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Unusual Influence of the Structures of Transition Metal Complexes on Catalytic C–S and C–Se Bond Formation Under Homogeneous and Heterogeneous Conditions

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In the presence of transition metal catalysts, hydrothiolation and hydroselenation reactions, as well as bisthiolation and bisselenation reactions, have been successfully carried out with high selectivities and yields. New transition metal-catalyzed synthetic methods have been developed for the preparation of vinyl sulfides and vinyl selenides of various types. Mechanistic study has revealed that a homogeneous catalytic system based on phosphine complexes of palladium is the best choice for carrying out stereoselective additions of disulfides and diselenides to alkynes. A heterogeneous Ni-catalyzed reaction with a unique self-organized nanostructured catalyst was superior for carrying out regioselective additions of thiols and selenols to alkynes.

1. Introduction

Increasing demand for vinyl sulfides and vinyl selenides in organic chemistry[1–3] and materials science[4] has furthered the development of new preparative methods for these target compounds. Several synthetic approaches have so far been developed, including halogen substitution in vinyl halides,[5] preparation from olefins[6] and carbonyl[7] compounds, rearrangement of propargylic aryl chalcogenides,[8] selenodecarboxylation,[9] utilization of In,[10] Al,[11] Li,[12] Ti,[13] and Ga[14] reagents, and some other methods.[1]

The best solution to the problem would be provided by addition reactions of element-hydrogen (E–H) and element-element (E–E) bonds to easily available acetylenic hydrocarbons (E = S, Se). Such addition reactions are performed with 100% atom efficiency and can be carried out without any by-products. Unfortunately, addition of disulfides[15] and diselenides[16] to alkynes carried out under photochemical or basic conditions usually gives mixtures of *Z* and *E*

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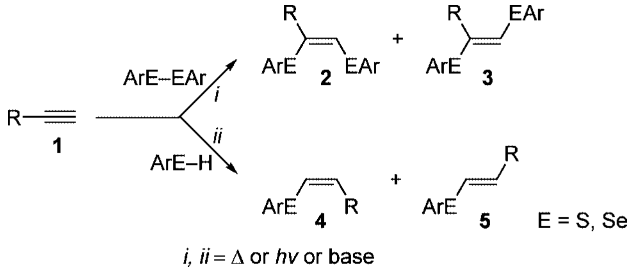
isomers **2** and **3** (Scheme 1), while addition of thiols[17] and selenols[18] to C≡C bonds mostly results in mixture of *cis* and *trans* anti-Markovnikov species **4** and **5** (Scheme 1). Selective transformations have been reported only in a few specific cases.[19,20]



Scheme 1.

A more convenient methodology can be created based on transition metal-catalyzed transformation, and has been successfully applied for addition of E–E and E–H bonds to alkynes (for E = B, Si, Sn, P, Ge, etc.).[21] Complexes of platinum group metals (mostly Pd, Pt, and Rh, and in some cases Ni) have been utilized in these catalytic reactions. In such cases, high atom efficiency of the addition reaction can be combined with high selectivity of the catalytic transformation, resulting in cost-efficient and environmentally friendly synthetic procedures in agreement with green chemistry requirements.[22]

However, there is an important difference between S and Se and the other elements. Sulfur compounds, RSSR and RSH, are dangerous poisons for catalytic reactions employing platinum group metals in the active site.[23] Due to formation of strong metal-sulfur bonds in monomeric and polymeric metal sulfides, even low concentrations of sulfur compounds may cause significant deactivation of the catalyst. From practical experience the concentration of the sulfur species should be <10 ppb to maintain high catalytic activity,[23a] which requires deep desulfurization of hydrocarbons. The same is applicable for the Se analogues, which also form a broad range of stable metal derivatives.

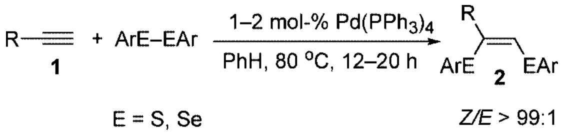
The obvious question is: if sulfur and selenium species are catalyst poisons even at very low concentrations, how can we employ these species as reagents in transition metal-catalyzed reactions?

In this review we address this problem in detail and describe recent developments in this fascinating field. An attempt has been made to analyze both the synthetic potential and the mechanistic aspects of the catalytic reactions and to provide reliable comparison with the other elements. Finally, we discuss some problems that still remain unsolved in the field.

2. Transition Metal-Catalyzed E–E Bond Addition to Alkynes (E = S, Se)

2.1 Pd-Catalyzed E–E Bond Addition to Alkynes

In their pioneering work in 1991, Ogawa, Sonoda, et al.[24] showed that the phosphine (the term "phosphine" is used throughout this review as in the original articles) complex of palladium $Pd(PPh_3)_4$ is an efficient catalyst for ArE–EAr bond addition to terminal alkynes (E = S, Se). It was found that, in the presence of 1–2 mol-% of $Pd(PPh_3)_4$, diaryl dichalcogenides (Ar_2S_2 and Ar_2Se_2) can be added to the triple bonds of terminal alkynes (benzene, 80 °C, 12–20 h) with good yields of 54–98% (Scheme 2). The catalytic reaction was performed with excellent stereoselectivity in a *syn* addition manner, resulting in the formation of *Z* isomers. Only diaryl dichalcogenides showed good reactivity in the studied reaction, while $n\mathrm{Bu}_2\mathrm{Se}_2$ (24% yield; R = $n\mathrm{C}_6\mathrm{H}_{13}$) and $(PhCH_2Se)_2$ (no product) were dramatically less active.[24,25]

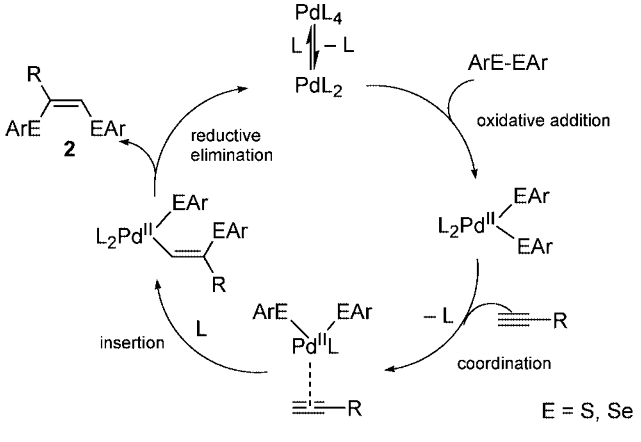


Scheme 2.

The catalytic system was not sensitive to the alkyne substituents: various terminal alkynes reacted with good to high yields (54–99%) and *Z*/*E* selectivities (> 90:10), except in the case of activated alkynes (R = Ar), where competitive noncatalytic reactions resulted in mixtures of **2** and **3**, thus decreasing the overall selectivity of the addition reaction (see Scheme 1).

Only the low-valent palladium complex $Pd(PPh_3)_4$ showed the desired catalytic activity, while derivatives of Pd^{II} – $PdCl_2(PPh_3)_2$, $PdCl_2(PhCN)_2$, and $Pd(OAc)_2$ – were inactive under these conditions.[24]

A plausible catalytic reaction mechanism involves the following steps (Scheme 3): 1) oxidative addition of the E–E bond to Pd^0, 2) alkyne coordination to the metal center, 3) alkyne insertion into the M–E bond, and 4) C–E reductive elimination to afford the product **2** and to regenerate Pd^0. This represents a general framework of transition metal-catalyzed E–E bond addition to unsaturated molecules.[21]



Scheme 3.

Detailed investigation of this catalytic reaction showed that the yield of product **2** strongly depended on the quality of catalyst.[26,27] Commercially available complex $Pd(PPh_3)_4$ (partially oxidized, as evident from the presence of

O=PPh_3 in the ^{31}P NMR spectrum) usually gave 50–60% yields. Better results were achieved with freshly prepared $Pd(PPh_3)_4$ catalyst, although the yields of **2** did not reach the quantitative level even in this case.

It was found that the yields of product **2** in the Pd-catalyzed reaction depended on the amount of free PPh_3 ligand in solution – an increase in the amount of added PPh_3 ligand resulted in a greater yield of **2**. Excellent isolated yields of **2** (83–98%) were achieved by utilizing an excess of the PPh_3 ligand: $[Pd(PPh_3)_4/PPh_3]$ = 1:4 for ArS–SAr addition and $[Pd(PPh_3)_4/PPh_3]$ = 1:6 for ArSe–SeAr addition to alkynes.[27] It should be noted that this is the first example of facilitation of E–E bond addition to unsaturated molecules by an excess of the ligand. Available data on the other elements (for E = B, Si, Sn, P, Ge, etc.) indicate that an excess of the ligand retards the catalytic reaction, since ligand dissociation should occur prior to coordination of the unsaturated molecule (Scheme 3). In some studies the best results were achieved by use of low-ligated transition metal complexes $[Pd(PPh_3)_2$ etc.] as catalyst precursors.[21]

2.2 Other Metals in Catalytic E–E Bond Additions to Alkynes

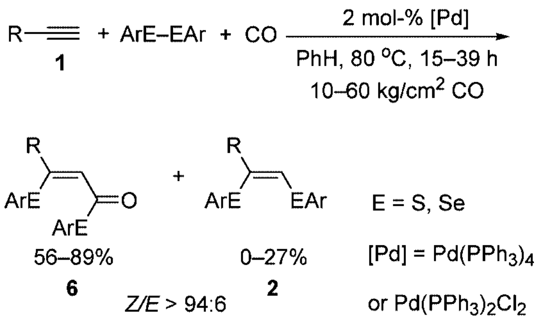
Surprisingly, the platinum analogue $Pt(PPh_3)_4$ has not shown good catalytic activity in the ArE–EAr addition reaction. Rather small yields of 9% (R = COOMe)[26] and 21% (R = $n\text{-}C_6H_{13}$)[24] of **2** were reported for the Pt-catalyzed transformation. An addition of an excess of PPh_3 ligand did not further increase the yield in the case of Pt-catalyzed reaction. Use of $Rh(PPh_3)_3Cl$, $Ni(PPh_3)_2Cl_2$, and $Ru(PPh_3)_3Cl_2$ as the catalysts resulted in 24%, 0%, and 0% yields of **2**, respectively (Ph_2S_2 addition to oct-1-yne).[24] Therefore, palladium was found to be the best catalyst for E–E bond addition of diaryl dichalcogenides to alkynes (E = S, Se).

Yamaguchi et al. have shown that rhodium complexes catalyze S–S bond additions of dialkyl disulfides to terminal alkynes.[28] In the presence of 3 mol-% of $RhH(PPh_3)_4$, 12 mol-% of tris(*p*-methoxyphenyl)phosphine, and 3 mol-% of trifluoromethanesulfonic acid, catalytic addition of various dialkyl disulfides to terminal alkynes (acetone, 56 °C, 10 h) was performed in 66–99% yields. The stereoselectivity of the addition reaction was high and only the formation of *Z* isomers was detected.[28]

The rhodium complex $RhH(PPh_3)_4$ with the dppf ligand catalyzed selenothiolation of alkynes with a mixture of diaryl disulfide and diaryl diselenide.[29] The reaction results in selective formation of 1-seleno-2-thio-substituted alkenes.

2.3 Catalytic Carbonylative Addition of E–E Bonds to Alkynes

Performing the catalytic reaction under CO (benzene, 80 °C, 10–60 $kg\,cm^{-2}$) affords the product corresponding to addition of the ArE and ArECO fragments to the alkyne (Scheme 4).[24] The formation of the carbonylative addition product **6** made the major contribution to the reaction, though a small amount of a direct addition product **2** was also observed in some cases. In contrast to the direct addition reaction (see Section 2.1), not only $Pd(PPh_3)_4$, but also $PdCl_2(PPh_3)_2$ has shown good catalytic activity in the carbonylative addition reaction, even under low pressure of CO. The carbonylative addition reaction was performed with excellent stereoselectivity and resulted in preferable formation of *Z* isomer **6** ($Z/E > 94{:}6$).[24]



Scheme 4.

Treatment of propargylic or homopropargylic alcohols with diaryl dichalcogenides and CO in the presence of $Pd(PPh_3)_4$ resulted in lactonization, giving the corresponding lactones with β-arylthio or β-arylseleno groups.[30]

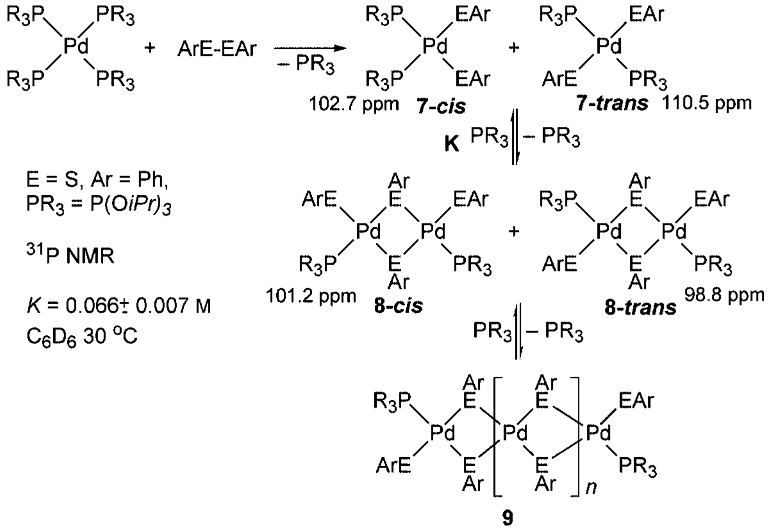
2.4 Mechanistic Study of the Catalytic E–E Bond Addition to Alkynes

Detailed mechanistic study revealed several important features not covered within the generally accepted framework. It was found that oxidative addition of S–S and Se–Se bonds to Pd^0 resulted in the formation of dinuclear derivatives $[Pd_2(EAr)_4(PAr'_3)_2]$, which were isolated and characterized by X-ray analysis.[31,32] However, mechanistic study of the catalytic reaction in solution was hardly possible, due to strong overlapping of the Ar and Ar′ signals in the NMR spectra. To solve this problem a new catalytic system based on phosphite ligands was developed.[33] The model system with phosphite ligands L = $P(O\textit{i}Pr)_3$ was found to be very convenient for mechanistic studies, since the L/EAr ratio could easily be determined by NMR spectroscopy.

Investigation of the first step of the catalytic cycle – oxidative addition – showed that E–E bond cleavage by palladium gives a mixture of *cis*/*trans* mononuclear and dinuclear complexes as well as oligomeric species (Scheme 5).[33,34]

The structures of complexes **7-*trans*** and **8-*trans*** were determined by X-ray analysis, complexes **7-*cis***, **7-*trans***, **8-*cis***, and **8-*trans*** were detected in solution by NMR, and the equilibrium constant of the dissociation of the dinuclear complexes into mononuclear form – $K = 0.066 \pm 0.007$ M – was measured.

It is interesting to find out which of the complexes **7**–**8** can catalyze the addition reaction. As we have already mentioned, an excess of the ligand is required to achieve



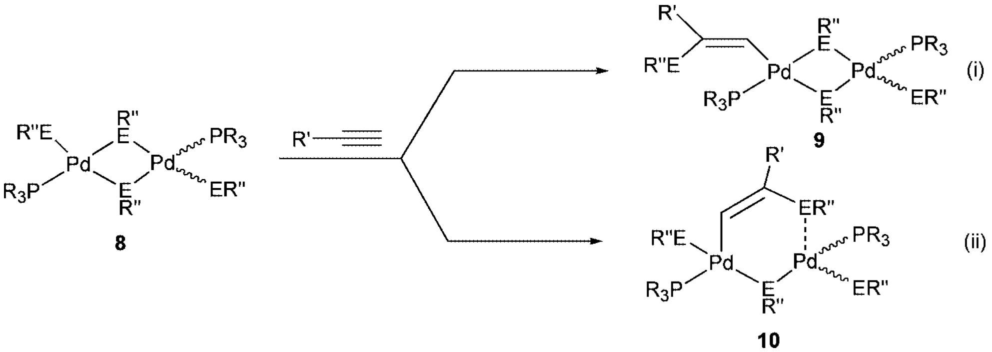
Scheme 5.

high yields of the E–E addition reaction to alkynes. In the absence of the extra ligand, the reaction was carried out under heterogeneous conditions, due to the formation of insoluble $[Pd(EAr)_2]_n$ polymer (**9**). It was shown that the polymeric species **9** did not catalyze the E–E bond addition reaction to alkynes. Therefore, if the amount of the ligand was not enough, palladium species were precipitated in this polymeric form and the catalytic reaction stopped. An excess of the ligand prevents catalyst polymerization and ensures homogeneous reaction conditions.[27,33]

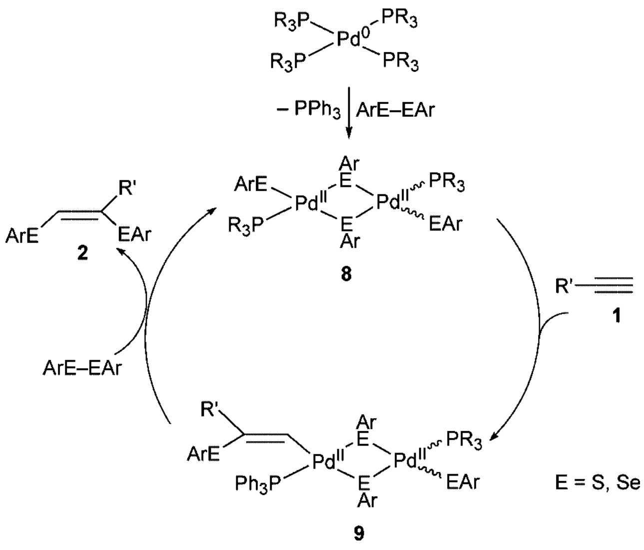
It is more difficult to distinguish catalytic activity of complexes **7**–**8**. It was proposed that complexes containing the *cis*-ArE–Pd–EAr unit (**7-*cis***, **8-*cis***, **8-*trans***) catalyzed this transformation, while **7-*trans*** was inactive. The absence of catalytic activity of *trans*-mononuclear derivative **7-*trans*** was presumed after analysis of the reactivity in the analogous platinum-catalyzed reaction with $Pt(PPh_3)_4$ as a catalyst precursor (see below).

After oxidative addition, the next step is alkyne insertion into the M–E bond. At the moment we do not know whether one or both palladium atoms are involved in the catalytic cycle, but we can compare the reactivities of different M–E bonds of dinuclear complexes. For dinuclear derivatives two different pathways are possible: i) insertion into the terminal M–E bond, and ii) insertion into the bridged M–E bond (Scheme 6). The relative reactivities of terminal and bridged M–E bonds were estimated by theoretical calculations at the B3LYP/Lanl2dz level.[35] According to theoretical calculations performed on a small model system (R = R′ = R′′ = H),[36] the reaction by pathway (i) requires an activation barrier of $\Delta E^{\neq} = 9.5$ kcal mol^{-1} to be overcome and is exothermic by $\Delta E = -9.6$ kcal mol^{-1} (Scheme 6). Reaction by pathway (ii) requires a much higher barrier of $\Delta E^{\neq} = 20.7$ kcal mol^{-1} to be overcome and it is endothermic by $\Delta E = 1.2$ kcal mol^{-1}. According to the calculations, pathway (i) is more favorable and we will depict only this pathway in further schemes.

A plausible mechanism for palladium-catalyzed addition of S–S and Se–Se bonds to alkynes is shown in Scheme 7. As we have established, the formation of polymeric species should be avoided in order to achieve high performance in the catalytic reaction. It should be noted that the mononuclear complex (which is stable only in the presence of an excess of PR_3 ligand) with *cis* geometry (**7-*cis***) can also make some contribution to the product formation according to the mechanism shown in Scheme 3.

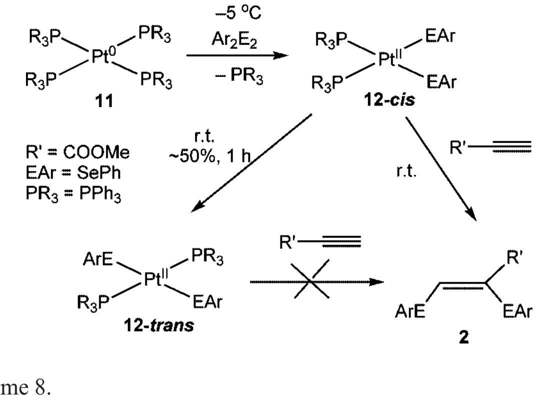


Scheme 6.



Scheme 7.

Unusual results were obtained upon comparing the catalytic activities of $Pd(PPh_3)_4$ and $Pt(PPh_3)_4$. Platinum complex **11** also underwent oxidative E–E bond addition with diaryl dichalcogenides, but dinuclear derivatives were not formed (Scheme 8). Complex **12-*cis***, with a *cis* ligand arrangement, was a kinetic product, which rapidly isomerized to the *trans* derivative **12-*trans***. The isomerization reaction was followed by NMR,[26] while the structures of the complexes **12-*cis*** and **12-*trans*** were established by X-ray analysis.[26,37] Complex **12-*cis*** reacted with alkynes to afford the expected products **2**, while complex **12-*trans*** was inactive. Most likely an insertion into the Pt–Se bond is possible for both *cis* and *trans* complexes (**12-*cis*** and **12-*trans***), but a *cis* arrangement of the PhSe and vinyl ligands is required for reductive elimination to take place. This assumption explains the observed differences in the reactivities of **12-*cis*** and **12-*trans*** in the studied reaction. The studied Pt derivatives represent a convenient model system and we think that the same reactivity should be expected for Pd analogues. Direct measurements for the mononuclear complexes of Pd are not possible, due to quick isomerization to the dinuclear form.



Scheme 8.

An important issue is the regioselectivity of the alkyne insertion step. In the studied system, alkyne insertion occurs only according to Markovnikov's rule: the metal atom is bonded to the terminal carbon atom, while an EAr group is bonded to the internal carbon atom (see **9**, Scheme 7). The structure of the carbonylative product **6** (Scheme 4) confirms this regioselectivity of the insertion step (if we accept that CO insertion occurs into the M–C bond of the vinyl complex **9**[38]).

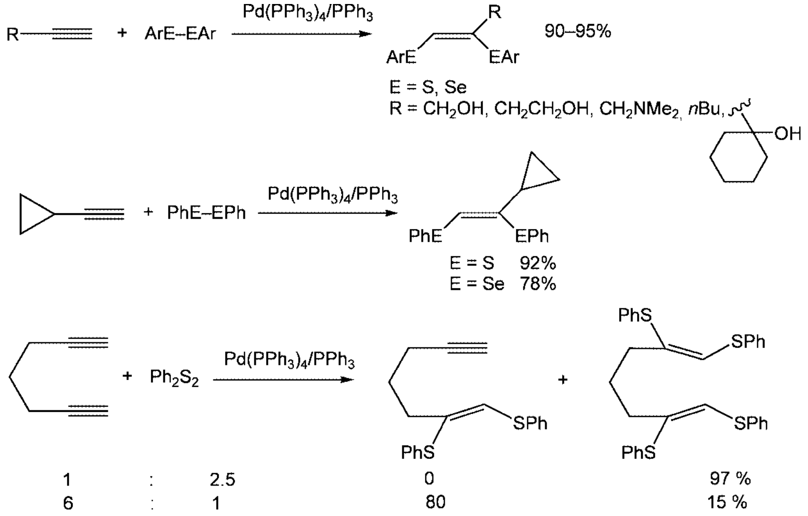
2.5 Synthetic Application of the E–E Bond Addition Reaction to Alkynes

Several important approaches were investigated in order to develop practical synthetic procedures for the preparation of disubstituted thio(seleno)alkenes **2**. The dinuclear palladium complexes were prepared not only by the oxidative addition reaction (Scheme 5), but also by chloride ligand substitution in Pd^{II} by ArE^- generated in situ.[26,27] By this approach, the Pd^0 catalyst precursor can be replaced with air-stable and easily available Pd^{II} species such as $Pd(PPh_3)_2Cl_2$, $PdCl_2$, and $Pd(OAc)_2$.[26,27,39]

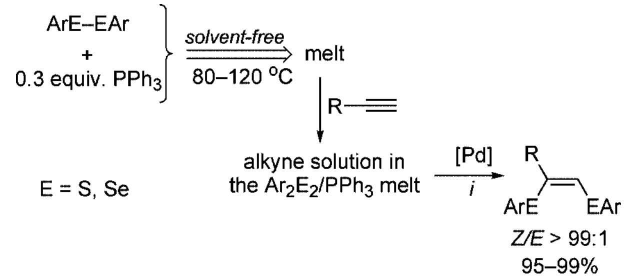
The scope of Pd-catalyzed additions of S–S and Se–Se bonds to terminal alkynes is illustrated in Scheme 9.[33,27,39–43] It was shown that the catalyst was tolerant to various functional groups in alkynes and diaryl dichalcogenides. An important issue was to carry out the reaction with an alkyne bearing an amino group, since the products were easily crystallized as oxalic salts. Corresponding X-ray structures were obtained for the first time for both cases E = S[27] and E = Se.[26] The crystal structures provided important information concerning nonbonded S···O and Se···O interactions.[26,27] Such interactions are of primary importance for understanding of the mechanisms of biological action of sulfur and selenium species in living cells.[40]

The addition reaction was successfully performed in the case of cyclopropylacetylene (without breaking of the cyclopropyl ring). Depending on the alkyne/Ph_2S_2 ratio, one or both triple bonds of hepta-1,6-diyne were involved in the reaction, with high stereoselectivities and yields (Scheme 9). These facts provide independent confirmation of the regioselectivity of the alkyne insertion step according to Markovnikov's rule (see 2.4). If the insertion step were to occur with opposite regioselectivity, the cyclopropyl ring should be involved in a homoallylic rearrangement, while the formation of cyclic products should be expected for hepta-1,6-diyne.

Performing the reaction under solvent-free conditions (Scheme 10) made it possible to increase the temperature to 100–140 °C [41] and to decrease the reaction time to 3–5 min or the catalyst loading to 0.1–0.001 mol-%.[42,39] Catalytic addition of Ar_2E_2 to alkynes under solvent-free conditions was performed with good isolated yields of 85–90% and excellent stereoselectivities ($Z/E > 97:3$).[42] It was possible to separate the catalyst by rapid flash chromatography and to repeat the addition reaction using this recycled catalyst without lowering the product yield and selectivity. The catalytic system under solvent-free conditions was easily scaled for the preparation of 0.3–3 g of product.[42]



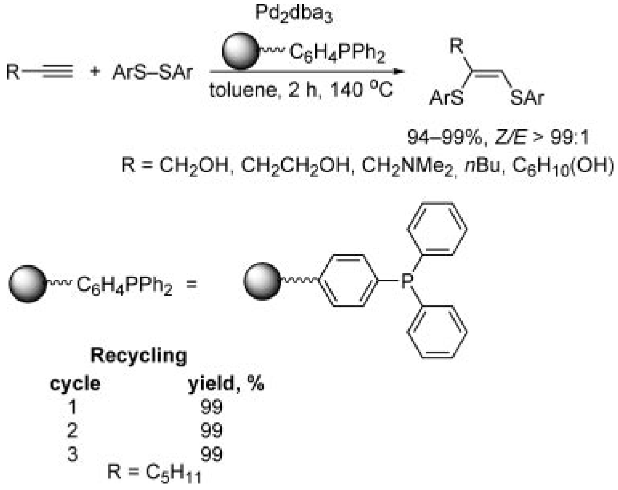
Scheme 9.



Scheme 10. Solvent free conditions (melt): i = 0.01 mol-% of $Pd(PPh_3)_4$, 140 °C, 1 h. Cf. with regular conditions in solvent: i = 3 mol-% of $Pd(PPh_3)_4$, 100 °C, 3 h.

The easiest practical opportunity for catalyst recycling was achieved with polymer-supported palladium catalyst (Scheme 11).[43] In this case the catalyst was separated by filtration and the final product of 96–98% purity was obtained in high isolated yields (94–99%) without any special purification procedure ($Z/E > 99:1$). The polymer-supported catalytic system was applicable only for the addition of diaryl disulfides to alkynes. In the presence of diaryl diselenides the catalyst was quickly deactivated due to selenation of the polymeric support, with the formation of P=Se bonds.[43]

The reaction times for Ar_2E_2 addition to alkynes can be decreased to as little as 10 min by using microwave irradiation under solvent-free conditions.[39] High yields and selectivities were achieved with use of as little as 0.1 mol-% of the catalyst generated in situ from various precursors – $Pd(PPh_3)_4$, $PdCl_2$, and $Pd(OAc)_2$ in the presence of PPh_3. The catalyst and triphenylphosphine ligand were recycled by flash chromatography and reused without noticeable lost of activity and selectivity.[39] Increasing the power of the microwave irradiation made it possible to activate not only the E–E bond, but also the C–E bond (E = S, Se) in catalytic fashion.[44,45] Mechanistic investigations have shown that the formation of dinuclear[44] and polynuclear[46] palladium complexes is a key factor for the activation of the C–E bond.



Scheme 11.

An interesting Pd-catalyzed one-pot, four-component coupling of diphenyl diselenide, alkyne, carbon monoxide, and sulfenamide was described by Meyer et al.[47] The catalytic reaction results in the formation of (Z)-β-selenylacrylamides via the intermediate palladium complex PhSe–PdL_2–CO–CH=C(R)EPh.

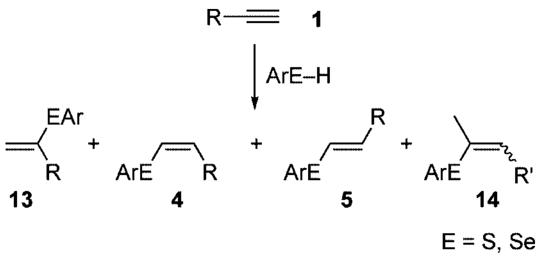
An unusual Rh-catalyzed reaction between the alkynes and disulfides has been reported: C–H bond breakage and thiolation of alkynes took place instead of addition to the triple bond.[48]

3. Transition Metal-Catalyzed E–H Bond Addition to Alkynes (E = S, Se)

Ogawa, Sonoda et al. carried out the first transition metal-catalyzed E–H bond addition to alkynes.[49] The catalytic reaction gave the desired Markovnikov-type product with good selectivity. However, to achieve good yields, high temperatures and long reaction times were required, which provoked several side-reactions (noncatalytic addition, isomerization, etc.). Further development of the field has revealed several approaches to solving this problem, as is reviewed below.

3.1 Pd-, Pt-, and Rh-Catalyzed E–H Bond Additions to Alkynes

Using $Pd(OAc)_2$ as a catalyst precursor made it possible to obtain Markovnikov-type product **13** with good yields and selectivities (Scheme 12).[50,51] ArSH addition to terminal alkynes was carried out with 55–87% product yields and >11:1 selectivities with regard to Markovnikov/anti-Markovnikov products (THF, 67 °C, 12–16 h). Depending on reaction temperature, up to 14% of **14** was obtained due to an isomerization side-reaction. Another side-reaction – noncatalytic addition – gave by-products **4** and **5** in <5% yield. It was also possible to carry out this reaction with internal alkynes, although in nonselective fashion and with a broad range of *E*/*Z* ratios. In the same manner, $Pd(OAc)_2$ catalyzed regioselective PhSeH addition to alkynes, which took place in benzene solution at 80 °C.[51] The catalytic reaction resulted in 62–73% yields of the α isomer **13**, depending on the nature of the substituent R, except in the case of activated phenylacetylene, which gave significant amounts of anti-Markovnikov species (33% of **13** and 64% of **4** + **5**).



Scheme 12.

Much better results in the synthesis of Markovnikov product were achieved by using $Pd(OAc)_2$ catalyst in pyridine to perform the hydroselenation reaction.[52] The reaction was carried out at high temperature (100 °C) for 15 h and gave 53–99% yields of **13**. It is interesting to point out that in THF or benzene solutions the Pd-catalyzed reaction gave mixtures of **13**, **4**, **5**, and **14**, while in pyridine solution the by-products **4**, **5**, and **14** were not detected. The performance of the $Pd(OAc)_2$/pyridine catalytic system for the addition of S–H bonds to alkynes has not yet been studied.

At high temperatures (80–100 °C) and with long reaction times (12–16 h) it is rather difficult to suppress the isomerization side-reaction. An attempt was made to use this feature of the catalytic system to design a sequential addition/isomerization process.[58] Utilizing $Pd(PhCN)_2Cl_2$ catalyst, a one-pot synthetic procedure was developed for the preparation of **14** through the addition of ArSH to alkynes; unfortunately, the reaction was not selective and gave a mixture of *cis* and *trans* isomers of **14**.[58]

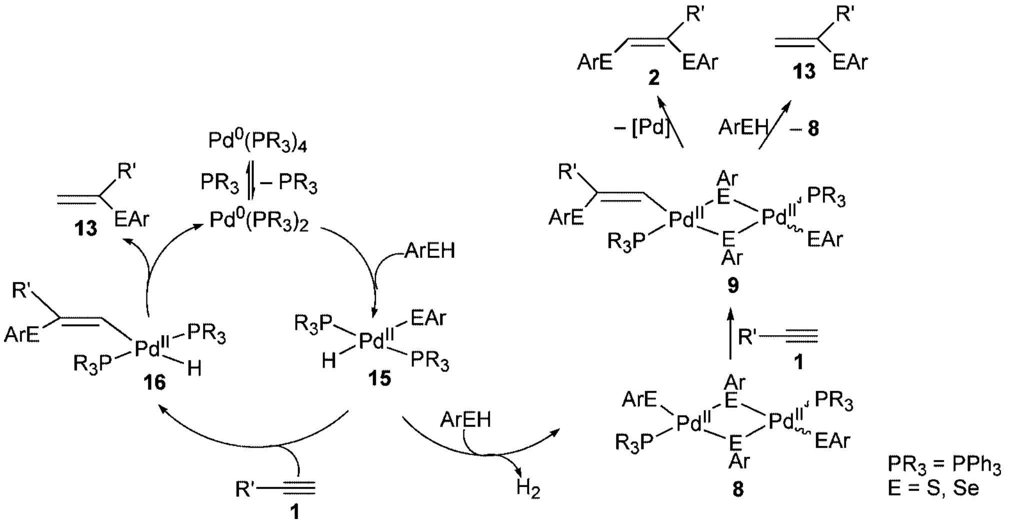
Phosphine complex $Pd(PPh_3)_4$ catalyzed regioselective addition of PhEH to terminal alkynes to afford the Markovnikov-type product **13** in 20–49% yields (Scheme 13).[53,54] Surprisingly, significant amounts of the bis-chalcogen-substituted alkene **2** (25–40%) were also obtained in this reaction. Since compounds **13** and **2** are rather difficult to separate from each other with conventional purification technique, this reaction is only poorly applicable for synthetic purpose.

If we consider the mechanism of transition metal-catalyzed S–H (Se–H) bond addition to alkynes, the first stage is the formation of a metal-sulfur (metal-selenium) bond. The oxidative addition of ArEH to Pd^0 would give hydride complex **15** (Scheme 13). Although the hydride complex was not observed, we do not rule out the mechanism involving alkyne insertion into the Pd–E bond of **15**, followed by reductive elimination from **16** to afford the desired product **13**. As is evident from spectroscopic data in the studied system, the mononuclear complex **15** was converted into the dinuclear derivatives **8**.[55] The formation of complexes **8** was confirmed by ^{31}P NMR spectroscopy.[53,56] The process was accompanied by H_2 evolution, which was detected by ^1H NMR for both E = S[56] and E = Se.[53] Alkyne insertion into the Pd–E bond of dinuclear complex **8**, followed by protonolysis of the Pd–C bond, gives Markovnikov-type alkene **13** (Scheme 13). A competitive side-reaction involves C–E reductive elimination from **9** and results in bis-chalcogen-substituted alkene **2**.

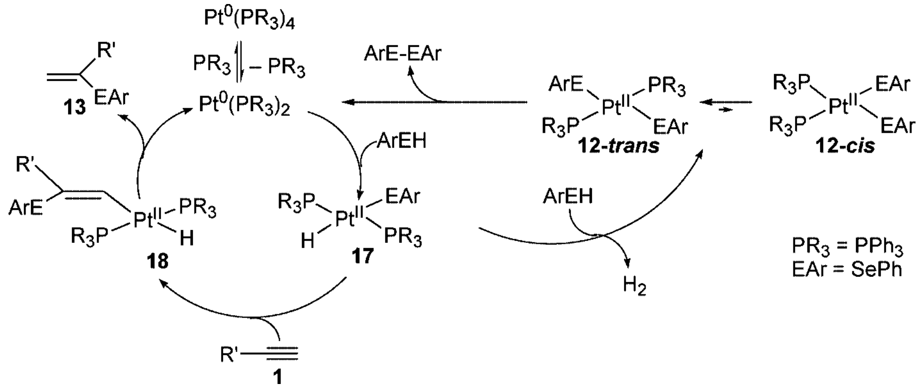
$Pt(PPh_3)_4$ was a more successful catalyst precursor than $Pd(PPh_3)_4$ for addition of Se–H bonds to alkynes. In the case of the Pt catalyst, the Markovnikov-type product **13** was obtained with excellent regioselectivity and in moderate yields of 51–60%, while the formation of compound **2** was not detected (Scheme 14).[53] We think that in the case of the Pt catalyst the Markovnikov-type product **13** was obtained by the same sequence of ArEH oxidative addition (**17**), alkyne insertion into the Pt–E bond (**18**), and C–H reductive elimination (Scheme 14).[57] The hydride complex **17** was more stable in the case of platinum and was detected by ^1H NMR spectroscopy. Platinum complexes do not form dinuclear species, and further transformation of **17** involving hydride ligand substitution and H_2 evolution affords the mononuclear derivatives **12-*cis*** and **12-*trans***. The presence of the thermodynamically more stable complex **12-*trans*** was confirmed by ^{31}P NMR, and the formation of molecular hydrogen was observed by ^1H NMR spectroscopy.[53]

Due to conversion of PhSeH into Ph_2Se_2 it was not possible to achieve quantitative yields of **13** in the Pt-catalyzed reaction. An attempt to involve arylthiols was unsuccessful; in the case of S–H bond addition the Pt-catalyzed reaction resulted in a complicated mixture of compounds with a rather low yield of **13**.[56]

Rhodium complexes catalyzed selective hydrothiolation reactions, but afforded the anti-Markovnikov β isomers (Scheme 11; R′ = H for terminal alkynes). The Wilkinson complex $Rh(PPh_3)_3Cl$ was found to be an excellent catalyst for reactions of alkynes (**19**) with arylthiols, resulting in products **20** with good to high yields 62–97%.[58] The reaction was carried out not only with terminal, but also with internal alkynes (**19**) at low temperatures (20–40 °C). An



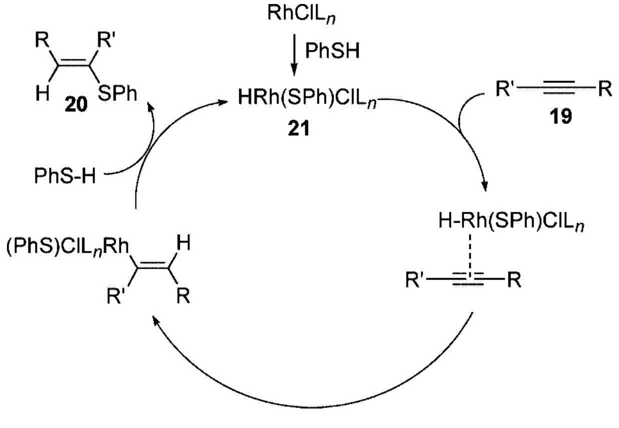
Scheme 13.



Scheme 14.

active form of the rhodium catalyst was represented by hydride complex $HRh(SPh)ClL_n$ (**21**), with alkyne insertion into the Rh–H bond as a key stage (Scheme 15).[58] It should be noted that the reaction was performed as a *syn* addition and that in the case of terminal alkynes (R′ = H) the metal atom was bonded to the less substituted carbon atom of the alkyne group (the same as discussed for Pd and Pt above). The complex $HRh(SPh)Cl(PPh_3)_2$ was synthesized and its catalytic activity in the PhSH addition to *n*-$C_{10}H_{21}$–C≡CH has been confirmed [the yield of E–*n*-$C_{10}H_{21}$–CH=CH(SPh) was 55%].[58] It is important to mention that this Rh-catalyzed transformation does not involve protonolysis (cf. with Pd-catalyzed reaction).

To summarize, phosphine complexes of Pd, Pt, and Rh did not solve the problem of selective Markovnikov-type addition of ArEH to alkynes in good yields. Use of Pd catalyst resulted in an unusual by-product **2**, while use of Pt catalyst gave moderate yields due to conversion of PhEH into Ph_2E_2. Depending on the type of Rh complex, different products were obtained in the addition reaction.



Scheme 15.

A few notes concerning the addition of alkanethiols should be made. The study of E–E bond addition to alkynes indicated that Rh complexes are active catalysts for involving alkyl-substituted substrates (Alk_2E_2) in the reaction (see 2.2). This finding was confirmed for the addition of AlkEH to alkynes as well. The rhodium complex $Tp^*Rh(PPh_3)_2$ with a pyrazolyl-borate ligand [Tp* = hydrotris(3,5-dimethylpyrazolyl)borate] was shown to activate the S–H bonds of thiols.[59] Based on this finding, catalytic hydrothiolation of alkynes, involving both aromatic and aliphatic thiols, was performed under mild conditions.[60] It was shown that the pyrazolyl-borate complex activates not only the S–H, but also the S–S bond, although the formation of **2** was not reported.[61]

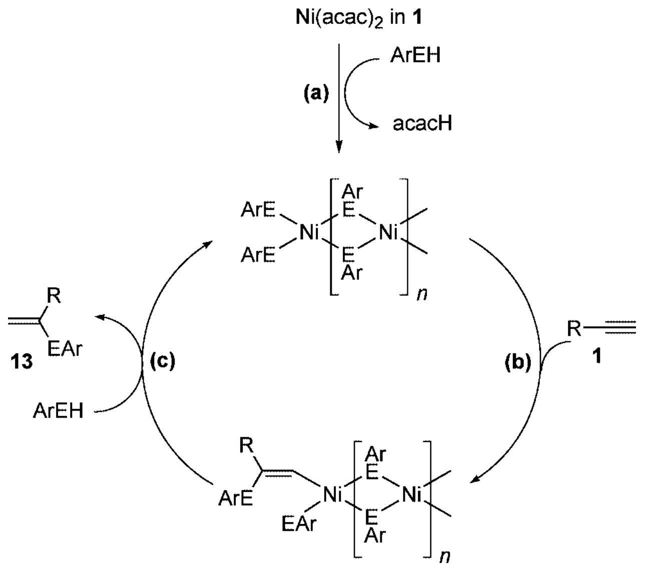
3.2 Ni-Catalyzed E–H Bond Addition to Alkynes

We have found that $NiCl_2$ is an efficient catalyst for the alkyne hydrothiolation reaction.[53] Dramatic acceleration of the catalytic reaction was observed in the presence of base (Et_3N).[62] Under optimized conditions, the Ni-catalyzed reaction was performed with different alkynes, resulting in the Markovnikov-type product **13** in good yields (60–85%) and selectivities (18:1–7:1). Noncatalytic side reactions resulting in anti-Markovnikov products and double bond isomerization were suppressed by addition of a radical trap (γ-terpinene) to the catalytic system.[53]

A remarkable catalytic system was discovered when $Ni(acac)_2$ was employed as a catalyst precursor.[63,64] ArSH and PhSeH addition to terminal alkynes was carried out with high yields (75–98%) and gave the Markovnikov-type isomer **13** with excellent selectivity. The catalytic transformation was performed under extraordinarily mild conditions (20–40 °C) in short reaction times. The catalyst was so active that even internal alkynes reacted with PhSeH with good yields and stereoselectivities.[64] Undoubtedly, it is very important to answer the question: why do various catalyst precursors [$NiCl_2$, $Ni(acac)_2$, etc.] give catalysts with dramatic differences in catalytic activity?

Mechanistic study showed that the catalytic reactions involving the $NiCl_2$ catalyst precursor without phosphine ligands took place under heterogeneous conditions.[63,64] The substitution reaction $NiCl_2 + 2\,ArEH \rightarrow [Ni(EAr)_2]_n$ took place directly in the reaction mixture and was facilitated by the presence of base (Et_3N), which reacted with the forming hydrochloric acid to give the $[Et_3NH]^+Cl^-$ salt. The polymer $[Ni(EAr)_2]_n$ was insoluble in common organic solvents. The same behavior was also observed for the polymers obtained from other metal salts such as $Ni(OAc)_2$, $PdCl_2$, and $Pd(OAc)_2$.

Due to the possibility of protonolysis of the Ni–vinyl intermediate (formed after alkyne insertion into the Ni–E bond) this polymer was an active catalyst for E–H bond addition to alkynes. The mechanism of the catalytic reaction has been studied in a series of stoichiometric reactions[63,64] and was shown to involve (Scheme 16): a) ligand replacement, b) alkyne coordination and insertion, and c) protonolysis.



Scheme 16.

The answer to the question of why the catalysts obtained from different metal salts (MX_2, X = Cl, OAc, acac; M = Ni, Pd) showed dramatically different activity was obtained after combined scanning electron microscopy and NMR studies.[63,64] It was revealed that the size and morphology of the catalyst particles played a crucial role for the yield and selectivity of the catalytic reaction (Figure 1). Although the catalyst had the same chemical formula $[M(EAr)_2]_n$, the sizes of the particles differed dramatically. Poor results were obtained for $NiCl_2$ precursor, which gave catalyst particle sizes of 3–10 µm. Better results were observed with $Pd(OAc)_2$ and $Ni(OAc)_2$ precursors, with particles sizes of 3–6 µm and 2–5 µm, respectively. A unique heterogeneous catalytic system was formed in the presence of Et_3N, with $[M(EAr)_2]_n$ particles supported on the $[Et_3NH]^+Cl^-$ crystals.[64] The presence of support prevents aggregation of catalyst particles, keeping the size in the 0.3–1.5 µm range. The best results were achieved with $Ni(acac)_2$; with this catalyst precursor a novel self-organized catalytic system with nanostructural organization was formed in situ.[63,64] According to scanning electron microscopy, the catalyst particles consisted of nanosized building units with sizes in the 300 ± 90 nm range. Due to the uniform shape of the par-

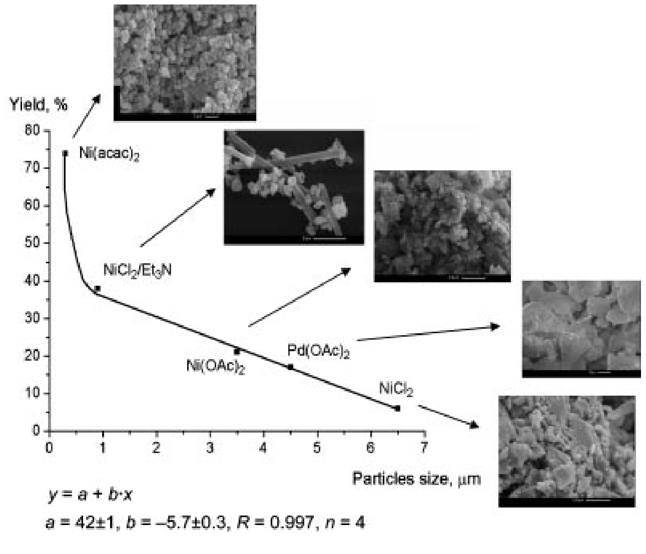
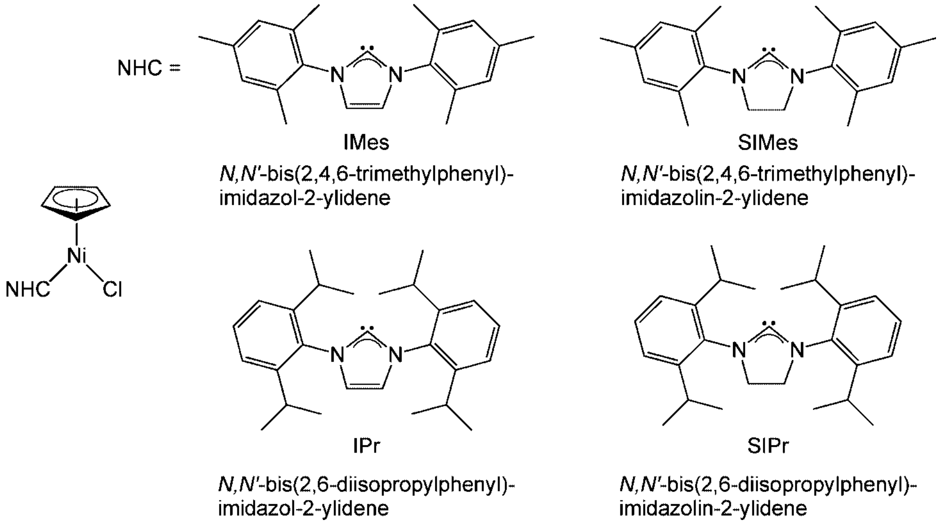


Figure 1. Plot of yields of the product **13** (EAr = SePh) measured after 10 min reaction time vs. average size of the $[M(SePh)_2]_n$ catalyst. The catalyst precursor is shown for each point; linear regression analysis was performed for all points except $Ni(acac)_2$ (see ref.[64] for details).



Scheme 17.

ticles the catalyst was stable enough without any additional support.

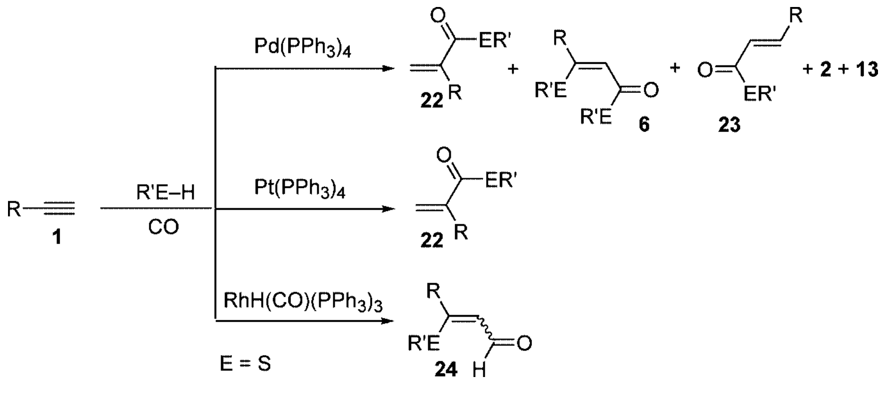
Detailed analysis of the Ni-catalyzed reaction revealed the presence of by-products with diene skeletons, resulting from the coupling of two alkyne molecules and one molecule of ArEH.[65]

Two other homogeneous Ni-based catalytic systems for hydrothiolation of alkynes were also reported. It was found that the phosphine complex $Ni(PPh_2Me)_4$ in the presence of $Ph_2P(O)OH$ catalyzed hydrothiolation of hept-1-yne.[66] The role of $Ph_2P(O)OH$ in this hydrothiolation reaction remains unclear. An analogous system was successfully utilized by Tanaka et al. for the hydrophosphination reaction.[67]

The N-heterocyclic carbene complex Cp(NHC)NiCl was used as a catalyst precursor to perform alkyne hydrothiolation reactions under homogeneous conditions (Scheme 17).[68] Several N-heterocyclic carbene ligands were tested in the reaction, and NHC = IMes showed the best results. An advantage of this catalyst is the presence of only one ligand, which can be substituted by ArE^- (i.e., chloride ligand). Therefore, this catalyst may transfer only one ArE group and one would not expect the formation of bis-substituted product **2**. The reaction catalyzed by this type of complexes proceeded smoothly and afforded products in good yields, but required higher temperatures (80 °C) and longer times (5 h). The developed homogeneous catalytic system provides good potential for mechanistic study by conventional spectral methods. The formation of the intermediate Ni-vinyl complex was not observed by NMR monitoring. The results suggest that alkyne insertion into the Ni–S bond is an equilibrium, which is shifted by protonolysis with PhSH.[68]

3.3 Catalytic Carbonylative Addition of E–H Bonds to Alkynes

Different products were obtained depending on the catalyst type (Scheme 18).[69,70] Use of palladium complexes resulted in the formation of complex mixtures of compounds including both mono- (25% of **22** + **23**) and bisthiolation (7% of **6**) products.[69] Use of platinum as a catalyst resulted in selective formation of α,β-unsaturated thioester **22** in good yields (70–94%) and regioselectivities.[70] Rhodium catalyst gave reversed regioselectivity, providing product **24** in good yields of 52–82% and in a broad range of *E*/*Z* ratios depending on the substituents (*E*/*Z* = 1:99–86:14).



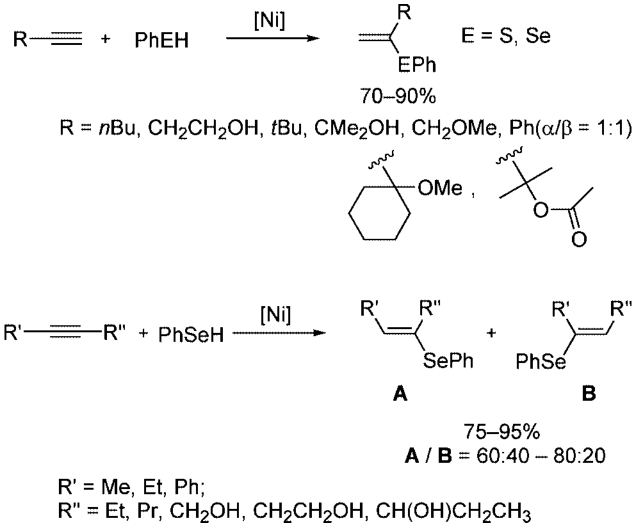
Scheme 18.

$Pt(PPh_3)_4$ also showed good catalytic activity in carbonylative lactonization of 5-hydroxypent-1-yne with various aromatic thiols.[71]

As we established in the case of E–E addition reactions (see 2.3), it is of great interest to compare direct addition reactions and carbonylative addition reactions. The structure of the carbonylative product may in some cases give important information about the binding point of the metal atom to the vinyl group in intermediate transition metal complexes, not observable by direct methods.

3.4 Synthetic Application of the E–H Bond Addition Reaction to Alkynes

The catalytic system based on the $Ni(acac)_2$ precursor is superior for practical application from the cost/performance point of view.[63,64] With this catalytic system, several alkenes were prepared from terminal and internal alkynes with high yields of 70–95% (Scheme 19). For all terminal alkynes very good regioselectivity was observed (>95:5, except for phenylacetylene, which undergoes quick competitive noncatalytic addition). For the internal alkynes the reaction was highly stereoselective, while regioselectivity depended on electronic and steric effects of the substituents.



Scheme 19.

It was shown that synthetic procedure can be scaled from 5 to 300 mmol of reagents, resulting in 0.8–49 g of product, without any decrease in the yield and selectivity.[63] Carrying out catalytic PhSH and PhSeH addition to *N*,*N*-dimethylpropargylamine and crystallization of the products as oxalic acid salts gave crystals of **13** (E = S, Se; R = CH_2NMe_2) of sufficient quality for X-ray analysis. The molecular structures of both products E = S[56] and E = Se[53] were established.

4. Conclusions

Mechanistic study has revealed the principal differences between the reactions involving S, Se, and the other elements (B, Si, Sn, P, Ge, etc.). Dinuclear and polynuclear species are formed if sulfur or selenium compounds react with transition metals. In fact, this is one of the possible reasons for catalyst poisoning with sulfur and selenium species. Neither E–E nor E–H bond addition reactions involving the other elements have been reported to proceed through the formation of di- and polynuclear derivatives.

Special care should be taken to avoid the formation of polynuclear species in the case of transition metal-catalyzed addition of E–E (E = S, Se) bonds to alkynes. Insoluble polymer $[M(ER)_2]_n$ without phosphine ligands does not catalyze the reaction of interest. We have established that phosphine ligands are required in order to facilitate the formation of 1,2-bis(arylthio)- and 1,2-bis(arylseleno)alkenes. Addition of an excess of PR_3 ligand solves both problems, preventing catalyst polymerization and facilitating C–E bond formation at the reductive elimination stage. Phosphine PPh_3 and phosphite $P(OAlk)_3$ can be utilized for this purpose, as well as polymer-bound phosphine PPh_2Ar ligands, and have made it possible to carry out the catalytic transformation with excellent stereoselectivities and high yields.

On the other hand, the polymers of general type $[M(ER)_2]_n$ are the catalysts of choice for addition of E–H bonds to alkynes. The presence of phosphine ligand is not required in this case, since protonolysis is the last stage of the catalytic cycle (instead of reductive elimination as discussed above for the E–E bond addition). Nanostructured nickel complexes formed in situ showed the best performance for carrying out regioselective hydrothiolation and hydroselenation of terminal alkynes and stereoselective hydroselenation of internal alkynes. Creating the catalyst particles with appropriate morphology dramatically increases the activity and selectivity of the addition reaction. It should be pointed out that this is a rare example of higher activity and selectivity in a heterogeneous catalyst system than in a similar homogeneous system.

From the practical point of view, the E–H bond addition reaction is much more difficult to carry out in selective fashion than the E–E bond addition. Noncatalytic E–H bond addition affording anti-Markovnikov isomers takes place under milder conditions than noncatalytic E–E bond addition. Despite the noncatalytic addition, another side-reaction – isomerization of the Markovnikov product to the internal alkene – was observed in the case of transition metal-catalyzed E–H bond addition. No similar transformation was observed for 1,2-bis(arylthio)- or 1,2-bis(arylseleno)alkenes. Therefore, to carry out selective transition metal-catalyzed E–H bond addition to alkynes, more careful optimization of reaction conditions should be performed.

To summarize, using transition metal catalysts provided an excellent opportunity to develop synthetic methods for selective addition of S–S, Se–Se, S–H, and Se–H bonds to alkynes.

Finally, we would like to mention some remaining problems in this field: i) the catalytic E–E bond addition has been performed only for terminal alkynes, while internal alkynes were inactive; the origin of this dramatic difference in reactivity remains unclear, ii) rather expensive rhodium catalysts are required for the addition of AlkE–EAlk and AlkE–H to alkynes; for practical reasons less expensive (Ni, etc.) alternatives should be developed, and iii) the catalytic system should be developed to carry out Te–Te and Te–H bond addition to alkynes.

Acknowledgments

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