

Addition reactions of E–E and E–H bonds to triple bond of alkynes catalyzed by Pd, Pt, and Ni complexes (E=S, Se)*

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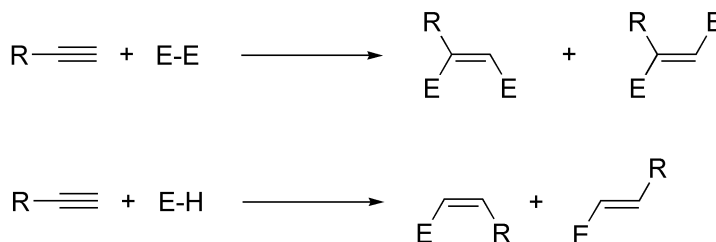
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Abstract: The synthetic application and mechanistic aspects of transition-metal (Ni, Pd, Pt) catalyzed addition of E–E and E–H (E=S, Se) bonds to alkynes were investigated in detail. This study revealed major factors controlling the selectivity of such addition reactions. A new Ni-based catalytic system with a self-organized nanostructured catalyst has been designed to perform chemical transformation in high yield, under mild conditions.

Keywords: addition reactions; green chemistry; transition-metal catalysis; sulfur species; selenium species.

INTRODUCTION

Addition reactions of E–E and E–H bonds to alkynes proceed with 100 % atom efficiency and are thus more compatible with the principles of green chemistry than comparable substitution reactions [1–4]. Noncatalytic addition of E–E bonds (E=S, Se) to alkynes leads to a mixture of *Z*- and *E*-isomers (Scheme 1) [5]. Radical or base-initiated addition of E–H bonds to alkynes also proceeds nonstereoselectively and gives β -isomers (anti-Markovnikov products) [6].



Scheme 1

Catalytic process may proceed by two different mechanisms (Scheme 2). One of them is based on the activation of triple bond by M^{n+} to *trans*-nucleophilic attack (as in Wacker-type process). The other involves activation of E–E and E–H bonds by $M(0)$ and insertion of the alkyne triple bond into

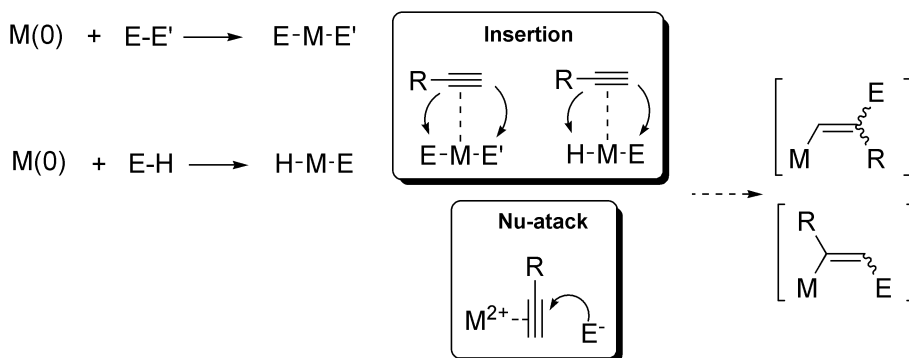
*Paper based on a presentation at the 18th International Conference on Physical Organic Chemistry (ICPOC-18), 20–25 August 2006, Warsaw, Poland. Other presentations are published in this issue, pp. 955–1151.

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the resultant E–M or H–M bonds. Insertion proceeds through *syn*-addition, and its regioselectivity depends on electronic and steric factors of reagents.

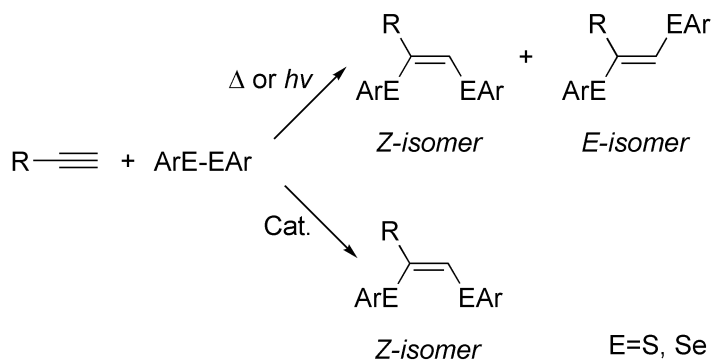
As model reactions for our study of the mechanism of addition reactions, we have chosen catalytic transformation involving alkynes and diaryl diselenides/diaryl disulfides (E–E = S–S, Se–Se) as well as arylselenols/arylthiols (E–H = S–H, Se–H).



Scheme 2

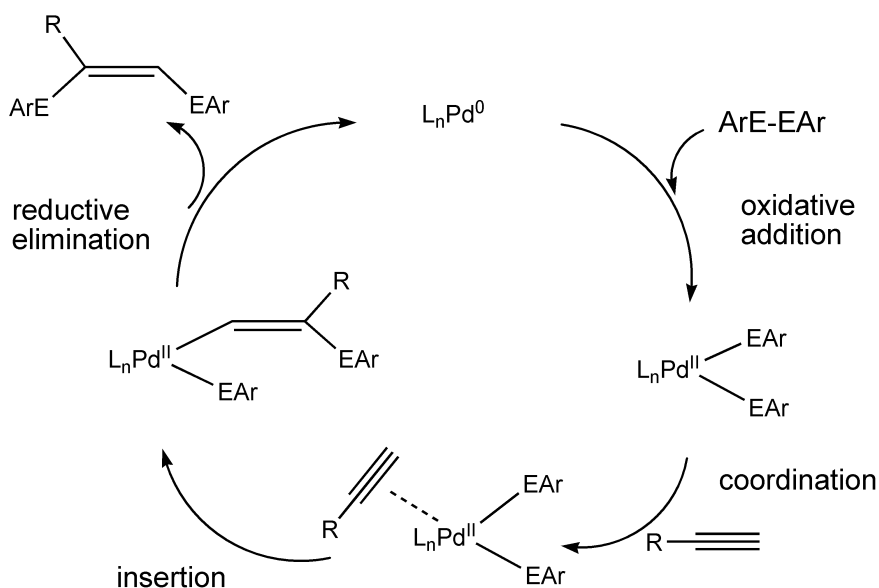
ADDITION OF ArE–EAr (E=S, Se) TO ALKYNES

Noncatalytic reaction (thermal or radical) can be performed with high yield for both diselenides and disulfides, but gives mixtures of *cis*-/*trans*-isomers (Scheme 3). Reactions of Ar₂Se₂ and Ar₂S₂ catalyzed by Pd(PPh₃)₄ require elevated temperature for long periods (80 °C, 12–20 h), but furnish in *syn*-products with high selectivity and 54–98 % yields [7]. In our hands, the yields in these reactions under similar conditions have not exceeded 60–65 % [8,9]. We decided to analyze the reasons of this limitation.



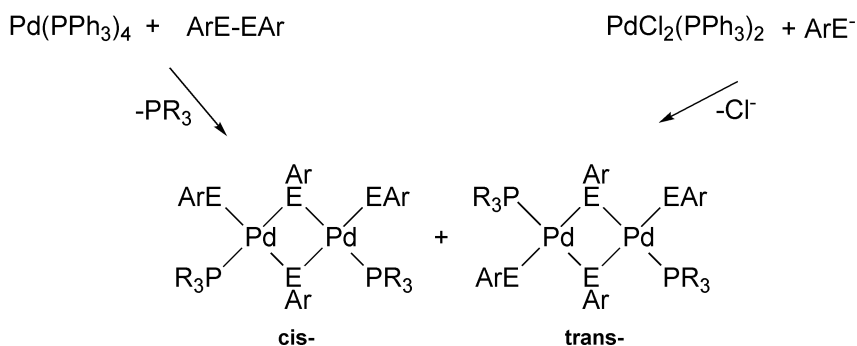
Scheme 3

An earlier proposal for the catalytic cycle of this reaction (Scheme 4) includes: (i) oxidative addition of Ar₂E₂ to Pd(0); (ii) formation of π-complex with the alkyne; (iii) insertion of the coordinated alkyne into the M–E bond; and (iv) reductive elimination with C–E bond formation. This provides a general framework for transition-metal-catalyzed addition of E–E bonds to unsaturated molecules [1–4].



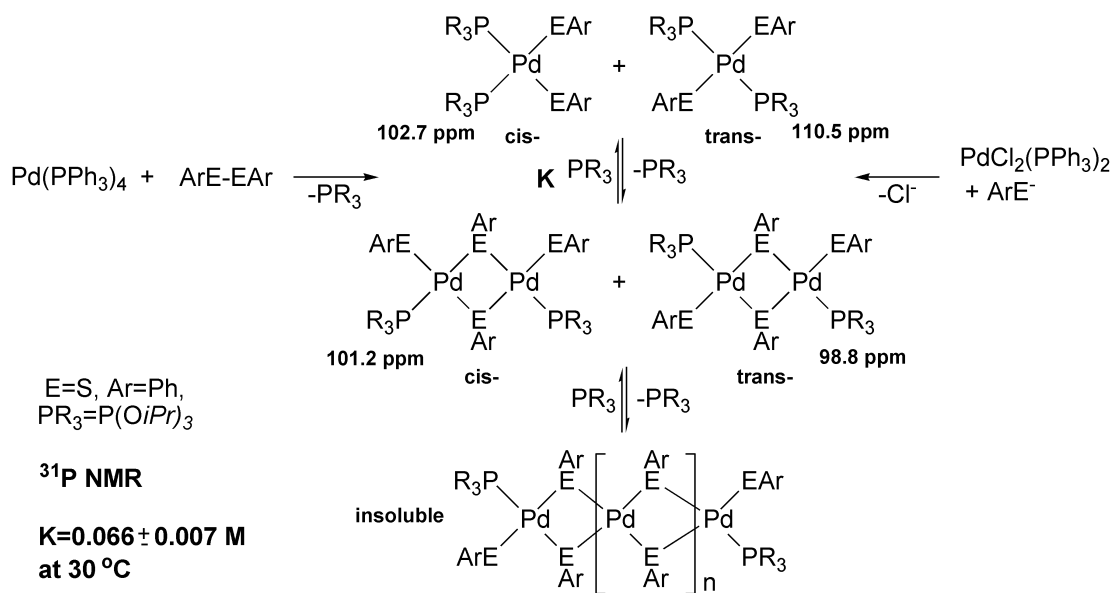
Scheme 4

We have found that in real systems, dinuclear Pd complexes are formed and are involved in the catalytic cycle [8,9]. The same dinuclear complexes are obtained independently on the way of their formation: either as a result of oxidative addition of Ph_2E_2 to $\text{Pd}(\text{PPh}_3)_4$ or as a result of a ligand exchange reaction between $\text{PdCl}_2(\text{PPh}_3)_2$ and PhE^- (Scheme 5). In reactions performed at elevated temperature, the dinuclear complexes tend to form oligomeric or polymeric material, which is insoluble and inactive in the catalytic reaction [8–10]. This is the pathway of catalyst deactivation in the systems investigated.



Scheme 5

We have found that instead of Ph_3P , the catalytic reaction can be carried out using less toxic phosphite ligand $(i\text{-PrO})_3\text{P}$ [11]. Investigation of the first step of the catalytic cycle—oxidative addition has shown that E–E bond cleavage by Pd leads to a mixture of *cis*-/*trans*- mononuclear and dinuclear complexes as well as oligomeric species. Model system with phosphite ligands $\text{L}=\text{P}(\text{O}i\text{Pr})_3$ is very convenient for the mechanistic studies, since the ratio L:EAr can easily be determined with NMR spectroscopy (Scheme 6).



Scheme 6

In this system, we have studied the equilibrium between the mononuclear and dinuclear complexes, and we have found that equilibrium constant of dinuclear complexes dissociation to mononuclear form is rather small $K = 0.066 \pm 0.007$ M. The structures of *trans*-mononuclear and *trans*-dinuclear complexes with phosphite ligands were determined by X-ray analysis; *cis*- and *trans*-complexes (mononuclear and dinuclear) were detected in solution by NMR.

For the system with phosphine ligands ($L = \text{PPh}_3$), it is rather difficult to determine the L:EAR ratio in solution with NMR spectroscopy due to overlapping of signals in the aromatic region. Dinuclear complexes *trans*-[Pd₂(EAR)₄(PPh₃)₂] have been characterized by X-ray crystallography [12], and the formation of [Pd(EAR)₂]_n polymeric species has been reported [13]. Heating of the dinuclear complexes [Pd₂(EAR)₄(OiPr)₂] without an excess of the ligand also initiated degradation leading to polymer formation.

Theoretical calculations at density functional theory (DFT) level have shown that alkyne insertion into the terminal Pd–Se bond of the model dinuclear complex requires overcoming $\Delta E^\ddagger = 9.5$ kcal/mol activation barrier and is an exothermic reaction with energy gain of $\Delta E = -9.6$ kcal/mol (Fig. 1). For the alkyne insertion into the bridged Pd–Se bond, much higher activation energy has been calculated $\Delta E^\ddagger = 20.7$ kcal/mol, and the process has been predicted to be endothermic $\Delta E = 1.2$ kcal/mol. Therefore, terminal M–E bonds most likely make the major contribution to the product formation under catalytic conditions.

We have established why platinum analog Pt(PPh₃)₄ is unreactive in the catalytic reaction of interest. Oxidative addition of PhSe–SePh to Pt(PPh₃)₄ first gives the mononuclear complex *cis*-Pt(SePh)₂(PPh₃)₂ (Scheme 7), which is a kinetic product that rapidly isomerizes to the *trans*-derivative. The isomerization reaction has been followed with the aid of NMR spectroscopy [8], and the structures of both the *cis*- and *trans*-complexes have been established by X-ray analysis [8,14]. *Cis*-complex reacts with alkynes leading to the expected product, whereas the *trans*-derivative is unreactive.

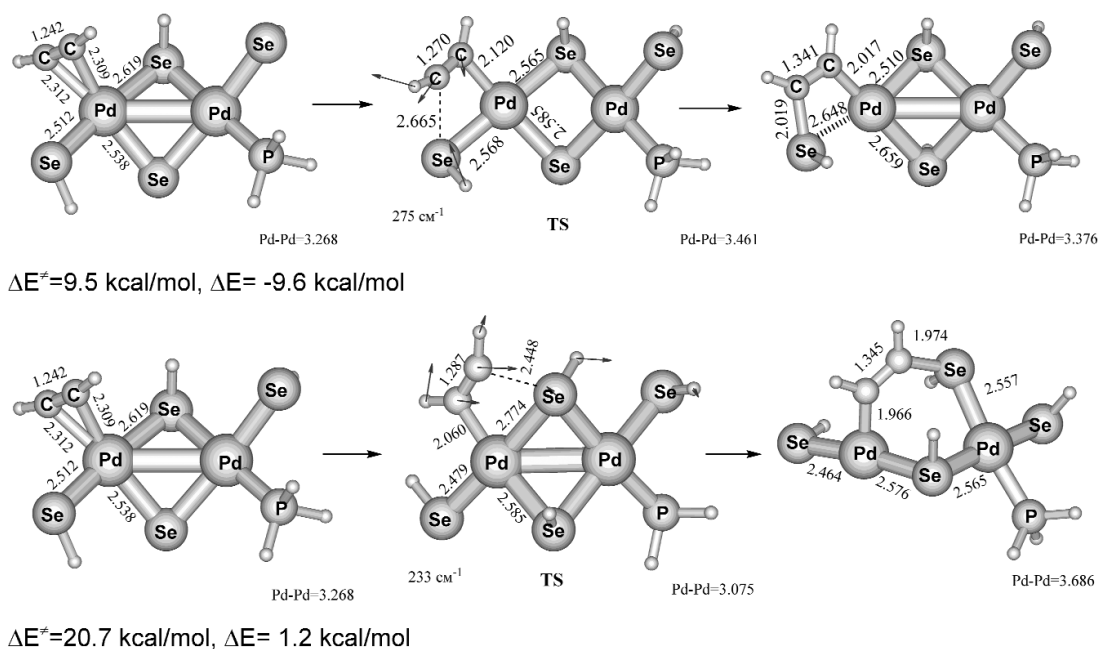
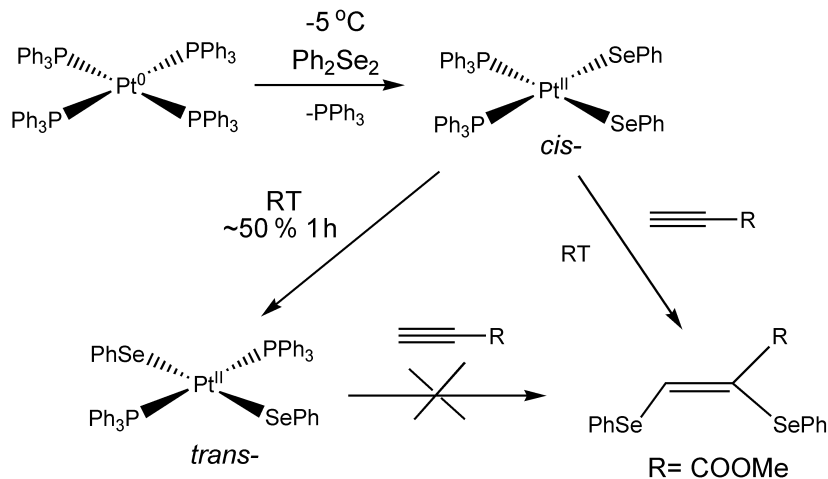
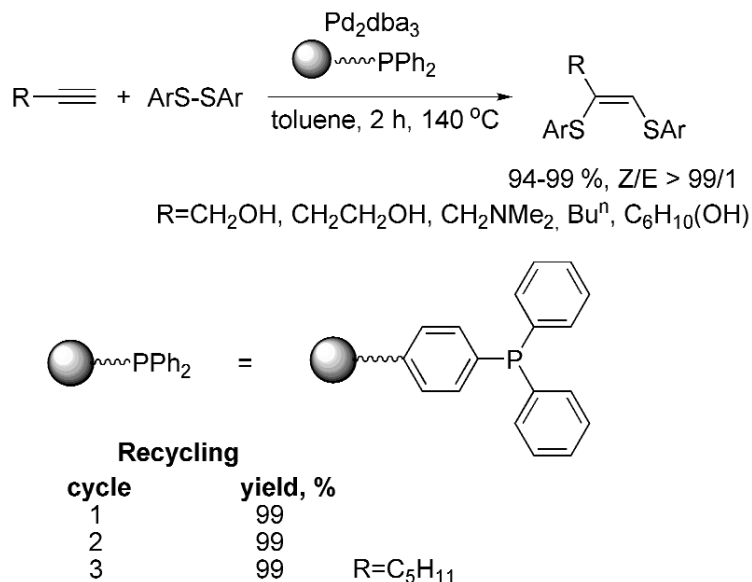


Fig. 1 Calculated pathways of acetylene insertion into the terminal (top) and bridged (bottom) Pd–Se bonds of the model complex at B3LYP/Lan12dz level.



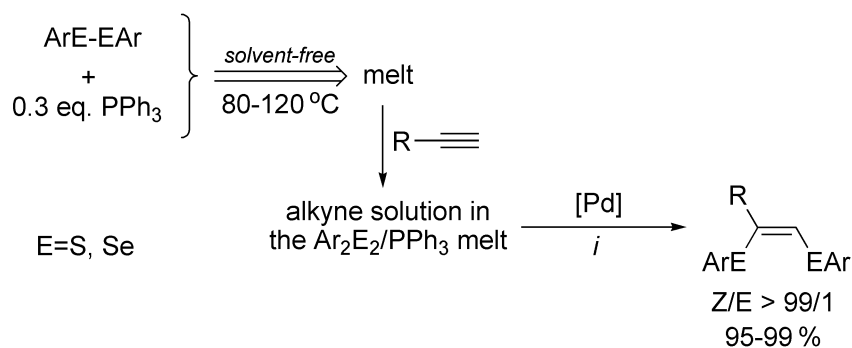
Scheme 7

We have tried to find the optimal conditions to make these reactions more convenient for synthetic applications. We have found that Pd-phosphine complex on polystyrene resin is an efficient catalyst for the addition of Ar_2S_2 to alkynes at 140°C (Scheme 8) [15]. The reaction has proceeded very smoothly with high product yield (94–99 %) and selectivity. The catalyst has been easily separated after completing the reaction by filtration and after drying the final product did not need any additional purification (the purity >98 %). However, this procedure is not applicable for the Ph_2Se_2 addition to alkynes, because at this temperature phosphorus atom was oxidized by Ph_2Se_2 to give $\text{Se}=\text{PR}_3$ and Ph_2Se .



Scheme 8

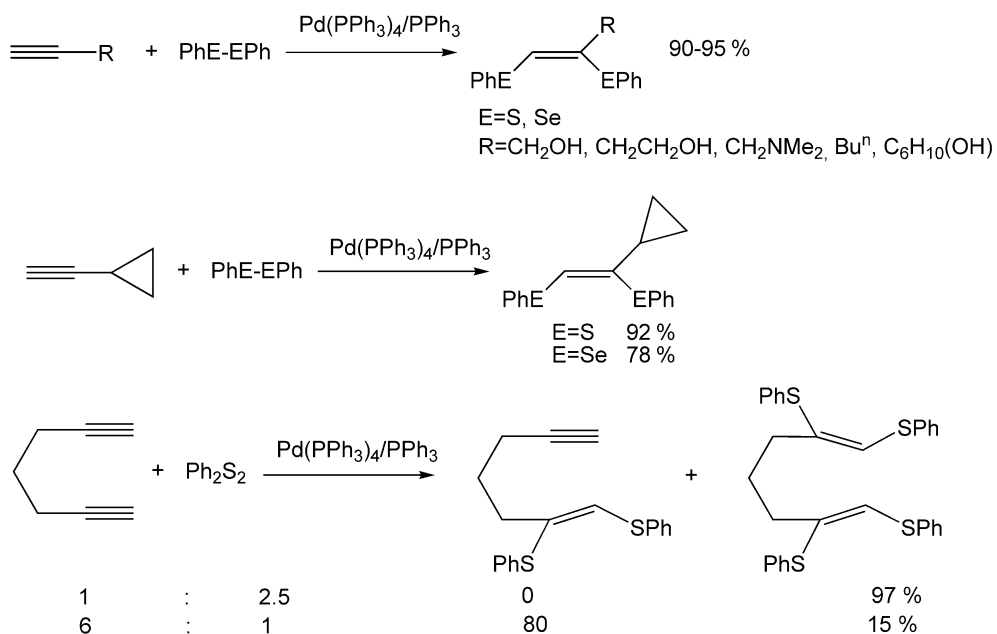
We succeeded in overcoming these difficulties when we carried out the reaction without a solvent in the presence of an excess of Ph₃P at 80–140 °C (for both E=S and Se) [16]. Excellent yield and selectivity have been achieved performing the addition reaction in a melt under solvent-free conditions (Scheme 9). Compared to the reaction in solvent significant enhancement of reaction rate, improved efficiency and remarkable catalyst stability have been observed under solvent-free conditions. For the Ph₂S₂ addition performed at 120 °C with 1 mol % of the catalyst, the reaction was completed in 5 min and at 140 °C with as small as 0.01 mol % of the catalyst in 1 h. The catalyst in this system has been also easily recovered. It is interesting to note that in the molten state the nature of the catalyst remained the same as in solution—dinuclear Pd species with *cis*- and *trans*-geometry [16] (Scheme 5).



Scheme 9

As a result, we have developed very efficient method for the synthesis of substituted alkenes from a variety of terminal alkynes (Scheme 10). However, the reaction did not proceed with internal alkynes.

In the E–E bond addition reaction, it is difficult to know the regioselectivity of the insertion step. We have investigated a couple of reactions to answer this question (Scheme 10). The reaction with cyclopropylacetylene proceeded without opening the three-membered ring that, in our opinion, can be considered as evidence that Pd is attached to a terminal position (otherwise one could expect homo-

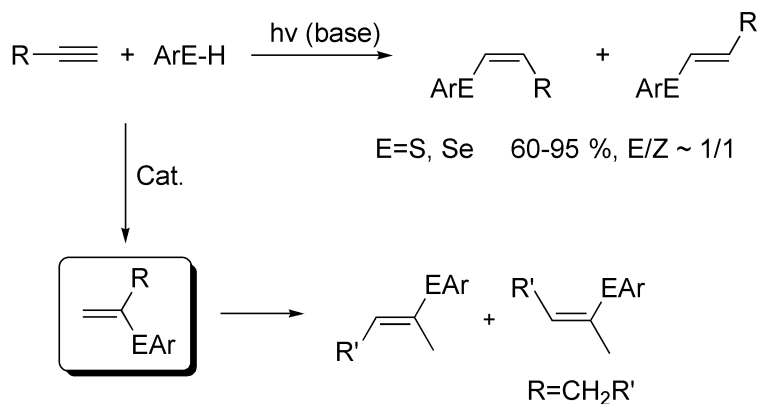


Scheme 10

allylic rearrangement). Another evidence is E–E bond addition to heptadiyne-1,6. Both triple bonds react independently without formation of cyclic products, which should be expected if Pd would attach to an internal carbon atom.

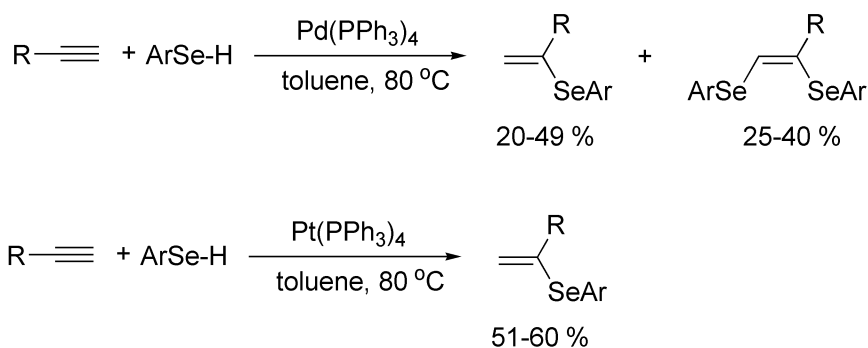
ADDITION OF ArE–H (E=S, Se) TO ALKYNES

Noncatalytic addition of ArS–H and ArSe–H to alkynes can be mediated by irradiation or by base to give a mixture of *E*- and *Z*-isomers (Scheme 11). It was shown that Pd(OAc)₂-catalyzed reaction gives Markovnikov-type product, thus changing the regioselectivity of the E–H bond addition [17,18]. In some cases, the addition reaction has been followed by double-bond isomerization resulting in internal alkenes with C–E bond [17,18].



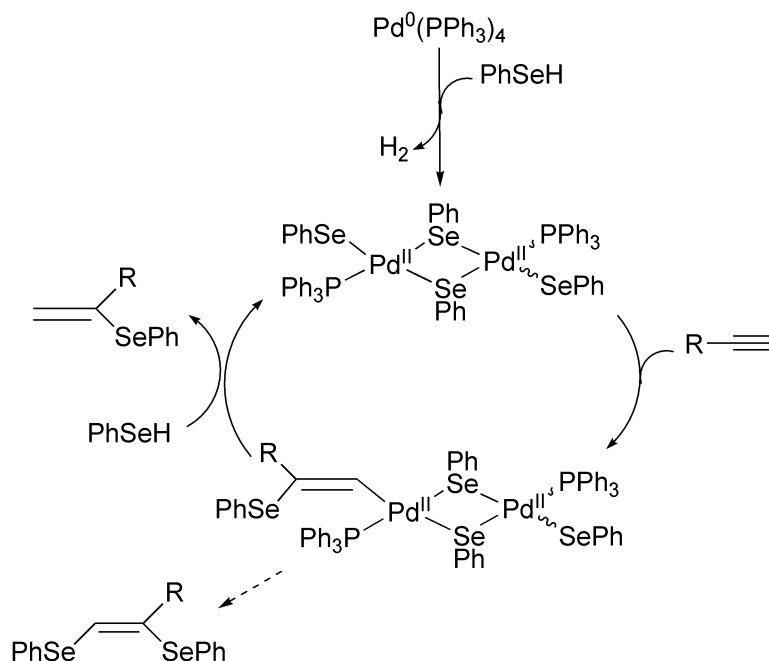
Scheme 11

Again, we failed to achieve high yields of Markovnikov-type product using $\text{Pd}(\text{PPh}_3)_4$ as catalyst precursor (Scheme 12), since a significant amount (25–40 %) of disubstituted product was formed in addition to desired α -vinyl sulfide (20–49 %) [19]. Better yield has been obtained with Pt catalyst (51–60 %), but it is still not quantitative (Scheme 12).



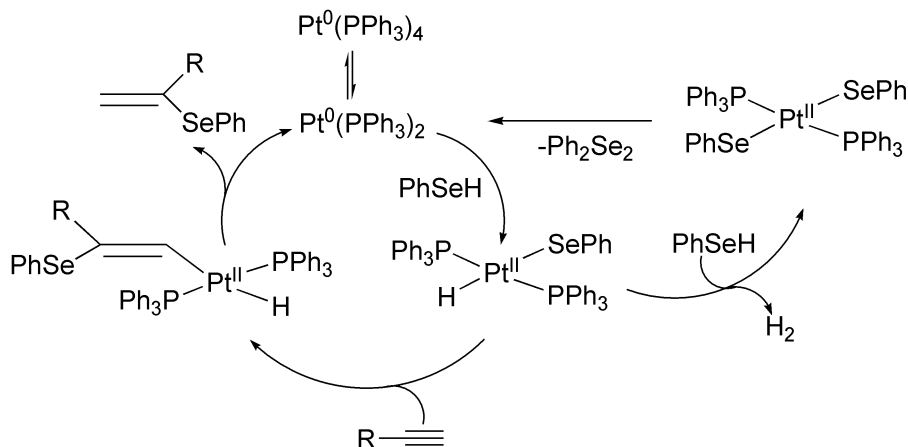
Scheme 12

Mechanistic study has shown that in the reaction of $\text{Pd}(\text{PPh}_3)_4$ with PhSeH (and PhSH), the same dinuclear complexes are formed as discussed above for the case of Ph_2Se_2 addition (Scheme 13). Molecular hydrogen elimination has been observed in ^1H NMR [19]. The reaction catalyzed by dinuclear Pd complex gave two products—monosubstituted α -isomer and disubstituted olefin. The former product has been formed as a result of protonolysis of Pd–C bond by PhSeH .



Scheme 13

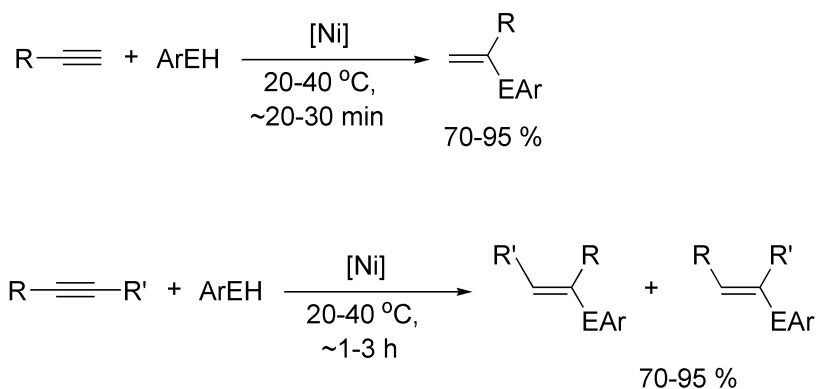
In contrast to Pd, hydride complex of Pt is more stable and we have observed it in ^1H NMR (Scheme 14). Although mononuclear Pt complexes are unreactive in Se–Se bond addition to alkynes, still we have a by-product formation of Ph_2Se_2 . In the system involving phosphine complexes of Pt and Pd, the formation of monosubstituted α -isomer may be achieved either via the reductive C–H elimination from hydride complex or via the protonolysis of metal-carbon bond.



Scheme 14

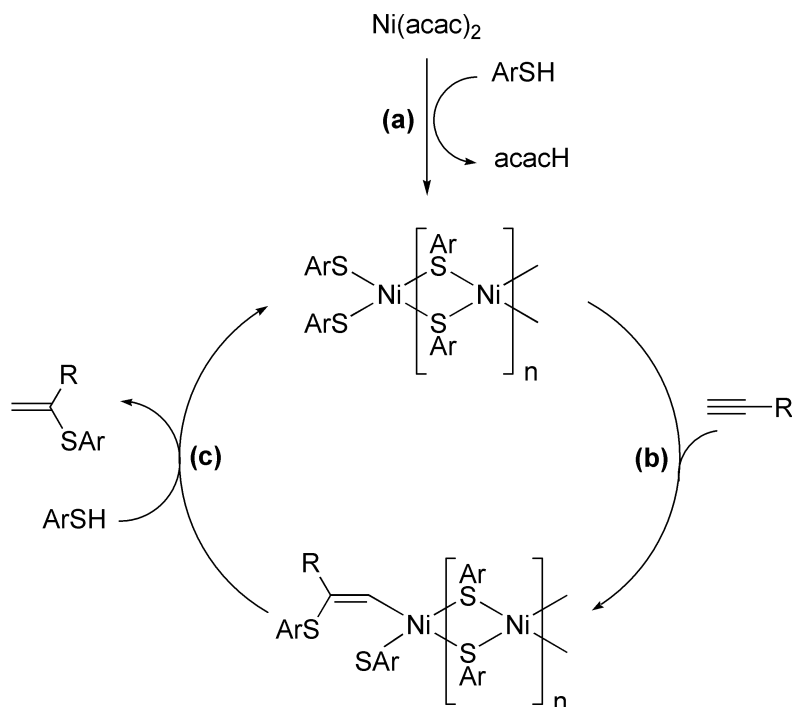
The regioselectivity of the addition reaction (E=S, Se) was proved by X-ray structure analysis performed for the products obtained from *N,N*-dimethylaminopropyne in a complex with oxalic acid [19,20]. The structures of the other products have been determined with 2D ^1H - ^{77}Se NMR spectroscopy [21].

Our study has shown that Pd or Pt systems are not the catalysts of choice to solve the synthetic problem of S–H and Se–H bonds addition to alkynes. Earlier, we have shown that activation of P–H of P–Cl bonds by Ni complexes is more efficient than with Pd compounds [22]. A unique heterogeneous catalytic system based on Ni complexes has been developed to perform E–H bond addition reaction at low temperature for a short time (Scheme 15) [23,24]. Unlike Pd- or Pt-catalyzed reactions, in this case not only terminal, but also internal alkynes undergo the reaction under mild conditions.



Scheme 15

Remarkable heterogeneous catalyst has been discovered using $\text{Ni}(\text{acac})_2$ as a precursor. With this catalyst, PhSH addition to alkynes has been performed under mild conditions (20–40 °C) with high selectivity (>97/3) and good yield (79–98 %). The mechanism of the catalytic reaction has been studied utilizing a series of stoichiometric reactions and has been shown to involve (Scheme 16): (a) ligand replacement; (b) alkyne coordination and insertion; and (c) protonolysis. We want to mention that utilizing NiCl_2 we have also achieved good yields in the S–H and Se–H bond addition reactions, however, it required Et_3N for activation and radical trap for suppressing the side-reactions [20]. According to elemental analysis, the catalysts obtained from the NiCl_2 and $\text{Ni}(\text{acac})_2$ precursors have a similar polymeric nature $[\text{Ni}(\text{SPh})_2]_n$, however, they possess rather different activity.



Scheme 16

It is interesting to question: Why is the efficiency of the catalysts with the same composition— $[\text{Ni}(\text{EAr})_2]_n$ —dramatically different? The answer to this question has been achieved after applying scanning electron microscopy (SEM) to study the structure and morphology of the catalysts (Fig. 2). The images obtained by SEM for these catalysts (including Pd-polymer) are quite different. Only the polymer made from $\text{Ni}(\text{acac})_2$ had nanostructured particles with building units of 300 ± 90 nm size. Much larger particles in the micrometer scale have been formed from NiCl_2 and $\text{Pd}(\text{OAc})_2$ precursors. It should be pointed out that the reaction of NiCl_2 with PhSH in the presence of Et_3N leads to the formation of better-structured particles supported on the $\text{Et}_3\text{NH}^+\text{Cl}^-$ salt (the support and the catalyst have been formed in the same reaction). A linear dependence between the particle size and catalyst activity in E–H bond addition reaction to alkynes has been found [24].

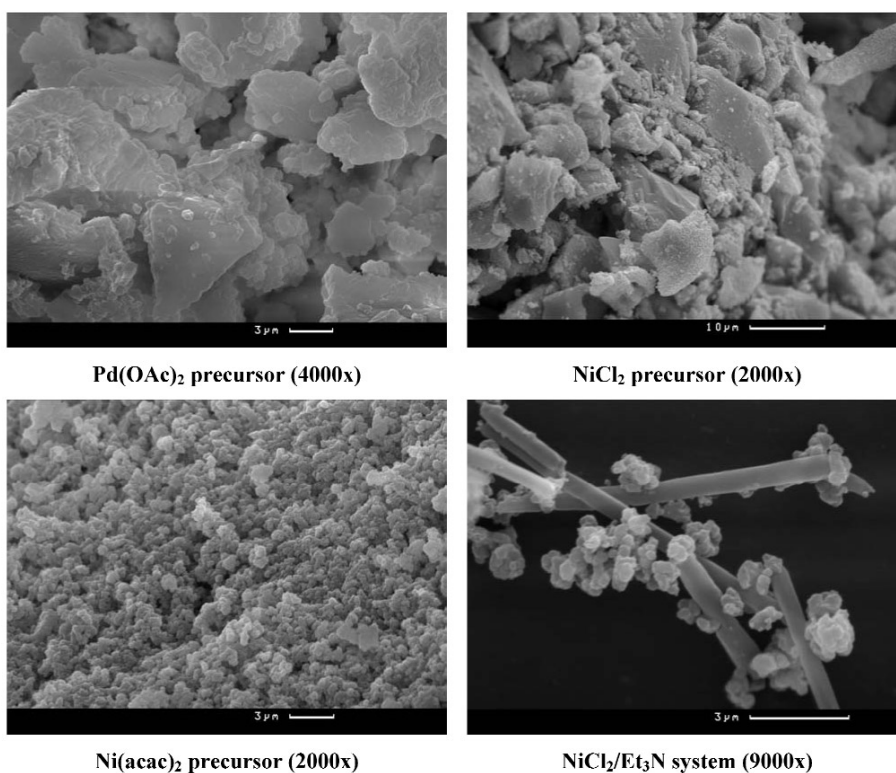
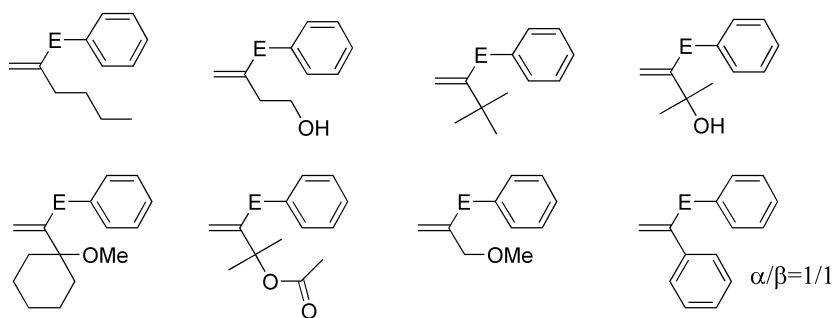


Fig. 2 SEM images of the $[\text{Ni}(\text{SPh})_2]_n$ catalysts from different precursors [24].

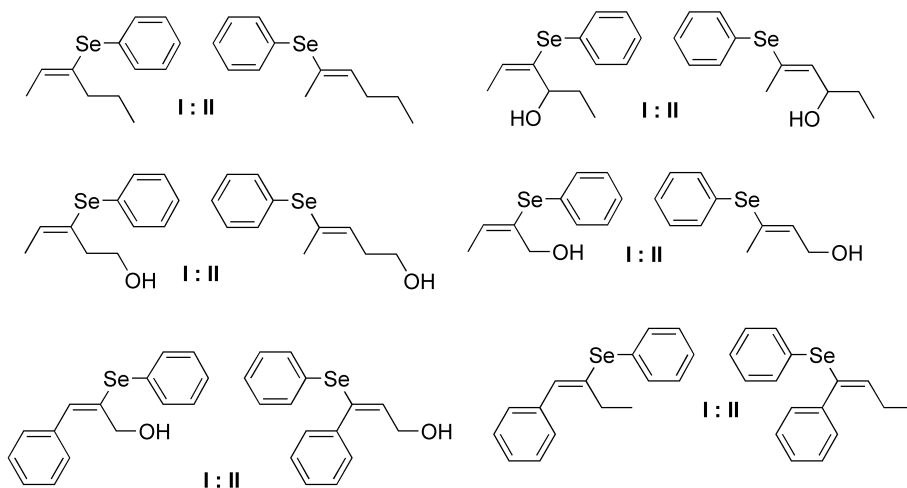
Using this remarkable nanosized catalyst, we carried out the reaction of PhSeH and PhSH with variety of terminal alkynes. In all cases (except phenylacetylene), excellent yield and selectivity were observed (Scheme 17).

Developed synthetic procedure is very practical and can be scaled up from 5 mmol of the reagents to 300 mmol, resulting in 0.8–49 g of product with the same yield of 81–84 %. As we mentioned already, the catalytic system can be applied to internal alkynes under mild conditions (Scheme 17). The stereoselectivity of the addition reaction was very high for all studied cases, while the regioselectivity depended on the alkyne.

Thus, we have developed a very efficient and inexpensive method for the synthesis of vinyl-sulfides and vinylselenides. We have revealed also the reasons of high activity of heterogeneous catalysts. Of course, it is interesting to compare this heterogeneous system with Ni-based homogeneous catalytic system. We have chosen heterocarbene $\text{Cp}(\text{NHC})\text{NiCl}$ complex as a precursor for the homogeneous catalyst (Scheme 18) [25]. We expected that the catalyst formed in this system will not produce polymers, and the presence of one EAr group will prevent the formation of disubstituted product. The reaction catalyzed by this complex proceeds smoothly and affords product in a high yield, but requires higher temperature (80 °C) and prolonged time (5 h).

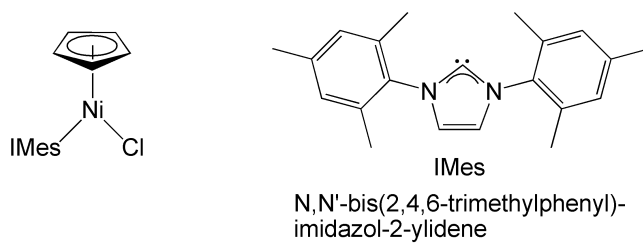
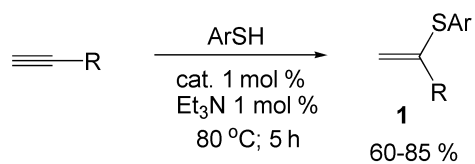


Isolated yields 70-90 % (E=S, Se)



Isolated yields 75-95 % (I : II = 60 : 40 – 80 : 20)

Scheme 17



Scheme 18

We have tried several carbene complexes (saturated and unsaturated with various steric effects) and found that CpNi(IMes)Cl is the best one (Fig. 3). The possible mechanism of the reaction involves the exchange of Cl ligand by SPh group, insertion of alkyne, and protonolysis (Scheme 19).

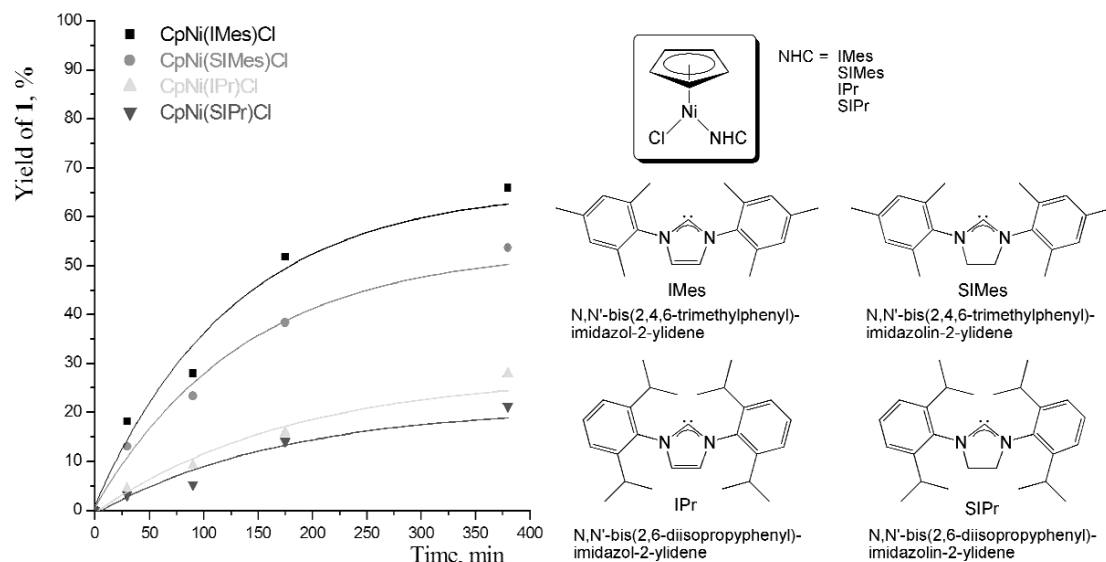
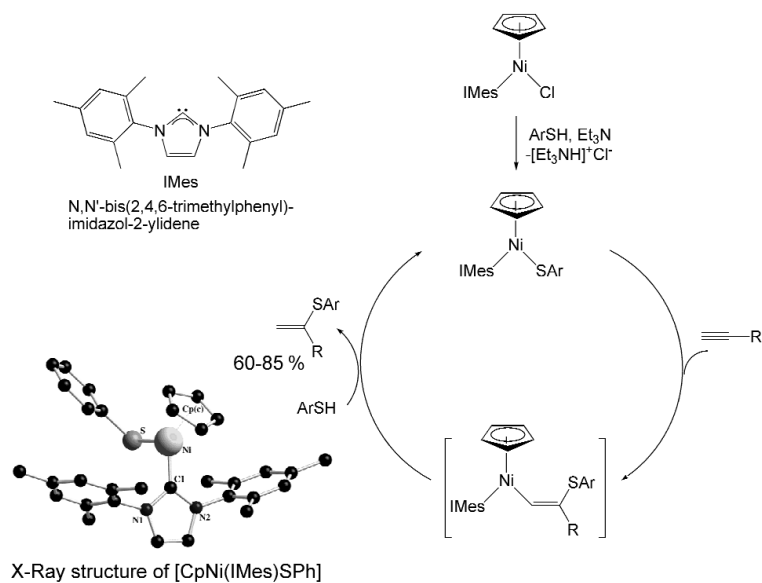
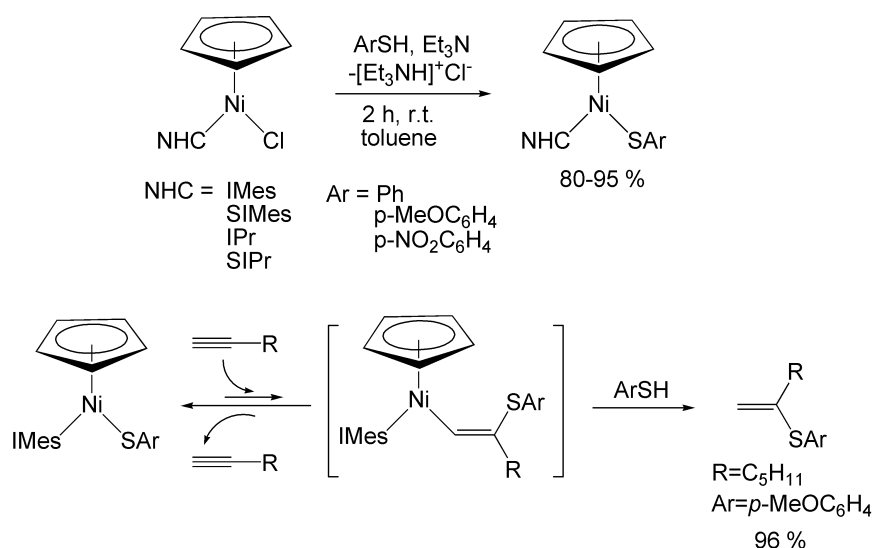


Fig. 3 Product yields vs. time for different ligands in Ni catalyst.



Scheme 19

To support this mechanism, we carried out a series of stoichiometric reactions with different ArSH under the same experimental conditions (Scheme 20). The reaction with alkyne took place only in the presence of arylthiol, and vinyl-Ni intermediates have not been observed in NMR spectra. It may suggest that coordination or insertion of the alkyne is a reversible process shifted toward the initial compound. Trapping the vinyl complex of Ni by ArSH shifts the reaction toward the product formation. As a by-product in this reaction, a small amount of dienes was formed. The formation of dienes took place via the reaction of intermediate Ni complex with a second acetylene molecule. The formation of dienes was not observed in the case of Pd-catalyzed reaction. This outlines an important difference between Pd- and Ni-based catalytic systems. The nature of the process leading to dienes will be addressed in our future studies.



Scheme 20

CONCLUSIONS

In the present article, we have shown that catalytic E–E and E–H bond additions to alkynes combine high atom economy of the addition reaction with ecological and economical benefits of the solvent-free conditions and polymeric (or polymer-supported) catalysts. Another advantage of the studied system is excellent selectivity of the catalytic transformations. Based on this methodology, a new generation of synthetic procedures may be developed in agreement with green chemistry requirements.

The study has clearly shown that separate consideration of E–E and E–H bond additions to alkynes makes it difficult to rationalize the nature of these fascinating reactions. To gain an insight into the mechanism of the catalytic cycle, both reactions should be analyzed in a comparative manner. The next important question is the origin of different catalytic activity and selectivity of Ni, Pd, and Pt complexes.

It is very important to note that Ni complexes can provide useful replacement for traditional Pd catalysts. As we have found, Ni-based catalyst is more efficient and selective for the E–H bond addition to alkynes. Unique nanostructured organization of the $[\text{Ni}(\text{EAr})_2]_n$ catalyst is a key feature that provides high activity and selectivity under mild conditions.

ACKNOWLEDGMENTS

The research was supported in part by the Russian Foundation for Basic Research (Projects No. 05-03-34888 and 07-03-00851) and the Division of Chemistry and Material Sciences of the Russian Academy of Sciences (under program “Theoretical and Experimental Investigation of the Nature of Chemical Bond and Mechanisms of the Most Important Chemical Reactions and Processes”). We also would like to acknowledge our present and former students for their contributions at various stages of the research: Dr. Nickolay Orlov, Michael Kabeshov, Denis Malyshev, and Sergej Zalesskij.

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