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Catalysis and regioselectivity in hydrofunctionalization reactions of unsaturated carbon bonds. Part III

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The review addresses the possibility of obtaining Markovnikov and anti-Markovnikov isomers in the reactions of unsaturated hydrocarbons with organophosphorus and organosulfur compounds having P – H and S – H bonds using metal salts or complexes as catalysts.
The bibliography includes 247 references.

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1. Introduction

To continue our reviews[1,2] dedicated to the memory of V.V.Markovnikov and addressing addition reactions of carbon – element bonds to unsaturated bonds of alkenes, alkynes, allenes and dienes (hydroformylation, hydrosilylation, and hydroamination), in the present review, we address reactions of this type involving organophosphorus and organosulfur compounds containing P – H and S – H bonds. These reactions also represent the most direct, efficient and economic processes for the synthesis of important classes of P- and S-containing aliphatic compounds. The reactions can follow either radical or polar mechanism; in the latter case, catalysis is often required not only to enable the reaction to proceed, but also to make the reaction selective. Like in the previous reviews, we are interested in the reaction regioselectivity, *i.e.*, exclusive or predominant formation of either Markovnikov (iso, branched, or α) or anti-Markovnikov (linear, or β) isomer and the related issues of enantioselectivity (for the Markovnikov isomer) and stereoselectivity (for the anti-Markovnikov isomer). We also endeavoured to find published examples of divergent regioselectivity, that is, the possibility of preparing either of the isomers by making relatively small changes in the catalyst (metal or ligand modification) or reaction conditions. We would like to remind the readers that V.V.Markovnikov's discovery of isomerism not only contributed to the development of A.M.Butlerov's structural theory of organic compounds, but also affected the current understanding of the reaction selectivity.

Dedicated to the memory of V.V.Markovnikov.

The following abbreviations are used in the review:
(*R*)-DTBM-Segphos — (*R*)-(−)-5,5′-bis[di(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-4,4′-bi-1,3-benzodioxole,
(*R*,*R*)-Ph-BPE — (−)-1,2-bis[(2*R*,5*R*)-2,5-diphenylphospholano]ethane,
(*R*,*R*)-QuinoxP — (*R*,*R*)-(−)-2,3-bis(*tert*-butylmethylphosphino)quinoxaline,
(*S*)-Xyl-Binap — (S)-(−)-2,2′-bis[bis(3,5-dimethylphenyl)phosphino]-1,1′-binaphthyl,
acac — acetylacetonate,
Alk — alkyl,
Am — amyl,
Ar — aryl,

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Binaphos — (11b*S*)-4-[[(1*R*)-2′-(diphenylphosphino)[1,1′-binaphthalene]-2-yl]oxy]dinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphosphepine,
Bn — benzyl,
Boc — *tert*-butoxycarbonyl,
Bu — butyl,
Bz — benzoyl,
Cod — 1,5-cyclooctadiene,
Cp* — 1,2,3,4,5-pentamethylcyclopentadienyl,
Cy — cyclohexyl,
Dba — dibenzylideneacetone,
DCE — 1,2-dichloroethane,
Dipp — 2,6-diisopropylphenyl,
Dmba — dimethylbenzylamine,
DMF — *N*,*N*-dimethylformamide
DMSO — dimethyl sulfoxide,
Dppben — 1,2-bis(diphenylphosphino)benzene,
Dppe — 1,2-bis(diphenylphosphino)ethane,
Dppf — 1,1′-bis(diphenylphosphino)ferrocene,
DTBP — di(*tert*-butyl) peroxide,
ee — enantiomeric excess,
EWG — electron-withdrawing group,
Hal — halogen,
HBPin — 4,4,5,5-tetramethyl-1,3,2-dioxaborolane, pinacolborane,
Het(Ar) — heteroaryl,
Hmpa — hexamethylphosphoramide,
IMe — 1,3-dimethylimidazolin-2-ylidene,
IPr — 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene,
JosiPhos — (*R*)-1-[(SP)-2-(dicyclohexylphosphino)ferrocenyl]ethyldicyclohexylphosphine,
LiHMDS — lithium bis(trimethylsilyl)amide,
m-CPBA — *m*-chloroperbenzoic acid,
MOM — methoxymethyl,
MTBE — methyl *tert*-butyl ether,
MW — microwave radiation,
neat — without a solvent,
NHC — *N*-heterocyclic carbene ligand,
n-Hex — n-hexyl,
NMP — *N*-methylpyrrolidone,
OTf — trifluoromethanesulfonate,
n-Pen — n-pentyl,
PG — protecting group,
PTC — phase transfer catalyst,
PTSA — *p*-toluenesulfonic acid,
Py — pyridyl,
rt — room temperature,
TBDMS — *tert*-butyl(dimethyl)silyl,
TBHP — *tert*-butyl hydroperoxide,
TFA — trifluoroacetic acid,
THF — tetrahydrofuran,
THP — tetrahydropyran,
TIPS — triisopropylsilyl,
TMS — trimethylsilyl,
Ts — tosyl (*para*-toluenesylfonyl)
Xantphos — 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

2. Hydrophosphinylation and hydrophosphorylation

The chemistry of organic phosphorus derivatives is an important area of organic chemistry, covering various P^{III} and P^{V} compounds. Phosphorus-containing organic compounds possess a broad range of biological activities and, therefore, they are used in medicine and agrochemistry. Unfortunately, nerve agents — second generation chemical weapons — also belong to this class of compounds, which is evidence for their potent biological action. Meanwhile, organophosphorus compounds devoid of high toxicity are widely used in industry as extractants and flame retardant additives. Organic derivatives of phosphorus are frequently used in organic synthesis; suffice it to mention the Wittig reaction (Nobel Prize of 1956) or the Horner–Evans reaction. These compounds have played an immense role in the development of transition metal catalysis and organocatalysis. A special mention should be made of the use of phosphines as ligands. Chiral phosphines enabled chemists to accomplish asymmetric catalysis (Knowles and Noyori, Nobel Prize of 2001).

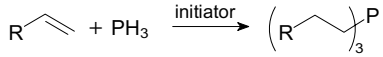
The methods of synthesis of organophosphorus compounds are also very diverse. Russian scientists, A.E.Arbuzov, B.A.Arbuzov, A.N.Pudovik, M.N.Kabachnik, A.V.Kirsanov, and many other made a significant contribution to the development of this area.

In view of the subject matter of this review, we will discuss the synthesis of organic derivatives of phosphorus by addition reactions of P–H and P(O)–H bonds to the unsaturated bonds of alkenes, alkynes, allenes and dienes. Theoretically, this is the most atom-economic way for the generation of C–P bonds. However, these methods are faced with the selectivity, first of all, regioselectivity problem.

As mentioned above, the addition reactions of P–H and P(O)–H bonds to unsaturated carbon–carbon bonds can follow different mechanisms. The most widely known are radical reactions using a variety of initiation methods,[3–13] including photoredox and electrochemical processes. These reactions usually give anti-Markovnikov products and are often accompanied by cyclization.[10,14–16] Reactions catalyzed by bases[17–21] and Lewis acids[22] proceed in a similar way, while Brønsted acid catalysis result in the formation of Markovnikov products.

A separate group of reactions is the addition to activated alkenes (P-analogues of the Michael reaction). These reactions can proceed without catalysts,[23,24] but at higher temperature or with microwave assistance, or can be conducted in the presence of organocatalysts.[25,26] All of such reactions result in the formation of anti-Markovnikov products.[27] These reactions are important for the preparation of a number of phosphorus compounds, for example, the reaction shown below represents the synthesis of trialkylphosphine (Scheme 1).

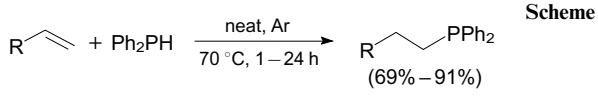
Scheme 1



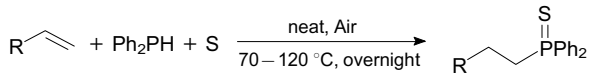
Alonso and co-workers[28] (see also a review[29]) demonstrated a very simple method for the preparation of tertiary phosphines in good yields by the reaction of terminal alkenes and alkynes with diphenylphosphine without a catalyst and solvent under fairly mild conditions. Treatment of the resulting phosphine with sulfur furnishes stable phosphine sulfide. The reaction has an anti-Markovnikov regioselectivity and, in the case of alkyne, the β-*Z*-isomer is formed (Scheme 2).

However, these reactions are beyond the subject of our review, since there is a priori no way for a different selectivity. Below we consider catalysis by metal salts and

Scheme 2



R = Ar, Het(Ar), Alk, EWG; neat means without a solvent



R = Ar, Het(Ar), Bn, Alk, SPh

complexes, especially catalysis, resulting in the formation of both isomers.[30]

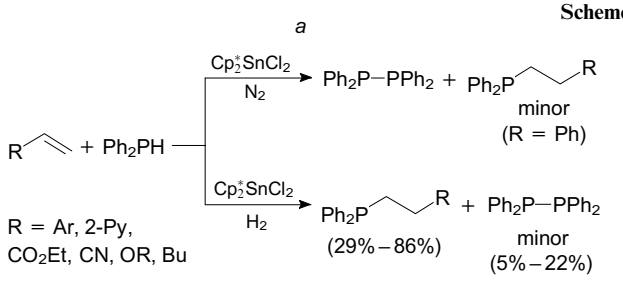
2.1. Alkenes

First, we will consider the addition reactions of phosphines (PH_3, Ph_2PH, RPH_2). For more reactive alkenes such as norbornene and vinylarenes, the reactions can be catalyzed by calcium phosphide,[31] zinc complexes,[32] other Lewis acids such as $Cp^*_2SnCl_2$ in H_2 atmosphere (Scheme 3*a*)[33] or lanthanide complexes (Scheme 3 *b*,*c*).[34–36] All these reactions afford anti-Markovnikov adducts.

Transition metal salts, particularly, platinum and nickel salts, were used by Pringle and co-workers[37] and Togni and co-workers[38] to carry out reactions with acrylo- and methacrylonitriles (Scheme 4).

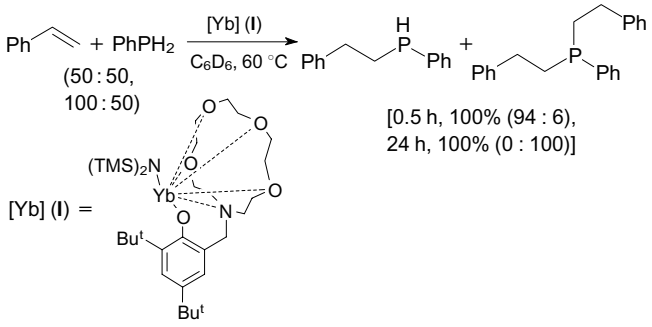
Scheme 3

a

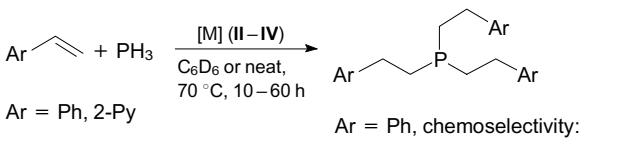


R = Ar, 2-Py, CO_2Et, CN, OR, Bu

b

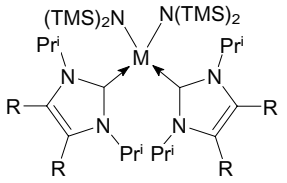


c



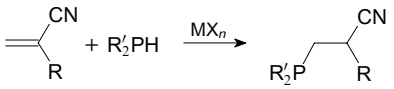
Ar = Ph, 2-Py

Ar = Ph, chemoselectivity:
[Ca]: R = H (up to 99%);
[Yb]: R = H (up to 85%);
[Sm]: R = H, Me (up to 99%)



R = H, Me;
[M] = [Ca] (**II**), [Yb] (**III**), [Sm] (**IV**)

Scheme 4

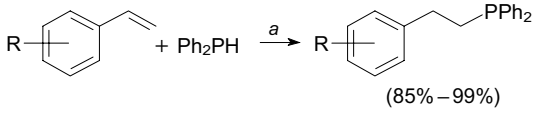


R = H, Me;
M = Pt, Ni

Note that the reaction of methacrylonitrile with $(1\text{-Ad})_2PH$ in the presence of a chiral catalyst was highly enantioselectivity (94% *ee*).[38]

Corma and co-workers[39] were the first to perform the hydrophosphination of alkenes under the action of the copper salts $(CuOTf)_2 \cdot$ toluene or CuCl. Styrene and its derivatives substituted in the benzene ring were converted exclusively to anti-Markovnikov products in high yields. However, substitution at the double bond, the use of aliphatic alkenes, or the use of Cy_2PH instead of Ph_2PH sharply decreased the product yields, and stilbene proved to be almost inactive (Scheme 5).

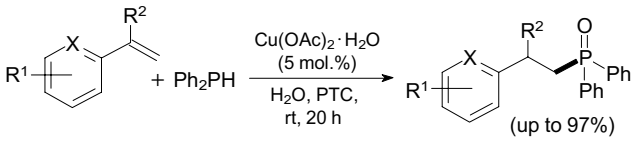
Scheme 5



(*a*) $(CuOTf)_2 \cdot$ toluene (10 mol.%), 1,4-dioxane (2 M), 100 °C, 18–24 h;
R = H, F, CF_3, MeO, m-NO_2

Copper(II) acetate catalyzed the addition of diphenylphosphine to vinylarenes in water in the presence of a phase transfer agent to give the oxidation product in high yield (Scheme 6).[40]

Scheme 6

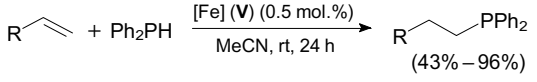


X = CH, N; R^1 = Hal, OMe; R^2 = H, Alk, Ar; rt is room temperature

Iron(II) complex (**V**) is a good catalyst for the phosphination of various types of alkenes. The reaction takes place at room temperature with a low concentration of iron complex (Scheme 7).[41]

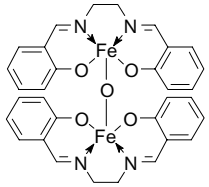
The anti-Markovnikov selectivity was also observed for the reactions of diphenylphosphine with vinylarenes (heter-

Scheme 7

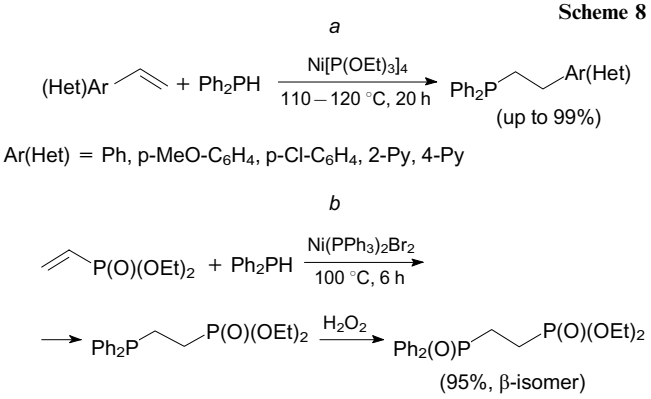


R = Ar, Het(Ar), CO_2Me, $CO_2(Bu^n)$;

[Fe] (**V**) =



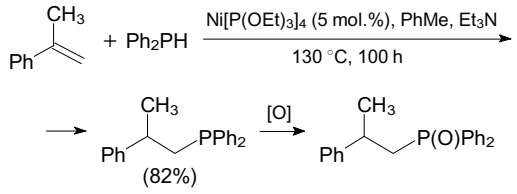
Scheme 8



oarenes) (Scheme 8 *a*) and with diethyl vinyl phosphite (Scheme 8 *b*) catalyzed by nickel complexes.[42]

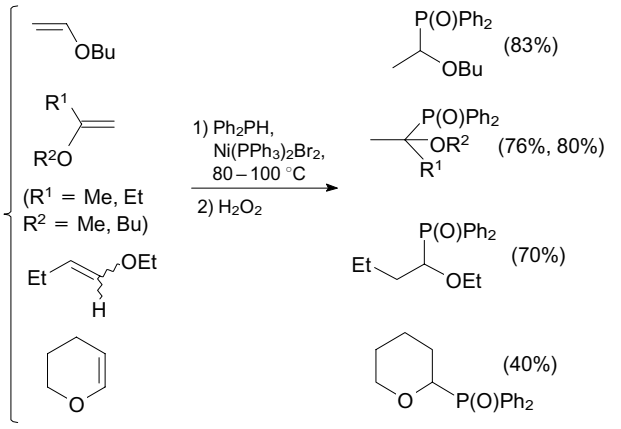
2-Methylstyrene reacted slowly even at 130 °C, but the yield of the product was high (82%) (Scheme 9).[43]

Scheme 9



However, if the alkene contains alkoxy groups, the regioselectivity of the reaction with Ph_2PH changes, and only the Markovnikov product (α-isomer) is formed (Scheme 10).[44]

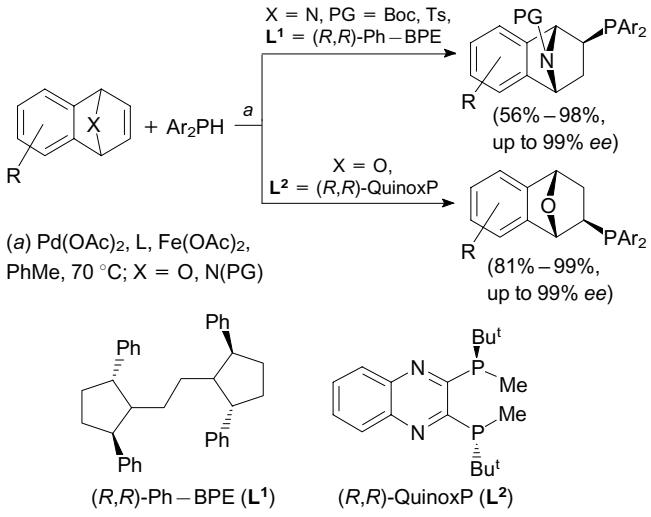
Scheme 10



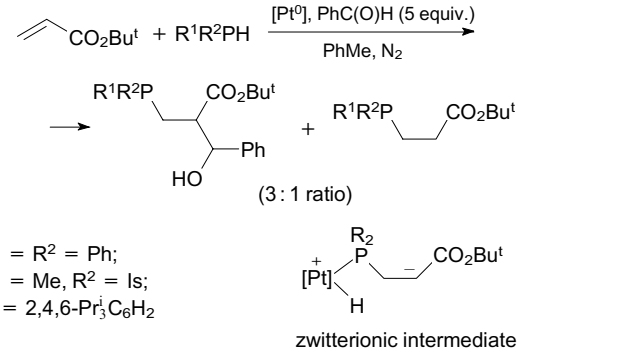
The palladium-catalyzed reactions of heterobicyclic benzonorbornadienes with Ar_2PH give products in high yields and, in the presence of a chiral ligand ($\mathbf{L}^1$ or $\mathbf{L}^2$), also with high enantioselectivity (Scheme 11).[45]

It is noteworthy that the resulting phosphine can add to activated alkenes, thus activating them towards the nucleophilic attack (now this is used as phosphine catalysis). In 2006, Glueck and co-workers[46] demonstrated that the reaction of Ph_2PH with *tert*-butyl acrylate in the presence of benzaldehyde and a platinum catalyst affords two products of addition, which are presumably formed *via* a zwitterionic intermediate (Scheme 12).

Scheme 11

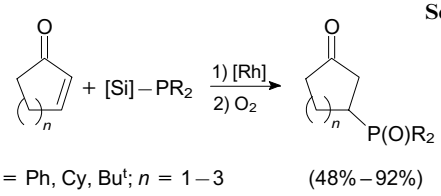


Scheme 12



Rhodium-catalyzed addition of $R_2P-[Si]$ to cyclic enones was reported by Trepohl and Oestreich[47] (Scheme 13).

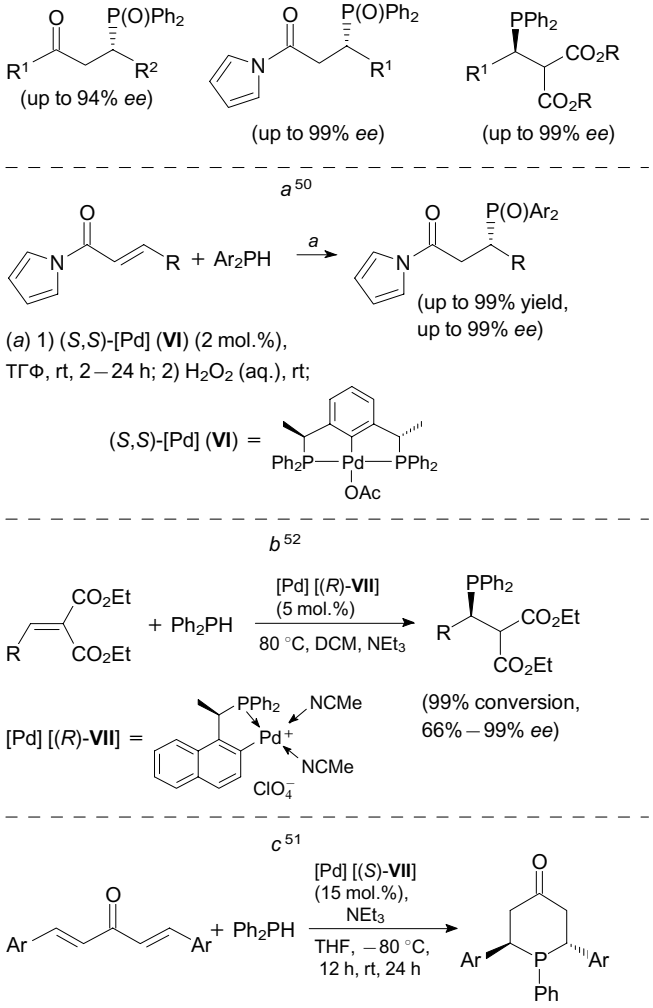
Scheme 13



We have already mentioned the addition of Ph_2PH to the activated bond of alkenes, which is catalyzed by Pt, Ni, Pd and organocatalysts. Below we present examples of the Michael reactions: asymmetric phosphination of α,β-unsaturated ketones and esters, including substituted methylidenemalonates, catalyzed by chiral palladacycles[48–53] or palladium[54–58] and nickel[55] pincer complexes, resulting in the formation of chiral tertiary phosphines (after oxidation, phosphine oxides) (Scheme 14).[48,49]

The phosphorylation of alkenes carried out under a variety of conditions (radical and basic, without a solvent, or with microwave assistance) and in the presence of a variety of catalysts has been studied more extensively than reactions of easily oxidizable phosphines, but still insufficiently systematically. Most often, the reactions were carried out with activated alkenes (such as norbornene and

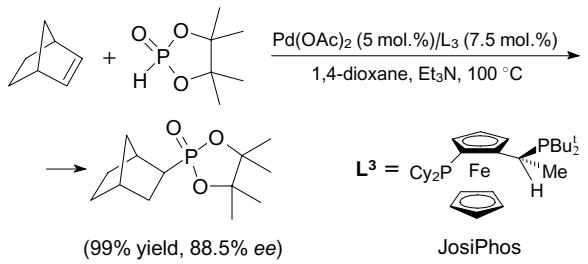
Scheme 14



vinylarenes). The reactions can be accompanied by cyclization and rearrangements.

A JosiPhos type ligand ($\mathbf{L}^3$) was used in the palladium-catalyzed reaction of pinacol H-phosphonate with norbornene.[59] Norbornyl phosphonate was obtained in high yield and with high enantioselectivity (Scheme 15).

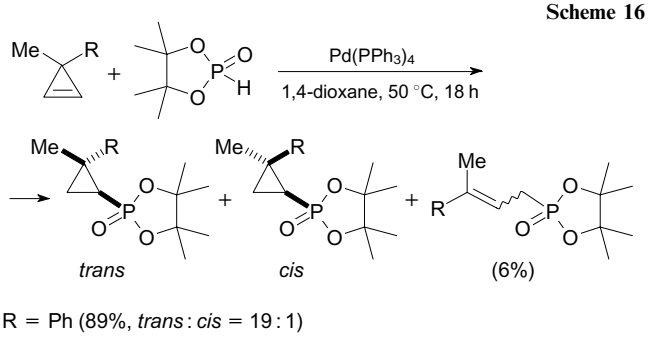
Scheme 15



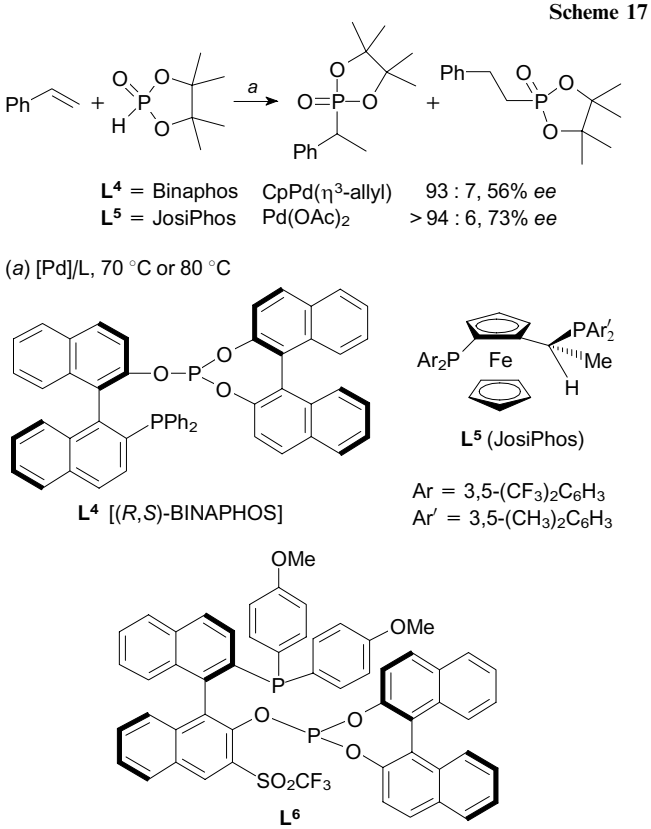
The reaction of cycloalkenes giving mixtures of stereoisomers, mainly with *trans*-configuration, was studied in a similar way (Scheme 16).[60]

The addition of pinacol H-phosphonate to vinylarenes catalyzed by palladium complexes mainly gives the Markovnikov isomer. Therefore, the asymmetric version of this reaction was studied; the obtained results are depicted in Scheme 17. Among the chiral ligands used, only in the case

Scheme 16



Scheme 17



of Binaphos ($\mathbf{L}^4$), the product was formed in a high yield with moderate enantioselectivity (56% *ee*).[61] Subsequently, this result was improved using JosiPhos ($\mathbf{L}^5$), but the enantioselectivity was still insufficient (73% *ee*).[59]

The use of ligand $\mathbf{L}^6$ slightly increased the enantioselectivity (up to 74%).[62]

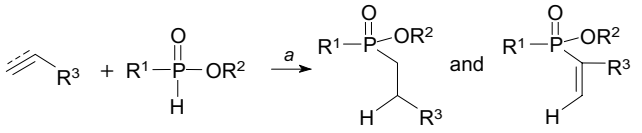
The palladium-catalyzed hydrophosphinylation of alkenes and alkynes with H-phosphinic acids[63,64] gives anti-Markovnikov products, although for alkynes there are some exceptions in which the Markovnikov isomer is formed (Scheme 18).

As in the case of phosphines, radical addition results in the preparation of the β-isomer in a high yield.[65]

The conjugate addition of diphenyl phosphite to substituted acrylic esters catalyzed by $Ti(OPr^i)_4$ gives very high yields of products (up to 100%) (Scheme 19).[22]

Cai and Gu[66] observed oxyphosphorylation in the reaction of dialkyl phosphite with vinylarenes (heteroarenes) in the presence of di(*tert*-butyl) peroxide and a Cu/Fe

Scheme 18

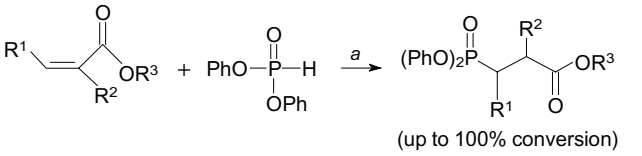


(*a*) Pd_2dba_3 (2 mol.% – 5 mol.%)/ nixantphos polymer, PhMe or $HO(CH_2)_2OH$, 110 °C; R^1 = Ph, Alk, Bn, H; R^2 = H, Et, CH_2CH_2OH; R^3 = Alk

(26% – 99% ^{31}P NMR, 46% – 71% isolated yield)

(89% – 99% ^{31}P NMR, 75% – 99% isolated yield)

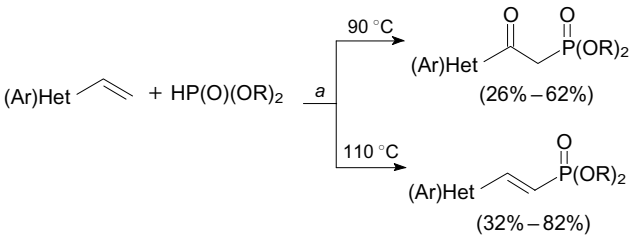
Scheme 19



(up to 100% conversion)

(*a*) $Ti(O^iPr)_4$, 25 – 105 °C; R^1 = H, Me, Ph; R^2 = H, Me; R^3 = Me, Et, Bu^t, Ph

Scheme 20



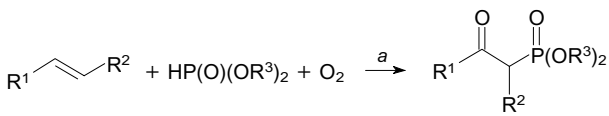
(*a*) CuCl (10 mol.%), $FeCl_3$ (20 mol.%), DTBP, NEt_3, DMSO, Ar; DTBP is di(*tert*-butyl) peroxide

catalyst at 90 °C. However, at 110 °C, oxidative cross-coupling took place (Scheme 20).

Thus, temperature control offers the possibility of selective chemodivergent reactions, giving either β-keto phosphonates or alkenylphosphonates.

Ji and Wei [67] also reported the formation of β-keto phosphonates in the $CuBr_2/FeBr_3$-catalyzed reaction conducted in the presence of O_2 (Scheme 21).

Scheme 21

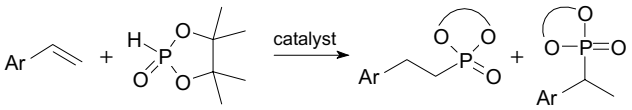


(*a*) $CuBr_2$ (2.5 mol.%), $FeBr_3$ (5 mol.%), NEt_3, DMSO, 55 °C; R^1 = Ar, Het(Ar), Alk; R^2 = H, Me, *etc.*; R^3 = Pr^i, Et, Bu^n

(26% – 81%)

As we have already noted, the amount of available data is still insufficient to discuss the regioselectivity problems, the dependence of regioselectivity on the catalyst and conditions and, the more so, the divergent selectivity. Nevertheless, there is an example of divergent formation of anti-Markovnikov or Markovnikov product depending on the use of either rhodium or palladium metal complex.[61] In this reaction, the palladium catalysis affords the Markovnikov isomer, while rhodium catalysis leads to the anti-Markovnikov isomer with a high regioselectivity (Scheme 22).

Scheme 22



Ar = Ph, 4-ClC_6H_4, 2-naphthyl, 6-CH_3O-2-naphthyl

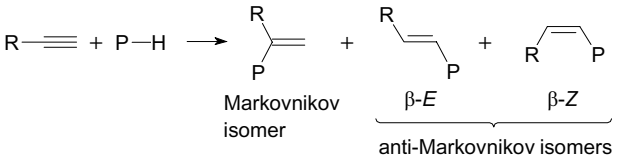
Ar	Catalyst	Yield (%)	Regioselectivity	
			β	α
4-ClC_6H_4	$RhCl(PPh_3)_3$	82	99	1
4-ClC_6H_4	$CpPd(\eta^3\text{-All})/\mathbf{L^7}$	84	6	94

$\mathbf{L^7}$ = $CyPPh_2$

2.2. Alkynes

The addition of the P – H bond to terminal acetylenes gives alkenylphosphines, which can exist as the Markovnikov isomer (α), two anti-Markovnikov isomers (β-*E* and β-*Z*) or their mixture (Scheme 23).[68]

Scheme 23



Alkenylphosphines serve as ligands [69 – 71] and are extensively utilized in catalysis, particularly, asymmetric catalysis.[72, 73] They can be prepared under radical conditions [12, 74] or in superbasic media,[20, 75] on treatment with main group phosphides, including catalytic reactions,[76 – 82] or by organocatalysis, in particular, by carbenes.[83]

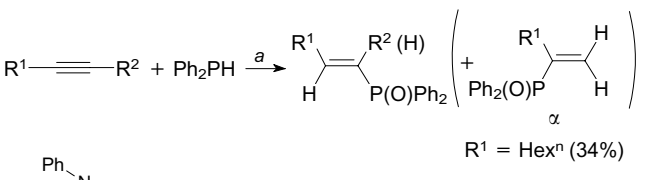
The intramolecular reactions involving P – H bonds were first studied by Marks and co-workers,[84 – 87] who used catalysis by lanthanide complexes able to form the P – Ln phosphide bond into which the triple bond is inserted. The subsequent transmetallation regenerates the catalyst and yields a P-containing heterocycle.

Takaki *et al.*[88] accomplished the intermolecular reaction of diphenylphosphine with alkynes catalyzed by ytterbium complex **VIII**. The reaction gave the β-isomer with stereoconfiguration depending on the nature of substituent in the alkyne (Scheme 24).

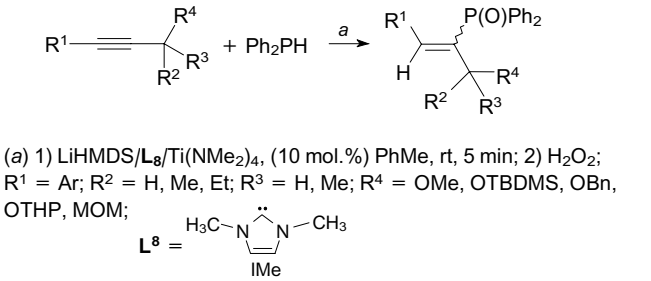
The lanthanum complex $La(Dmba)_3$ (Dmba is dimethylbenzylamine) catalyzes the reaction of Ph_2PH with terminal alkynes to give exclusively the anti-Markovnikov adduct with the predominant *E*-configuration.[89] The catalysis by europium complex also resulted in the anti-Markovnikov isomer, predominantly with *Z*-configuration.[36]

The phosphination of propargyl derivatives was carried out using a titanium complex with a carbene ligand ($\mathbf{L^8}$) as the catalyst and gave the products in high yields (Scheme 25).[90]

Scheme 24

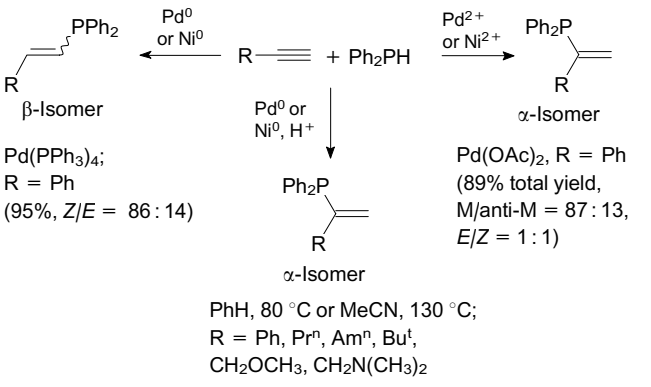


Scheme 25



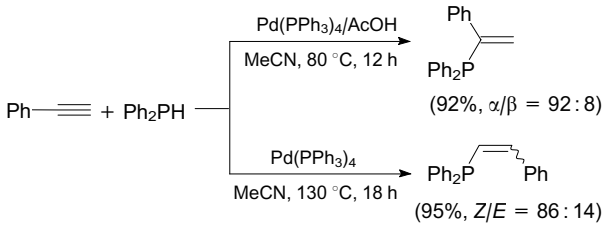
Beletskaya and co-workers [91] studied the hydrophosphination reactions catalyzed by palladium and nickel. Both reactions occurred as the *syn*-addition, and Ni proved to be a more efficient catalyst than Pd. Depending on the nature of the catalyst precursor, isomer mixtures with different ratios of the Markovnikov and anti-Markovnikov products were formed. However, the use of $Pd(PPh_3)_4$ in MeCN in the reaction with phenylacetylene resulted in the formation of only anti-Markovnikov isomer, mainly with *Z*-configuration, while in the case of Pd or Ni salts as catalysts, the Markovnikov isomer was formed as the major product (Scheme 26).

Scheme 26



The addition of a catalytic amount of an acid into the reaction mixture completely changed the reaction regioselectivity towards the formation of only the Markovnikov isomer. The authors attributed this outcome to participation of the $[H-Pd-X]L_2$ intermediate in the catalytic cycle. Thus, it is possible to compose a regiodivergent pair in this case (Scheme 27).

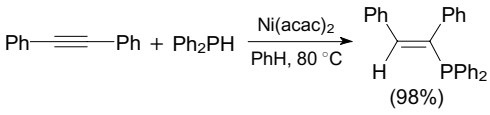
Scheme 27



This change in the regioselectivity was observed for the first time by Tanaka and co-workers,[92,93] who added the acid $Ph_2P(O)(OH)$ to the reaction of 1-octyne with diphenylphosphine oxide catalyzed by *cis*-$[PdMe_2(PPhMe_2)_2]$. The reaction gave the α-isomer with a selectivity of 95%, with the total yield being 92%.

A high product yield was obtained upon the addition reaction of diphenylphosphine with an internal alkyne catalyzed by a nickel salt (Scheme 28).[91]

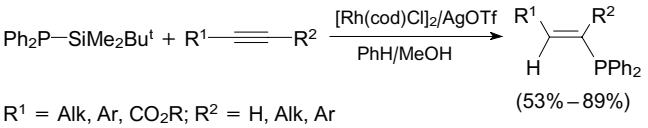
Scheme 28



The addition of diphenylphosphine to alkynes, including aliphatic ones, catalyzed by the $BuLi-Co(acac)_2$ system has *syn*-selectivity, but gives a mixture of α- and β-isomers, with a predominant amount of the anti-Markovnikov product.[94]

For rhodium-catalyzed addition to alkynes, diphenylphosphine was replaced by its silyl derivative.[95] The reaction had high selectivity for the anti-Markovnikov isomer (Scheme 29).

Scheme 29



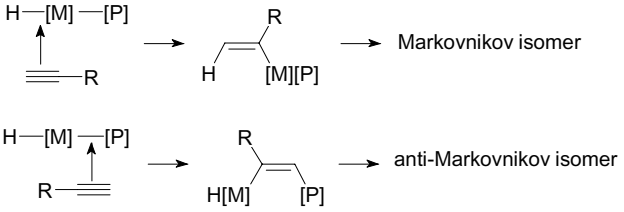
The ruthenium-catalyzed addition of Ph_2PH to propargyl alcohol proceeding *via* the formation of ruthenium vinylidene complex also results in the anti-Markovnikov product.[96]

Presumably, the reactions catalyzed by transition metal complexes include the oxidative addition of the P–H bond to M^0, with the regioselectivity being determined by the step of alkyne insertion into the H–M or P–M bond (Scheme 30).[97]

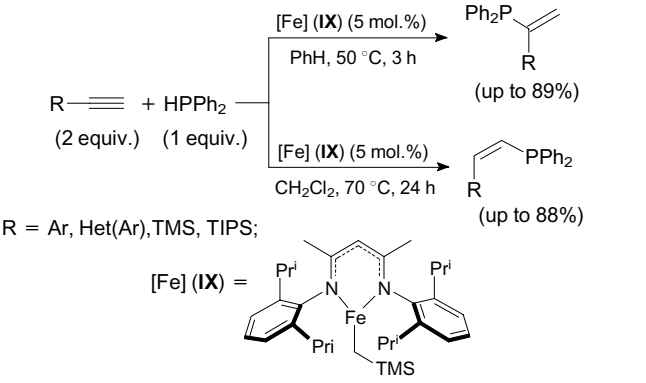
Nakazawa and co-workers [98] reported the addition of diphenylphosphine to alkynes catalyzed by an iron complex, which gave the anti-Markovnikov product, predominantly having *Z*-configuration.

Using iron imidate complex **IX**, Webster and co-workers [99] found that replacement of the solvent in this reaction brings about a change in the regioselectivity: in benzene, the Markovnikov isomer is formed with high selectivity (9 : 1), while in dichloromethane, the anti-Markovnikov isomer with *Z*-configuration is obtained. This divergent pair is

Scheme 30



Scheme 31



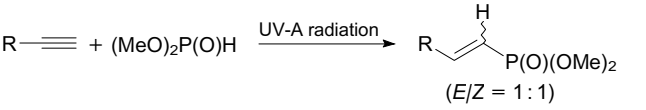
depicted in Scheme 31. The authors attributed the reversal of regioselectivity to the change in the oxidation state of iron (from Fe^{2+} to Fe^{3+}).

The addition of the HP(O) bond to alkynes provides the synthesis of important classes of phosphorus alkenyl derivatives (alkenylphosphine oxides and alkenyl phosphites). These compounds possess a broad range of biological activities;[100–102] they are used as flame retardant additives[103, 104] and ligands in homogeneous catalysis,[105] including asymmetric catalysis.[106] They can be prepared without a catalyst in a superbasic medium[20, 75] or in radical reactions,[12] often only using activated alkynes. However, the application of these methods is rather limited.[107–109] The use of transition metal-based catalysts makes it possible to obtain these compounds with high regio- and stereoselectivity under fairly mild conditions.[110–118]

Trofimov and co-workers[119] demonstrated that phosphine chalcogenides (S or Se) add to alkynes on heating to 80 °C without a solvent to give anti-Markovnikov products.

The radical addition of the H—P(O) bond to alkynes gives anti-Markovnikov products with high regioselectivity, but with poor stereoselectivity;[74, 120] an example is shown below (Scheme 32).

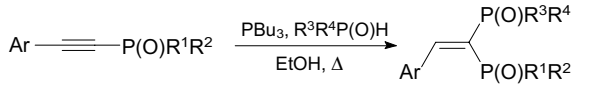
Scheme 32



There are organocatalyzed reactions of alkynes with electron-withdrawing substituents, for example, tri(n-butyl)phosphine-catalyzed reactions with diethyl phosphites, diphenylphosphine oxide and ethyl phenylphosphinate (Scheme 33).[121]

The use of $La(Dmba)_3$ to catalyze the reaction of $Ph_2P(O)H$ with terminal and internal alkynes afforded

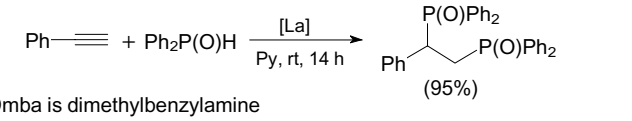
Scheme 33



$R^1 = R^2 = OEt$, Ph;
$R^1 = Ph$, $R^2 = OEt$;
$R^3 = R^4 = OEt$, Ph; $R^3 = Ph$, $R^4 = OEt$

(53%–97% yields, *Z*/*E* from 70 : 30 to 100 : 0)

Scheme 34



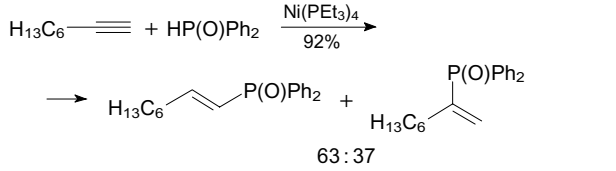
Dmba is dimethylbenzylamine

double hydrophosphinylation products; an example is the reaction of phenylacetylene with diphenylphosphine oxide (Scheme 34).[89]

The addition of the H—P(O) bond to alkynes catalyzed by nickel, palladium, rhodium and copper complexes has been extensively studied. The selectivity of these reactions is determined by both the metal and the ligand used.

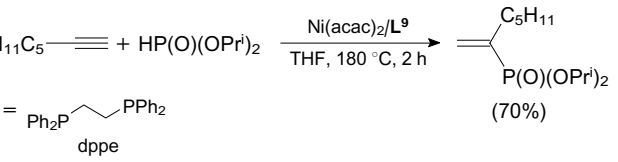
For example, the addition of diphenylphosphine oxide to 1-octyne catalyzed by the nickel complex results in a high product yield, but has insufficient selectivity, although predominant amounts of the anti-isomer are formed (Scheme 35).[122]

Scheme 35



However, the use of $Ni(acac)_2$/dppe ($\mathbf{L}^9$) in a similar reaction with diisopropyl phosphite afforded the Markovnikov isomer with a high regioselectivity (Scheme 36).[123]

Scheme 36

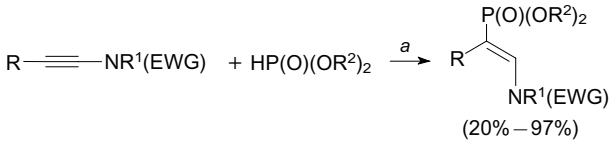


High regio- and stereoselectivity was attained in the nickel salt-catalyzed addition of dialkyl phosphites to ynamides (Scheme 37).[124]

By varying the ligand environment in the nickel catalyst and the reaction conditions, it is possible to find a regiodivergent pair for the reaction involving dimethyl phosphite, which would give either the anti-Markovnikov or Markovnikov isomer as the major product (Scheme 38).[122]

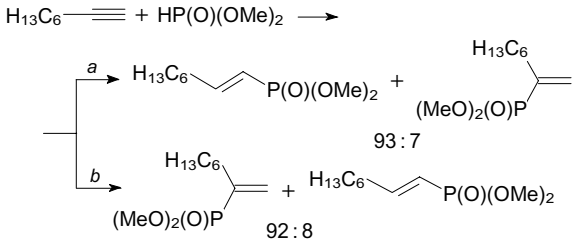
Palladium is an especially active catalyst for the addition of dialkyl phosphites to the triple bond. Like in the case of diphenylphosphine addition, Pd catalysis promotes the formation of the anti-Markovnikov isomer, but the addition of the acid $Ph_2P(O)OH$ completely changes the regio-

Scheme 37



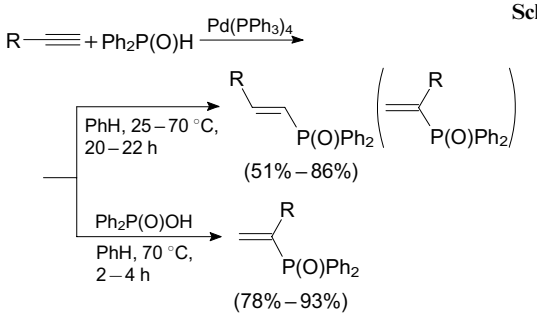
(*a*) $NiBr_2$ (10 mol.%), PhMe, Δ, 2–6 h; R = Alk, Ar, Het(Ar);
$NR^1(EWG)$ = NTs(Bn), $NTs(CH_2)_2Ph$, NTsPh, , *etc.*;
R^2 = Me, Et, Pr^i, Ph

Scheme 38



(*a*) $Ni(PPh_2Me)_4$, EtOH, 20 °C, 5 h (96%);
(*b*) $Ni(cod)_2$/$PPhMe_2$, $Ph_2P(O)OH$, THF, rt, 2 h (91%)

Scheme 39

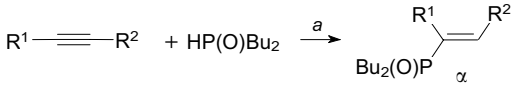


selectivity, resulting in the formation of the Markovnikov isomer (Scheme 39).[93, 125]

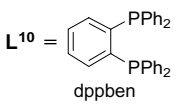
Dibutylphosphine oxide adds to alkyne in the presence of palladium with a chelating phosphine ligand (**L**[9] or **L**[10]) and a Brønsted acid to afford also the Markovnikov isomer (Scheme 40).[126]

Ananikov and Beletskaya[97,127,128] demonstrated that using an ordinary Pd catalyst and a catalytic amount of trifluoroacetic acid (TFA) under appropriately selected conditions, it is possible to attain high yields and excellent regio- and stereoselectivity of the reactions (Scheme 41).

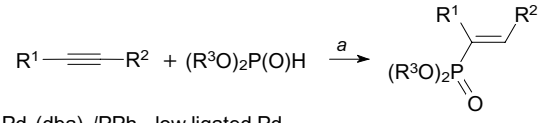
Scheme 40



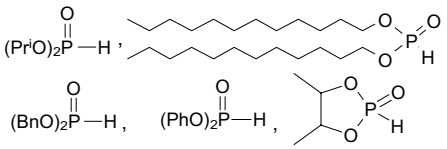
(*a*) CpPd(η^3-All) (5 mol.%)/**L**[10] (5 mol.%),
3,5-$(CF_3)_2C_6H_3P(O)OH$ (5 mol.%), EtPh, 130 °C, 30 min, N_2;
R^1 = Alk, Bn, Ph; R^2 = H, Ph;
R^2 = H: R^1 = Ph, **L**[10] (80%, 68% isolated yield);
R^2 = H: R^1 = C_6H_{13}, **L**[9] (95%, 86% isolated yield);

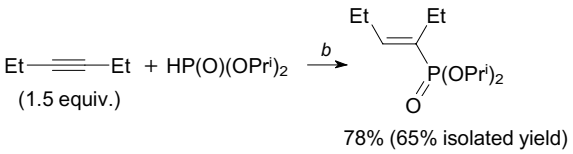

dppben

Scheme 41



(*a*) $Pd_2(dba)_3$/PPh_3, low ligated Pd, cat. TFA (10 mol.%), THF, 50–120 °C, 3–8 h;
[up to 96% yield, up to 99 : 1 selectivity (R^2 = H)]

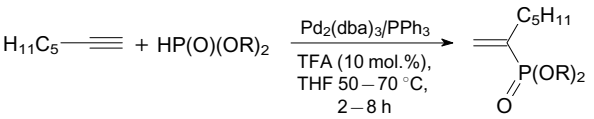
$(R^3O)_2P(O)$–H: 



(*b*) $Pd_2(dba)_3$/PPh_3, TFA (10 mol.%), THF, 120 °C, 8 h

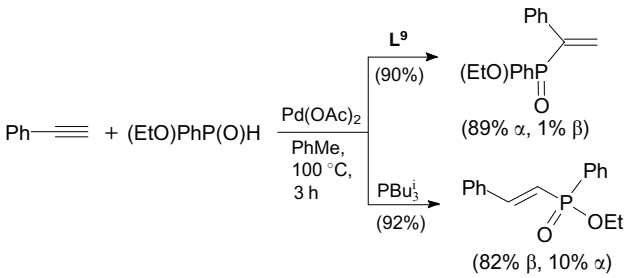
Under these conditions at $R^1 = C_5H_{11}$ and R^2 = H, the Markovnikov isomer was obtained almost exclusively (Scheme 42).[127]

Scheme 42



Tanaka and Nune[129] showed that variation of the ligand on palladium in the reaction of phenylacetylene with ethyl phenylphosphinate (EtO)PhP(O)H allows regioselective preparation of both α (Markovnikov) and β (anti-Markovnikov) isomers (Scheme 43).

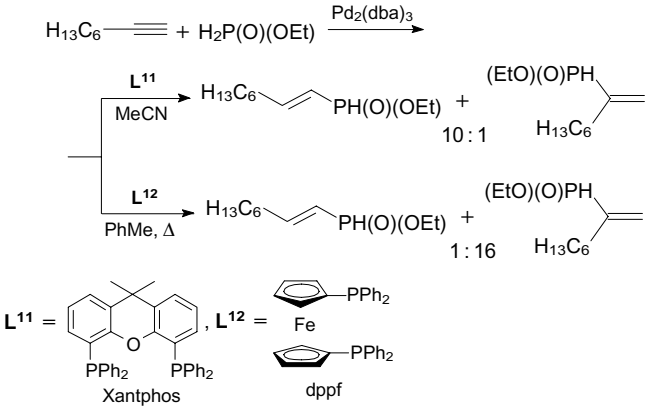
Scheme 43



One more example of divergent pair was obtained by variation of the ligand (**L**[11] or **L**[12]) and the solvent in the Pd-catalyzed addition of ethyl phosphinate to 1-octyne (Scheme 44).[130]

Note that in all cases, *syn*-addition takes place, while the change in the catalyst and reaction conditions can control the insertion of alkyne both into the M–H bond and into the M–P bond.[97]

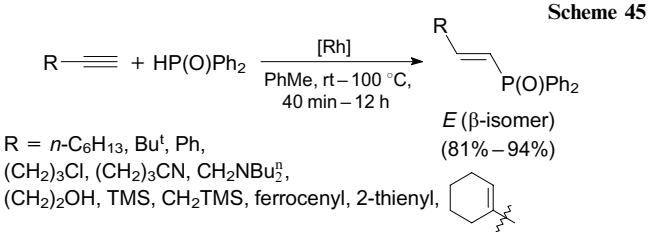
Scheme 44



The linear, anti-Markovnikov isomer is formed in a moderate yield upon the addition reaction of diphenylphosphine oxide to terminal alkyne catalyzed by the rhodium complex Tp*Rh(PPh_3)$_2$ [Tp* is hydrotris(3,5-dimethylpyrazolyl)borate].[131]

The use of the Wilkinson complex RhX(PPh_3)$_3$ (X = Br) results in the formation of the anti-Markovnikov product in high yield and with *E*-stereoselectivity (Scheme 45).[132]

Scheme 45



A high yield and an excellent β-selectivity were found in the reaction of pinacol phosphine oxide with phenylacetylene (91%, >98% selectivity) and 1-octyne (93%, >98% selectivity) catalyzed by RhCl(PPh_3)$_3$.[132]

Guo and Han[133] described the application of heterogenized Rh-, Pd- and Ni-based catalysts immobilized on polystyrene-bound triphenylphosphine (**L**^{13}). The reactions of alkynes with $R^1R^2P(O)H$ gave products in high yields and regioselectivity, with the catalyst being reused several types without considerable deactivation. For the point of our interest, it is significant that Ni and Pd catalysts lead to the Markovnikov product, while the Rh catalyst gives the anti-Markovnikov isomer (Scheme 46).

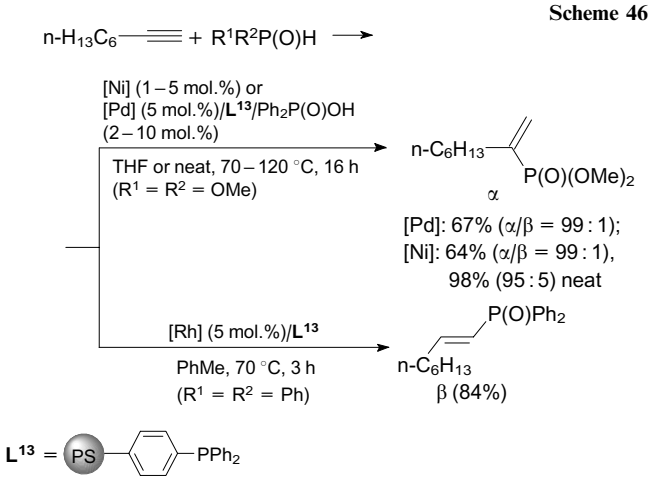
The addition of dialkyl phosphites $(RO)_2P(O)H$ to alkyne has been studied no less thoroughly.

Han, Tanaka and co-workers[134,135] showed that the reaction catalyzed by the palladium complex, *cis*-$PdMe_2(PPh_2Me)_2$, furnishes the Markovnikov product, while catalysis by the rhodium complex affords the *E*-configured anti-Markovnikov isomer.

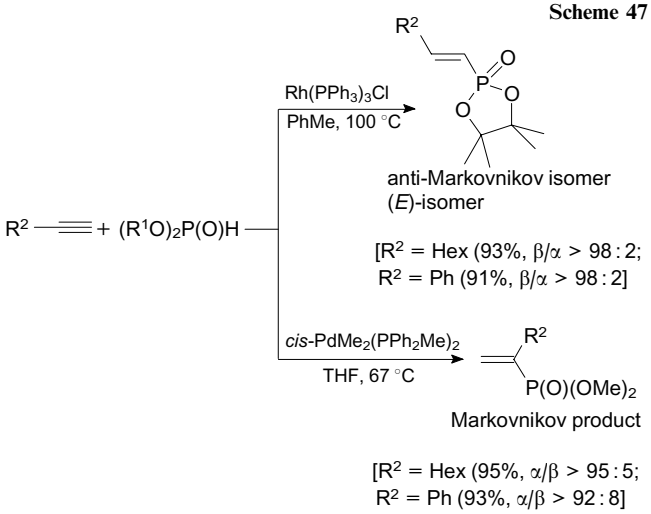
Hence, these reactions form a divergent regioselective pair (Scheme 47).

Han, Tanaka and co-workers[136] carried out the addition of chiral (R_p) phenylphosphinate to terminal alkynes using the $Me_2Pd(PPhMe_2)_2$ catalyst in the presence of $Ph_2P(O)(OH)$. In all cases except for R^2 = TMS, the reaction gave Markovnikov products with stereochemical retention of the configuration at phosphorus. Thus, the authors prepared, for the first time, a P-chiral organophosphorus

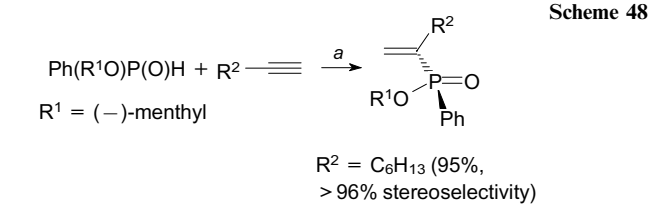
Scheme 46



Scheme 47



Scheme 48



(*a*) $PdMe_2(PPhMe_2)_2$ (5 mol.%), $Ph_2P(O)(OH)$ (10 mol.%), PhMe, 70 °C, 4 h

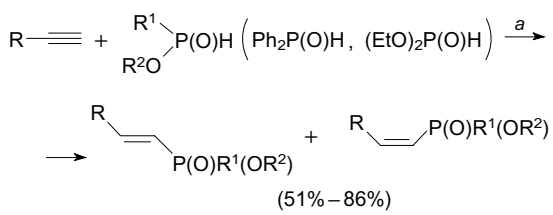
compound by metal-catalyzed hydrophosphinylation (Scheme 48).

Later, it was shown that the Markovnikov isomer can be obtained in the reaction of arylalkynes with dialkyl phosphites using a simpler Pd complex.[137] By asymmetric hydrogenation of the obtained Markovnikov product, the authors performed highly enantioselective synthesis of P-analogues of naproxen and ibuprofen.

Zhao and co-workers[138] showed that $R^1R^2P(O)H$ adds to alkyne in the CuI/ethylenediamine system to give the anti-Markovnikov isomer. Later, it was found[139] that the reactions should better be conducted in an inert atmosphere, since in the presence of oxygen, oxidative coupling takes place to give $R{\equiv}P(O)R^1R^2$. The addition of diphe-

nylphosphine oxide and diethyl phosphite to aromatic and aliphatic alkynes catalyzed by copper(II) acetylacetonate gives a high yield of the product with anti-Markovnikov selectivity, but containing both *E* and *Z* isomers. However, the stereoselectivity of the reaction can be controlled by using either aprotic or protic solvents. High regio- and stereoselectivity was also observed for the addition of H-phosphinates and diethyl phosphite (Scheme 49).[140]

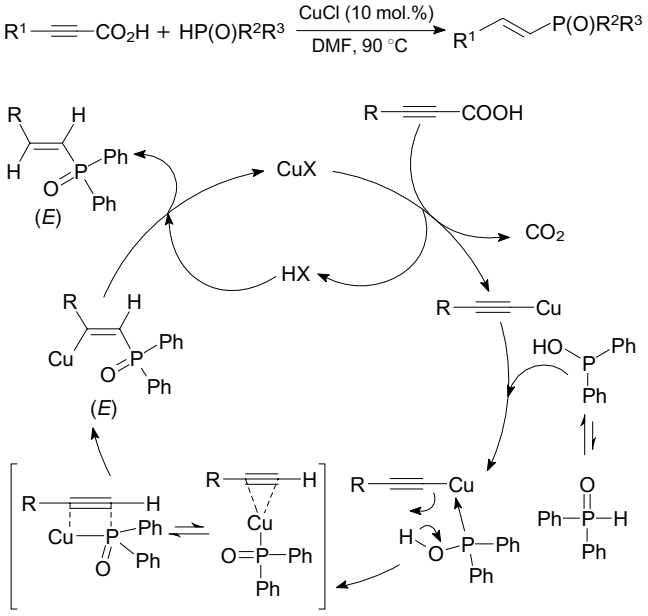
Scheme 49



(*a*) $Cu(acac)_2$ (5 mol.%), DMF/THF (3 : 1), 70 °C; R = C_6H_{13}, Ph

On treatment with CuCl in an inert medium, decarboxylation of propargyl acids takes place, which is followed by triple bond activation and nucleophilic addition. The reaction products were formed in high yields.[141] The catalytic cycle proposed by the authors is shown in Scheme 50.

Scheme 50



A similar regioselectivity was attained in the oxidative phosphorylation of a terminal alkyne (Scheme 51 *a*)[142] and acetylenecarboxylic acid (Scheme 51 *b*).[143]

Scheme 52 shows an example of hydrophosphorylation followed by cyclization.[144]

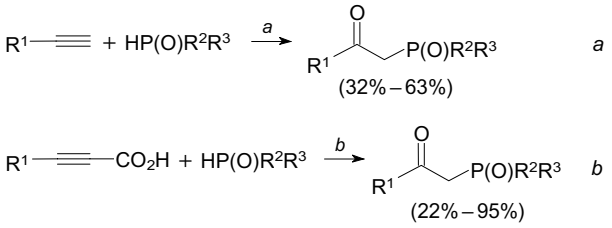
The addition of $R^1R^2P(O)H$ to propargyl alcohols can be catalyzed by Lewis acid in the presence of $Ph_2P(O)(OH)$ (Scheme 53).[145]

Han and co-workers[146] carried out the cyclization–phosphonylation reaction in the presence of Cu^I catalyst to give 2-phosphorylmethylbenzofurans (Scheme 54).

A similar reaction without copper catalysis, but in the presence of K_2CO_3 was reported by Zhao and co-workers,[147] who thus obtained a different P-isomer (Scheme 55).

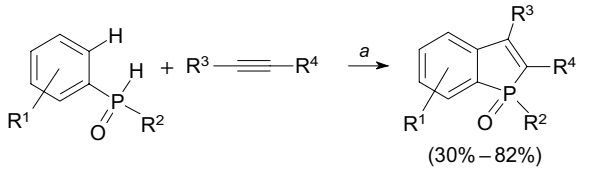
Xiao and co-workers[148] accomplished the cascade cyclization involving 2-propynylphenol with a copper complex as a catalyst, which resulted in the formation of 4-phosphorylated 2*H*-chromene (Scheme 56).

Scheme 51



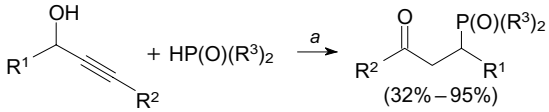
(*a*) $Cu(acac)_2$, $FeCl_3$, Et_3N, DMSO, O_2, 70 °C;
(*b*) $CuSO_4 \cdot 5H_2O$ (10 mol.%), TBHP, $NH_3 \cdot H_2O$, MeCN, Air;
TBHP is *tert*-butyl hydroperoxide

Scheme 52



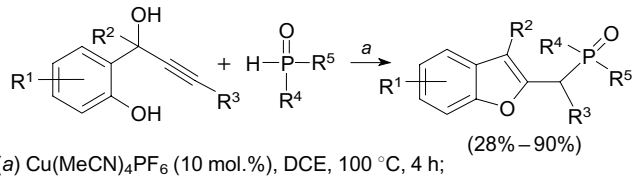
(*a*) $CuSO_4 \cdot 5H_2O$ (2 mol.%), TBHP, $NH_3 \cdot H_2O$, MeCN, 60 °C

Scheme 53



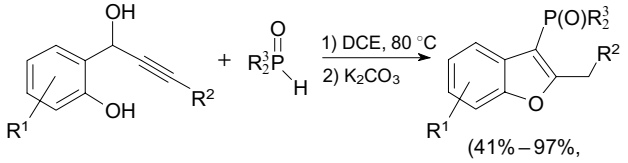
(*a*) $Zn(OTf)_2$ (40 mol.%), $Ph_2P(O)OH$ (20 mol.%), PhCl, 100 °C, 4 h, Ar;
R^1 = Ar; R^2 = Ar, Alk; R^3 = p-CH_3-C_6H_4, p-Cl-C_6H_4, OEt

Scheme 54

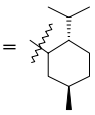


(*a*) $Cu(MeCN)_4PF_6$ (10 mol.%), DCE, 100 °C, 4 h;
R^1 = H, 4-Me, 4-Cl, 6-OMe, 4-F, 2,4-Br_2, *etc.*;
R^2 = H, Ph, C_2H_5, CH═CHPh; R^3 = H, Alk, Ar; R^4 = R^5 = Ar

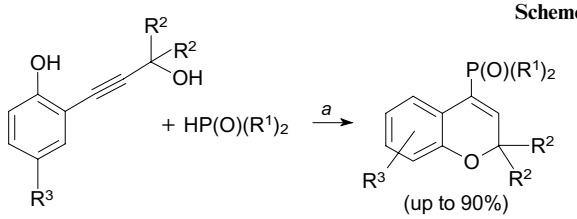
Scheme 55



R^1 = H, Alk, Hal, NO_2; R^2 = R^3 = Ph;

R^2 = Ph, R^3 = Men; Men = 

Scheme 56



(*a*) Cu(OTf)Ph (20 mol.%), DCE, 100 °C, 4 h, Ar

Phosphonylation accompanied by cyclization was observed for many molecular systems such as diynes, dienes, enynes and propargyl derivatives. For instance, Tanaka and co-workers [149] studied the palladium-catalyzed reaction of 1,6-diynes with $H(O)PR^1R^2$. More complex tricyclic structures were obtained by oxidative phosphonylation of 1,6-enynes catalyzed by a silver salt.[150]

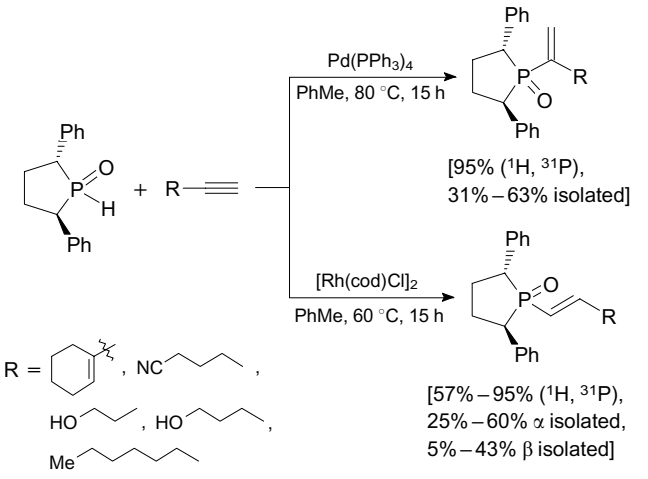
The phosphorylation reactions of propargyl derivatives can be accompanied by isomerization to allene [151, 152] or diene structures.[153, 154]

The isomerization and epoxide ring opening to give allene was observed in the Ag^I-catalyzed phosphorylation of propargyl epoxides studied by Han and co-workers.[152]

As noted above, we did not set ourselves the task to consider the mechanism of addition of the H–P or HP(O) bonds to acetylenes or other unsaturated compounds. It is quite evident that in this case, the initial organophosphorus compounds can form some intermediates with the catalysts, while the products should behave as ligands; this brings more complexity to the intricate pattern of catalysis of addition reactions. We would only like to note that Han and co-workers [155] studied many intermediates and made attempts to find out whether they are involved in the catalytic cycle. However, each particular case requires special investigation.

To conclude this Section, consider an interesting study dealing with the palladium- and rhodium-catalyzed addition of *trans*-2,5-diphenylphospholene to terminal alkynes (aromatic and aliphatic).[156] This reaction is regioselective for both catalysts. In the case of Pd catalyst, the Markovnikov product (α-isomer) is formed, while in the case of Rh catalyst, the *E*-anti-Markovnikov adduct is produced with complete selectivity (Scheme 57).

Scheme 57



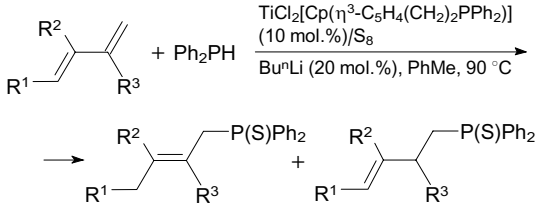
It is of interest that $Pd(OAc)_2/\mathbf{L}^9$ and $Pd_2(dba)_3/\mathbf{L}^9$ proved to be inactive under these conditions.

2.3. Allenes. Dienes

The addition of the H–P and H–P(O) bonds to allenes and dienes has been studied for a moderate number of examples.

The addition of diphenylphosphine to 1,3-dienes was performed using titanium complexes as catalysts.[157] The authors succeeded in conducting the reaction after an alkyl substituent containing a phosphine group was introduced into the Cp ligand. The 1,4-addition products were formed in high yields and with high selectivity (Scheme 58).

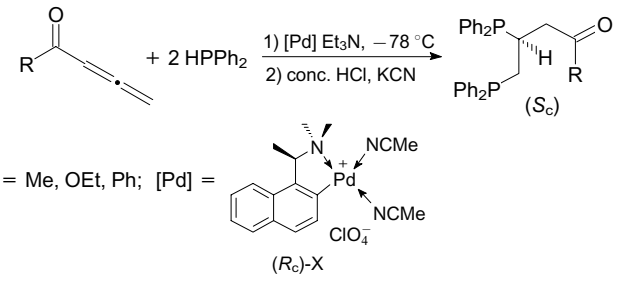
Scheme 58



Starting compound	Product	Yield (%)	Isomer ratio
	P(S)Ph2	96	97 : 3
	P(S)Ph2	91	> 98 : 2
	P(S)Ph2	97	> 98 : 2
	P(S)Ph2	89	> 98 : 2

The reaction of $HPPh_2$ with ketoallene promoted by chiral cyclopalladate [(R_c)-**X**] used in a stoichiometric amount includes the addition of two phosphine molecules and affords chiral diphosphine (Scheme 59).[158]

Scheme 59

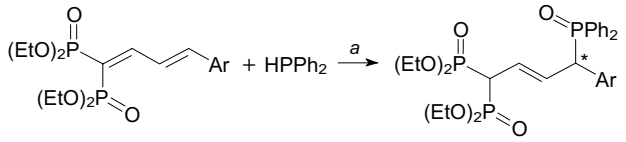


The diphenylphosphine addition to activated diene can be catalyzed by chiral palladium complex **VI** and gives 1,4-addition products in high yields and with high enantioselectivity (Scheme 60).[159]

The hydrophosphorylation of isoprene with diethyl phosphite was reported by Hirao *et al.*[160] back in 1982. The $Pd(PPh_3)_4/\mathbf{L}^9$- catalyzed reaction conducted at 150 °C proceeded as 1,4-addition, but the product yield was only 10%.

The same result was obtained by Tanaka and co-workers.[161, 162] However, the use of more reactive pinacolyl

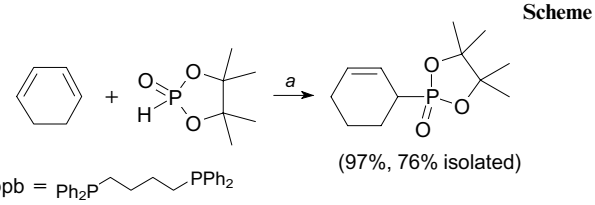
Scheme 60



(up to 96% yield, 91% *ee*)

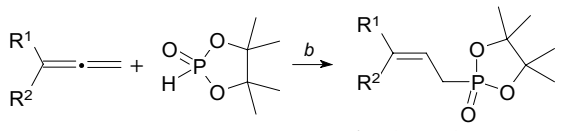
(*a*) 1) (*S*,*S*)-[Pd] (**VI**) (2 mol.%), MTBE, 0 °C, 2) H_2O_2;
MTBE is methyl *tert*-butyl ether

Scheme 61



(97%, 76% isolated)

dppb = Ph_2P–$(CH_2)_4$–PPh_2



(61%–92%,
R^1 = H: *E*/*Z* up to 99 : 1)

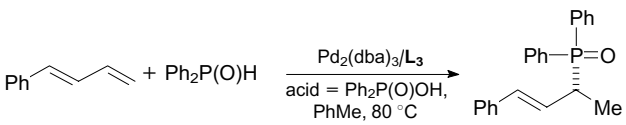
(*a*) $PdMe_2$dppb (5 mol.%), 1,4-dioxane, 100 °C, 12 h;
(*b*) $PdMe_2$dppf or $PdMe_2$dppb (3 mol.%–5 mol.%), 1,4-dioxane,
80–100 °C, 1–18 h; R^1 = H, Ph, Me, $-(CH_2)_5-$;
R^2 = Bu^n, Bu^t, Cy, Ph, Me

derivative allowed the authors to successfully carry out this reaction both with a cyclic diene and with terminal allenes (Scheme 61).

The enantioselective hydrophosphorylation of terminal 1,3-dienes by treatment with $R_2P(O)H$ was carried out for a wide range of substrates, which gave products in good to high yields with high regio- and enantioselectivity.[163] Taking into account the results of Tanaka and Han,[161] the authors chose the most active $\mathbf{L}^3$ ligand among the Josiphos family (Scheme 62).

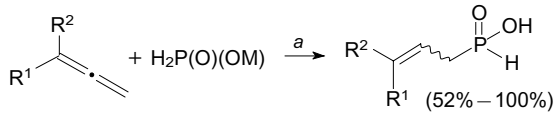
It was shown that in the presence of palladium complex, phosphinic acids (salts) add to allenes at the unsubstituted terminal position (anti-Markovnikov isomer) to give allyl derivatives (Scheme 63).[164, 165]

Scheme 62



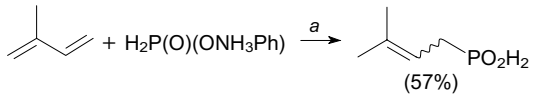
(91%, 95 : 5 *er*)

Scheme 63



(*a*) $Pd_2(dba)_3$, $\mathbf{L}^{11}$ (1 mol.%), MeCN, reflux or DMF (85 °C),
8–14 h, then acid treatment; R^1 = Ph, Cy; R^2 = H;
$R^1 + R^2 = -(CH_2)_5-$; M = H, $PhNH_3$

Scheme 64



(57%)

(*a*) $Pd_2(dba)_3$, $\mathbf{L}^{11}$ (1 mol.%), DMF (85 °C), then acid treatment

The reaction of isoprene with the same catalyst occurs as non-stereoselective 1,4-addition (Scheme 64).

3. Hydrothiolation (hydroselenation)

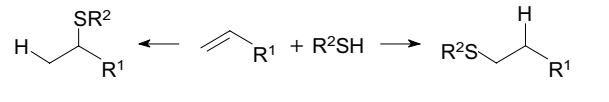
Compounds with the carbon–sulfur bond are present among natural products;[166] they find use in medicine [167–169] and are often encountered as intermediates in organic synthesis,[170] in particular, for the preparation of heterocyclic compounds.[171–174]

Owing to high efficiency of hydrothiolation reactions and ready availability of the starting compounds, these reactions have been widely used in recent decades for the fabrication of bioconjugates and new materials, including the synthesis of polymers and surface modification.[175–178]

Since sulfur can exist in different valence states, the chemistry of organic derivatives of sulfur is highly diverse.[179] However, a special place in this diversity belongs to thioethers (sulfides), which are used to prepare sulfoxides and sulfonium derivatives. Sulfides, including vinyl sulfides, can be synthesized by various routes and, in view of the ability of sulfur to form cationic, anionic and radical intermediates, these reactions can follow different mechanisms: electrophilic, radical and nucleophilic.[180]

It is clear that the addition of thiols to the alkene double bond is the primary method for the synthesis of aliphatic sulfides. The metal-free radical addition [181–184] and base-catalyzed nucleophilic addition [185] usually give the anti-Markovnikov products, while the electrophilic addition catalyzed by Brønsted acids [186, 187] or Lewis acids [188] affords the Markovnikov isomer. The metal-catalyzed reactions of thiols with alkenes have not been adequately studied and, in most cases, they result in the formation of anti-Markovnikov isomers.[178] The organocatalyzed thiolation reactions of alkenes with electron-withdrawing groups have been thoroughly studied and their regioselectivity is easily predictable (Scheme 65).[189]

Scheme 65

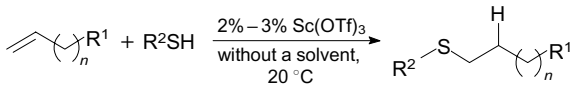


Markovnikov isomer — anti-Markovnikov isomer

The addition of aromatic and aliphatic thiols to vinylarenes and functionalized alkenes catalyzed by the Lewis acid $Sc(OTf)_3$ proceeds without a solvent at room temperature to give the anti-Markovnikov isomer in high yield and with high selectivity (Scheme 66).[190]

Under the same conditions, the reaction of RSH with alkenes catalyzed by $CeCl_3$ also yields the anti-Markovnikov product in high yield (78%–97%).[191] The same outcome is obtained upon the addition of thiols to electron-

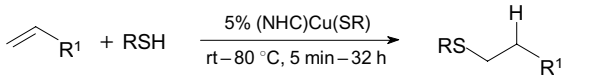
Scheme 66



(up to 100% selectivity, 80%–97% yield)

R^2 = Alk, Ar; R^1 = Alk, Ar, TMS, Hal, OH, OR″, OC(O)R″; n = 0–8

Scheme 67



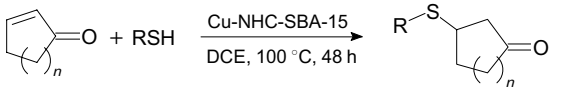
(> 95% conversion)

R = Ph, CH_2Ph;
R^1 = CN, C(O)Me, C(O)OMe, *p*-$NO_2C_6H_4$, *etc.*;
NHC is *N*-heterocyclic carbene ligand

deficient alkenes in the presence of the thiolate copper complex (NHC)Cu(SR) (Scheme 67).[192, 193]

When a copper carbene complex immobilized on SBA-15 was used as the catalyst in the reaction of thiols with α,β-unsaturated cyclohexenone and cyclopentenone, a number of anti-Markovnikov products were obtained. In the case of aromatic thiols, the yields were high (97%–99%), while for aliphatic thiols, the yields ranged from 61% to 69% (Scheme 68).[194]

Scheme 68

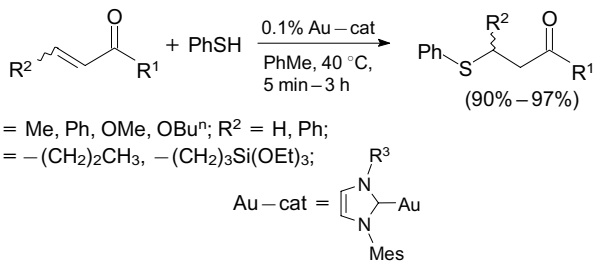


R = Ar, CH_2Ph, n-C_5H_{11}; n = 1, 2

R = Ar (97%–99%), CH_2Ph, n-C_5H_{11} (61%–69%)

The addition of thiophenol to α,β-unsaturated compounds is also catalyzed by the cationic gold carbene complex.[195] The reaction in toluene at 40 °C proceeds regioselectively giving the anti-Markovnikov product in up to 97% yield (Scheme 69).

Scheme 69



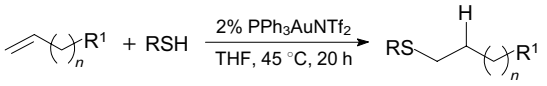
(90%–97%)

R^1 = Me, Ph, OMe, OBu^n; R^2 = H, Ph;
R^3 = $-(CH_2)_2CH_3$, $-(CH_2)_3Si(OEt)_3$;

Ogawa and co-workers[196] were able to carry out the addition of thiols to unactivated alkenes using another cationic gold complex, PPh_3AuNTf_2. The reaction was also regioselective and gave only the linear isomer (Scheme 70).

The magnetic Fe_3O_4 nanoparticles served as the heterogeneous recyclable catalyst in the reaction of thiols with

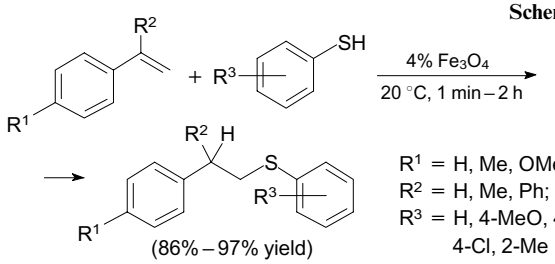
Scheme 70



(31%–92% yield)

R = Ar, CH_2Ph, Cy, *n*-$C_{12}H_{25}$;
R^1 = Alk, Ph, OPh, CN, OH, Cl; n = 1–7

Scheme 71



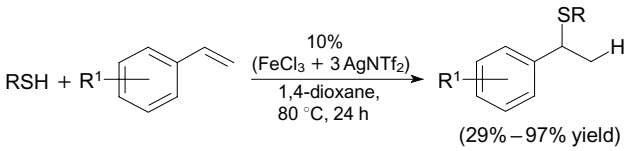
(86%–97% yield)

R^1 = H, Me, OMe, Cl;
R^2 = H, Me, Ph;
R^3 = H, 4-MeO, 4-Me, 4-Cl, 2-Me

styrenes; this gave the anti-Markovnikov products in high yields (Scheme 71).[197]

The predominant formation of the Markovnikov isomer in the reactions of thiols with alkenes is quite a rare case and is mainly observed for activated alkenes such as vinylarenes. Corma and co-workers,[198] who carried out the reactions of styrenes with thiols catalyzed by iron(III) salts varying the nature of the anion, obtained the Markovnikov isomers as the major products (Scheme 72).

Scheme 72



(29%–97% yield)

R = Ar, $ArCH_2$, $Ar(CH_2)_2$, Cy, Alk, PhC(O)
R^1 = 4-Cl, 4-F, 4-CF_3, 4-OMe, 4-PhC≡C, 4-CO_2H, 3-Me, 3-NO_2

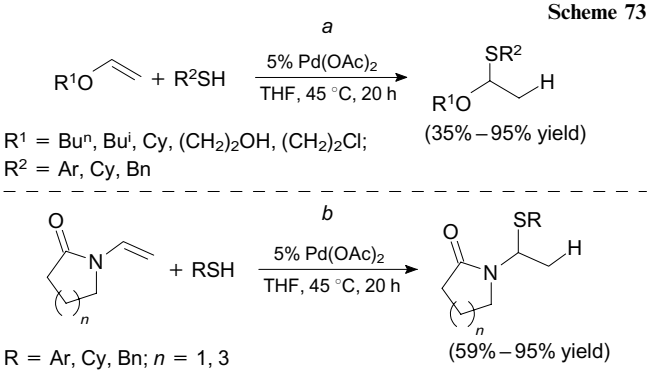
Ogawa and Tamai[199] found that the addition of aromatic thiols to alkenes containing heteroatoms (O or N) catalyzed by $Pd(OAc)_2$ gave the Markovnikov product in high yield and with high regioselectivity. In the case of aliphatic thiols, the yields sharply decreased (Scheme 73 *a*,*b*). In 2016, Ogawa and co-workers[200] performed palladium-catalyzed selenation of N-vinyllactams, which afforded the Markovnikov product — N,Se-acetal (Scheme 73 *c*,*d*).

The reactions of heteroaromatic thiols with styrenes catalyzed simultaneously by $Pd(OAc)_2$ and $Cu(OTf)_2$ gives the Markovnikov isomer (Scheme 74).[201]

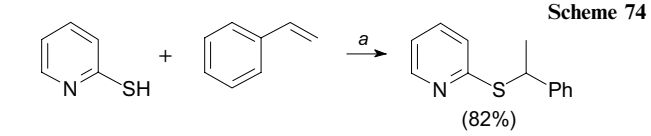
Hull and co-workers[202] studied the hydrothiolation of allylamines catalyzed by rhodium complexes and showed that, depending on the nature of the ligand, either Markovnikov or anti-Markovnikov isomer is formed. In other words, ligand-controlled divergent regioselectivity is observed (Scheme 75).

Wang and Bian and co-workers[203] carried out enantioselective selenation of heterobicyclic alkenes with diselenides catalyzed by chiral rhodium complexes. Due to the presence of diphenylphosphine oxide in the reaction mixture, the required reagent R^1SeH is formed *in situ*. The reaction is highly selective and gives high yields of products (Scheme 76).

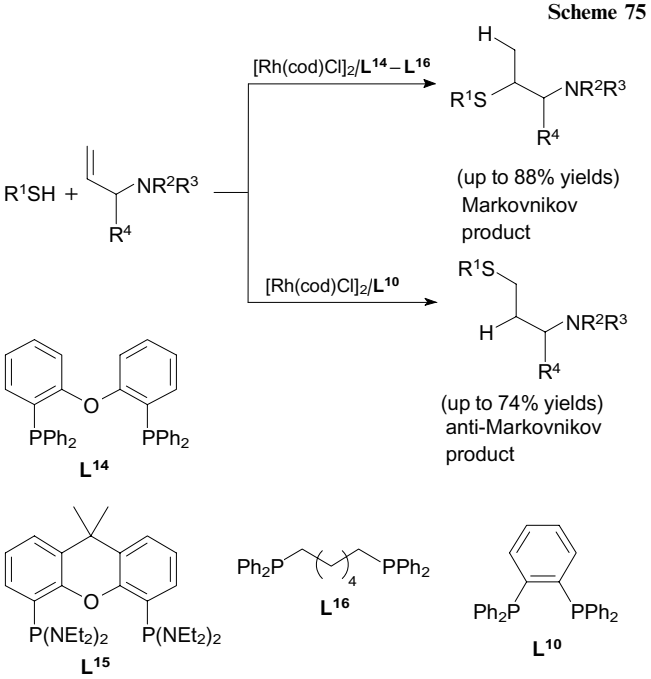
Scheme 73



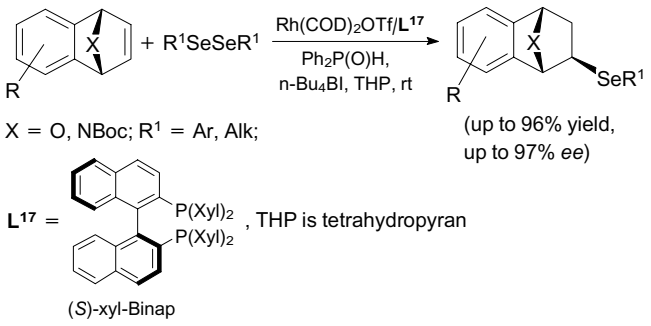
Scheme 74



Scheme 75

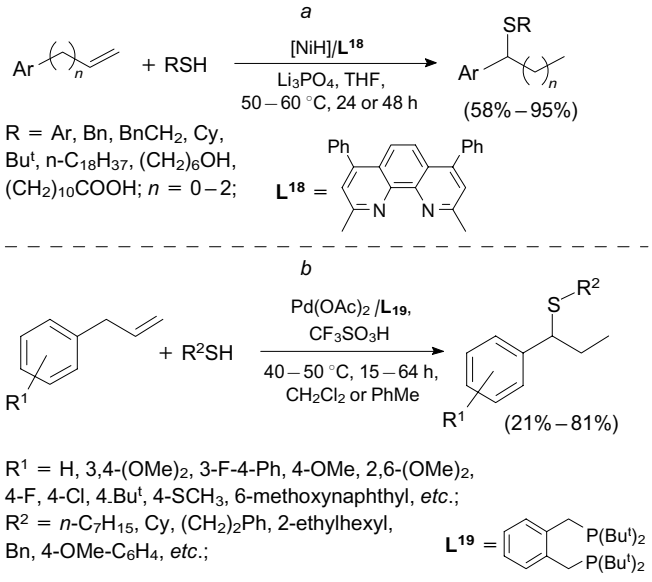


Scheme 76



It was shown that hydrothiolation of the alkene double bond remote from the aryl group can be catalyzed by nickel hydride ($NiI_2 + HBpin$). This is accompanied by migration of the double bond, giving α-substituted product in high yield and with high selectivity (Scheme 77 *a*).[204] The thiolation of allylbenzenes catalyzed by $Pd(OAc)_2$ in the presence of trifluoromethasulfonic acid proceeds in a similar way, being accompanied by bond migration (Scheme 77 *b*).[205]

Scheme 77

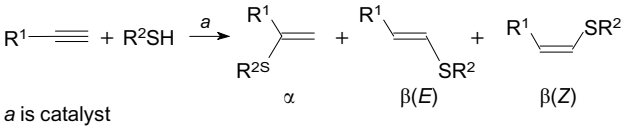


The pioneering studies of metal-catalyzed reactions of thiols with alkynes were published in the 1990s by Ogawa and Sonoda.[206–208] Certainly, these reactions are less significant than the hydroformylation, hydrosilylation and hydroboration reactions considered above, but they are of considerable interest as methods for the preparation of vinyl sulfides and selenides and as excellent objects for studying the mechanism of addition reactions to unsaturated bonds; therefore, studies of these reactions are now in progress.[171,173,177,209–213]

The reactions of thiols with terminal alkynes in the presence of metal-containing catalysts normally give mixtures of α (Markovnikov) and β (anti-Markovnikov) products, with the latter usually predominating and comprising *E*-and *Z*-isomers (Scheme 78).

The mechanism of thiolation reaction taking place in water, which results in the anti-Markovnikov product with different *E* and *Z* stereoisomer ratios in the case of terminal

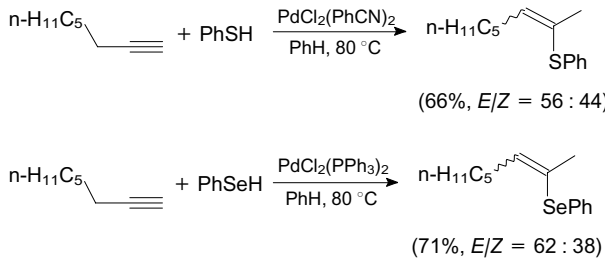
Scheme 78



alkynes, is still unclear. An ionic mechanism was proposed, according to which water molecules increase the thiol nucleophilicity.[214] However, the reaction mechanism of this radical cannot be ruled out either.[215]

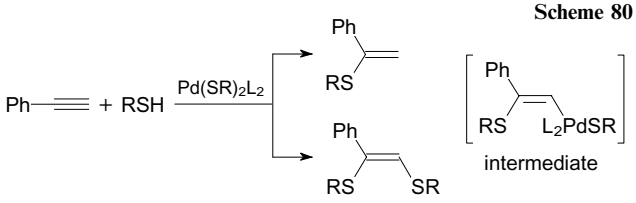
The formation of Markovnikov isomer in the reaction of thiols with aliphatic alkynes is additionally complicated by isomerization of the double bond in the product. Ogawa and co-workers[216,217] demonstrated that the palladium-catalyzed reactions of PhSH and PhSeH afford mainly Markovnikov products, but with double bond isomerization and formation of the *E*- and *Z*-isomers (Scheme 79).

Scheme 79



Depending on the type of the catalyst, the reaction can follow two mechanisms, in which either $M(SR)_2$ or the H–M–SR hydride complex serves as the catalytically active species. In the former case, alkene is inserted into the M–SR bond, while in the latter case, one more option — insertion into the M–H bond — is possible, which may change the regioselectivity of the reaction. Later it was shown that the reactions of alkynes with RSH catalyzed by the PdX_2L_2 complexes lead to unstable palladium hydride, which disproportionates to give $Pd(SR)_2L_2$. In the presence of this complex, two competing reactions of thiols with phenylacetylene take place, resulting in mono- and dithiolation products.[216,218,219] Both products arise from the same intermediate, one as a result of protonolysis and the other as a result of reductive elimination. The latter process is favoured by the presence of ligands, especially phosphines (Scheme 80).[220]

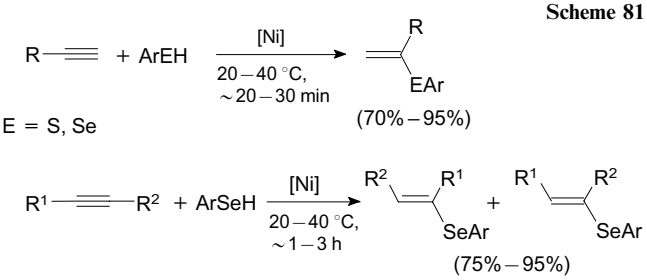
Scheme 80



Conduction of the reaction without a ligand affords the insoluble polymer $[Pd(SR)_2]_n$, which catalyzes only the reaction that gives rise to α-thiolated alkene (Markovnikov isomer) in a virtually quantitative yield.[221] The reactions with RSeH proceed in a similar way.[218]

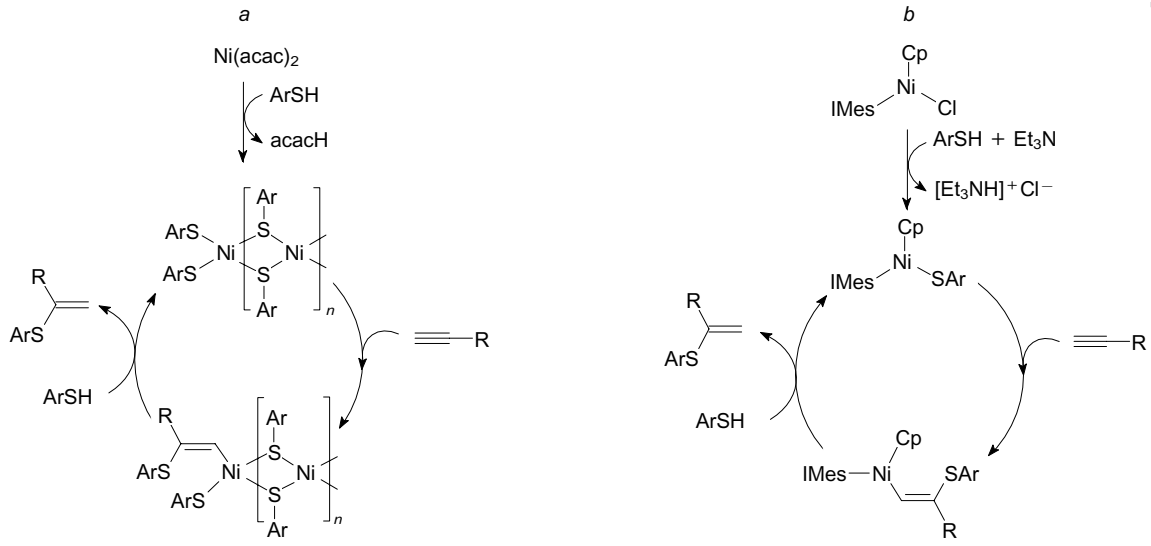
It was found that the nickel complexes $[Ni(SR)_2]_n$, prepared from $Ni(acac)_2$ are more efficient catalysts for the reactions of PhSH and PhSeH with alkynes, which are completed in a matter of minutes at room temperature.[222,223] Moreover, in the case of PhSeH, this reaction can be carried out under mild conditions also for internal alkynes (Scheme 81).[223]

Scheme 81



The mechanism of thiolation reaction catalyzed by $[Ni(SR)_2]_n$ is shown in Scheme 82 *a*. The hydrothiolation of terminal alkynes catalyzed by the nickel carbene complex

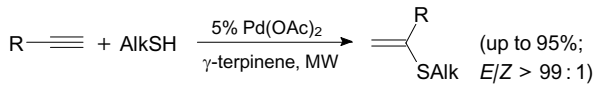
Scheme 82



was accomplished under homogeneous conditions (Scheme 82 *b*).[219]

A different picture was found for the reaction of alkynes with aliphatic thiols. In this case, Pd-based catalytic species were more efficient (Scheme 83).[221]

Scheme 83



R = Ph, Bu^n, $C(CH_3)_2OH$, $C(CH_3)OAc$, CH_2NMe_2; Alk = Cy, Bn

Elucidation of the cause for this activity demonstrated that it is related to the size and morphology of the arising nanostructured species (Fig. 1).[221, 223]

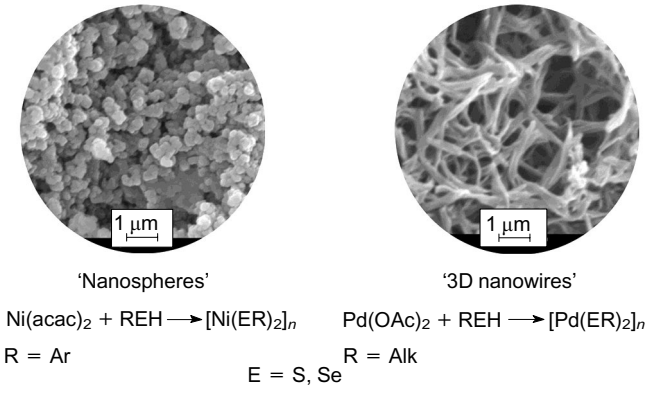
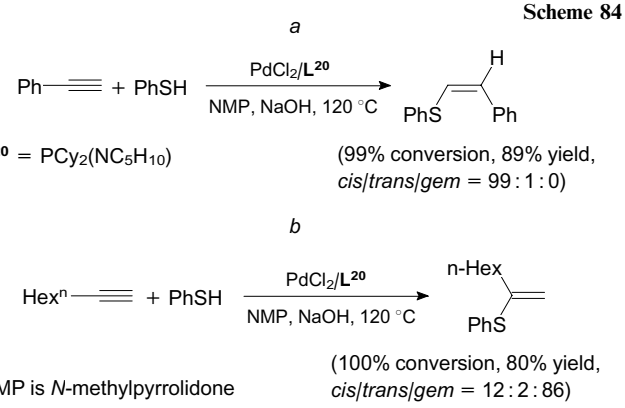
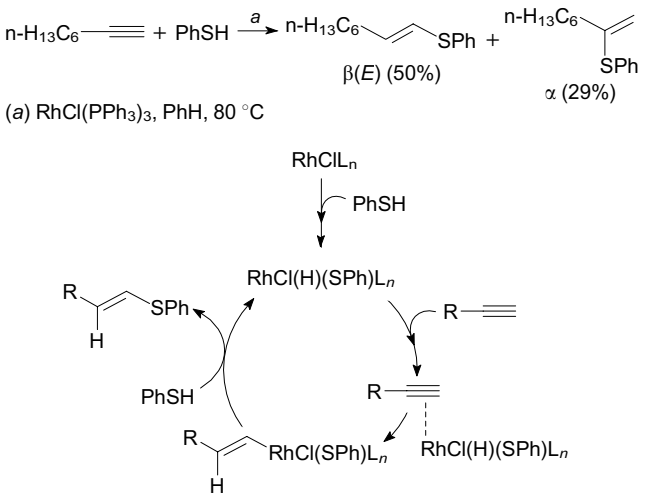


Figure 1. Nanoparticles of Ni and Pd sulfides with different morphology.

Scheme 84



Scheme 85



Ananikov and co-workers [224] found that the palladium carbene complex (IMes)Pd(Cl)(acac) without phosphine ligands can catalyze reactions of alkynes not only with primary, but also with secondary and tertiary alkanethiols to give the Markovnikov products, like in an earlier study.[221]

The reactions of thiols with aromatic and aliphatic alkynes are catalyzed in different ways by the $PdCl_2$ mixed aminophosphine complex. In the case of aromatic alkynes, the *Z*-vinyl sulfides are formed in high yields and with anti-Markovnikov selectivity.[225] In the case of aliphatic alkynes, the Markovnikov products (α-substituted vinyl sulfides) are formed less rapidly, but also in high yields, although less selectively. In the authors' opinion, nucleophilic addition takes place in the former case, and the alkyne insertion into the Pd–S bond occurs in the latter case, although other explanations are also possible (Scheme 84 *a*,*b*).

The use of Rh^I complex (Wilkinson catalyst) to catalyze the hydrothiolation of alkynes gives rise to the anti-Markovnikov isomer as the major product.[216] When the reaction is carried out in ethanol, the yield of the anti-Markovnikov product increases to 58%, while in the presence of radical inhibitors (25 °C), it is formed in 73% yield. In the reaction of phenylacetylene with thiophenol (ethanol, 40 °C), the yield of the β(*E*)-isomer is 97%. The catalytic cycle for this reaction is shown below (Scheme 85).

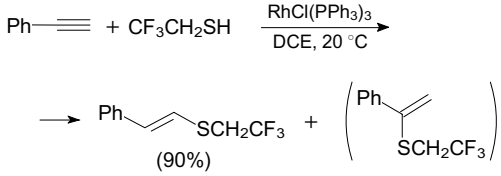
This reaction involves the rhodium hydride complex formed upon the oxidative addition of PhSH to Rh^I. The alkyne is inserted into the H–Rh bond, and the subsequent reductive elimination gives rise to the anti-Markovnikov product — β-thiolated alkene. Note that the Rh^{III} hydride–thiolate complex was previously reported by Wilkinson.[226]

The rhodium catalyst immobilized on mesoporous SBA-15, a heterogeneous analogue of the Wilkinson catalyst, showed high regioselectivity (98%–99% of the anti-Markovnikov product) and high stereoselectivity (up to 100% of the *E* isomer) and was recycled six times in the reaction of aromatic thiols with terminal alkynes.[227]

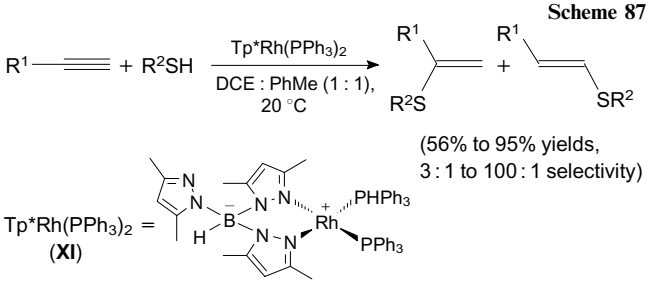
Love and co-workers [228] accomplished the hydrothiolation of alkynes with aliphatic thiols catalyzed by $RhCl(PPh_3)_3$ and thus obtained the anti-Markovnikov product with exclusive selectivity (Scheme 86).

When the cationic rhodium catalyst $Tp^*Rh(PPh_3)_2$ (**XI**) was used in this reaction, the regioselectivity was reversed, that is, the Markovnikov product was formed predominantly (or exclusively). However, the selectivity of the

Scheme 86



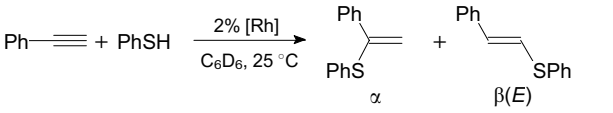
Scheme 87



reaction may vary over a broad range depending on the alkyne and the thiol (Scheme 87).[229, 230]

Castarlenas and co-wokers[231] showed that the carbene complexes Rh–NHC are also efficient catalysts for the hydrothiolation of alkynes. The use of binuclear complexes $[Rh(\mu\text{-}Cl)(IPr)(\eta^2\text{-alkene})]_2$ (**XII**) (alkene is cyclooctene, ethylene) in the reaction of thiophenol with phenylacetylene results in the predominant formation of the linear β(*E*)-isomer. The use of mononuclear complexes $RhCl(IPr)(Py)(\eta^2\text{-alkene})$ (**XIII**) induces a change in the regioselectivity, with the α isomer being formed as the predominant product. The preparation of the mononuclear complex *in situ* by adding 10 equiv. of pyridine to the binuclear complex increases the α/β(*E*) isomer ratio to 94/6 (Scheme 88).

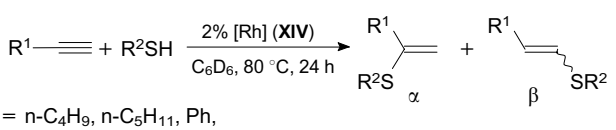
Scheme 88



	(99% conversion, selectivity
[Rh] (**XII**) = $[Rh(\mu\text{-}Cl)(IPr)(\eta^2\text{-}C_2H_4)]_2$	33 : 67
[Rh] (**XIII**) = $RhCl(IPr)(Py)(\eta^2\text{-}C_2H_4)$	89 : 11

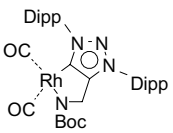
The rhodium complexes with 1,2,3-triazolyl-5-ylidene ligands containing electron-withdrawing aminoalkyl substituents were reported; the use of these complexes also results in the predominant formation of the Markovnikov isomer (Scheme 89).[232]

Scheme 89



R^1 = n-C_4H_9, n-C_5H_{11}, Ph, CH_2NH_2, CH_2NHBoc, CH_2OH, Mes, Fc; R^2 = n-C_5H_{11}, Ph;

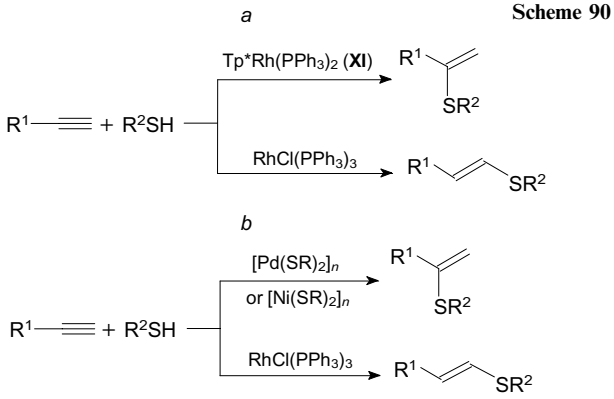
(40% – 91% conversion, 71 : 29 to > 99 : 1 selectivity)

[Rh] (**XIV**) = 

; Dipp is 2,6-diisopropylphenyl

It can be seen from the presented examples that the regiodivergence in the reactions of thiols with alkynes can be associated with both the nature of the ligands in the complexes with the same metal (electronic and steric factors) (Scheme 90 *a*) and the change in the reaction mechanism (Scheme 90 *b*).

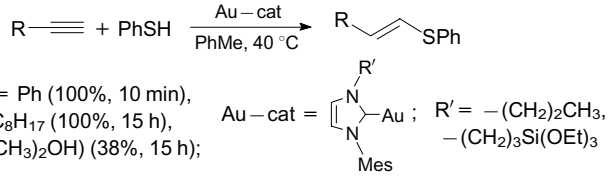
Scheme 90



The cationic gold carbene complex catalyzes the reaction of thiophenol with alkynes, which follows, like in the case of reactions with alkenes, the anti-Markovnikov pathway with a high regio- and stereoselectivity (Scheme 91).[195]

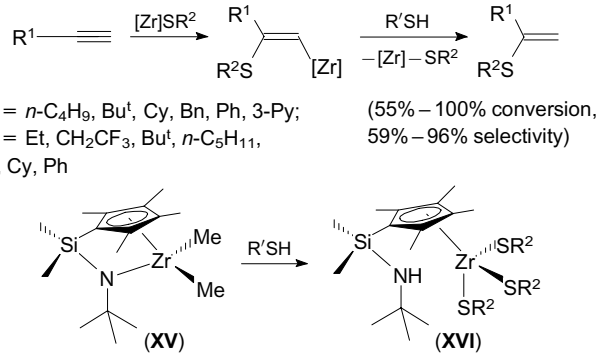
In the case of the heterogeneous grafted complex, the catalyst can be recycled three times without the loss of activity.

Scheme 91



There are examples of reactions of RSH with alkynes catalyzed by zirconium complexes, *e.g.*, complexes **XVI**, to give the Markovnikov product in high yield (up to 90%) and with high regioselectivity (up to 99%) (Scheme 92).[233]

Scheme 92



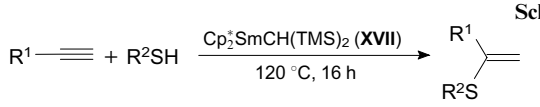
Lanthanide complexes catalyze the thiolation of alkynes in a similar way (Scheme 93).[234]

Relatively recently, it was shown that copper salts are excellent catalysts for the thiolation of alkynes to give the anti-Markovnikov product (Scheme 94).[235]

The reaction in DMF or THF gives the β(*Z*)-isomer, while in a mixture of protic solvents, the β(*E*)-isomer is formed for a variety of alkynes and thiols.

The anti-Markovnikov product was also obtained when the copper carbene complex immobilized on SBA-15 is used. The reaction of thiols with terminal alkynes carried

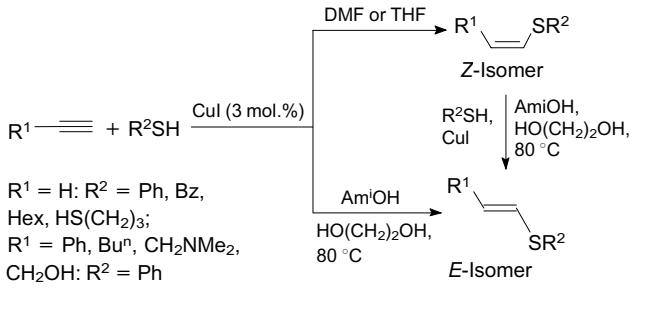
Scheme 93

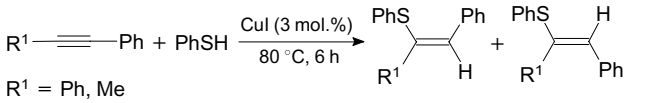


R^1 = n-C_4H_9, Cy, $CyCH_2$, Bn, 3-Py;
R^2 = Et, n-C_5H_{11}, Bn, Cy, Ph

(11%–95% conversion, 72%–99% selectivity)

Scheme 94

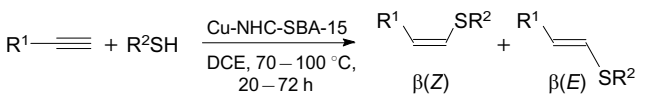




R1 = Me (90%, *Z*/*E* = 5 : 1), Ph (100%, *Z* 80%)

out in 1,2-dichloroethane at 70 or 100 °C afforded a mixture of *Z*- and *E*-isomers, *Z*-isomer being the major product.[194] It was shown that in the reaction of phenylacetylene with thiophenol, the catalyst can be recycled six times without significant loss of activity and selectivity (Scheme 95).

Scheme 95



R^1 = Ar, n-C_5H_{11}, n-$C_{10}H_{21}$, $(CH_2)_2OH$, $(CH_2)_2Cl$;
R^2 = Ar, $PhCH_2$, n-C_6H_{13}, Cy

(51%–99% yields, 80 : 20 to 93 : 7 selectivity)

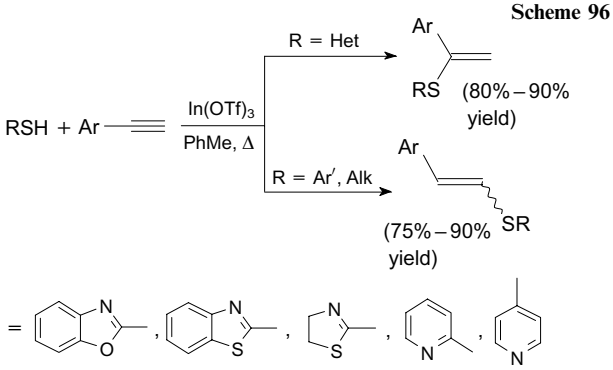
The reaction pathway is often determined by not only the nature of the catalyst, but also the thiolating agent. A very vivid example is the reaction of aromatic alkynes with thiols catalyzed by $In(OTf)_3$. In this reaction, heteroaromatic thiols are converted only to the Markovnikov products, while aromatic and aliphatic thiols give anti-Markovnikov products (Scheme 96).[236]

Huang and co-workers[201] carried out the reaction of heteroaromatic thiols with aromatic alkynes using joint catalysis by $Pd(OAc)_2$ and $Cu(OTf)_2$. In all cases, the α-isomer was formed (Scheme 97).

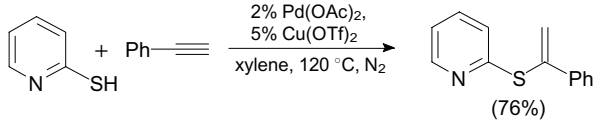
Apart from the hydrothiolation of alkenes and alkynes, metal-catalyzed reactions of thiols with allenes were studied. The reactions of RSH with allenes can, in principle, give four isomers (vinylic and allylic) (Scheme 98). These reactions provide allyl sulfides — an important class of sulfur compounds.[237, 238]

The radical reaction furnishes a mixture of β- and γ-isomers. Palladium catalysis of the reaction of alkyl-substituted allenes with thiophenol results mainly in the

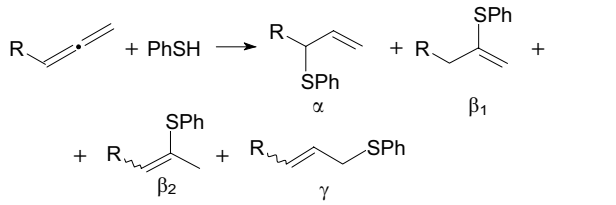
Scheme 96



Scheme 97

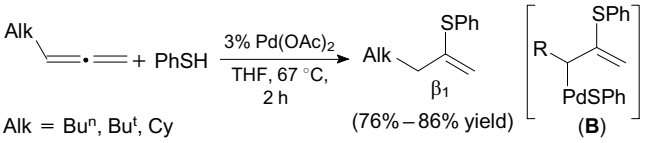


Scheme 98

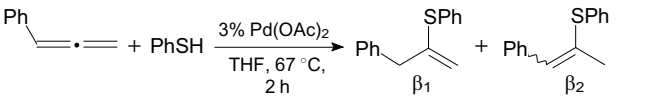


formation of vinylic β_1-isomer, that is, the reaction involves the formation of intermediate **B**.[239] The reaction of phenyl-substituted allene produces a mixture of β_1- and β_2-isomers, with the latter being the major product and the conversion being moderate (Scheme 99).

Scheme 99



Alk = Bu^n, Bu^t, Cy

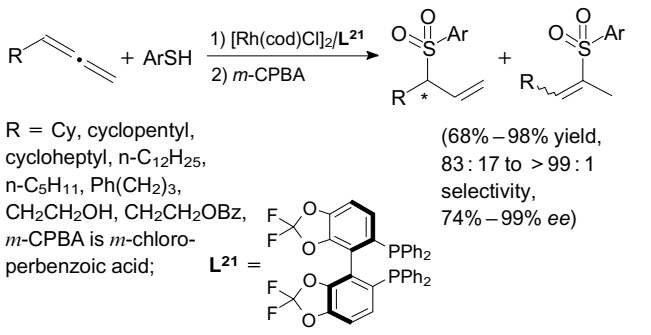


(8% yield) (36% yield, *E*/*Z* = 50 : 50)

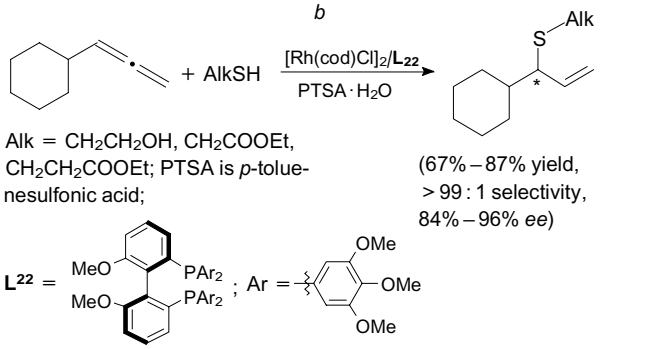
The asymmetric addition of thiols to the terminal allenes catalyzed by chiral rhodium complexes is highly regio- and enantioselective and affords α-allyl sulfides.[240] Aryl-substituted α-allyl sulfides are then oxidized to chiral sulfones to prevent the double bond isomerization, which is typical of aryl substituents (Scheme 100 *a*,*b*). For alkyl substituents, no isomerization takes place (Scheme 100 *b*). The ligand **L**[21] proved to be the chiral ligand of choice for the reaction of PhSH with allene (for R^1 = Cy). The yield of thioether was 92%, while the selectivity was >99% and *ee* was 92%. In the case of aliphatic thiols, the best result was attained for

Scheme 100

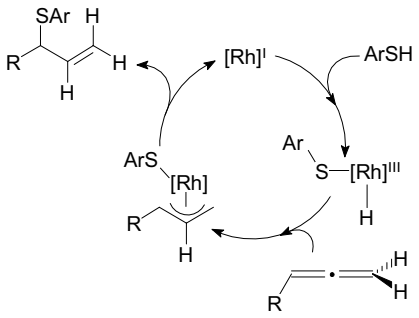
a



b



c



L[22]. In the reaction with 2-mercaptoethanol, the enantioselectivity reached 96%. A mechanism proposed for this reaction includes the oxidative addition of thiol to the rhodium complex ion, insertion of the allene into the Rh–H bond to give the rhodium allyl complex and reductive elimination (Scheme 100 *c*).

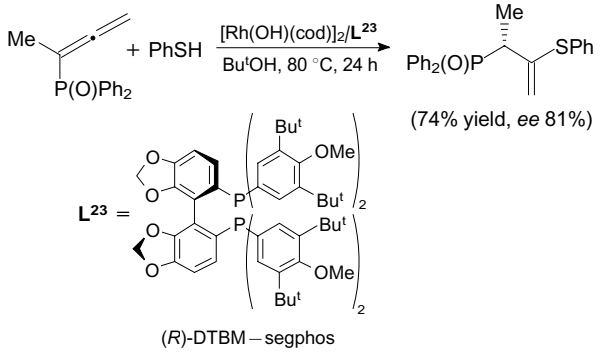
The same authors investigated the reaction with 1,3-disubstituted allenes and found that *Z*-isomer is formed as the major product.[241]

The asymmetric Rh-catalyzed thiolation of 1-methyl-1-diphenylphosphorylallene with PhSH also involves the internal carbon–carbon bond and affords the β_1-isomer (Scheme 101).[242]

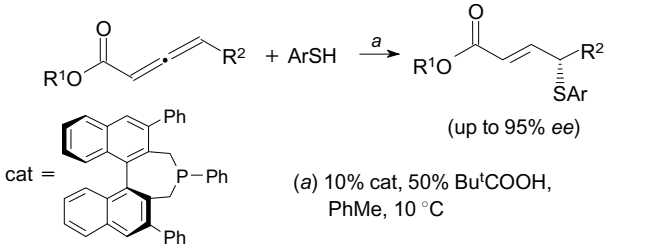
Fu and co-workers[243] accomplished the addition of arylthiols to activated 1,3-disubstituted allenes with high enantioselectivity using a chiral phosphine as the catalyst (Scheme 102).

The reactions of thiols with allenes and 1,3-dienes are also catalyzed by gold salts and complexes. Hydrothiolation of aromatic allenes with aromatic thiols catalyzed by 5 mol.% $AuBr_3$ yields dithioketal as the double addition product (Scheme 103).[244] The use of 1 mol.% $AuBr_3$ leads to a mixture of *E*- and *Z*-alkenes.

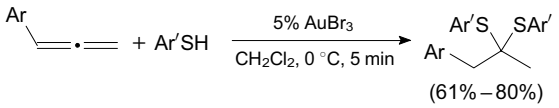
Scheme 101



Scheme 102

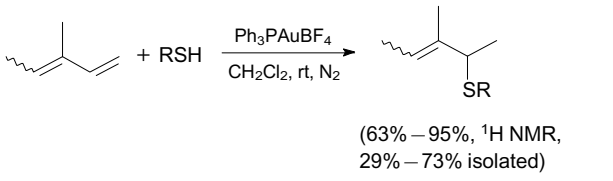


Scheme 103



The Markovnikov selectivity and high product yields were found for the reaction of 1,3-diene with thiols catalyzed by the cationic Au^I complex (Scheme 104).[245]

Scheme 104

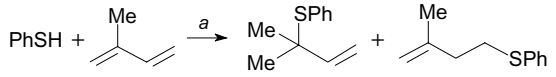


The use of rhodium complexes in the reactions of thiophenol with 1,3-dienes may give either 1,2-Markovnikov or 3,4-anti-Markovnikov product, depending on the anion present in the complex (Scheme 105).[246]

Thus, the data described in the literature provide the conclusion that the regio- and stereoselectivity of the metal-catalyzed hydrothiolation of compounds with unsaturated bonds may depend on the types of the metal, the ligand and the counter-ion that form the complex and on the natures of the thiolating agent and the unsaturated substrate.

Interesting results were obtained in the thiolation reaction of 1,1-aryl-1,3-diene catalyzed by Lewis acids [catalysts: $B(C_6F_5)_3$ and $BF_3 \cdot Et_2O$].[247] Owing to the formation of a boron complex with thiol, the latter becomes capable of protonating the diene, and the reaction follows the Markovnikov rule, giving rise to the Markovnikov isomer (Scheme 106).

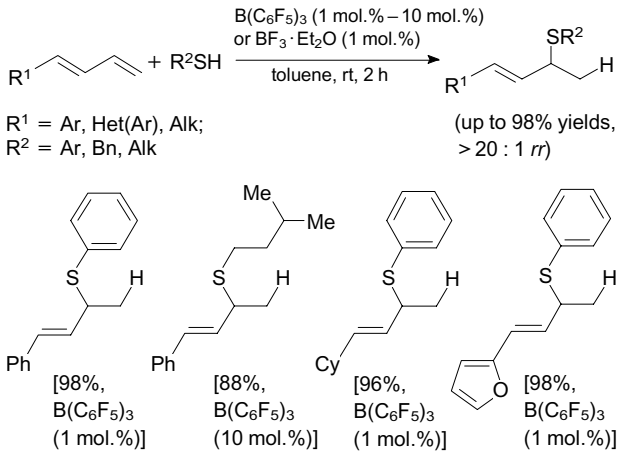
Scheme 105



(*a*) 5% [Rh], 5% **L**[11], DCE, 30 °C

[Rh] = $Rh(cod)_2SbF_6$ (83%, > 20 : 1), $[Rh(cod)Cl]_2$ (74%, > 20 : 1)

Scheme 106



R^1 = Ar, Het(Ar), Alk;
R^2 = Ar, Bn, Alk

(up to 98% yields, > 20 : 1 *rr*)

[98%, $B(C_6F_5)_3$ (1 mol.%)] [88%, $B(C_6F_5)_3$ (10 mol.%)] [96%, $B(C_6F_5)_3$ (1 mol.%)] [98%, $B(C_6F_5)_3$ (1 mol.%)]

The regioselectivity of the 4,3-addition to substituted 1,3-dienes reaches > 20 : 1.

4. Conclusion

The review addresses reactions of various organophosphorus compounds with P–H bonds and reactions of aromatic and aliphatic thiols with unsaturated hydrocarbons (alkenes, alkynes, dienes and allenes). Compounds with the P–H and S–H bonds are prone to radical addition reactions, since they easily form phosphorus- and sulfur-centred radicals. Their reactions can also be catalyzed by bases or by Lewis and Brønsted acids. However, the mechanisms inherent in these reactions dictate the formation of one isomer; the radical and base-catalyzed reactions afford the anti-Markovnikov product (the reactions with alkynes face the stereoselectivity problem). The use of transition metal salts and complexes as catalysts increases the activity, ensures milder conditions for the reactions and decreases the amount of undesirable products. Also, what is most important, this type of catalysis allows the selective preparation of either of the isomers, *i.e.*, it is possible to perform regiodivergent reactions. This fact is especially important, because not only the anti-Markovnikov, but also Markovnikov isomer is needed for both fundamental research and industrial purposes. Moreover, the anti-Markovnikov isomer is required only stereoselectively in either *E*- or *Z*-configuration, while the Markovnikov isomer is required in the enantiomerically pure state. Certainly, this sophisticated and interesting field needs further development and elaboration of theories and concepts with a predictive power and, moreover, the design of cheaper catalysts.

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