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Review

Activation and reactivity of Group 16 inter-element linkage — transition-metal-catalyzed reactions of thiols and selenols

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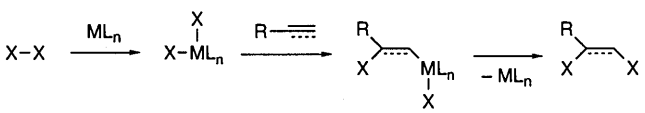
Abstract

This review deals with new synthetic methods for introducing Group 16 elements into organic molecules, especially, synthetic reactions based on the activation of Group 16 heteroatom compounds by transition metal catalysts. In these transition-metal-catalyzed reactions, metal chalcogenides (RY-ML_n, Y = S, Se) play an important role. Chalcogen compounds with inter-element linkage such as S–S, Se–Se, Se–Si, etc. add to terminal alkynes regio- and stereoselectively in the presence of palladium(0) catalyst. The addition of thiols and selenols to alkynes can be catalyzed by a lot of transition metal catalysts. In the presence of $Pd(OAc)_2$, alkynes undergo Markovnikov addition with thiols, whereas the $RhCl(PPh_3)_3$-catalyzed reaction of alkynes provides *anti*-Markovnikov adducts regio- and stereoselectively. Moreover, the introduction of carbon monoxide into these transition-metal catalyzed addition reaction systems leads to the development of novel carbonylation reactions with simultaneous introduction of chalcogen functions. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Group 16 inter-element linkage; Regio- and stereoselective addition; Carbonylation; Transition metal catalyst; Thiol; Selenol; Carbon–carbon unsaturated bond

1. Introduction

Transition-metal-catalyzed addition of heteroatom compounds bearing heteroatom–heteroatom linkage (X–X) or heteroatom–hydrogen linkage (X–H) to carbon–carbon unsaturated bonds such as alkynes, alkenes, allenes, etc. is one of the most useful methods for introducing heteroatom functions into organic molecules [1]. A possible catalytic pathway for these reactions may involve the inter-element species bearing a heteroatom–metal linkage as a key intermediate, which can be formed from the oxidative addition of heteroatom compounds to transition metals. The subsequent heterometallation of unsaturated compounds, followed by the reductive elimination leads to the corresponding hetero-functionalized organic molecules (Eq. (1)).



(1)

1.1. Group 16–Group 16 inter-element linkage

Along this line, a series of bismetallations of carbon–carbon unsaturated compounds such as bissilylation [2], bisgermylation [3], bisstannation [4], bisboration [5], etc. have been developed as transition-metal-catalyzed reactions. In contrast, transition-metal-catalyzed reactions of Group 16 inter-element compounds with carbon–carbon unsaturated compounds has remained largely undeveloped very recently. This might be partly due to the widespread prejudice that Group 16 inter-element compounds often bind strongly to the catalysts, thus poisoning them and making the catalytic reactions ineffective. On the con-

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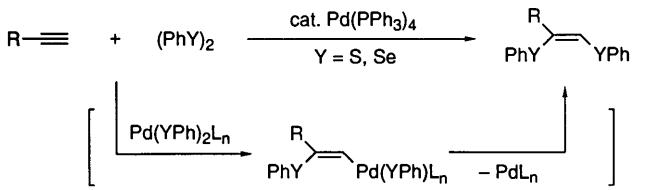
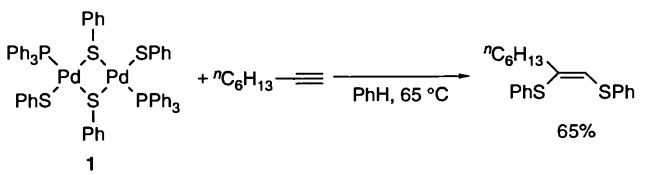
trary, we have recently revealed a series of reactions made up of such mismatched combinations of transition metal catalysts and Group 16 inter-element compounds like organic disulfides and diselenides. For example, diphenyl disulfide and selenide are found to add to alkynes in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0), giving the corresponding *vic*-bis(phenylthio)alkenes and *vic*-bis(phenylseleno)alkenes, respectively, with high stereoselectivity (Eq. (2)) [6]. The procedure can be employed with a variety of alkynes[1]. However, $Pd(PPh_3)_4$ exhibits no catalytic activity toward the addition to alkenes. Recently, Cp*RuCl(cod) is reported to work as an excellent catalyst for the vicinal dithiolation of alkenes [8].



(2)

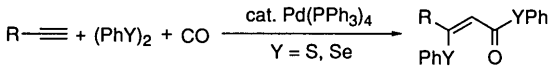
Diphenyl disulfide is reported to add oxidatively to $Pd(PPh_3)_4$ generating the complex (**1**) formulated as a dimer bearing both terminal and bridged sulfide groups [9]. The stoichiometric reaction of the complex (**1**) isolated with 1-octyne affords *vic*-1,2-bis(phenylthio)-1-octene in moderate yields (Eq. (3)).



(3)

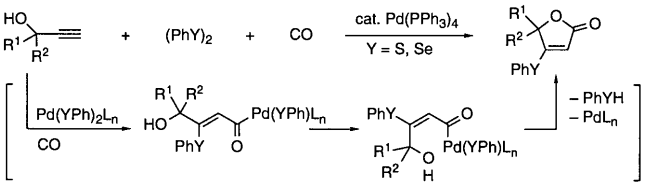
These results strongly suggest that the $Pd(PPh_3)_4$-catalyzed bisthiolation of alkynes proceeds via (i) oxidative addition of $(PhS)_2$ to $Pd(PPh_3)_4$; (ii) insertion of alkynes to the Pd–S inter-element linkage of $Pd(SPh)_2L_n$; (iii) reductive elimination of *vic*-bis(phenylthio)-alkenes with regeneration of the catalyst.

Since the $Pd(PPh_3)_4$-catalyzed bisthiolation of alkynes involves vinylpalladium species as a key intermediate, the same reaction in the presence of carbon monoxide may lead to the carbonylative bisthiolation of alkynes. Indeed, the $Pd(PPh_3)_4$-catalyzed reaction of alkynes with diphenyl disulfide under pressurized carbon monoxide gives rise to the corresponding carbonylative bisthiolation products in high yields with excellent stereoselectivity (Eq. (4)) [6]. The method can be also employed with diphenyl diselenide. In both cases, carbon monoxide is introduced into the terminal carbon of alkynes regioselectively.



(4)

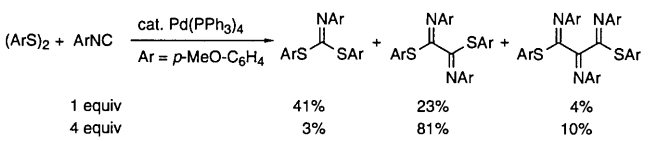
When the palladium-catalyzed carbonylation with $(PhY)_2$ (Y=S, Se) and CO is applied to propargyl alcohols, carbonylative lactonization takes place under higher pressure of CO to provide the corresponding γ-lactone in good yields (Eq. (5)) [10].



(5)

The reaction may involve double bond isomerization process of α,β-unsaturated acylpalladium species, followed by intramolecular cyclization to give the corresponding lactones. Considering that the carbonylative addition of disulfides (or diselenides) to alkynes bearing no hydroxy group provides (*Z*)-carbonylative addition products with excellent stereoselectivity (Eq. (4)), the result may indicate that the presence of a hydroxyl group in alkynes is crucial for the double bond isomerization. Probably, intramolecular coordination of the hydroxyl group to the palladium may contribute to the double bond isomerization.

Isocyanides is known to have an isoelectronic structure with carbon monoxide. Recently, insertion reaction of isocyanides into the sulfur–sulfur inter-element linkage of organic disulfides is reported to proceed in the presence of $Pd(PPh_3)_4$, as exemplified in Eq. (6) [11].



(6)

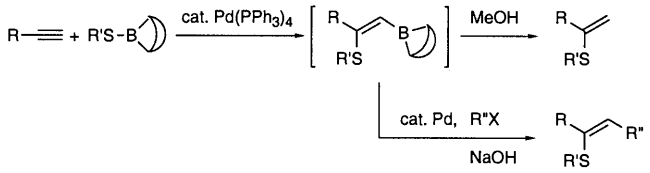
The equimolar reaction of $(ArS)_2$ with ArNC provides the mono-insertion product as the major product, whereas the use of 4 equiv of ArNC leads to the formation of the corresponding double-insertion products in 81% yield.

1.2. Group 16–Group 13 inter-element linkage

Although the reactions mentioned above include the activation of Group 16–Group 16 inter-element linkage by transition-metal catalysts, one of the most interesting application of this methodology is the simultaneous introduction of two different heteroatoms into unsaturated compounds. A highly selective thioboration of

[1] With dialkyl disulfides in place of diaryl ones, the palladium-catalyzed dithiolation of alkynes results in lower yield of the desired *vic*-dithiolation products. For an improved method, see [7].

alkynes with 9-(alkylthio)-9-borabicyclo[3.3.1]nonanes, which bear a Group 16–Group 13 inter-element linkage, is reported to take place in the presence of $Pd(PPh_3)_4$ catalyst (Eq. (7)). The reaction is regio- and stereoselective, and the subsequent protonolysis with methanol produces the Markovnikov adducts of thiols to alkynes [12].

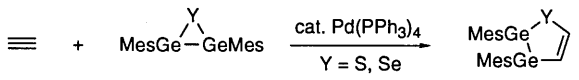


(7)

The palladium-catalyzed thioboration, followed by the palladium-catalyzed cross-coupling with organic halides leads to the regio- and stereoselective one-pot synthesis of vinyl sulfides.

1.3. Group 16–Group 14 inter-element linkage

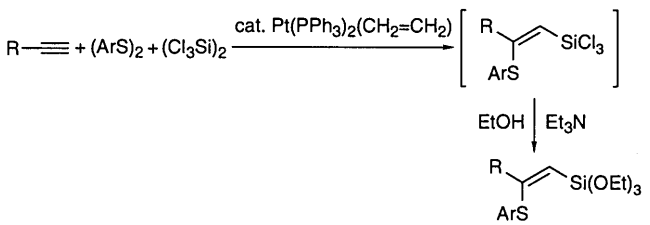
The first example of the transition-metal-catalyzed addition of Group 16–Group 14 inter-element linkage to alkynes is shown by using thia- and selena-digermiranes as strained molecules (Eq. (8)) [13].



(8)

The regio- and stereoselective addition of Group 16–Group 14 inter-element linkage to alkynes is demonstrated by the $Pd(PPh_3)_4$-catalyzed reaction of $PhSeSiMe_3$ and $PhSeGeMe_3$ with aromatic acetylenes, but the yields of the adducts are relatively low (e.g. (*Z*)–Ar(PhSe)C=CH($GeMe_3$), 35%) [14].

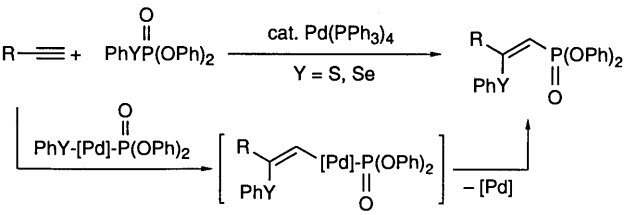
Very recently, a novel mixed system of $(ArS)_2$ and $(Cl_3Si)_2$ in the presence of $Pt(PPh_3)_2(CH_2{=}CH_2)$ is reported to work well for the regio- and stereoselective thiosilylation of various alkynes (Eq. (9)) [15]. At the initial stage, platinum-catalyzed disproportionation of $(ArS)_2$ with $(Cl_3Si)_2$ may take place to form $ArSSiCl_3$, which adds oxidatively to the low-valent platinum. Thus formed ArS–[Pt]–$SiCl_3$ then reacts with alkynes.



(9)

1.4. Group 16–Group 15 inter-element linkage

Palladium complexes such as $Pd(PPh_3)_4$, $Me_2Pd(PPh_3)_4$, and $Pd(PPh_3)_2(CH_2{=}CH_2)$ efficiently catalyze the addition of *O*,*O*,*S*-triphenyl phosphorothioate, which bears a Group 16–Group 15 inter-element linkage, to terminal alkynes to produce (*Z*)-1-(diphenoxyphosphinyl)-2-(phenylthio)alkenes in high yields with high regio- and stereoselectivity (Eq. (10)) [16]. The procedure can be applied to the regio- and stereoselective selenophosphorylation of alkynes with $PhSeP(O)(OPh)_2$ [17].



(10)

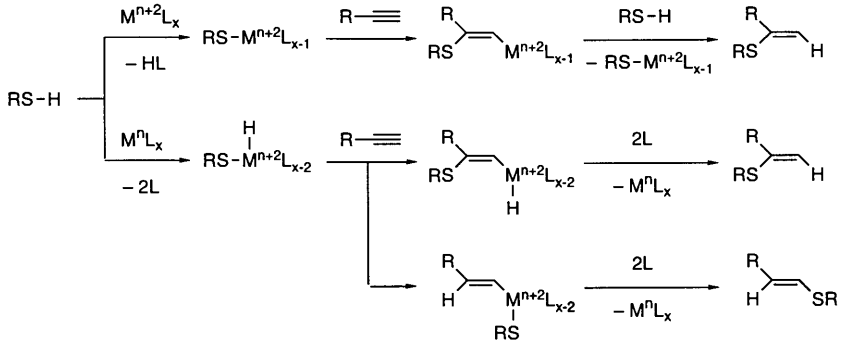
As mentioned in this introduction, activation of inter-element linkage involving Group 16 elements by transition metal catalysts and highly selective addition to alkynes based on this activation have been developed. These new reactions clearly indicate the utility of transition metal catalysts in the synthetic reactions of Group 16 heteroatom compounds.

In this review, we wish to describe a series of transition-metal-catalyzed reactions of thiols and selenols, as a Group 16 element–hydrogen bond compounds, with carbon–carbon unsaturated compounds.

2. Transition-metal-catalyzed hydrochalcogenation of alkynes

Transition metal-catalyzed addition reaction of compounds bearing a main group element–hydrogen linkage to carbon–carbon unsaturated bonds is an important methodology for the synthesis of main group compounds, as represented by the hydrosilylation [18], hydrostannation [19], and hydroboration [5] of olefins, acetylenes, and conjugated dienes. In these reactions, the hydrogen of silanes, stannanes, and boranes is more electronegative than the heteroatoms. On the other hand, thiols and selenols have an acidic proton, and it is of much interest to investigate the reactivity of these chalcogenol toward transition metal catalysts in the presence of carbon–carbon unsaturated bonds.

Thiols and selenols have been widely employed as the sources of ligands for various transition metals [20]. In the stoichiometric reactions of thiols (or selenols) with transition metal complexes, two types of processes are generally operative. One is the ligand-exchange reaction between high-valent transition metals and thiols (or selenols) to give the complexes bearing only thiolate (or selenolate) ligands (Scheme 1). The other is the oxidative addition of thiols (or selenols) to low-valent transition metals to give the corresponding complexes



Scheme 1.

bearing both hydride and thiolate (or selenolate) ligands.

The reaction of the former complexes (RS-$M^{n+2}L_{x-1}$) with alkynes may proceed via thiometallation, in which relatively more bulky $M^{n+2}L_{x-1}$ is bonded at the terminal carbon of alkynes. On the other hand, both hydrometallation and thiometallation processes are possible in the reaction of the latter complexes (RS-$HM^{n+2}L_{x-2}$) with alkynes.

Thus, the reaction of benzenethiol with 1-octyne is examined by using a variety of transition metal catalysts and the results are summarized in Table 1 [21]. It is 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 [22]. Indeed, the reaction of benzenethiol with 1-octyne in the absence of transition metal catalyst (entry 12) or in the presence of acetic acid (entry 2) provides *anti*-Markovnikov adduct (**4a**) regioselectively with the E/Z ratio of ca. 1:1, most probably via the radical process induced by trace amounts of oxygen existed in the reaction system. The radical addition of thiols to alkynes sometimes seems to proceed even in the presence of transition metal catalysts. Accordingly, when the *anti*-Markovnikov adducts are obtained with approximately equal amounts of (*E*)- and (*Z*)-isomers, the following possibility is present: the *anti*-Markovnikov adducts are formed by the radical process, regardless of the presence of transition metal catalysts.

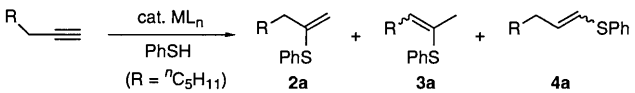
As indicated in Table 1, a variety of transition metal complexes do catalyze the hydrothiolation of 1-octyne with PhSH. Among them, palladium acetate exhibits excellent catalytic activity toward the Markovnikov-type hydrothiolation of 1-octynes (entry 1).

When $PdCl_2(PhCN)_2$ is used as a catalyst, a novel Markovnikov addition and double bond isomerization reaction of benzenethiol with terminal alkynes is found to take place sequentially to give the corresponding internal vinylic sulfides (**3a**) (entry 3). More interestingly, switching the catalyst simply from $Pd(OAc)_2$ to $RhCl(PPh_3)_3$ leads to a sharp reversal of regioselectivity in the addition of PhSH to alkynes providing *anti*-Markovnikov-type vinylic sulfides (**4a**) with the *trans* configuration (entry 11).

2.1. $Pd(OAc)_2$-catalyzed hydrothiolation

The results of the $Pd(OAc)_2$-catalyzed hydrothiolation of several alkynes with PhSH are shown in Table 2 [21a]. Functionalities such as hydroxy, amino, and alkenyl groups [21c] are tolerant toward the regioselective hydrothiolation (entries 1, 2 and 4). The hydrothio-

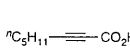
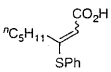
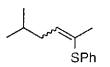
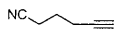
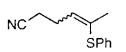
Table 1
Transition-metal-catalyzed addition of PhSH to 1-octyne [a]



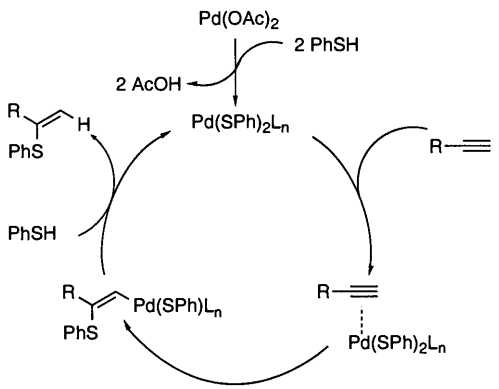
Entry	Catalyst	Yield (%) [b]		
		2a	**3a** [E/Z]	**4a** [E/Z]
1 [c]	$Pd(OAc)_2$	85	Trace	Trace
2	AcOH	0	0	78 [53/47]
3	$PdCl_2(PhCN)_2$	1	66 [56/44]	0
4	$PdCl_2(MeCN)_2$	2	58 [64/36]	23 [51/49]
5	$Pd(PPh_3)_4$	17	2	16 [91/9]
6	$Pt(PPh_3)_2(CH_2{=}CH_2)$	19	38 [63/37]	17 [50/50]
7 [d]	$Pt(PPh_3)_2(CH_2{=}CH_2)$	41	10 [76/24]	5 [40/60]
8	$RhH(CO)(PPh_3)_3$	49	0	16 [76/24]
9 [d]	$RhH(CO)(PPh_3)_3$	19	26 [61/39]	14 [89/11]
10 [e]	$RhH(CO)(PPh_3)_3$	2	58 [67/33]	7 [43/57]
11	$RhCl(PPh_3)_3$	29	0	50 [100/0]
12 [f]		0	0	65 [48/52]

[a] Reaction conditions: 1-octyne (1 mmol), PhSH (1 mmol), catalyst (5 mol%), benzene (0.5 ml), 80°C, 20 h.
[b] Determined by ^{1}H-NMR.
[c] Catalyst (2 mol%), THF (0.5 ml), 40°C.
[d] Catalyst (3 mol%).
[e] Catalyst (0.5 mol%).
[f] In the absence of catalyst.

Table 2
$Pd(OAc)_2$- or $PdCl_2(PhCN)_2$-catalyzed regioselective hydrothiolation [a]

entry	alkyne	catalyst	product, 2	yield, %[b]	[E/Z][c]
1		$Pd(OAc)_2$		86	
2[d]		$Pd(OAc)_2$		65	
3		$PdCl_2(PhCN)_2$		69	
4		$Pd(OAc)_2$		70	
5		$Pd(OAc)_2$		72	[34/66]
6					[92/8][e]
7		$Pd(OAc)_2$		29	[48/52]
				53	[63/37]
8		$Pd(OAc)_2$		87	[98/2]
9		$PdCl_2(PhCN)_2$		77	[58/42]
10		$PdCl_2(PhCN)_2$		63	[40/60]
11		$PdCl_2(PhCN)_2$		70	[45/55]
12		$PdCl_2(PhCN)_2$		68	

[a]Condition A: alkyne (1.0 mmol), $Pd(OAc)_2$ (2 mol%), PhSH (1.0-1.3 mmol), THF (0.5 mL), 67 °C, 12-16 h. Condition B: alkyne (1.0 mmol), $PdCl_2(PhCN)_2$ (5 mol%), PhSH (1.0 mmol), PhH (0.5 mL), 80 °C, 20 h. [b]Isolated yield. [c]Determined by ^{1}H NMR. [d]24 h. [e]10 min.



Scheme 2.

lation also proceeds smoothly with internal acetylenes to give a mixture of stereoisomers (entry 5), although the (*E*)-isomer is predominantly formed at the beginning of the reaction (entry 6). Interestingly, the addition to 2-octynoic acid affords the corresponding adduct with high regio- and stereoselectivity (entry 8).

To obtain some insight of active catalyst of the $Pd(OAc)_2$-catalyzed hydrothiolation, the reaction of $Pd(OAc)_2$ with 2 equivalents of PhSH in THF-d_8 in the presence or absence of 1-octyne is monitored by ^{1}H-NMR spectroscopy. In both cases (in the presence or absence of 1-octyne), the mixture immediately deposited dark brown precipitates (**A** or **B**) with the formation of ca. 2 equivalents of AcOH. The elemental analysis of the dark brown precipitates (**A** or **B**) strongly suggests the formation of $[Pd(SPh)_2]_n$ from the ligand-exchange reaction between $Pd(OAc)_2$ and PhSH (Eq. (11)). The catalytic hydrothiolation of 1-octyne with PhSH is examined by using the dark brown precipitates (**A** or **B**) prepared by the reaction in the presence or absence of 1-octyne. Interestingly, the dark brown precipitates (**A**) exhibits good catalytic activity toward the hydrothiolation, whereas the catalytic activity of the dark brown precipitates (**B**) is less effective (Eq. (12)).

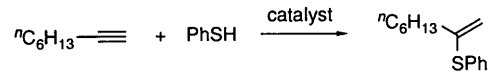
$$Pd(OAc)_2 + 2PhSH \longrightarrow [Pd(SPh)_2]_n + 2AcOH$$

dark brown solid

in the presence of 1-octyne — **A**

in the absence of 1-octyne — **B**

(11)



catalyst : dark brown solid **A** 62%

B 32%

(12)

A possible explanation for these results is as follows: palladium sulfide ($[Pd(SPh)_2]_n$) has a polymeric structure bearing both terminal and bridged sulfide groups [23], and therefore insoluble in most of organic solvents. This strongly suggests that the $Pd(OAc)_2$-catalyzed hydrothiolation of alkynes with PhSH proceeds on the surface of the precipitated palladium sulfide. Probably, the palladium sulfide (**B**) prepared by the reaction in the absence of 1-octyne might be much more polymeric than the palladium sulfide (**A**) prepared by the reaction in the presence of 1-octyne, because the polymerization by the sulfur bridging may be retarded by the coordination of 1-octyne to the palladium. If the terminal sulfide groups are more reactive than the bridged sulfide groups, the palladium sulfide (**A**), which has much terminal sulfide groups compared with the palladium sulfide (**B**), is expected to be catalytically more active than the palladium sulfide (**B**).

To ascertain the stereochemistry of this $Pd(OAc)_2$-catalyzed hydrothiolation, the reaction of PhSH with 1-octyne-*1-d* (containing $>93\%$ *d*) is followed by ^{1}H-NMR spectroscopy. The *E*/*Z* ratio of the thiolation products changes from 100/0 (6% conversion) after 15 min to 86/14 (81% conversion) after 8 h. Thus, (*E*)-isomer can be accepted as the kinetic product, which gradually isomerized to (*Z*)-isomer. This clearly indicated that *syn*-addition of PhSH to 1-octyne proceeds at least at the initial stage (Scheme 2).

Thus, a mechanistic proposal includes: (1) ligand-exchange reaction of AcO ligand with PhS group in the presence of alkyne to give AcOH and the active catalyst; (2) coordination of alkyne to the palladium; (3) *syn*-thiopalladation to alkyne to form *cis*-vinylpalladium; (4) trapping of the vinyl group by PhSH or AcOH with retention of the stereochemistry to give the product with regeneration of the catalyst.

2.2. $PdCl_2(PhCN)_2$-catalyzed hydrothiolation

Table 2 also represents the sequential addition/isomerization reactions of terminal alkynes in the presence of $PdCl_2(PhCN)_2$ [21b]. In general, alkynes bearing propargylic protons ($R'CH_2C{\equiv}CH$) undergo sequential addition/isomerization reaction to provide the internal vinylic sulfides ($R'CH{=}C(SAr)CH_3$) regioselectively (entries 9–11). However, hydrothiolation of propargyldimethylamine provides only Markovnikov adduct regioselectively in 69% yield; namely, this indicates that the presence of a basic amino group inhibits the double bond isomerization entirely (entry 3). Phenylacetylene, which bears no propargylic protons, undergoes regioselective hydrothiolation to provide Markovnikov adduct in good yield (entry 12). On the other hand, the hydrothiolation of inner alkynes is not regioselective.

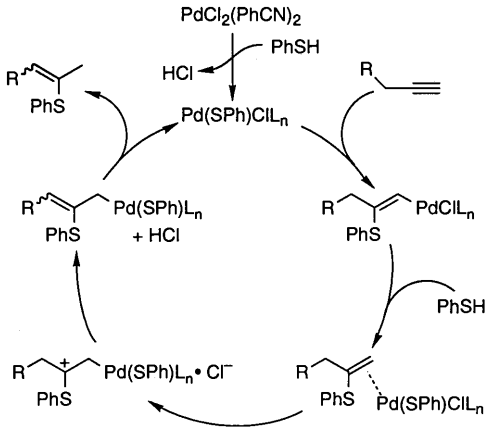
To get some information about the real catalyst in this sequential addition/isomerization reaction, stoichiometric reaction using $PdCl_2(PhCN)_2$ is conducted, as shown in Eq. (13). The reaction of $PdCl_2(PhCN)_2$ with PhSH (2 equiv) in benzene at room temperature provides brown solid (**A**), which is insoluble in most organic solvents such as THF, $CHCl_3$, CH_3CN, etc. but slightly soluble in DMF. The elemental analysis and measurement of the molecular weight of **A** by using GPC suggests that A is monomeric or dimeric but does not have a polymeric (or oligomeric) structure.

$$PdCl_2(PhCN)_2 + \underset{\text{2 equiv}}{PhSH} \longrightarrow \underset{\text{Complex A}}{[PdCl(SPh)(PhSH)]_n} \quad (n = 1 \text{ or } 2) \qquad (13)$$

$$^nC_5H_{11}{-}{\equiv} + \underset{\text{1 equiv}}{PhSH} \xrightarrow{\text{cat. complex A}} \underset{\textbf{3a, 42\%}}{^nC_5H_{11}\text{(SPh)}C{=}CH_2} \qquad (14)$$

The reaction of benzenethiol with 1-octyne by using the complex **A** as a catalyst affords the corresponding addition/isomerization product in 41% yield (Eq. (14)). Furthermore, upon treatment of the Markovnikov adduct ($^nC_6H_{13}(PhS)C{=}CH_2$, **2a**) with a catalytic amount of complex **A**, double bond isomerization takes place to give **3a** in almost quantitative yield.

On the other hand, the reaction of $PdCl_2(PhCN)_2$ with 3 equiv of PhSH provides the complex **B**, the elemental analysis of which indicates oligomeric structure such as $[Pd_2(SPh)_3(PhSH)]_n$. Compared with the complex **A**, the complex **B** exhibits lower catalytic activity toward the present sequential addition/isomerization reaction of 1-octyne with PhSH (the yield of **3a**, 28%).



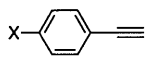
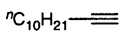
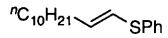
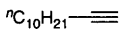
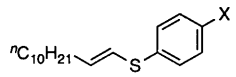
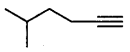
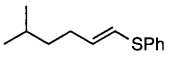
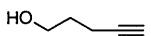
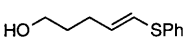
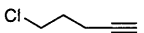
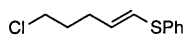
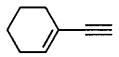
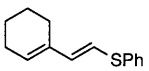
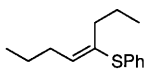
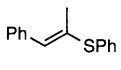
Scheme 3.

Scheme 3 illustrates a possible reaction pathway for the $PdCl_2(PhCN)_2$-catalyzed hydrothiolation of alkynes, which includes the following: (i) ligand-exchange reaction of $PdCl_2(PhCN)_2$ with PhSH forms $Pd(SPh)ClL_n$, which adds to alkyne, providing vinylic palladium intermediate; (ii) protonation of the vinylic palladium intermediate with PhSH leads to Markovnikov type adduct; (iii) double bond isomerization of the Markovnikov type adduct takes place via cationic intermediate [24], followed by deprotonation to give allylpalladium intermediate; (iv) protonation of the allylpalladium intermediate with HCl provides the sequential addition/isomerization product with regeneration of the catalyst.

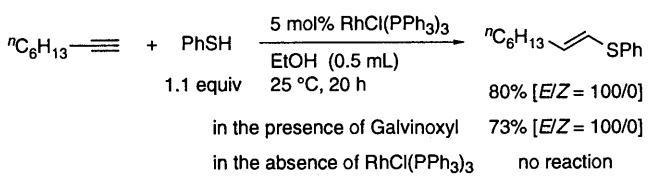
2.3. $RhCl(PPh_3)_3$-catalyzed hydrothiolation

As the results of the detailed investigation on the $RhCl(PPh_3)_3$-catalyzed hydrothiolation of alkynes with PhSH, the best regio- and stereoselectivities are observed, when slightly excess PhSH is added dropwise at 25°C over 1 h to the solution of 1-octyne and $RhCl(PPh_3)_3$ (5 mol%) in EtOH (Eq. (15)). To rule out the possibility that radical mechanism contributes to this *anti*-Markovnikov addition process, the rhodium-catalyzed reaction of PhSH to alkynes is examined in the presence of a radical inhibitor such as Galvinoxyl, which proceeds smoothly to provide the *anti*-Markovnikov adduct regio- and stereoselectively. In the absence of the rhodium catalyst, the reaction of PhSH with alkynes in EtOH resulted in only recovery of the starting materials. These observations clearly indicate that the present *anti*-Markovnikov addition proceeds as a catalytic reaction of $RhCl(PPh_3)_3$.

Table 3
$RhCl(PPh_3)_3$-catalyzed selective hydrothiolation[a]

entry	alkyne	temp, °C	vinyl sulfide	yield, %[b]
1		40	X = H	97
2		20	X = Me	94
3		20	X = F	75
4		25		80[c]
				
5[d]		30	X = MeO	72[c]
6[e]		40	X = Cl	86[c]
7		25		66[c]
8		25		60
9		40		60
10		20		73
11		20		80[c]
12		20		97[c]

[a]Reaction conditions: alkyne (1 mmol), PhSH (1.1 mmol), $RhCl(PPh_3)_3$ (1-3 mol%), EtOH (1 mL), 20 h. [b]Isolated yield based on the thiol used. [c]Thiol was added dropwise over 1 h. [d]p-MeO-C_6H_4SH was used. [e]p-Cl-C_6H_4SH was used.

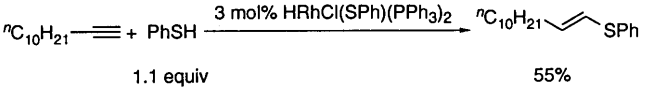


(15)

Table 3 represents the results of the $RhCl(PPh_3)_3$-catalyzed hydrothiolation of a series of alkynes with ArSH [21b]. The procedure can be applied to both aromatic and aliphatic alkynes. Functionalities such as fluoro, chloro, hydroxy, methoxy, and olefinic groups tolerate the reaction conditions (entries 3, 5, 6, 8, 9, and 10). In all cases listed in Table 3, the hydrothiolation proceeds with excellent regio- and stereoselectivity to provide only (*E*)-isomer of *anti*-Markovnikov adduct.

To explore the reaction pathway for this $RhCl(PPh_3)_3$-catalyzed hydrothiolation, the stoichiometric reaction of $RhCl(PPh_3)_3$ with benzenethiol is examined. The equimolar reaction of $RhCl(PPh_3)_3$ with PhSH at 20°C in dichloromethane under argon atmosphere affords a yellow solid, which can be identified unambiguously with *trans*-$HRhCl(SPh)(PPh_3)_2$ reported in the literature [25].

The catalytic reaction of 1-dodecyne with PhSH in the presence of 3 mol% of *trans*-$HRhCl(SPh)(PPh_3)_2$ affords the *anti*-Markovnikov adduct in a good yield (Eq. (16)).



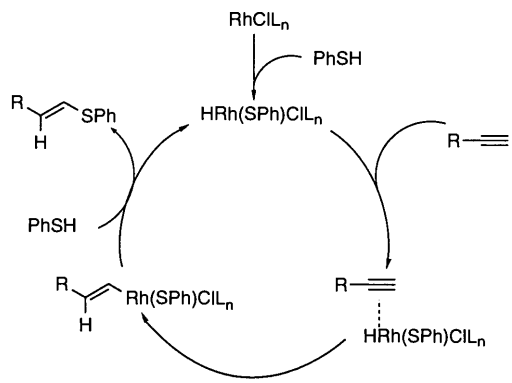
(16)

Furthermore, the $RhCl(PPh_3)_3$-catalyzed hydrothiolation of 1-dodecyne with PhSH is monitored by ^{1}H-NMR spectrometer: the reaction of $HRhCl(SPh)(PPh_3)_2$ with equimolar amount of 1-dodecyne at room temperature results in disappearance of both Rh–*H* (δ −16.4) and acetylenic H, and instead, a new doublet peak appears at δ 5.1 (probably as the vinylic proton). The new peak disappears by the addition of PhSH (1 equiv) to the solution, producing vinylic sulfide after standing for 6 h.

Based on these results, a possible catalytic cycle for this rhodium-catalyzed hydrothiolation of alkynes is shown in Scheme 4. Formation of $HRh(SPh)ClL_n$ via the oxidative addition of PhSH to $RhClL_n$, followed by the stereoselective insertion of alkynes into the Rh–H bond to form *trans*-vinylrhodium intermediate. The subsequent reductive elimination of the *anti*-Markovnikov adduct in the presence of excess PhSH, regenerates $HRh(SPh)ClL_n$.

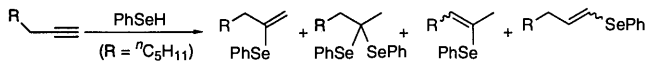
2.4. Transition-metal-catalyzed hydroselenation

The hydroselenation of alkynes with PhSeH provides the simple route to produce vinyl selenides, and therefore the hydroselenation is attempted using transition metal catalysts. Compared with the transition-metal-catalyzed hydrothiolation, the corresponding hydroselenation is less selective. For example, the hydro-



Scheme 4.

selenation of 1-octyne with PhSeH in the presence of $Pd(OAc)_2$ at 80°C for 15 h gives rise to 2-(phenylseleno)-1-octene as the major product along with some other addition products (Eq. (17)) [26]. Sequential addition/isomerization reaction takes place in the presence of $PdCl_2(PhCN)_2$, whereas $RhCl(PPh_3)_3$ does not exhibit good catalytic activity toward the selective *anti*-Markovnikov addition reaction.

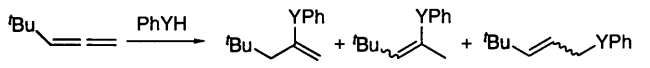


catalyst :	$Pd(OAc)_2$	62%	13%	7%	3%
	$PdCl_2(PhCN)_2$	4%	-	68%	-
	$RhCl(PPh_3)_3$	15%	-	7%	15%

(17)

3. Palladium acetate-catalyzed hydrochalcogenation of allenes

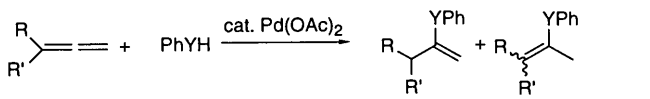
The addition reaction of organic chalcogenols to allenes is one of the most straightforward access to vinylic and/or allylic chalcogenides, and the radical addition of thiols and selenols is already known to produce the corresponding regioisomeric mixtures as illustrated in Eq. (18) [27].



Y = S	O_2	38%	37%	25%
Se	O_2	8%	70%	-
S	cat. $Pd(OAc)_2$	85%	-	-
Se	cat. $Pd(OAc)_2$	74%	-	-

(18)

In contrast, palladium acetate exhibits excellent catalytic activity toward the highly regioselective hydrothiolation [28] and hydroselenation [29] of *t*-butylallene.



Y = S	R = ^{n}Bu	R' = H	86%	-
S	cyclohexyl	H	76%	-
S	Ph	H	8%	36% [50/50]
S	Me	Me	67%	-
Se	^{n}Bu	H	63%	16% [44/56]
Se	cyclohexyl	H	69%	20% [50/50]

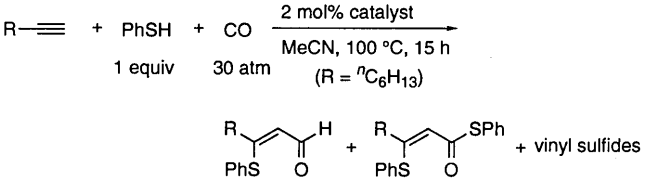
(19)

Similarly, *n*-butyl-, cyclohexyl-, and 1,1-dimetylallenes undergo regioselective addition of benzenethiol successfully to provide the corresponding terminal vinylic sulfides in high yields (Eq. (19)). With phenylallene as an aromatic allene, however, the hydrothiolation affords regioisomeric mixtures. Since no double bond isomerization reaction is observed under the reaction conditions, the formation of the regioisomers may be account for by the preferential coordination of more electron-rich terminal double bond, compared with the inner one, to palladium(II) species. On the other hand, the $Pd(OAc)_2$-catalyzed hydroselenation of *n*-butyl- and cyclohexylallenes proceeds preferentially via the internal addition, but the reaction is accompanied by the formation of small amounts of the regioisomers.

A mechanistic proposal includes the following (see Scheme 5): (i) ligand-exchange reaction of the acetoxyl groups of $Pd(OAc)_2$ with PhS groups to give the palladium sulfide complex (as an active catalyst) with the concomitant formation of AcOH; (ii) coordination to the palladium species, of the allene double bond bearing higher electron density; (iii) *syn*-thiopalladation to form σ-allylpalladium; (iv) without changing into π-allylpalladium, the σ-allylpalladium intermediate is immediately quenched by PhSH [30], giving the desired adduct with regeneration of the catalyst. As shown in Scheme 5, the addition to alkyl-substituted allenes takes place selectively at the inner double bond of allenes, because the inner double bond is more electron-rich than the terminal one.

4. Rhodium-catalyzed thioformylation of alkynes with thiols and carbon monoxide

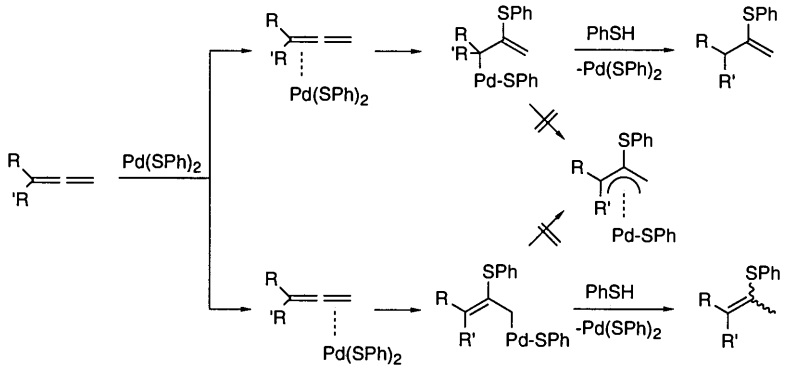
As mentioned already, the transition-metal-catalyzed hydrothiolation of alkynes may involve the formation of vinylic metal complexes as a key intermediates. Therefore, it is of great interest to examine the catalytic hydrothiolation in the presence of carbon monoxide, because a novel carbonylative hydrothiolation is expected to take place.



catalyst :	$Pd(OAc)_2$	-	7%	22%
	$PdCl_2(PhCN)_2$	-	7%	9%
	$RhCl(PPh_3)_3$	24%	3%	7%

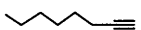
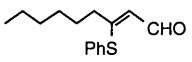
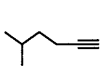
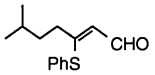
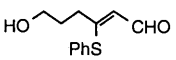
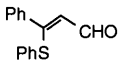
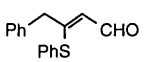
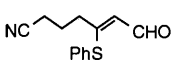
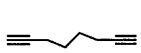
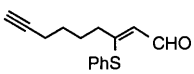
(20)

Thus, the reaction of 1-octyne with benzenethiol and carbon monoxide in the presence of $Pd(OAc)_2$ or $PdCl_2(PhCN)_2$ is conducted, but the both reactions afford only small amounts of the carbonylated product along with the hydrothiolation products (Eq. (20)). On the other hand, the rhodium(I) catalyst is found to permit simultaneous introduction of a formyl and a sulfide units into alkynes. Moreover, several rhodium catalysts is examined for this 'thioformylation' reaction, and rhodium(I) complexes bearing phosphine ligands work well as the catalysts. In particular, RhH(CO)-



Scheme 5.

Table 4
Rhodium-catalyzed thioformylation of alkynes with thiols and CO[a]

entry	acetylene	product	yield, %	E/Z
1			82	13/87
2			80	14/86
3			76	86/14
4			35	29/71
5			63	54/46
6			61	23/77
7			57	1/99

[a] Reaction were conducted under the condition of 7.5 mmol of acetylene, 5.0 mmol of PhSH and CO (30 atm) in the presence of 3 mol% of catalyst at 120°C for 5 h in acetonitrile (5 ml).

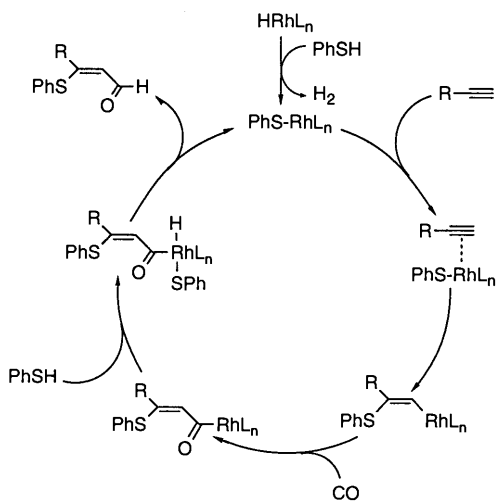
$(PPh_3)_3$ is the most effective catalyst: the reaction of 1-octyne with PhSH and CO (30 atm) in the presence of 3 mol% of $RhH(CO)(PPh_3)_3$ at 120°C for 5 h leads to the high yield formation of the thioformylation product (82%). $RhCl(PPh_3)_3$ is also a good catalyst for the thioformylation, although prolonged reaction time is required (20 h, 70%).

Table 4 represents the $RhH(CO)(PPh_3)_3$-catalyzed thioformylation of various alkynes [31,32]. The reactions are highly regioselective, and CO is incorporated predominantly at the terminal carbon of alkynes.

To explore the mechanistic pathway of this thioformylation, equimolar reaction of $RhH(CO)(PPh_3)_3$ with PhSH at 15°C in acetonitrile under argon atmosphere is attempted, which affords a yellow solid with the evolution of molecular hydrogen. The measurement of ^{1}H-NMR spectra indicate the disappearance of the signal at δ −9.71 assigned to the hydride of $RhH(CO)(PPh_3)_3$ [33]. The IR spectra of the yellow solid shows that the CO absorption (1922 cm^{-1}) [33] of $RhH(CO)(PPh_3)_3$ disappears and a new carbonyl absorption appears at 1969 cm^{-1}. These results and elemental analysis of the yellow solid suggest the formation of $Rh(SPh)(CO)(PPh_3)_2$ (Eq. (21)).

$$HRh(CO)(PPh_3)_3 + PhSH \xrightarrow[15\ ^\circ C,\ 2\ h]{CH_3CN} \underset{\text{yellow solid}}{[Rh(SPh)(CO)(PPh_3)_2]_n} + H_2 \quad (21)$$

A possible catalytic cycle for this thioformylation is shown in Scheme 6. The rhodium sulfide complex ($PhS–RhL_n$) formed in situ according to Eq. (21), may add regioselectively to alkyne to give vinylrhodium intermediate. After CO insertion to the vinyl–rhodium bond, oxidative addition of thiol to acylrhodium species, followed by reductive elimination of the thioformylation product may regenerate the catalyst.

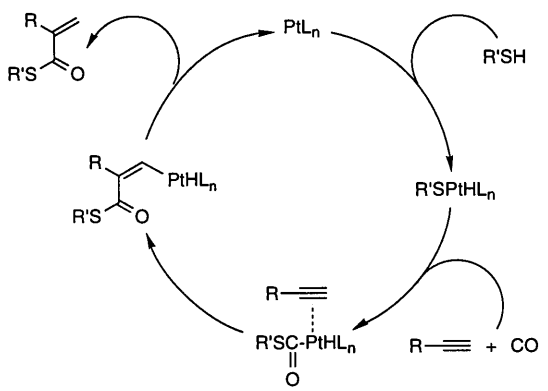


Scheme 6.

Table 5
Pt(0)-catalyzed hydrothiocarboxylation of alkynes with thiols and CO[a]

entry	acetylene	thiol (RSH)	molar ratio of alkyne/thiol	product	yield, %[b]
1	$^nC_6H_{13}$–≡	PhSH	7.5	$^nC_6H_{13}$, RS, O	83
2		$^nC_8H_{17}SH$	7.5		87
3		SH	7.5		94
4			1.0		99
5		PhSH	7.5	RS, O	70
6		SH	1.0		87
7	NC	PhSH	7.5	NC, RS, O	75
8		SH	1.0		62
9	Ph	PhSH	7.5	Ph, PhS, O	63
10	Ph–≡	SH	1.0	Ph, S, O	62

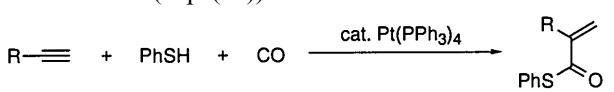
[a]Reaction conditions: PhSH (5 mmol), CO (30 atm), $Pt(PPh_3)_4$ (3 mol%), CH_3CN (5 mL), 120 °C, 1-7 h. [b]Based on the thiols employed.



Scheme 7.

5. Platinum-catalyzed hydrothiocarbonylation of alkynes with thiols and carbon monoxide

Organic thiols are known to add oxidatively to low-valent platinum complex forming platinum hydride complex bearing a sulfide ligand [34]. Detailed investigation on the reactions between thiols, alkynes, and carbon monoxide in the presence of platinum(0) catalysts leads to an interesting finding that switching the catalyst simply from $RhH(CO)(PPh_3)_3$ to $Pt(PPh_3)_4$ leads to a sharp reversal of regioselectivity of CO introduction (Eq. (22)).

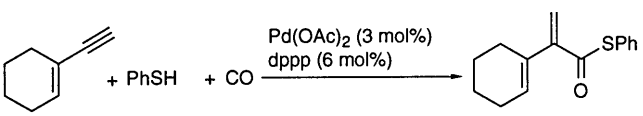


(22)

Table 5 represents the 'hydrothiocarboxylation' of alkynes, in which hydride and thiocarboxyl groups are introduced into the terminal and internal positions of alkynes, respectively [35]. The hydrothiocarboxylation product, which has an α,β-unsaturated carbonyl unit, is subject to conjugate addition of PhSH. However, the use of excess alkyne prevents the conjugate addition entirely. The procedure for this hydrothiocarboxylation can be employed with a variety of aromatic and aliphatic thiols, giving the corresponding α,β-unsaturated thioesters regioselectively in good to excellent yields (entries 1–10). In particular, the hydrothiocarboxylation with aliphatic thiols proceeds smoothly without using excess amounts of alkynes (entries 4, 6, 8 and 10). In the case of aromatic thiols, the higher acidity of aromatic thiols (compared with aliphatic ones) probably causes the competitive conjugate addition of thiols to α,β-unsaturated thioesters.

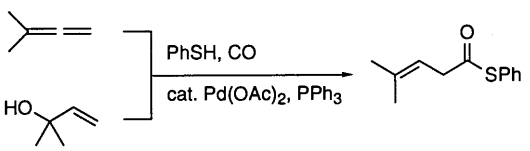
According to the literature [34], *trans*-$PtH(SPh)(PPh_3)_2$ is prepared from the equimolar reaction of $Pt(PPh_3)_4$ with PhSH at 20°C in acetonitrile under argon atmosphere. Moreover, the catalytic reaction of 1-octyne with PhSH and CO (30 atm) in the presence of 3 mol% of *trans*-$PtH(SPh)(PPh_3)_2$ in CH_3CN at 120°C for 1 h affords the hydrothiocarboxylation product in 77% yield. Although elucidation of the precise mechanism requires further detailed investigation, a possible reaction pathway for this hydrothiocarboxylation may include CO insertion to the Pt–S bond of $PtH(SPh)(PPh_3)_2$, followed by regioselective acylplatination of alkyne and reductive elimination of the product, as shown in Scheme 7.

The hydrothiocarbonylation with PhSH and CO (27 atm) can also proceed by using a palladium catalyst in THF at 110°C for 6 h, when 3 equiv of conjugated enynes are employed as the substrates (Eq. (23)) [36a]. A key step for this carbonylation is considered to be regioselective thiocarboxypalladation of enynes with $PhSC(O)–PdL_n–H$.



(23)

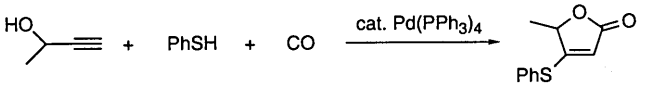
The procedure is applicable to the regioselective hydrothiocarbonylation of allenes [36b] and allylic alcohols [36c] (Eq. (24)).



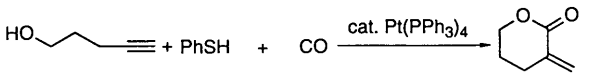
(24)

In the presence of $Pd(PPh_3)_4$, propargyl alcohols undergo carbonylative lactonization with PhSH and

CO to give β-thio-α,β-unsaturated-γ-lactone [37] (Eq. (25)). On the other hand, the $Pt(PPh_3)_4$-catalyzed carbonylative lactonization of 5-hydroxy-1-pentyne with CO proceeds in the presence of thiols to give α-methylene-δ-lactone [38] (Eq. (26)).



(25)



(26)

6. Conclusion

Highly selective methods using transition metal catalysts for introduction of Group 16 functions into carbon–carbon unsaturated bonds have been developed, which make it possible to synthesize various types of vinylic chalcogen compounds. A series of addition and carbonylation reactions mentioned in this review involve the formation of key species bearing a Group 16-transition metal inter-element linkage. These catalytic reactions are expected to open up a new field in transition-metal chemistry of organic chalcogen compounds.

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