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The Mechanism for Transition-Metal-Catalyzed Hydrochalcogenation of Unsaturated Organic Molecules

Akihiko Ishii and Norio Nakata

Abstract In this chapter, discussions are focused on two types of mechanisms of transition-metal-catalyzed hydrochalcogenation, Type I and Type II, which are classified by the initial behavior of precatalysts. In Type I mechanism, precatalyst M–X (M = Pd, Ni, Zr, Ln, and An) first undergoes protonolysis with REH (E = O, S, and Se) to generate active catalyst M–ER, which then undergoes insertion of alkyne into the M–ER bond (chalcogenometalation) to give 2-chalcogenovinyl complex, followed by protonolysis of M–C_{vinyl} with REH to produce the product and to regenerate active catalyst M–ER. Type II mechanism starts from oxidative addition of REH (E = S and Se) to complex [M] (M = Pd, Pt, Rh, and Ir) to give chalcogenolato–hydrido complex, [M]H(ER). In the next alkyne insertion, [M]–H insertion (hydrometalation) to give [M](ER)(vinyl) or [M]–E insertion (chalcogenometalation) to give [M]H(2-RE-vinyl) occurs and then reductive elimination of the resulting vinyl [M] complexes yields the product and [M]. Reactions where transition metal catalysts exert as Lewis acid to activate unsaturated bonds and those proceeding through vinylidene intermediates are mentioned only shortly.

Keywords Hydrochalcogenation · Oxidative addition · Protonolysis · Reductive elimination · Transition metal

Contents

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1 Introduction

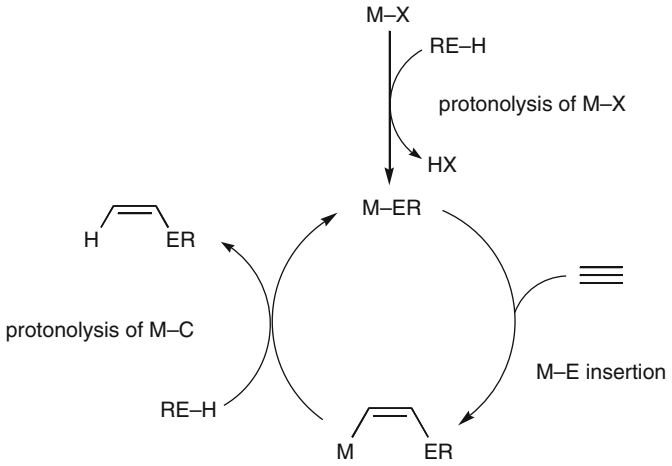
Introduction of organoelemento functionalities into organic molecules is an important reaction to prepare useful synthetic intermediates [1–8]. This chapter concerns the mechanism of transition-metal-catalyzed addition of chalcogenol (REH: E = O, S, and Se) to carbon–carbon unsaturated bonds. Conventional additions of REH, catalyzed by Brønsted acids or initiated by radical species, and chalcogenolate (RE^-) to unsaturated bonds are out of scope of this chapter. In the transition-metal-catalyzed hydrochalcogenation, discussions are focused on two types of mechanisms, Type I and Type II, which are classified by the initial behavior of precatalysts for convenience and involve at least one step of insertion of carbon–carbon unsaturated bond to metal–chalcogen (M–E) or metal–hydrogen (M–H) bonds. In some cases, this classification is ambiguous and there are hybrid type mechanisms of them. Reactions where transition metal catalysts exert as Lewis acid to activate unsaturated carbon–carbon bonds and those proceeding through vinylidene intermediates are mentioned only shortly in this introduction part.

1.1 Type I Mechanism

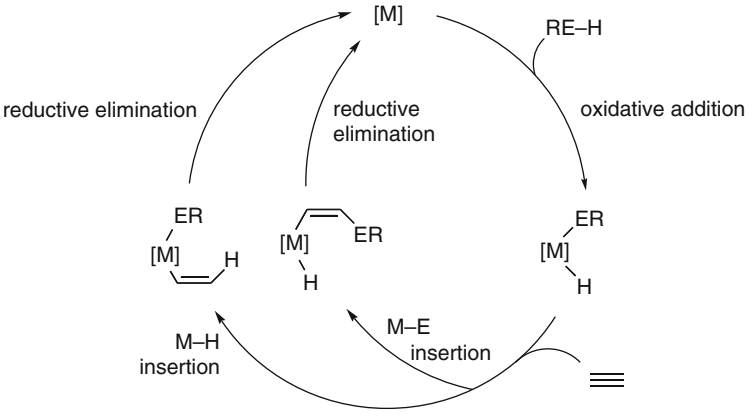
In the initial stage of this mechanism (Scheme 1), transition metal precatalyst M–X undergoes protonolysis of the M–X bond with REH to generate active catalyst M–ER. The chalcogenolato–metal complex then undergoes insertion of alkyne into the M–ER bond (chalcogenometalation) to give 2-chalcogenovinyl complex. In the final stage, protonolysis of $M–C_{vinyl}$ with REH produces the product and active catalyst M–ER.

1.2 Type II Mechanism

Type II mechanism starts from oxidative addition of REH to transition metal complex ([M]) to give chalcogenolato–hydrido metal complex, [M]H(ER) (Scheme 2). In the next step of alkyne insertion, there are two possible pathways, [M]–H insertion (hydrometalation) to give [M](ER)(vinyl) and [M]–E insertion (chalcogenometalation) to give [M]H(2-RE-vinyl). In the final stage, reductive



Scheme 1 Catalytic cycle for Type I mechanism comprising of protonolysis of M–X by REH, M–E insertion of alkyne, and protonolysis of M–C_{vinyl} by REH



Scheme 2 Catalytic cycle for Type II mechanism comprising of oxidative addition of REH to transition metal complex [M], insertion of alkyne into [M]–H or [M]–E, and reductive elimination of [M](ER)(vinyl) or [M]H(2-RE-vinyl)

elimination of the resulting vinyl [M] complexes yields the product and [M]. The [M]–H insertion corresponds to Chalk–Harrod Mechanism in hydrosilylation, and the [M]–E insertion to modified Chalk–Harrod Mechanism in hydrosilylation. In the hydrosilylation, theoretical study on the reaction of $PtH(SiR_3)PH_3$ with ethylene showed that ethylene is inserted into the Pt–H bond with a lower activation energy than into the Pt–SiR_3 bond [9].

1.3 Transition Metal Catalysts as Lewis Acids

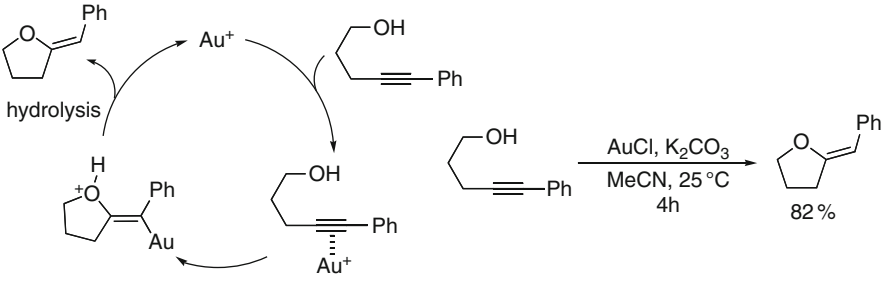
Alkynes, allenes, and alkenes in the presence of Au, Ag, or Pt complexes undergo intermolecular or intramolecular addition of X–H bond (X = O, S, and N) to yield respective hydroelementation products [10, 11]. Although mechanistic aspects are not always clarified, activation of multiple bonds with these noble metal complexes, as Lewis acids, by coordination, is proposed in some papers [12–18]. An example is shown in Scheme 3 [16].

1.4 Mechanism Through Vinylidene Intermediates

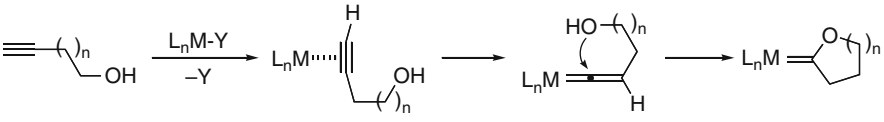
This pathway involves cycloisomerization of η^2-metal–alkyne complex to a vinylidene complex (Scheme 4) [19]. An example is shown in Scheme 5 [20]. The initial η^2-Mo–alkyne complex rearranges to vinylidene–Mo complex intermediate that undergoes an intramolecular nucleophilic attack of the hydroxy oxygen to give cyclic anionic intermediate, protonation of which yields 2,3-dihydrofuran.

2 Type I Mechanism

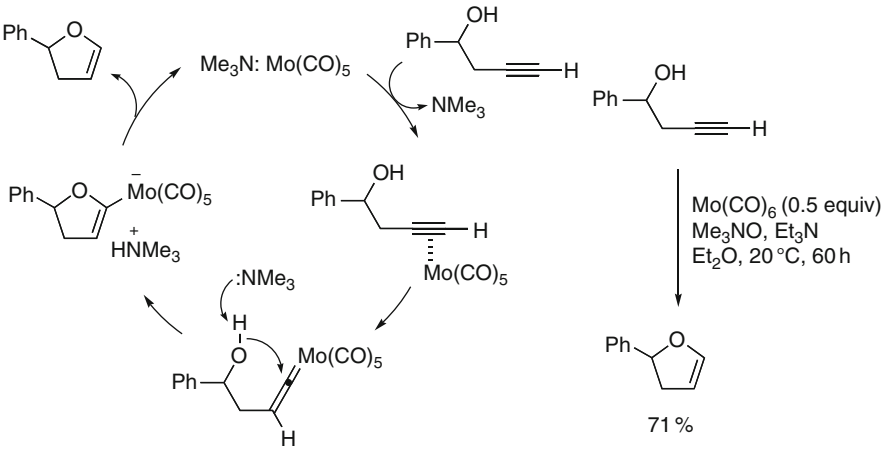
In 1992, the first examples of $Pd(OAc)_2$-catalyzed hydroselenation [21] and hydrothiolation [22] were reported by Ogawa and Sonoda and their coworkers of Osaka University. Extensive studies by the Osaka group on reaction mechanism



Scheme 3 Proposed catalytic cycle for AuCl-catalyzed intramolecular cyclization of 5-hydroxy-1-phenyl-1-pentyne



Scheme 4 Cycloisomerization of η^2-metal–alkyne complex to a vinylidene complex



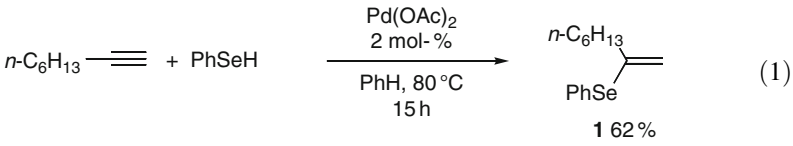
Scheme 5 Proposed catalytic cycle for Mo-catalyzed intramolecular cyclization of 4-hydroxy-4-phenyl-1-butyne

have established Type I mechanism. Subsequently, Ni(II) and groups III and IV transition-metals-catalyzed hydrochalcogenations categorized to Type I mechanism were reported.

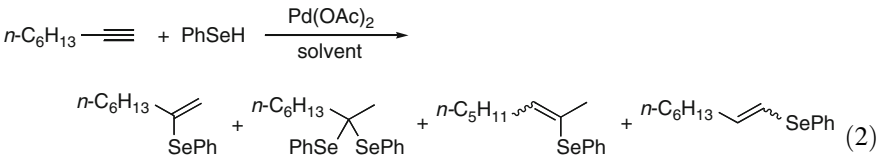
2.1 Group X Metal-Catalyzed Hydrothiolation and Hydroselenation

2.1.1 $Pd(OAc)_2$-Catalyzed Hydrothiolation and Hydroselenation

The reaction of 1-octyne with PhSeH in the presence of $Pd(OAc)_2$ in benzene at 80°C for 15 h provided the Markovnikov-type adduct, 2-(phenylseleno)-1-octene (**1**) in 62% yield (1) [21]. The reaction conducted in toluene with employing 40 mol% of pyridine or 2,2′-bipyridyl as an additive produced **1** in 38 or 63% yields, respectively. In addition, the solvent effect is remarkable and pyridine is the best solvent to form **1** (2).



(1)

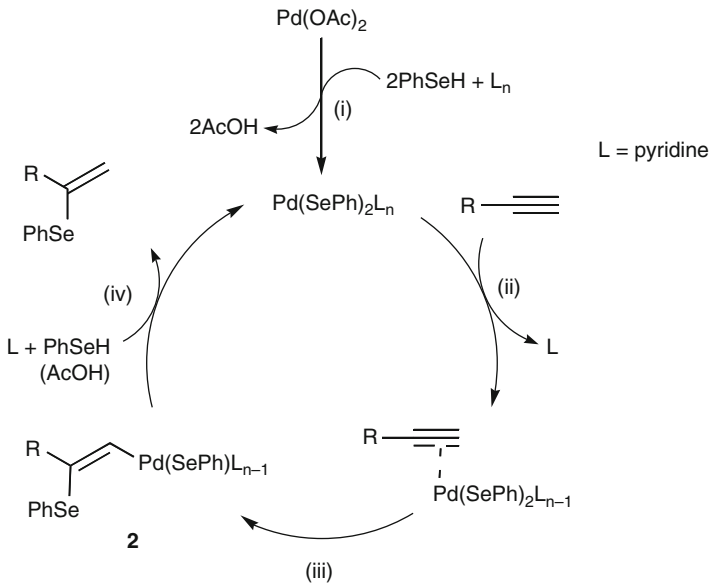


1

solv.				
THF	46	15	10	5
toluene	23	29	34	0
pyridine	77	0	0	0

These results strongly suggest that pyridine acts as a suitable ligand for an active palladium intermediate. In the absence of pyridine, palladium selenide [$Pd(SePh)_2$] molecules, a key species for this hydroselenation of alkynes, easily react with each other by the coordination of the selenide ligand to the other palladium center to form polymerized complex, which is insoluble in usual organic solvent and loses the catalytic activity. Therefore, pyridine is considered to inhibit the polymerization and protect the catalyst from the poisoning [23].

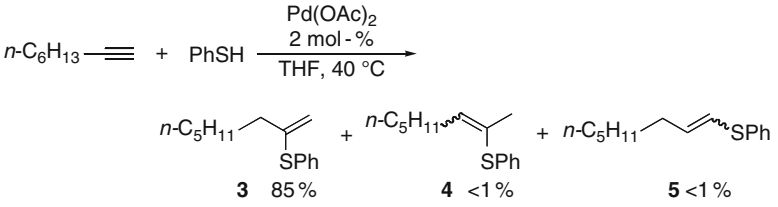
A mechanism shown in Scheme 6 was proposed [23], which involves (i) ligand exchange of the AcO group with the PhSe group to give $Pd(SePh)_2L_n$ as an active catalyst and AcOH; (ii) coordination of alkyne to the selenolato Pd(II) species; (iii) insertion of alkyne into the Pd–Se bond (*syn*-selenopalladation) to form (*Z*)-(2-phenylseleno)vinyl Pd(II) intermediate **2**; (iv) the protonolysis of the



Scheme 6 Catalytic cycle for $Pd(OAc)_2$-catalyzed hydroselenation of alkynes

vinyl Pd(II) complex **2** with PhSeH (or AcOH) to provide 2-phenylseleno-1-alkene with regeneration of the catalyst.

In the case of $Pd(OAc)_2$-catalyzed hydrothiolation of alkynes, THF was used as the solvent. Thus the reaction of 1-octyne with PhSH in the presence of $Pd(OAc)_2$ at 40°C gave **3**, **4**, and **5** in 85%, <1%, and <1% yields, respectively (3) [22].

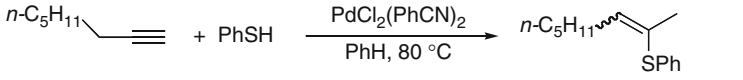


(3)

The reaction of $Pd(OAc)_2$ with 3 equiv of PhSH in THF-d_8 immediately gave dark brown precipitates and ca. 2 equiv of AcOH. This precipitate scarcely exhibited the catalytic activities for the addition of PhSH to 1-octyne. On the other hand, the precipitates prepared in the presence of 1-octyne had a moderate catalytic activity. *cis*-Addition of PhSH to 1-octyne was confirmed by the reaction employing 1-octyne-*1*-*d*. The (*E*)-isomer, (*E*)-*n*-C_6H_{13}(PhS)C=C(D)H, is the kinetic product and gradually isomerized to the (*Z*)-isomer. A mechanism similar to that shown in Scheme 6 was proposed [22].

2.1.2 $PdCl_2L_2$-Catalyzed Hydrothiolation and Hydroselenation

The reaction of terminal alkynes with a catalytic amount of $PdCl_2(PhCN)_2$ [24] or $PdCl_2(PPh_3)_2$ [25] in benzene at 80°C gave selectively **4** or **6**, respectively [(4) and (5)]. The stoichiometric reaction of $PdCl_2(PhCN)_2$ with PhSH (2 equiv) in benzene at room temperature gave a reddish brown solid with the composition of $[PdCl(SPh)(PhSH)]_n$ ($n = 1$ or 2), which catalyzes the addition of PhSH to 1-octyne in benzene at 80°C to lead to **4**. The complex also catalyzed the isomerization of Markovnikov-type adduct **3** to **4**. Scheme 7 shows a proposed catalytic cycle for $PdCl_2(PhCN)_2$-catalyzed hydrothiolation involving the isomerization of the initial Markovnikov-type adduct [24]. A similar mechanism was proposed for $PdCl_2(PPh_3)_2$-catalyzed hydroselenation [25].



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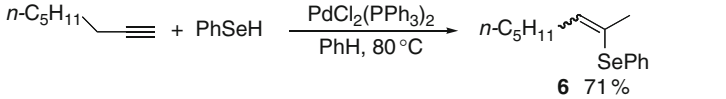

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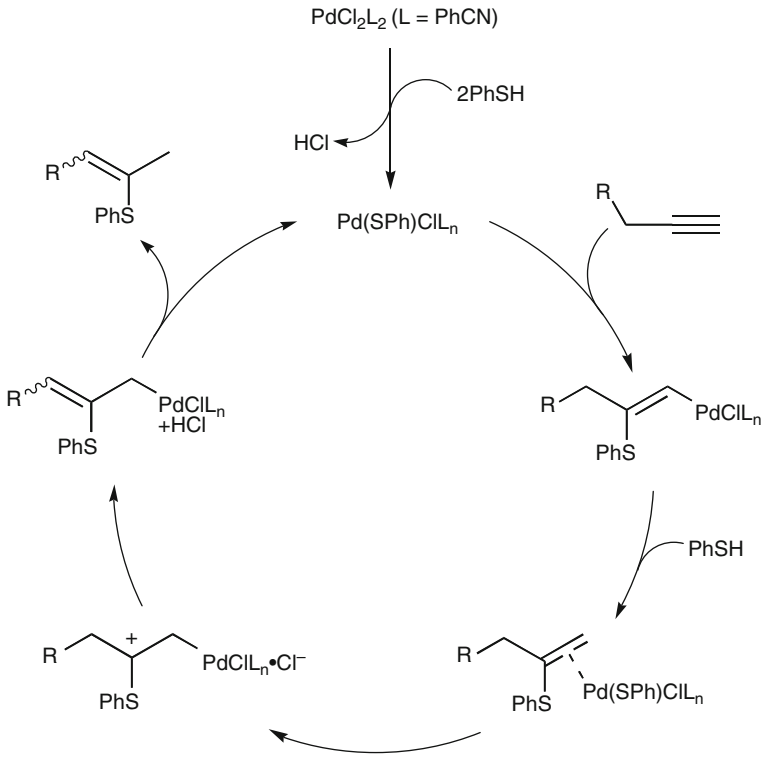
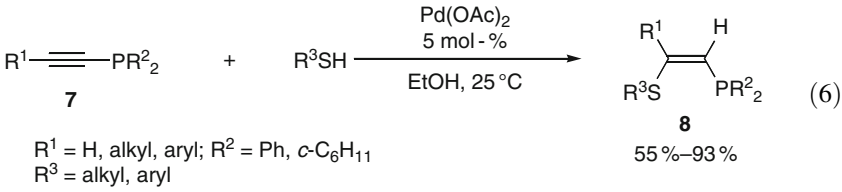


Scheme 7 Catalytic cycle for $PdCl_2(PhCN)_2$-catalyzed hydrothiolation of alkynes followed by isomerization of the resulting Markovnikov-type adduct

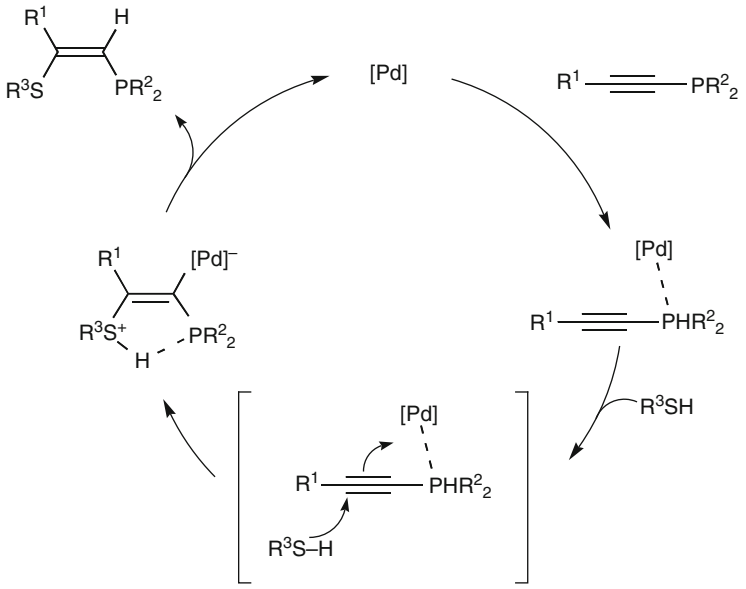
The $Pd(OAc)_2$-catalyzed hydrothiolation of 1-alkynylphosphines **7** was reported in 2007 [26]. This reaction yields (*Z*)-1-phosphino-2-thio-1-alkenes **8** regio- and stereoselectively in *anti*-hydrothiolation fashion (6). From the stereochemistry observed, the following mechanism was proposed, where Pd(II) coordinates on the phosphorus atom to induce the addition of RSH (Scheme 8).



(6)

2.1.3 Ni(II)-Catalyzed Hydrothiolation and Hydroselenation

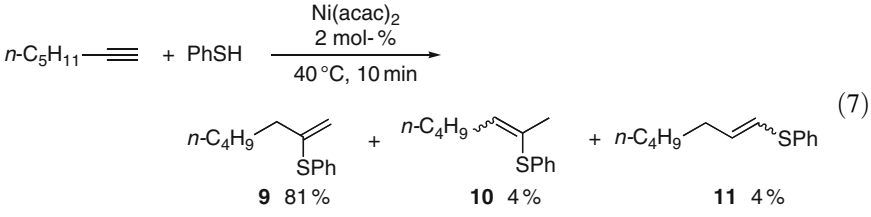
The hydrothiolation and hydroselenation of alkynes catalyzed by $NiCl_2$ [27] or $Ni(acac)_2$ [28–30] under heterogeneous conditions and by CpNi(NHC)Cl



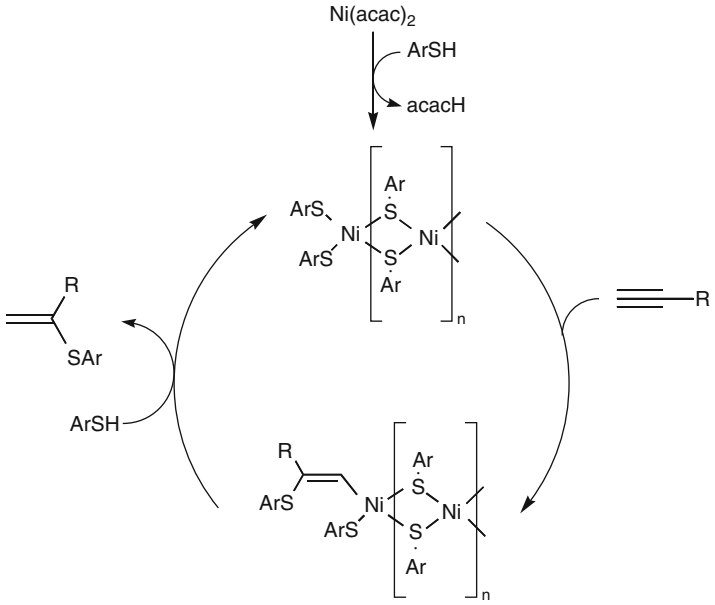
Scheme 8 Catalytic cycle for $Pd(OAc)_2$-catalyzed hydrothiolation of 1-alkynylphosphines

(Cp = C_5H_5, NHC = *N*-heterocyclic carbene) under homogeneous conditions [31] have been reported.

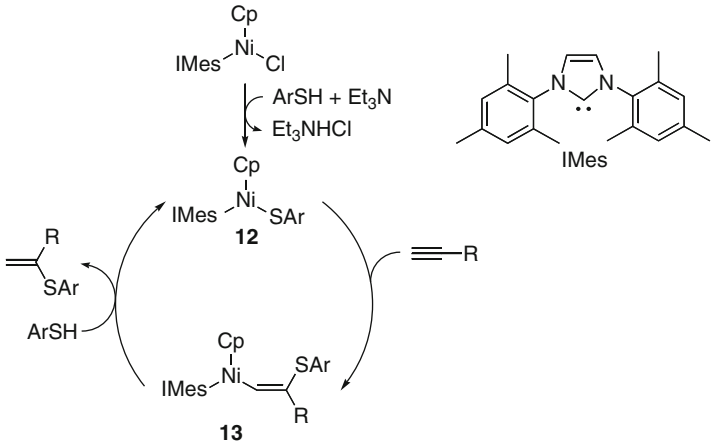
The hydrothiolation of 1-heptyne with PhSH (2 equiv) was catalyzed by Ni (acac) (2 mol%) at 40°C under solvent-free conditions to produce **9**, **10**, and **11** in 81%, 4%, and 4% yields, respectively (7). In the reaction, the formation of an insoluble dark brown polymer $[Ni(SAr)_2]_n$ was confirmed by elemental analysis [28], and it was verified that the polymer served as the catalyst for the reaction of HC≡CC(OH)Me_2 with PhSH to give the corresponding Markovnikov-type product in 95% yield. The structure and morphology of the particles of $[Ni(SAr)_2]_n$ were studied by scanning electron microscopy (SEM) [28, 30, 32]. A catalytic cycle for the Ni(acac)-catalyzed hydrothiolation was proposed as shown in Scheme 9 [28, 29]. The resulting *syn*-addition of thiols to alkynes was verified by the reactions employing internal alkynes [28, 29]. A similar mechanism was proposed for the Ni $(acac)_2$-catalyzed hydroselenation [30].



(7)



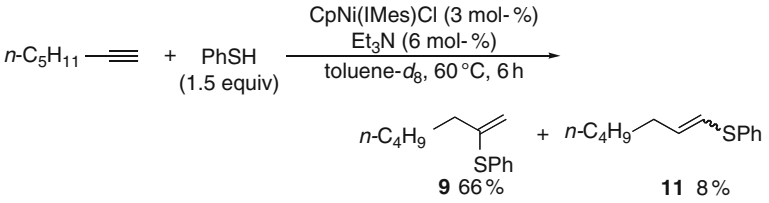
Scheme 9 Catalytic cycle for $Ni(acac)_2$-catalyzed hydrothiolation of alkynes



Scheme 10 Catalytic cycle for CpNi(IMes)Cl-catalyzed hydrothiolation of alkynes

Homogeneous hydrothiolation of alkynes was achieved by using CpNi(IMes)Cl (IMes = *N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene). Under the optimized conditions (8), CpNi(IMes)Cl catalyzed the reaction of PhSH with 1-heptyne in the presence of Et_3N in toluene-d_8 to give **9** (66%) and **11** (8%) without other byproducts. This catalytic reaction (Scheme 10) starts from the formation of the thiolato Ni(II)

complex **12**. Indeed, **12** (Ar = Ph) was prepared by the stoichiometric reaction of CpNi(IMes)Cl with PhSH in the presence of Et_3N (the structure was determined by X-ray crystallography) and was verified to catalyze the hydrothiolation of 1-heptyne with PhSH. Although the next intermediate **13**, formed by the insertion of alkyne to the Ni–S bond, was not observed by NMR in the reaction of **12** (Ar = *p*-$MeOC_6H_4$) with 1-heptyne, the authors proposed that **13**, being very unstable and in equilibrium with **12** and alkyne, was trapped by ArSH to give the product by protonolysis of the Ni–C_{vinyl} bond [31].

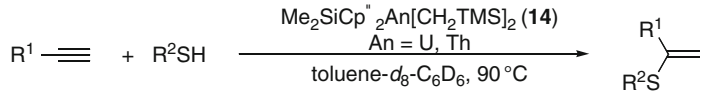


(8)

2.2 *Groups III and IV Metal-Catalyzed Hydrothiolation and Hydroalkoxylation*

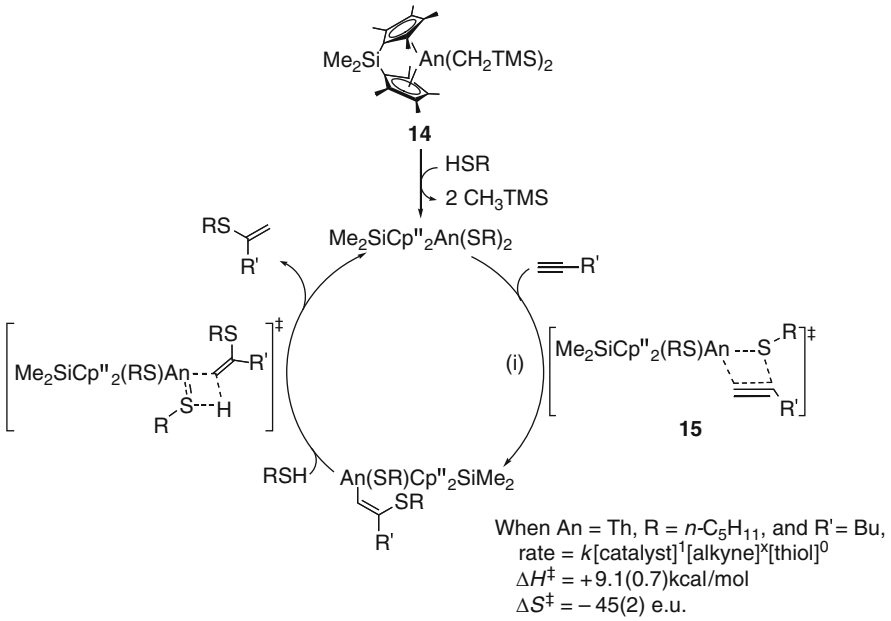
2.2.1 Organoactinide- and Organolanthanide-Catalyzed Hydrothiolation

Organoactinide complexes catalyze the hydrothiolation of alkanethiols and arenethiols into alkyl, aryl, and vinyl alkynes. The reaction catalyzed by $Me_2SiCp''_2An(CH_2TMS)_2$ (**14**) (An = U, Th; Cp″ = C_5Me_4) yields Markovnikov-type adducts regioselectively (9) [33].



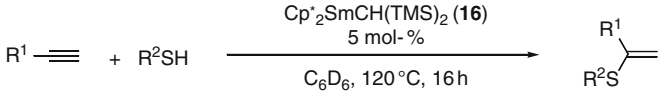
(9)

Monitoring the reaction reveled that $Me_2SiCp''_2Th(CH_2TMS)_2$ (**14**: An = Th) underwent fast Th–CH_2TMS bond protonolysis in the presence of excess thiol. The rate-limiting step in the catalytic cycle is the alkyne insertion step into Th–SR bond [Scheme 11, (i)], because kinetic study on the reaction of 1-pentanethiol with 1-hexyne in the presence of **14** (An = Th) showed that the reaction obeyed first-order in [**14** (An = Th)], first-order in [alkyne] at lower alkyne concentration and zero-order at higher [alkyne], and zero-order in [thiol]. Kinetic analysis between 60 and 110°C gave $\Delta H^{\ddagger}$ = +9.1(0.7) kcal mol^{-1} and $\Delta S^{\ddagger}$ = −45(2) e.u., suggesting a highly ordered (four-membered) transition state **15**. The kinetic isotope effect is k_H/k_D = 1.35(0.1) in the reaction. In the reaction of *n*-$C_5H_{11}SD$ with 1-hexyne in the presence of **14** (An = Th), deuterium was introduced at both *E* and *Z* positions because deuterium exchange between *n*-$C_5H_{11}SD$ with 1-hexyne occurred by reversible alkyne C–H activation.



Scheme 11 Catalytic cycle for organoactinide-catalyzed hydrothiolation

Marks and coworkers also reported in detail the Markovnikov-selective lanthanide-mediated, intermolecular hydrothiolation of terminal alkynes by aliphatic, benzylic, and aromatic thiols using $Cp^*_2LnCH(TMS)_2$ ($Cp^* = C_5Me_5$; Ln = La, Sm (**16**), and Lu) as precatalysts [34]. The Markovnikov selectivity and conversion rate of this transformation depend on the bulkiness of substituents of thiols and alkynes (10).



(10)

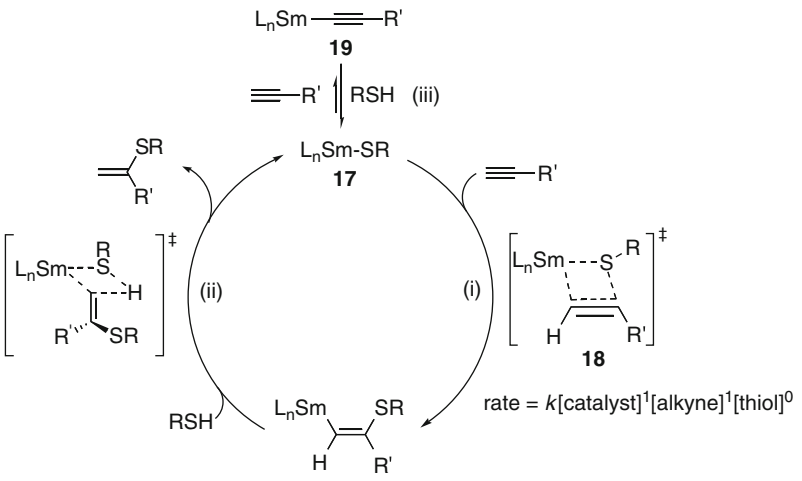
R^1 = *n*-C_4H_9, *c*-C_6H_{11}, *c*-$C_6H_{11}CH_2$, $PhCH_2$, Ph, 3-pyridyl, 1-cyclohexenyl

R^2 = Et, *n*-C_5H_{11}, *c*-C_6H_{11}, $PhCH_2$, Ph

conversion: 11 % – >95 %

Markovnikov selectivity: 32 % – >99 %

The proposed mechanism is shown in Scheme 12. The $Cp^*_2SmCH(TMS)_2$ (**16**)-mediated reaction between 1-pentanethiol and 1-hexyne was found to be first-order in catalyst concentration, first-order in alkyne concentration, and zero-order in thiol concentration by kinetic investigations. The reaction of **16** with >20 equiv of 1-pentanethiol and 1-hexyne in benzene-d_6 was monitored by NMR to show the formation of $H_2C(TMS)_2$ and 40–60% of Cp*H, indicating occurrence of the protonolysis of not only $CH(TMS)_2$ but also Cp* in **16** by thiol in the catalyst activation stage to generate **17**. The reactions employing thiols and terminal alkynes bearing a sterically demanding substituent showed the decrease of the

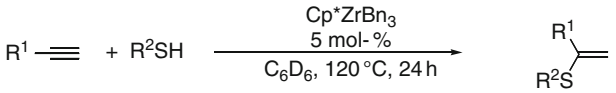


Scheme 12 Catalytic cycle for organolanthanide-catalyzed hydrothiolation

selectivity of Markovnikov addition to *anti*-Markovnikov addition, suggesting a strong dependence of hydrothiolation activity on the steric hindrance in the four-membered transition state **18**. The formation of *anti*-Markovnikov adducts is suppressed in the presence of γ-terpinene as a radical inhibitor, indicating that a free radical mechanism is operative for the *anti*-Markovnikov addition. The reaction with deuterium-labeled alkyne (Ph–C≡C–D) reveals a secondary kinetic isotope effect [$k_H/k_D = 1.40(0.1)$] and deuterium exchange between alkyne –C≡C–D and thiol RS–H. The kinetic isotope effect indicates that insertion of alkyne to Sm–SR bond (i) is the turnover-limiting process followed by fast thiol-induced Sm–C bond protonolysis (ii). Observed deuterium exchange between alkyne –C≡C–D and thiol RS–H shows the equilibrium between **17** and **19** (iii), favoring the Sm–SR species **17** under hydrothiolation conditions.

2.2.2 Organozirconium(IV)-Catalyzed Hydrothiolation

Organozirconium(IV)-catalyzed hydrothiolation of terminal alkynes was studied with $[Me_2Si(Cp'')N\text{-}t\text{-}Bu]ZrMe_2$ ($Cp'' = C_5Me_4$) (**20**), Cp^*ZrBn_3, $Cp^*ZrCl_2NMe_2$, $Cp^*_2ZrMe_2$, and $Zr(NMe_2)_4$ as the precatalysts [35]. The choice of ligands on zirconium is important for decongestion of the metal center for further reactions and for preventing the aggregation of the resulting thiolato-zirconium complexes leading to unfavorable precipitation. Thus, $Cp^*ZrCl_2NMe_2$, **20**, and Cp^*ZrBn_3, which have one cyclopentadienyl-based ligand, showed high reactivity and $Cp^*_2ZrMe_2$ showed low reactivity. $Zr(NMe_2)_4$ exhibited high initial activity but resulted in gradual precipitation. Equation (11) summarizes the hydrothiolation with Cp^*ZrBn_3 as the precatalyst. The hydrothiolation is highly Markovnikov-selective (up to 99%), and the formation of *anti*-Markovnikov products is suppressed by the addition of a radical inhibitor.

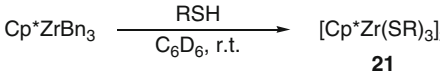


(11)

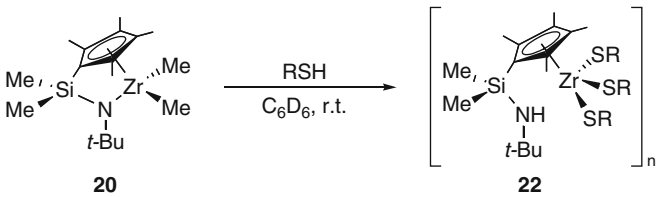
R^1 = *n*-C_4H_9, *c*-C_6H_{11}, *c*-$C_6H_{11}CH_2$, $PhCH_2$, Ph, 3-pyridyl, 1-cyclohexenyl — conversion: 79 % – quant; Markovnikov selectivity: 66 % – 99 %

R^2 = Et, CF_3CH_2, *n*-C_5H_{11}, $PhCH_2$, Ph

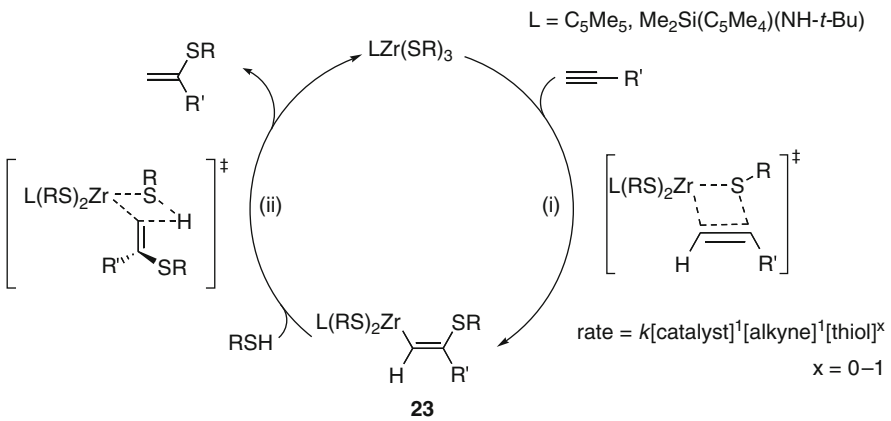
The formations of dimer **21** or oligomer **22** of tris(thiolato) Zr(IV) complexes were observed by ^{1}H NMR [(12) and (13)]. Kinetic studies on **20**-catalyzed reaction of 1-pentanethiol with 1-hexyne showed the empirical rate low expressed as rate $= k_{obs}$[**20**]^1[1-hexyne]^1[1-pentanethil]^x ($x = 1$ for $\leq$0.3 M and $x = 0$ for $\geq$0.3 M) with $\Delta H^{\ddagger} = +18.1(1.2)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -20.9(2.5)$ e.u. In addition, a secondary kinetic isotope effect [$k_H/k_D = 1.3(0.1)$] was observed in the reaction of 1-pentanethiol with PhC≡C–D catalyzed by **20**. These and other findings are consistent with the catalytic cycle shown in Scheme 13, involving alkyne insertion into the Zr–SR bond (i), which is the turnover-limiting process, followed by protonolysis of Zr–C in **23** by thiol (ii).



(12)



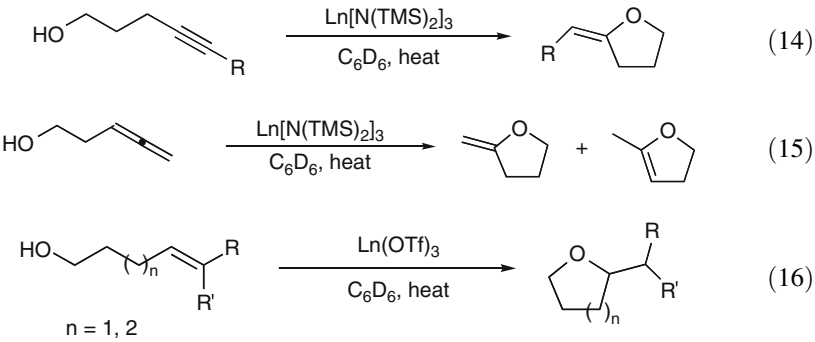
(13)



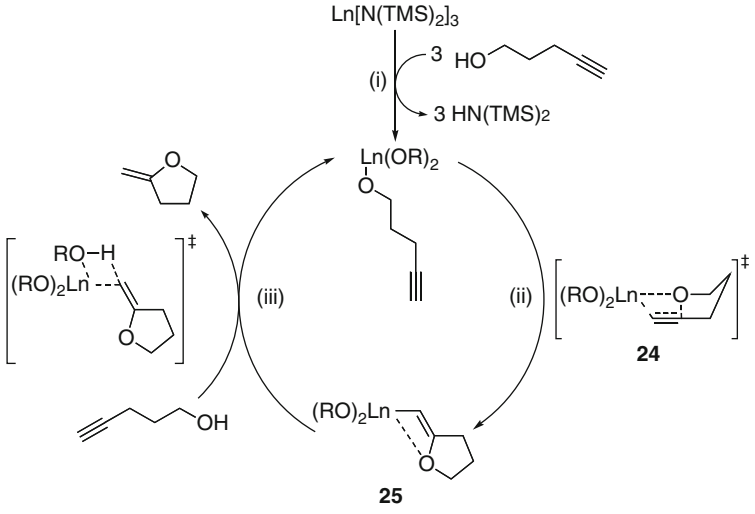
Scheme 13 Catalytic cycle for organozirconium(IV)-catalyzed hydrothiolation

2.2.3 Organolanthanide-Catalyzed Intramolecular Hydroalkoxylation

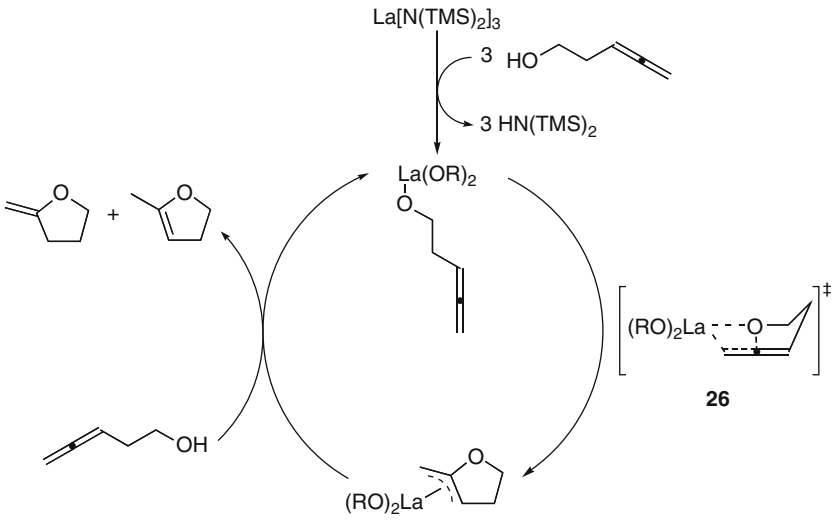
Marks and coworkers have reported the syntheses of oxygen-containing heterocycles by organolanthanide-catalyzed intramolecular hydroxyalkoxylation since 2007 (14)–(16) [36–41].



In the cyclization of γ-hydroxyalkynes [36–39], precatalyst, $Ln[N(TMS)_2]_3$ (Ln = La, Nd, Sm, Y, and Lu), is activated by alcohol-mediated protonolysis to give $Ln(OR)_3$ (Scheme 14, (i)), followed by intramolecular alkyne insertion (ii) that is the turnover-limiting process. The cyclization by alkyne hydroalkoxylation proceeds through π-complexation of the carbon–carbon triple bond [38] with high *exo* and *E*-selectivity as considered from the structure of the transition state **24**. Theoretical investigation was reported for this lanthanide-catalyzed cyclization, where a significant effect of metal ion size was obtained [38]. The activation parameters were $\Delta H^{\ddagger} = +20.2(1.0)$ kcal mol^{-1}, $\Delta S^{\ddagger} = -11.8(0.3)$ e.u., and $E_a = 20.9(0.3)$ kcal



Scheme 14 Catalytic cycle for $Ln[N(TMS)_2]_3$-catalyzed intramolecular hydroalkoxylation of γ-hydroxyalkyne (Ln = La, Nd, Sm, Y, and Lu)

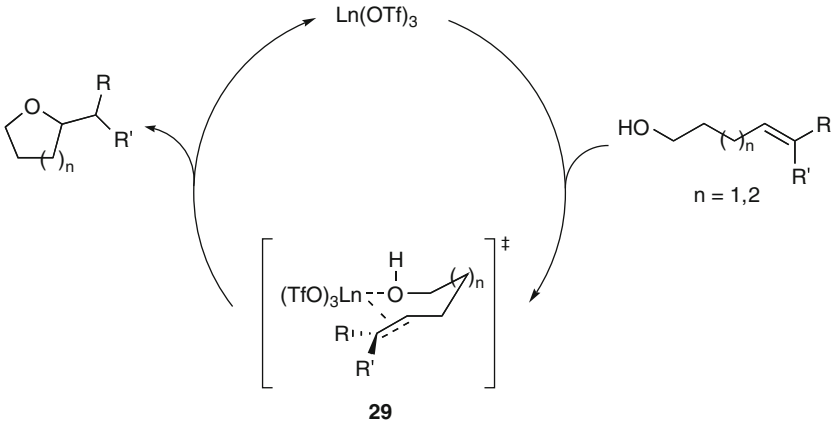


Scheme 15 Catalytic cycle for $La[N(TMS)_2]_3$-catalyzed intramolecular hydroalkoxylation of γ-hydroxyallene

mol^{-1} in the cyclization of $HO(CH_2)_3C{\equiv}CH$ with $La[N(TMS)_2]_3$ (40–80°C), indicating a highly-ordered transition state. The resulting cyclic vinyl ether **25** rapidly undergoes protonolysis by ROH (iii) to provide the product and the active catalyst. However, the structures of the active catalysts $Ln(OR)_3$ were not well-defined [42].

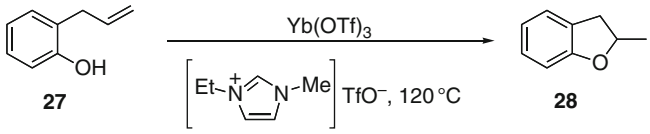
β-Hydroxy and γ-hydroxyallenes yield five-membered and six-membered rings, respectively, by $La[N(TMS)_2]_3$-catalyzed reactions [36]. As shown in Scheme 15, the addition of hydroxyl oxygen atoms takes place to the central allene carbon through **26**. The activity decreases compared with the case of hydroxyalkynes, which is explained in terms of the larger enthalpic barrier in the turnover-limiting process of the intramolecular insertion step [42]. A theoretical study by Tobisch [43] supports this mechanism and showed that reactive $La(OR)_3$ ($R = CH_2CH_2CH{=}C{=}CH_2$) undergoes energetically favorable coordination of ROH to form $La(OR)_3(ROH)_n$ (n = 1–6), where the forms having three η^1-RO ligands and those having one or two chelating η^2-RO ligands have almost similar stability in the range of 3.3 kcal mol^{-1}. Furthermore, the observed 5-*endo* cyclization ($\Delta G^{\ddagger}$ = 19.7 kcal mol^{-1}) is much more favorable than the unobserved 4-*exo* cyclization ($\Delta G^{\ddagger}$ = 37.5 kcal mol^{-1}) to give 2-vinyloxetane, and the 5-*endo* cyclization is followed by the protonolysis with the already coordinated ROH through a metathesis-like transition state ($\Delta G^{\ddagger}$ = ca. 10 kcal mol^{-1}).

Cyclization by hydroalkoxylation of γ- and δ-alkenols is achieved by lanthanide triflates as catalysts at 60–120°C in ion-liquids [40, 41]. In the cyclization of C_6H_4-*o*-$(OH)(CH_2CH{=}CH_2)$ **27** to **28** catalyzed by $Yb(OTf)_3$ in $[C_2mim][OTf]$ (17), the activation parameters were $\Delta H^{\ddagger}$ = +18.2(9) kcal mol^{-1}, $\Delta S^{\ddagger}$ = –17.0(1.4) e.u., and E_a = 18.2(8) kcal mol^{-1}, suggesting a highly organized transition state. A primary kinetic isotope effect of k_H/k_D = 2.48(9) was observed for the cyclization



Scheme 16 Catalytic cycle for $Ln(OTf)_3$-catalyzed intramolecular hydroalkoxylation of γ- and δ-alkenols (Ln = La, Nd, Sm, Yb, and Lu)

of CH_2=$CHCH_2CH_2CH_2OH$(D) catalyzed by $Yb(OTf_3)$ at 120°C, suggesting a catalytic pathway that involves kinetically significant intramolecular proton transfer. Proton scavenging experiments suggested the participation of an acidic proton in the catalytic cycle that originates from the hydroxy functionality. A free TfOH-catalyzed process as a major pathway was ruled out. An NMR study indicated hydroxyl and olefin coordination to Yb^{3+} (**29** in Scheme 16). Based on these experimental results, a catalytic cycle was proposed as shown in Scheme 16, which involves hydroxy and olefin activation by the electron-deficient Ln^{3+} center, followed by alkoxide nucleophilic attack with ring closure.



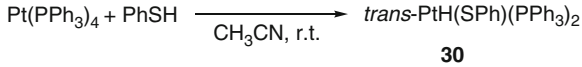
(17)

3 Type II Mechanism

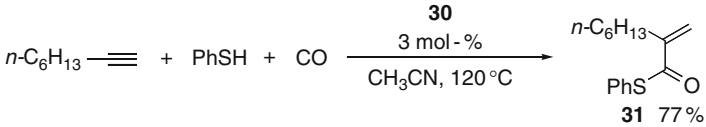
3.1 Pd(0) and Pt(0)-Catalyzed Hydroselenation of Alkynes

In 1992, when $Pt(PPh_3)_4$ was used instead of $Pd(OAc)_2$ [22], vinyl selenide **4**, derived from the Markovnikov-type product, was obtained as the major product in 80% yield. In this reaction, the generation of $PtH(SPh)(PPh_3)_2$ was considered. During the study on the hydrothiocarboxylation employing PhSH, 1-octyne, CO, and $Pt(PPh_3)_4$ as the catalyst [44], hydrido-thiolato Pt(II) complex **30** was isolated by the stoichiometric reaction of $Pt(PPh_3)_4$ with PhSH in acetonitrile at room

temperature (18). The complex was assigned as *trans*-PtH(SPh)(PPh_3)$_2$ (**30**) by ^{1}H NMR spectroscopic analysis [in $CDCl_3$: δ –10.01 (Pt–*H*, $J_{P–H}$ = 14 Hz, $J_{Pt–H}$ 961 Hz) [45]. The reaction of 1-octyne with PhSH and CO in the presence of 3 mol% of **30** gave the hydrothiocarboxylation product **31** in 77% yield (19).

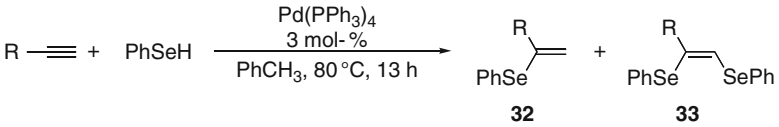


(18)



(19)

In 2003, Ananikov and Beletskaya and their coworkers proposed hydroselenation of terminal alkynes catalyzed by $Pd(PPh_3)_4$ and $Pt(PPh_3)_4$ [46]. In the case of $Pd(PPh_3)_4$, Markovnikov-type adducts **32** were obtained together with bis(selenide)s **33** (20).

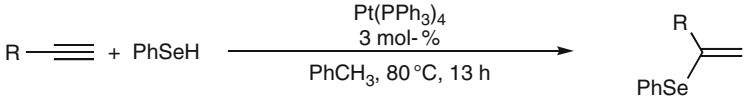


(20)

R = $HOCH_2$, Bu, Me_2NCH_2, *c*-C_6H_{10}(1-OH) 20%: 36% – 49%: 25%

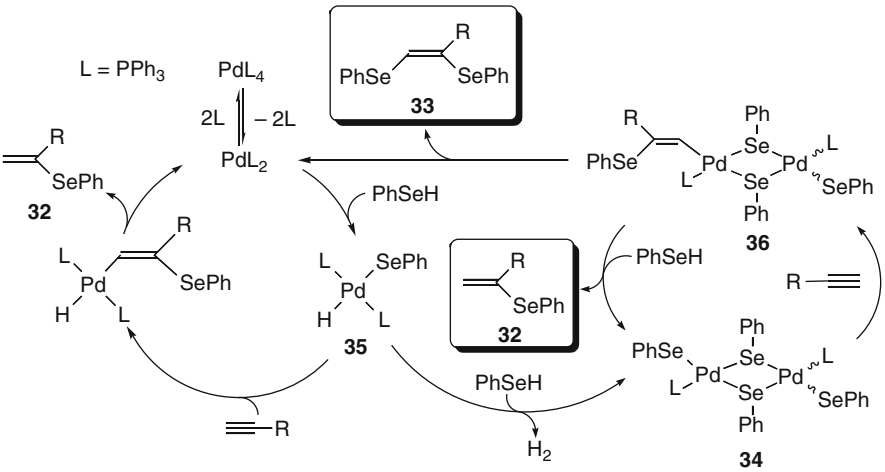
The reaction of $Pd(PPh_3)_4$ with PhSH took place rapidly with evolution of H_2, which was observed in ^{1}H NMR (δ 4.5). In the ^{31}P NMR, complexes assigned to dinuclear complexes *trans*- and *cis*-{Pd(SePh)(PPh_3)}$_2$(μ-SePh)$_2$ (**34**) at δ 28.2 and 26.8 in the relative ratio of 3:1. A mechanism involving both *trans*-PdH(SePh)(PPh_3)$_2$ (**35**) and dinuclear Pd(II) complexes **34** was proposed (Scheme 17). Two pathways are shown for the formation of vinyl selenide **32** there. Although they did not rule out the alternative pathway completely [3], Beletskaya and Ananikov proposed that the dominating pathway was protonolysis of selenovinyl Pd_2 complex **36** by PhSeH, based on observations: (1) hydrido Pd complex **35** was not observed in NMR experiments and (2) the reaction of HC≡CCH_2OH with a mixture of dinuclear Pd(II) complexes **34** in the presence of CF_3CO_2H yielded both bis(selenide) **33** (31%) and Markovnikov-type product **32** (15%).

On the other hand, the hydroselenation catalyzed by $Pt(PPh_3)_4$ provided only Markovnikov-type product **32** (21) [46].

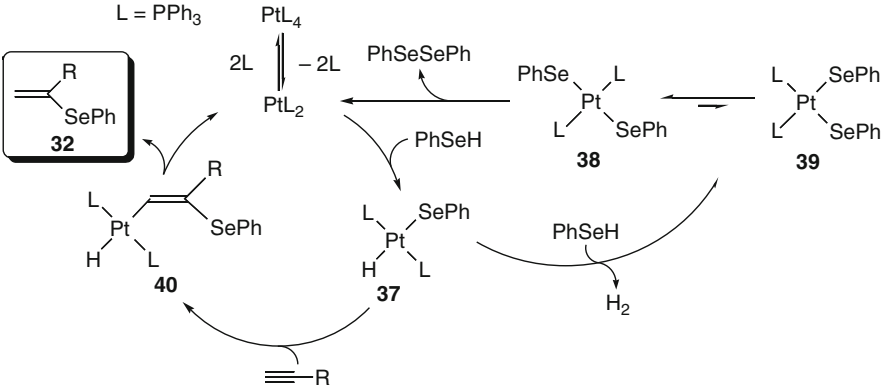


(21)

R = $HOCH_2$, Bu, Me_2NCH_2, *c*-C_6H_{10} (1-OH) 51% – 60%

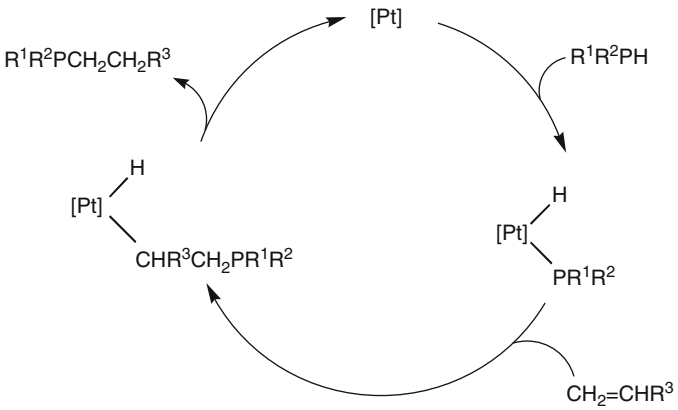


Scheme 17 Catalytic cycle for $Pd(PPh_3)_4$-catalyzed hydroselenation



Scheme 18 Catalytic cycle for $Pt(PPh_3)_4$-catalyzed hydroselenation

A key intermediate, *trans*-PtH(SePh)$(PPh_3)_2$ (**37**), was observed by ^{1}H NMR spectroscopy in the reaction of PhSeH with $Pt(PPh_3)_4$ in C_6D_6 (Pt–*H*: δ –8.77, $J_{Pt–H}$ 999.8 Hz, and $J_{Se–H}$ = 44.1 Hz). In ^{31}P NMR, signals assigned to *trans*- and *cis*-Pt$(SePh)_2(PPh_3)_2$ (**38** and **39**) were observed at δ 20.8 ($J_{Pt–P}$ = 2,842 Hz) and δ 18.5 ($J_{Pt–P}$ = 2,966 Hz), respectively, along with minor signals at δ 20.8, 23.7, and 30.6. *cis*-Pt$(SePh)_2(PPh_3)_2$ (**39**) very rapidly isomerized to *trans*-Pt$(SePh)_2(PPh_3)_2$ (**38**) at 80°C. Thus, a catalytic cycle shown in Scheme 18 was proposed [46]. Hydrido Pt (II) complex **37** undergoes insertion of alkyne into the Pt–Se bond to give *syn*-selenoplatination intermediate **40**, the reductive elimination from which yields the vinyl selenide **32** and $Pt(PPh_3)_2$. Incidentally, in a review [3], Beletskaya and Ananikov mentioned that the isomerization from *trans* to *cis* geometry of hydrido-(2-selenovinyl) Pt(II) complex **40** may be required for C–H reductive elimination.



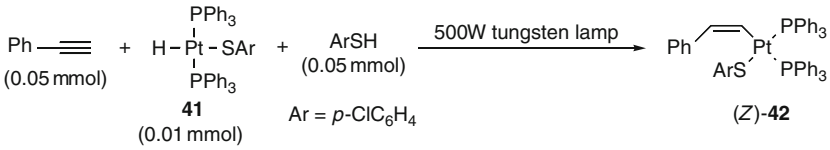
Scheme 19 Catalytic cycle for $Pt[P(CH_2CH_2CN)_3]_3$-catalyzed hydrophosphination

Importantly, while the reaction of PhSeH with 1-hexyne in the presence of *trans*-$Pt(SePh)_2(PPh_3)_2$ (**38**) gave $H_2C{=}C(SePh)Bu$ in 60% yield, the reaction of $HC{\equiv}CCH_2OH$ with **38** *in the presence of* CF_3CO_2H gave *only a trace amount (~0.5%) of* $H_2C{=}C(SePh)CH_2OH$. The latter result is quite in contrast with the case of the catalytic reaction with dinuclear Pd(II) complexes **34** (*vide supra*), ruling out the pathways involving protonolysis of vinyl Pt(II) intermediate **40** with acid.

In relation, Pringle and coworkers reported the reaction of PH_3 with acrylonitrile catalyzed by $Pt[P(CH_2CH_2CN)_3]_3$ to yield $P(CH_2CH_2CN)_3$ [47]. They proposed that the reaction proceeds through oxidative addition of the P–H followed by insertion of acrylonitrile into the Pt–P bond (not Pt–H) bond and a C–H reductive elimination (Scheme 19) [45].

3.2 Stoichiometric Reaction of Hydrido-Chalcogenolato Pt(II) Complexes with Alkynes

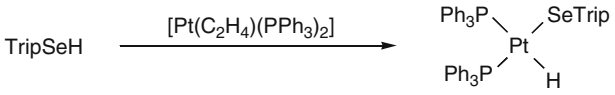
Kuniyasu and Kurosawa reported that, while hydrido-thiolato Pt(II) complex, *trans*-$PtH(SC_6H_4$-*p*-$Cl)(PPh_3)_2$ (**41**), did not react with phenylacetylene in C_6D_6 at room temperature, **41** did react with phenylacetylene *in the presence of p-*ClC_6H_4SH *under photoirradiation* to furnish (*Z*)-**42** in 77% yield (*cis*/*trans* = 73/27) in C_6D_6 or 85% yield (*cis*/*trans* = 85/15) in acetone-d_6 (22) [48]. In this reaction, (*Z*)-**42** is the kinetic product and the insertion of phenylacetylene to the Pt–H bond occurs in a *trans*-fashion (*anti*-addition). The reaction of phenylacetylene with **41** in the presence of AIBN and *p*-ClC_6H_4SH gave (*Z*)-**42** in 77% yield. *trans*-$PtH(X)(PPh_3)_2$ (X = Cl, Br, and I) also lead to similar reactions under photoirradiation or in the presence of AIBN to furnish the corresponding (*Z*)-insertion products. Although a pivotal role of thiyl radical is considered in this *trans*-insertion, the mechanism remains unclear.



(22)

In the case of dithiolato Pt(II) complex, *trans*-$Pt(SAr)_2(PPh_3)_2$, Kuniyasu and Kambe succeeded in the observation of stepwise double insertion of terminal alkynes followed by reductive elimination to give (*Z*,*Z*)-1,4-diarylthio-1,4-disubstituted-1,3-butadienes [49, 50]. They also obtained (2-chalcogenovinyl)-selenolato Pt(II) [51] and Pd(II) complexes [52] by other methods.

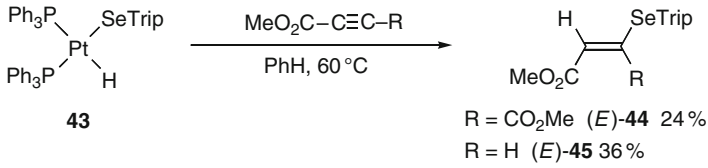
Ishii and coworkers investigated stoichiometric reaction of hydrido-selenolato Pt(II) complexes, *cis*-PtH(SeTrip)$(PPh_3)_2$ (**43**) (Trip = 9-triptycyl), with alkynes [53]. The hydrido-selenolato Pt(II) complex **43** is obtained by the reaction of TripSeH with $Pt(C_2H_4)(PPh_3)_2$ (23) [54].



43

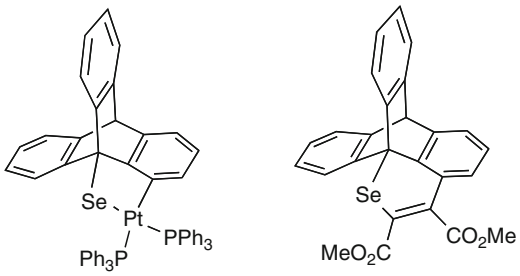
(23)

The reaction of **43** with activated alkynes, dimethyl acetylenedicarboxylate (DMAD), or methyl propiolate (MP), in benzene at 60°C, gave *syn*-adducts (*E*)-**44** and (*E*)-**45** in 24% or 36% yield, respectively, together with byproducts, selenaplatinacycle **46**, 1*H*-2-benzoselenin derivative **47** (in the case of DMAD), $(TripSe)_2$, and $[Pt(alkyne)(Ph_3P)_2]$ (alkyne = DMAD or MP) (24). The selenaplatinacycle **46** is a thermal reaction product of **43** as observed in other hydrido-selenolato Pt(II) [55–57], hydrido-thiolato Pt(II) [58], and hydrido-selenolato Pd(II) [59] complexes. 1*H*-2-Benzoselenin **47** is a carboselenation product of DMAD with **46** or TripSeH [53].



43

R = CO_2Me (*E*)-**44** 24%
R = H (*E*)-**45** 36%

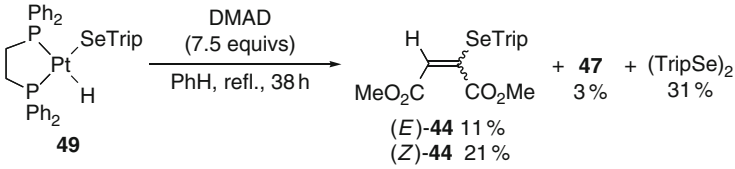


46 **47**

(24)

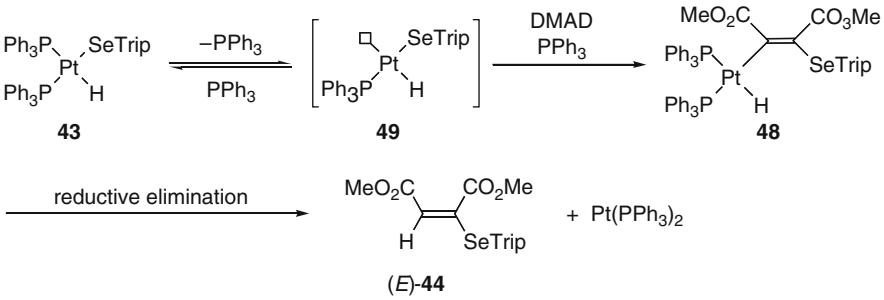
This result is in contrast with the report by Ananikov and Beletskaya on the reaction of PhSeH with methyl propiolate in the presence of $Pt(PPh_3)_4$ in toluene at 80°C to give a 1:7 mixture of the corresponding (*E*)- and (*Z*)-vinyl selenide ($PhSCH{=}CHCO_2Me$) by a non-catalytic reaction [46]. The reaction of *cis*-PtH(SeTrip)$(PPh_3)_2$ (**43**) with 1-hexyne, phenylacetylene, diphenylacetylene, or methyl 2-butynoate did not yield hydroselenation adducts, which is probably due to the steric hindrance of the bulky 9-triptycyl group and strong coordination ability of this alkaneselenolato ligand compared with benzeneselenolato ligand.

The regio- and stereoselective formation of (*E*)-**44** and (*E*)-**45** supports the *syn*-insertion of DMAD or MP into the Pt–Se bond of **43** to give (*Z*)-2-selenovinyl Pt(II) complex (**48** in Scheme 20), followed by reductive elimination. On the other hand, the reaction of PtH(SeTrip)(dppe) (**49**) [dppe = 1,2-bis(diphenylphosphino)ethane] with DMAD in benzene was sluggish at 60°C, and heating in refluxing benzene for 38 h was necessary for complete consumption of **49** to yield (*E*)-**44** (11%), (*Z*)-**44** (21%), 1*H*-2-benzoselenin **47** (3%), and $(TripSe)_2$ (31%) (23). These products are considered to be formed by the reaction of TripSeH, generated by reductive elimination of **49**, with DMAD.



(25)

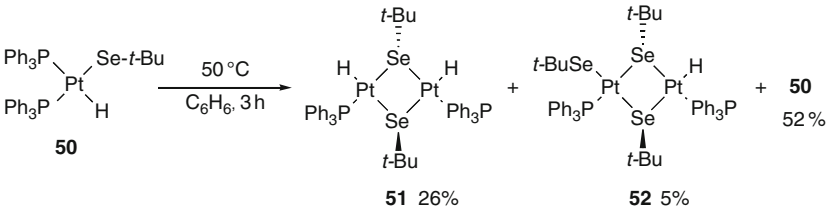
The difference between *cis*-PtH(SeTrip)$(PPh_3)_2$ (**43**) and PtH(SeTrip)(dppe) (**49**) in the reactivity toward DMAD is attributed to the weaker coordination ability of PPh_3 than that of dppe, that is, the dissociation of one phosphine ligand (PPh_3) from **43** is essential for the hydroselenation reaction. The reaction of **43** with DMAD in the presence of additional PPh_3 (2 molar equiv) to impede the formation (*E*)-**44** and to give $(TripSe)_2$ (39%), **43** (35%), and $Pt(dmad)(PPh_3)_2$ (53%). Thus, as depicted in Scheme 20, dissociation of one of the PPh_3 ligands from **43** occurs first to give coordination-unsaturated intermediate **49**, where the ligand *trans* to H would be



Scheme 20 Formation mechanism of *syn*-adduct (*E*)-**44** by the reaction of *cis*-PtH(SeTrip)$(PPh_3)_2$ (**43**) with DMAD

detached owing to the stronger *trans* effect of the H than that of the selenolato ligand. Then, **49** undergoes insertion of DMAD and re-coordination of PPh_3 to yield hydrido-(2-selenoalkenyl) Pt(II) intermediate **48**, from which reductive elimination provides the *syn*-adduct (*E*)-**44** and $Pt(PPh_3)_2$. Similar prior dissociation of a phosphine ligand was reported for the insertion of an alkyne into the Pt–S bond in *trans*-$Pt(SAr)_2(PPh_3)_2$ [49, 50]. *cis*-$PtH(SeTrip)(PPh_3)_2$ (**43**) did not work as the catalyst for the reaction of TripSeH with DMAD because it would undergo coordination of DMAD preferentially furnishing $Pt(dmad)(Ph_3P)_2$ persistent under the conditions.

cis-$PtH(Se\text{-}t\text{-}Bu)(PPh_3)_2$ (**50**) is an alternative isolable hydrido-alkaneselenolato complex, which is stable at room temperature in the absence of air and moisture [60]. Heating **50** in benzene at 50°C, two dinuclear hydrido Pt(II) complexes **51** and **52** were formed (26). The stoichiometric reaction of **50** with methyl propiolate gave a mixture of (*E*)- and (*Z*)-adducts in 28% and 6% yields, respectively, which are probably produced by the reaction of *t*-BuSeH, formed by the reductive elimination of **50**, with methyl propiolate. This low reactivity of **50** toward alkynes is similar to that of *cis*-$PtH(SeTrip)(PPh_3)_2$ (**43**) as mentioned above. The reactions of the two dinuclear hydrido Pt(II) complexes with methyl propiolate gave complex mixtures.

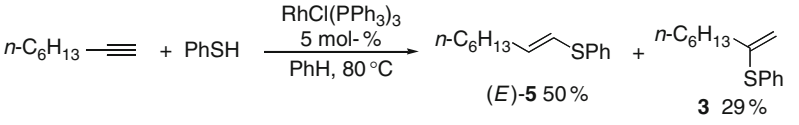


(26)

3.3 *Hybrid Type of Type I and Type II Mechanisms: Rh(I) and Ir(I) Complex-Catalyzed Hydrothiolation*

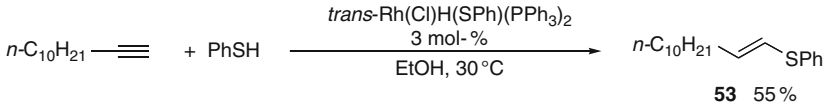
3.3.1 $RhCl(PPh_3)_3$-Catalyzed Hydrothiolation

The addition of PhSH to 1-octyne catalyzed by $RhCl(PPh_3)_3$ (Wilkinson catalyst) gives (*E*)-**5** (*anti*-Markovnikov adduct) as the main product together with **3** (27) [24]. The reaction carried out in EtOH provided the highest product selectivity [(*E*)-**5** 58%; **3** 0%]. When the reaction in EtOH was examined in the presence of galvinoxyl as a radical inhibitor, only (*E*)-**5** was formed in 73% yield, suggesting that a non-radical mechanism is operative for the formation of (*E*)-**5**.



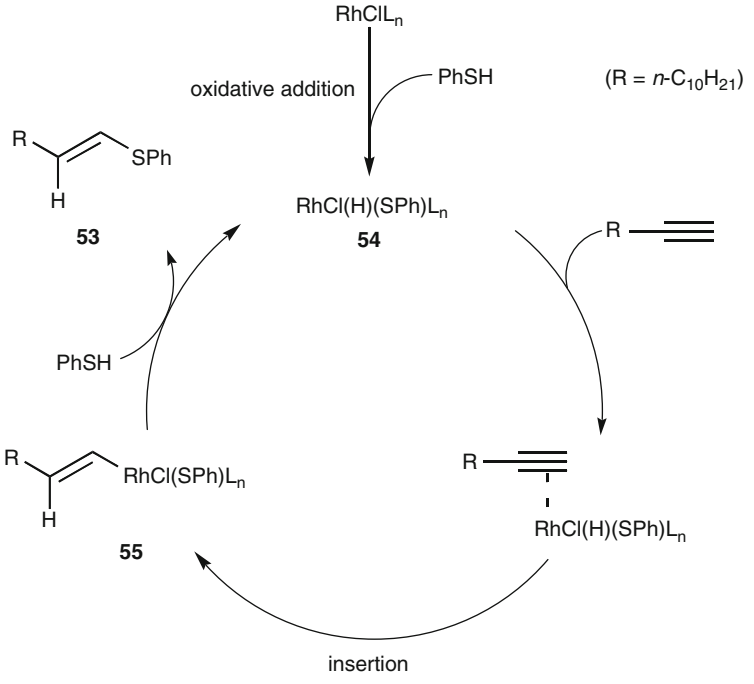
(27)

The stoichiometric reaction of $RhCl(PPh_3)_3$ with PhSH in dichloromethane at 20°C under argon atmosphere gave a hydrido-thiolato complex, *trans*-Rh(Cl)H(SPh)$(PPh_3)_2$ [61]. The reaction of PhSH with 1-dodecyne in the presence of *trans*-Rh(Cl)H(SPh)$(PPh_3)_2$ as the catalyst (3 mol%) gave **53** in 55% yield (26).



(28)

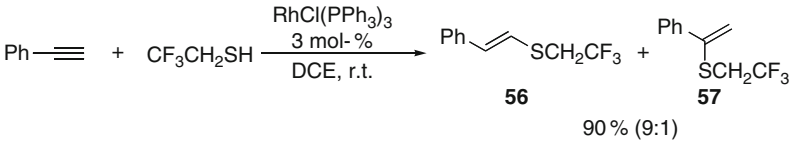
The proposed mechanism is shown in Scheme 21, where hydrido-thiolato Rh (III) complex **54** undergoes the stereoselective insertion of alkynes into the Rh–H bond to form the *trans*-vinyl Rh(III) complex **55** and the following reductive elimination of the complex in the presence of excess PhSH yields *anti*-Markovnikov-type, *syn*-adducts **53** and **54**. This catalytic cycle is based on the ^1H NMR observations. Thus, the ^1H NMR spectrum of a stoichiometric mixture of *trans*-Rh(Cl)H(SPh)$(PPh_3)_2$ with 1-dodecyne exhibited a doublet δ 5.1, probably due to a vinylic proton of *trans*-vinylrhodium intermediate (corresponding to **55**) with disappearance of signals due to Rh–*H* (δ –16.4) and *n*-$C_{10}H_{21}C{\equiv}C$–*H*. This doublet disappeared by the addition of PhSH giving the vinylic sulfide **53** after 6 h at room temperature. This observation supports that the insertion of alkynes occurs to the Rh–H bond and not to Rh–S bond of *trans*-Rh(Cl)H(SPh)$(PPh_3)_2$ and that the



Scheme 21 Catalytic cycle for $RhCl(PPh_3)_3$-catalyzed hydrothiolation of alkynes to give the *anti*-Markovnikov-type product

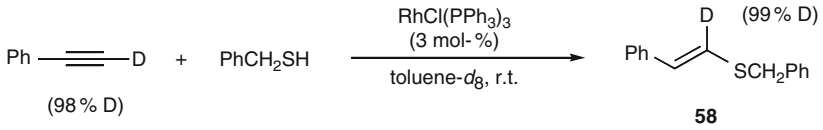
final product is produced not by a sole reductive elimination of *trans*-vinylrhodium intermediate **55** but by a *PhSH-assisted* reductive elimination.

In 2007, Love and coworkers reported the hydrothiolation of alkynes with alkanethiol using $RhCl(PPh_3)_3$ [62]. Under optimized conditions (in 1,2-dichloroethane at room temperature), the reaction of CF_3CH_2SH with phenylacetylene in the presence of 3 mol% of $RhCl(PPh_3)_3$ furnished *anti*-Markovnikov (**56**) and Markovnikov (**57**) adducts in a ratio of 9:1 in 90% yield (27), the regioselectivity of which is similar to the case of PhSH [see (28)].



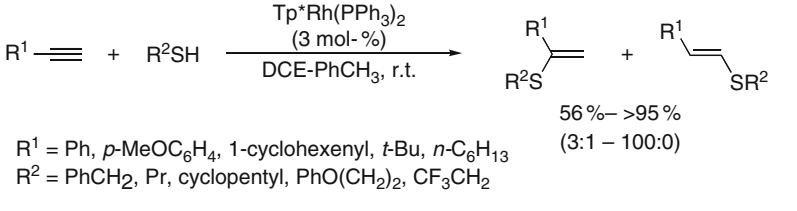
(29)

In the reaction employing deuterium-labeled phenylacetylene (PhC≡CD), only *syn*-addition product **58** was obtained (30), excluding the vinylidene pathway. Love suggested that the reactions involve alkyne insertion into the Rh–H bond of the intermediate, formed by oxidative addition of thiol to $RhCl(PPh_3)_3$, from steric reason.

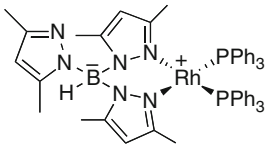


(30)

Love also reported $Tp^*Rh(PPh_3)_2$-catalyzed hydrothiolation of alkanethiol to alkynes (31) [63–65], in which the regioselectivity was opposite of that obtained with other Rh(I) catalysts mentioned above. In the reaction of arenethiols (ArSH: Ar = Ph, *p*-Tol, *p*-BrC_6H_4) with Ar′C≡CH (Ar′ = Ph, *p*-$MeOC_6H_4$, and *o*, *p*-$F_2C_6H_3$), the selectivity is lowered (1.4:1 to 6:1) [63].



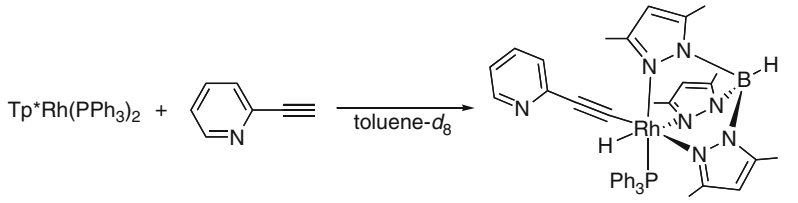
(31)



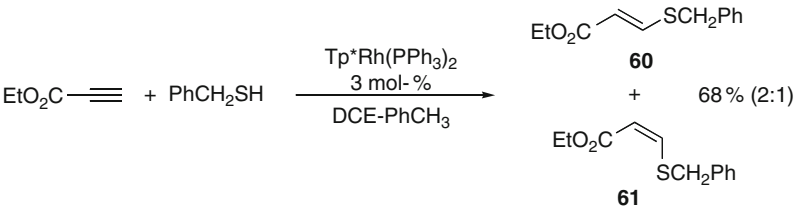
$Tp^*Rh(PPh_3)_2$

While the reactions of $PhCH_2SH$ with *para*-substituted phenylacetylenes (Ar′C≡CH) in the presence of $Tp^*Rh(PPh_3)_2$ provided Markovnikov-type adducts

$PhCH_2S(Ar')C{=}CH_2$ regioselectively in moderate to high yields, 2-pyridylacetylene was unreactive in hydrothiolation [66]. The stoichiometric reaction of $Tp^*Rh(PPh_3)_2$ with 2-pyridylacetylene in toluene-d_8 was investigated to reveal the formation of acetylido-hydrido complex **59** (32), the formation of which is rapid and irreversible to preclude the reaction of thiol with $Tp^*Rh(PPh_3)_2$. The reaction of $PhCH_2SH$ with ethyl propiolate catalyzed by $Tp^*Rh(PPh_3)_2$ yielded **60** and **61** in the ratio of 2:1 (33).



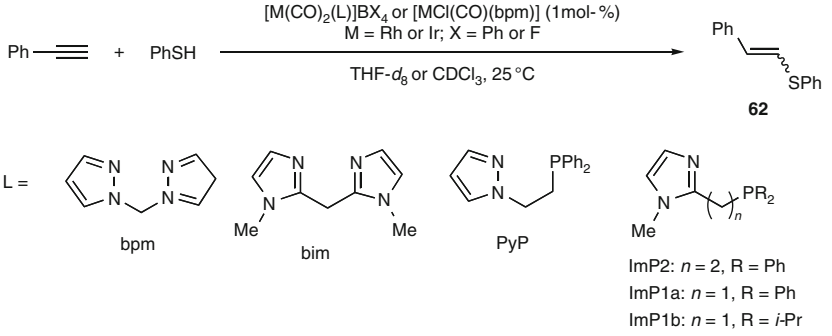
(32)



(33)

3.3.2 Cationic Rh(I) and Ir(I) Complex-Catalyzed Hydrothiolation

Hydrothiolation with cationic ($[M(CO)_2(L)]BX_4$; L = N,N and N,P bidentate ligands; bim, PyP, bpm, ImP2, ImP1a, IMP1b; X = Ph, F) or neutral ([MCl(CO)(bpm)]) Rh(I) and Ir(I) complexes as the catalysts were reported by Messerle and coworkers (34) [67, 68]. The catalytic reaction gave a mixture of (*E*)- and (*Z*)-*anti*-Markovnikov adducts **62** as the main products. Monitoring the course of the reaction by ^1H NMR showed that the (*Z*)-isomer was the kinetic product [67]. Although mechanism was not shown in the literatures, a mechanism similar to the cases of neutral Rh(I) and Ir(I) complexes described above may be operative.



(34)

4 Conclusion

Since the first reports of Pd(II)-catalyzed hydroselenation and hydrothiolation 1992, considerable investigations have accumulated experimental evidence for the mechanism, in particular for Type I mechanism. Each step of Type I mechanism, structures of active catalysts, the reaction of alkynes with the active catalysts, and the protonolysis of the resulting vinyl metal complexes, has been verified for Pd, Ni, Zr, Ln, and An-catalyzed hydrochalcogenations by isolation of intermediates, isotope-labeled experiments, and kinetic studies. With regard to Type II mechanism, while the initial oxidative addition of REH (E = S, Se) to a low-valent transition metal catalyst (metal = Pd and Pt) has been verified by direct (for Pt) or indirect (for Pd) experimental evidence, the following steps of alkyne insertion to chalcogenolate-hydrido complex and reductive elimination of resultant vinyl metal complexes leave room for further mechanistic investigations to obtain direct evidence. On the other hand, a hybrid mechanism of Type I and Type II has been clarified for the hydrothiolation with Rh(I) complexes.

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