclic conjugated enynes can be smoothly and regioselectively transformed into the corresponding 2-(phenylthiocarbonyl)-1,3-dienes in good yields. Attempts to thiocarbonylate enynes with internal triple bonds were unsuccessful. An enyne bearing a hydroxyl group in the allylic position afforded a sulfur-substituted lactone in 74% yield instead of an α,β-unsaturated thioester (eq 63).

$$\text{HO} \diagdown \diagup + \text{PhSH} + \text{CO at 400 psi} \xrightarrow[\text{THF, 110 }^\circ\text{C}]{\text{Pd(OAc)}_2 / \text{dppp}} \quad (63)$$
$$74\%$$

B. Insertion of Carbon Monoxide into Carbon–Sulfur Bonds

Phase-transfer catalysis is a useful method for effecting a variety of carbonylation reactions under remarkably mild conditions.[126] Of particular note are reactions involving halides and epoxides as substrates. However, little is known concerning transition metal complex-catalyzed reactions of thiiranes, which are sulfur analogues of epoxides. Recently, it was shown that [RhCl(CO)$_2$]$_2$ can catalyze the homogeneous desulfurization of thiiranes to alkenes.[127] A further effort to develop the transformations of thiiranes catalyzed by transition metal complexes can achieve the carbonylation of thiiranes to β-mercapto acids by cobalt carbonyl and phase-transfer catalysis.[128] For example, 2-phenylthiirane (styrene sulfide) was treated with carbon monoxide (bubbling), methyl iodide, potassium hydroxide (3 N), benzene as the organic phase, a catalytic amount of Co$_2$(CO)$_8$, and PEG-400 as the phase-transfer catalyst at room temperature to give the β-mercapto acid in 78% yield (eq 64). Superior to the use of a quaternary ammonium salt as the phase-transfer agent was the use
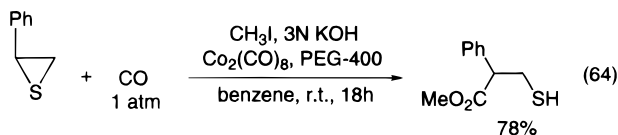
of poly(ethylene glycol)s (PEG-400) as the catalyst. Other synthetic approaches to β-mercapro acids are also known, including the reaction of unsaturated acids with benzyl mercaptan followed by debenzylation with sodium in liquid ammonia, but the present method has a number of advantages including simplicity of execution and workup as well as the regiospecificity.

Important classes of carbonylation reactions are those that involve the direct incorporation of one or two molecules of carbon monoxide into a heterocyclic substrate resulting in ring expansion. This method has been particularly successful when applied to three-membered-ring heterocycles. However, little is known concerning the direct conversion of four- to five-membered-ring heterocycles by carbonylation. $Co_2(CO)_8$ and $Ru_3(CO)_{12}$ together catalyze the regiospecific insertion of carbon monoxide into the least substituted carbon–sulfur bond of a thietane, affording thiobutyrolactones in fine yields (eq 65).[129]
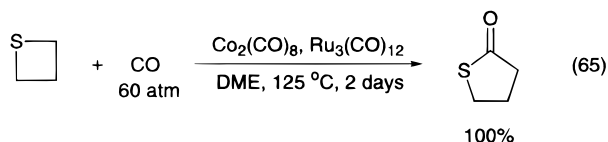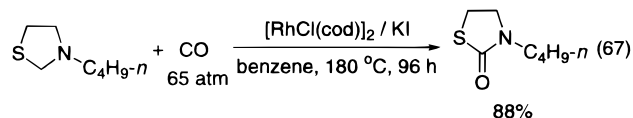

The insertion of carbon monoxide into carbon–heteroatom bonds can be effected by a variety of transition metal catalysts. In most cases, the reaction, which presumably begins by insertion of the metal into the carbon–heteroatom bond, is driven, or at least aided, by ring strain. A challenging problem in organosulfur chemistry is also the achievement of the carbonylation of acyclic, unstrained sulfur-containing compounds. N,S-Acetals appeared to be excellent candidates for such an investigation as the insertion could, in principle, occur in any of the carbon–sulfur or carbon–nitrogen bonds. It was gratifying to observe regiospecific rhodium(I)-catalyzed insertion of carbon monoxide into one of the two carbon–sulfur bonds, the regiosepecificity being dependent on the nature of the reactant.[130] The carbonylation of a series of N,S-acetals was carried out in dry benzene at 53 atm of carbon monoxide at 140 °C for 24 h in the presence of 1 mol % [RhCl-
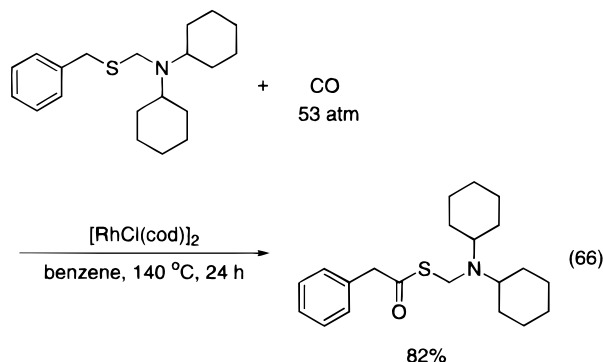
(cod)]$_2$ to give thioesters as the only products in high isolated yields (eq 66). A benzyl group attached to sulfur is required in order to effect the carbon monoxide insertion. No carbon monoxide insertion into the C–N bond was found, even when the amine is benzylated.

The regiospecific carbon monoxide insertion into the C–S bond in this series is quite unusual. In cyclic systems, the ease of carbonylation is in the order of C–N > C–S > C–O.[129,131] 1,3-Thiazolidines reacted with carbon monoxide in the presence of a catalytic amount of [RhCl(cod)]$_2$ and KI to give thiazolidinones exclusively in 56–88% yields (eq 67).[132] This process

involves a novel regiospecific insertion of carbon monoxide into one of two ring C–N bonds, as well as a metal-catalyzed ketene elimination process.

Although no carbonylation of the C–N bond is observed, the presence of this functionality is crucial to the success of insertion of CO into the C–S bond. Furthermore, not only is it necessary to have nitrogen in the molecule, it must be in a 1,3-relationship with respect to sulfur. 1,4-Thioamines are completely unreactive under the described conditions.

Palladium complex-catalyzed insertion of carbon monoxide into the C–S bond of various allylic sulfides affords thioesters in up to 88% yield (eq 68).[133] The
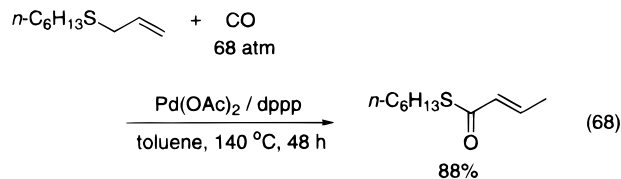
reaction is catalyzed by various palladium complexes, with concomitant isomerization of the olefin into conjugation with the carbonyl group. In these cases, only the trans isomer was detected by ^{1}H NMR spectroscopy. Ruthenium complexes also catalyzed the carbonylation, but the initially formed β,γ-thioesters were not isomerized.

C. Insertion of Carbon Monoxide and Isocyanides into Sulfur–Sulfur Bonds

While transition metal complex-catalyzed reactions of thiols, thiiranes, thietanes, N,S-acetals, and allylic sulfides with carbon monoxide have been extensively studied and described above, organic disulfides are another class of important organic sulfur compounds. Aromatic and benzylic disulfides reacted with carbon monoxide in the presence of a catalytic amount of $Co_2(CO)_8$ to give the corresponding thioesters and COS (eq 69).[134]
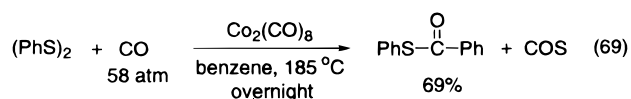
The first evidence of insertion of isocyanide into a Pd–S bond has been demonstrated by Kurosawa and Kuniyasu et al.[135] Pd(PPh$_3$)$_4$-catalyzed the reaction of diaryl disulfides, (ArS)$_2$, with isocyanides, Ar'NC, to produce the adducts (ArS)(C=NAr')$_m$(SAr). The mechanistic study reveals that the complex, Pd(SAr)$_2$-(CNAr')(PPh$_3$) is a resting state for giving the 1:1 adduct and converted it into the corresponding 1:1 insertion product, ArS(C=NAr')SAr, in the presence of another equivalent of (ArS)$_2$. The study on reactivities of isocyanide and thiolato ligands on platinum including the X-ray crystallographic analysis of the imidoyl platinum *trans*-Pt[(C=NAr')$_2$SAr](SAr)(PPh$_3$) obtained by the oxidative addition of the C–S bond of 1:2 adduct to Pt(PPh$_3$)$_4$ has also been reported.

VI. Concluding Remarks

This article compiled recent advances in transition metal complex-catalyzed carbon–sulfur bond forming reactions mainly from the standpoint of organic synthesis. Over the last two or three decades, the importance of heterochemistries in organic synthesis has grown dramatically. As mentioned in this review, silicone, tin, and boron chemistries as well as phosphorus chemistry were developed earlier and faster than sulfur and other chalcogen chemistries. The reluctance of organic chemists to handle sulfur compounds was probably in part responsible for this situation; however, this time is now over. A devoted chemist can no longer ignore the possibilities in organic synthesis offered by sulfur-based reagents, and the combination of organosulfur chemistry with organotransition metal complex catalysis will also open up new opportunities in this field. Hence, since the transition metal complex-catalyzed carbon–sulfur bond forming reaction is a very powerful and useful reaction, these catalytic processes introduced in this article could become a valuable tool in the field of organic synthesis.

Because of the space limitations, full details of each reaction, i.e., reaction mechanism, limitation of the applicable substrates, and synthetic applications, have not been described precisely in this article. For further details, refer to the review articles and original papers cited in the references.

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