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

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The review presents state-of-the-art data on the influence of catalysts (mainly transition metal complexes) on the regioselectivity of a number of reactions. The most important addition reactions to unsaturated bonds are considered, in particular, hydroformylation, hydrosilylation, hydroboration and hydroxy-, alkoxy- and aminocarbonylation, which give predominantly one product. Particular attention is given to reactions with divergent regioselectivity. The reaction conditions, the structures of metal complexes and the ligands involved are indicated and, in some cases, the reaction mechanism is discussed. Examples of industrial processes using homogeneous catalysis are given.
The bibliography includes 203 references.

Dedicated to the memory of V.V.Markovnikov.

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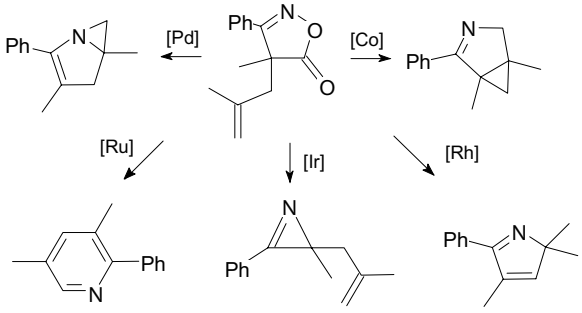
1. Introduction

The resource and nature conservation issues came to the forefront in the 21st century and the notions 'green chemistry' and 'sustainable development' became crucial factors determining the research trends in chemistry. Certainly, there are reactions that cannot proceed without waste even if the yield is 100% — in particular, this refers to substitution reactions. However, some transformations such as addition to unsaturated bonds could theoretically proceed without by-products. These reactions can, in principle, have 100% atom economy. However, it has been known since Markovnikov's time that the addition to multiple bonds usually gives different isomers, out of which only one is needed; therefore, it turns out that even a 100% atom economy does not ensure 'zero waste' for the reaction and, hence, for the whole process. It is Vladimir Vasil'evich Markovnikov, a great Russian scientist, who introduced the concept of isomerism and, simultaneously, a highly important notion of modern chemistry — reaction selectivity. Without the ability to selectively perform chemical reactions, one would never solve the environmental and economic challenges of chemical science. Generally, chemo-, regio-, stereo- and enantioselectivity are distinguished. In each particular case, for obtaining the desired outcome, it is necessary to find out what factors control the selectivity. In recent years, an important role for solving this problem has been played by catalysis, especially catalysis by transition metal complexes. The use of catalytic processes affects not only the reaction rate, but also the mere possibility for the reaction to proceed; catalysis often determines the reaction selectivity. Of special interest is divergent selectivity, which means that the reaction pathway can be diverged by varying the nature of the catalyst (metal or ligand), with the substrate being the same.

An unusual example of divergent catalytic transformations demonstrating the synthetic diversity of nitrogen-containing heterocyclic products that can be obtained upon variation of the nature of catalytic metal was reported by Ohe and co-workers [1] (Scheme 1).

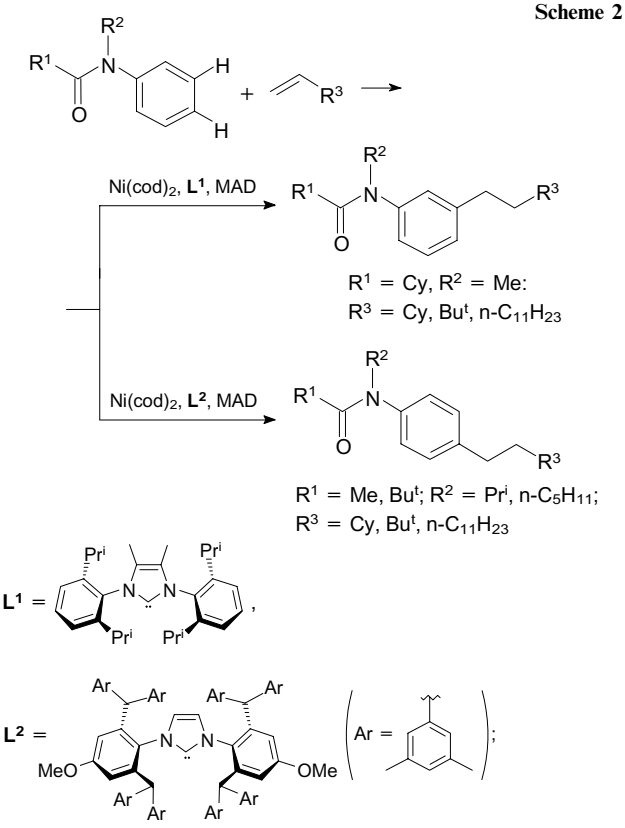
Alkylation of aromatic compounds with olefins into the *meta*- or *para*-position depending on the nature of the

Scheme 1



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Scheme 2



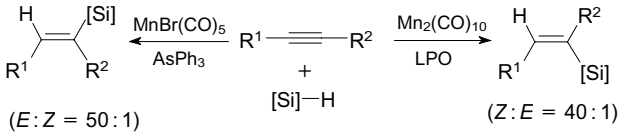
cod is cycloocta-1,5-diene, MAD is methylaluminium bis[2,6-bi-*tert*-butyl-4-methylphenoxide], Cy is cyclohexyl

carbene ligand in the Ni-Al complex ($\mathbf{L}^1$ or $\mathbf{L}^2$) is a remarkable example of divergent regioselectivity, which was also described in 2018 (Scheme 2).[2]

Hydrosilylation of internal alkynes catalyzed by manganese complexes under various conditions is an example of different *Z* – *E*-selectivity (Scheme 3).[3]

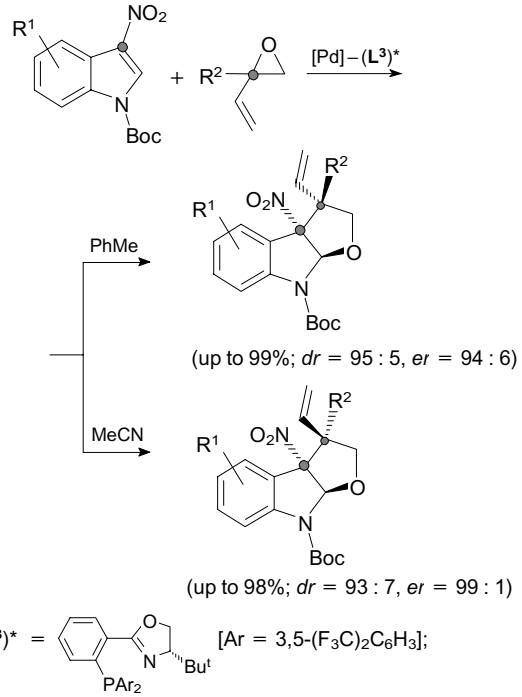
Quite a number of enantiodivergent reactions are presented in a recent review.[4] Cheng *et al.*[5] reported enantiodivergence induced by replacement of the solvent, while the chiral Pd catalyst with the ligand $\mathbf{L}^3$ remained the same (Scheme 4).

Scheme 3



R1 = Ar, Het, Alk; R2 = H, Ar, Alk; LPO is dilauryl peroxide

Scheme 4



R1 = 5-NO2, 5-Me, 5-Cl, 5-Br, 6-Me, 6-CO2Me, 6-F, 6-Cl, 6-Br, 6-CN, 7-F, *etc.*; R2 = H, Me; Boc is *tert*-butoxycarbonyl, *dr* is diastereometric ratio, *er* is enantiomeric ratio

This review, dedicated to the memory of V.V.Markovnikov, addresses the most important addition reactions to unsaturated bonds catalyzed by metal complexes and the possibility for these reactions to proceed regioselectively giving mainly or exclusively either Markovnikov or anti-Markovnikov isomers. The attention is focused on divergent regioselectivity of reactions.

The following abbreviations and designations are used in the review:

acac — acetylacetonate,

Ad — 1-adamantyl,

b and l — branched and linear isomers, respectively,

BARF — tetrakis[3,5-bis(trifluoromethyl)phenyl]borate,

BDPP — (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane,

(*R*,*R*)-BenzP* — (*R*,*R*)-(+)-1,2-bis(*tert*-butylmethylphosphino)benzene,

BINAP — 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl,

(*R*,*S*)-Binaphos — (*R*)-2-diphenylphosphino-1,1′-binaphthalen-2′-yl (*S*)-1,1′-binaphthalene-2,2′-diyl phosphite,

(*S*,*S*,*S*)-Bobphos — (11a*S*)-4,8-bis(*tert*-butyl)-1,2,10,11-tetramethyl-6-{[(2*S*,5*S*)-(2,5-diphenylphospholan-1-yl) methoxy]dibenzo[*d*,*f*][1,3,2]dioxaphosphepin},

Boc — *tert*-butoxycarbonyl,

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Translation: Z.P.Svitanko

B_2pin_2 — bis(pinacolato)diboron,
(*S*,*R*)-BPPFA — *R*-(*R**,*S**)]-1-[1-(dimethylamino)ethyl]-1′,2-bis(diphenylphosphino)ferrocene,
BTPP — biphenyl-2,2′,6,6′-tetrakis(dipyrrolylphosphoramidite),
Cat — catalyst,
Cat* — chiral catalyst,
CHIRAPHOS — 2,3-bis(diphenylphosphino)butane,
cod — cycloocta-1,5-diene,
Cp — cyclopentadienyl,
Cp* — pentamethylcyclopentadienyl,
Cy — cyclohexyl,
Dan — 2-(2,3-dihydro-1*H*-naphtho[1,8-*d*,*e*][1,3,2]diazaborinine),
dba — dibenzylideneacetone,
DFT — density functional theory,
DIOP — (+)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane,
DIPP — 2,6-diisopropylphenyl,
DMA — dimethylacetamide,
DME — 1,2-dimethoxyethane,
DPEphos — bis[(2-diphenylphosphino)phenyl] ether,
dppe — 1,2-bis(diphenylphosphino)ethane,
dppf — 1,1′-bis(diphenylphosphino)ferrocene,
dr — diastereomeric ratio,
DVDS — 1,3-divinyl-1,1,3,3-tetramethyldisiloxane,
ee — enantiomeric excess,
er — enantiomeric ratio,
Fu — furyl,
Hex^n — n-hexyl,
IAd — 1,3-bis(1-adamantyl)imidazol-2-ylidene,
IMes — 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene,
IPr — 1,3-bis(isopropyl)imidazol-2-ylidene,
Jospophos — (S_P)-1-[(*R*)-*tert*-butylphosphinoyl]-2-[(*R*)-1-(diphenylphosphino)ethyl]ferrocene,
(*R*,*R*)-Kelliphite — (*R*,*R*)-(−)-6,6′-[(1,1′-biphenyl-2,2′-diyl)]bis(4,8-di-*tert*-butyl-1,2,10,11-tetramethyl]dibenzo-[*d*,*f*][1,3,2]dioxaphosphepin,
LPD — dilauroyl peroxide,
MAD — methylaluminium bis(2,6-di-*tert*-butyl-4-methylphenoxide),
(*R*,*R*)-Me-DuPhos — (−)-1,2-bis[(2*R*,5*R*)-2,5-dimethylphospholano]benzene,
(*S*)-MeO-MOP — (*S*)-2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl,
Mes — mesityl (2,4,6-trimethylphenyl),
MOP — monodentate phosphine ligand,
Naph — α-naphthyl,
NHC — *N*-heterocyclic carbene,
NMP — *N*-methyl-2-pyrrolidone,
NORPhos — 2,3-bis(diphenylphosphino)bicyclo[2.2.1]-hept-5-ene,
NP — nanoparticle,
PCC — pyridinium chlorochromate,
(*S*,*S*)-Ph-BPE — (+)-1,2-bis[(2*S*,5*S*)-2,5-diphenylphospholano]ethane,
PHOX — phosphinooxazoline,
Phth — phthalimido,
Pg — protecting group,
PMP — *p*-methoxyphenyl,
Py — 4-pyridyl,
Pybox — 2,6-bis(oxazolin-2-yl)pyridine,
RuPhos — 2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl,
(*R*,*R*)-QuinoxP* — (*R*,*R*)-(−)-2,3-bis(*tert*-butylmethylphosphino)quinoxaline,
rr — regioselectivity ratio,
rt — room temperature,
(*R*)-SOP — (*R*)-[6-(*tert*-butylsulfinyl)-2-cyclohexyloxy-3-methoxyphenyl]diisopropylphosphine,
TADDOlPPh — (3a*R*,8a*R*)-(−)-4,4,8,8-tetrakis[3,5-di-(isopropyl)phenyl]tetrahydro-2,2-dimethyl-6-phenyl-1,3-dioxolo[4,5-*e*]dioxaphosphepin,
TBAI — tetra-n-butylammonium iodide,
TBDMS — *tert*-butyldimethylsilyl,
Tf — trifluoromethanesulfonyl (triflyl),
TFA — trifluoroacetic acid,
Th — thienyl,
TMS — trimethylsilyl,
Tol — *p*-methylphenyl (tolyl),
TOF — turnover frequency,
TON — turnover number,
TPPTS — trisodium 3-bis(3-sulfonatophenyl)phosphanylbenzenesulfonate,
TsOH — *p*-toluenesulfonic acid,
Xantphos — 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

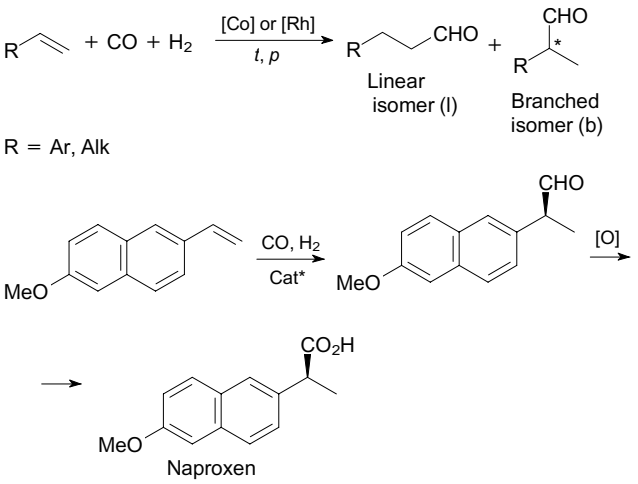
2. Hydroformylation and hydroxy(alkoxy, amino)carbonylation

Hydroformylation of olefins is a highly important reaction for the synthesis of aldehydes and alcohols and is performed in industry on an enormous scale (> 10 million tons of products per year).[6,7] A distinctive feature of these production processes is the use of homogeneous catalysis by transition metal complexes, namely, cobalt and rhodium complexes (currently, the latter predominate). Naturally, with this large scale of production, regioselectivity of reactions is a critical issue. Since linear aldehydes (anti-Markovnikov products) are required from big industry, the efforts of researchers have been directed towards increasing the ratio of the linear to branched isomers. This problem used to be solved by selecting appropriate ligands, first of all, phosphines and phosphites. Note that application of a Rh catalyst (which is markedly more expensive than the Co catalyst) sharply decreased the temperature and pressure of the process and provided a better control of regioselectivity.[8] Rhodium complexes played a special role in the synthesis of branched-chain aldehydes (Markovnikov isomers), which became in demand relatively recently for the preparation of some important pharmaceuticals (Scheme 5). It turned out that pharmaceutical industry is interested in these production processes (see, for example, the synthesis of naproxen shown in Scheme 5) and, although the production scale is smaller than that of some other hydroformylation products, this process is not less sophisticated, because the required isomer should be isolated in the enantiomerically pure state.

The regioselectivity is affected by not only the catalyst, but also the reaction conditions. Of no less importance is the nature and the structure of the olefin — whether it is terminal or internal, aliphatic or aromatic, functionalized or inactivated, mono- or 1,1-disubstituted, *etc*.

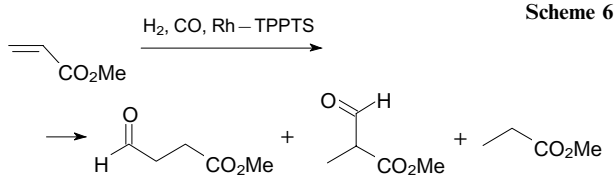
We will consider the hydroformylation of activated olefins in relation to methyl acrylate (Scheme 6). Depending on the ligand environment of rhodium, the reaction mainly affords either the Markovnikov or anti-Markovnikov isomer; the branched isomer is usually preferable.[9,10]

Scheme 5



Cat* is a chiral catalyst

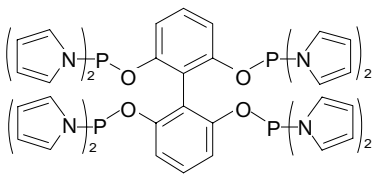
Scheme 6



TPPTS is trisodium 3-bis(3-sulfonatophenyl)phosphanylbenzenesulfonate

However, the use of the complex $Rh(acac)(CO)_2$ (acac is acetylacetonate) with a bulky donor ligand, biphenyl-2,2′,6,6′-tetrakis(dipyrrolylphosphoramidite) (BTPP, **L**[4]), results in an exceptional selectivity in favour of the linear isomer [the linear (l) to branched (b) product ratio is > 99 : 1] with high turnover number (TON) and turnover frequency (TOF) values.[11]

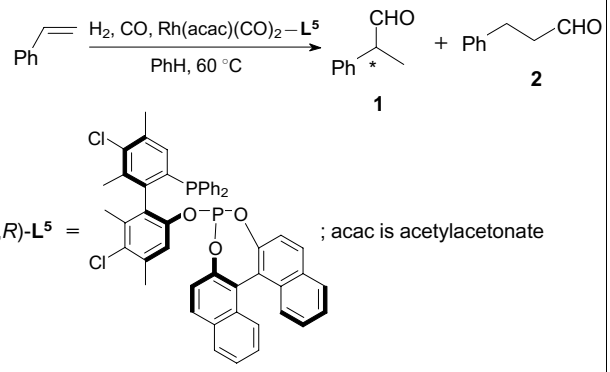
Structure L[4]



L[4]

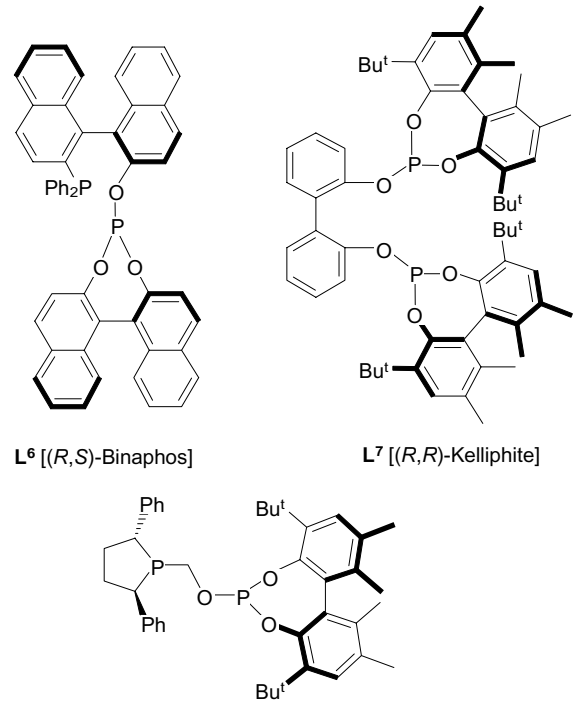
Since the formation of the Markovnikov isomer is especially typical of styrenes,[12] asymmetric hydroformylation of these compounds has been thoroughly studied.[8] A high optical purity [enantiomeric excess (*ee*) reaching 86%] was first attained for this reaction back in 1991 with the use of bis-phosphine platinum complexes in the $PtCl_2 - SnCl_2$ system.[13] In 1997, Nozaki *et al.*[14] made a step forward by using rhodium catalysts with chiral phosphine–phosphite ligands, *e.g.*, the ligand **L**[5] (Scheme 7). With styrene conversion being complete (> 99%), reaction products were formed in a 9 : 1 ratio of branched (**1**) to linear (**2**) isomers and high enantioselectivity (94% *ee*). A similar outcome (*ee* of up to 98%) was attained not only for styrenes, but also for hetero- and fluoro-substituted olefins.

Scheme 7



Ligands of this type such as (*R*,*S*)-Binaphos (**L**[6]), phosphite type ligands such as (*R*,*R*)-Kelliphite (**L**[7]) and phospholane–phosphite ligands such as (*S*,*S*,*S*)- or (*R*,*R*,*R*)-Bobphos (**L**[8])[15] found wide use in enantioselective hydroformylation reactions.

Structures L[6]–L[8]



L[6] [(*R*,*S*)-Binaphos]

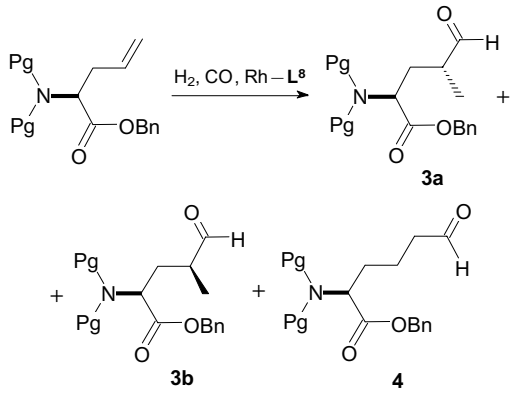
L[7] [(*R*,*R*)-Kelliphite]

L[8] [(*R*,*R*,*R*)-Bobphos]

(*R*,*S*)-Binaphos is (*R*)-2-diphenylphosphino-1,1′-binaphthalen-2′-yl (*S*)-1,1′-binaphthalene-2,2′-diyl phosphite; (*R*,*R*)-Kelliphite is (*R*,*R*)-(–)-6,6′-[(1,1′-biphenyl-2,2′-diyl)]bis(4,8-di-*tert*-butyl-1,2,10,11-tetramethyl]dibenzo[*d*, *f*][1,3,2]dioxaphosphepin; (*R*,*R*,*R*)-Bobphos is (11a*S*)-4,8-bis(*tert*-butyl)-1,2,10,11-tetramethyl-6-{[(2*S*,5*S*)-(2,5-diphenylphospholan-1-yl)methoxy]dibenzo[*d*, *f*][1,3,2] dioxaphosphepin}

Recently, the Markovnikov isomer was synthesized with a high diastereoselectivity by hydroformylation of protected allylglycine (Scheme 8).[16] When (*R*,*R*,*R*)-Bobphos (**L**[8]) was used as the ligand, this reaction showed good performance: the substrate conversion was 92%, the branched (**3**) to linear (**4**) isomer ratio was 6.8 : 1 and the diastereomeric ratio was 98 : 2.

Scheme 8



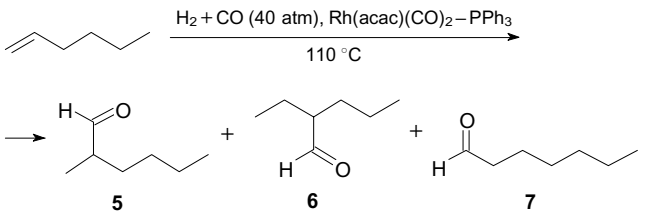
The Markovnikov isomer can be used to synthesize the antibiotic nemonoxacin.

As has already been noted, non-activated olefins (first of all, α-olefins) are the major feedstock for hydroformylation. It turned out that in this case, too, not only products with a linear structure are in demand, but branched oxygen-containing products are also required. These derivatives are used to prepare fragrances and flavouring additives and they also serve as intermediates for organic synthesis. There is extensive literature devoted to the Rh catalysis of the formation of branched aldehydes upon hydroformylation. However, it is by no means a trivial task. Under the action of Rh catalysts, double bond isomerization readily takes place, and the reaction gives a mixture of products, including not only a branched and linear isomer mixture, but also a mixture of Markovnikov isomers. For example, hydroformylation of hex-1-ene catalyzed by the $Rh(acac)(CO)_2 - PPh_3$ system gives a mixture of products **5** – **7**,† among which are two Markovnikov isomers (**5** and **7**), and the ratio of branched to linear products at 110 °C is 40 : 60 (Scheme 9).[17]

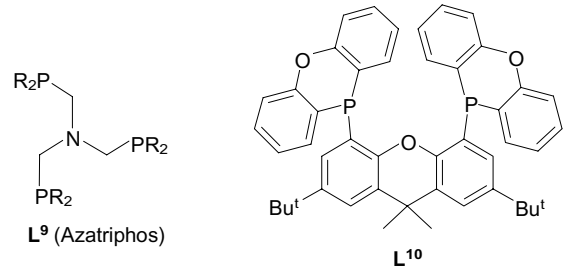
The application of phosphine ($PNaph_3$, where Naph is α-naphthyl) and phosphite [$P(ONaph)_3$] ligands results in a markedly higher proportion of branched isomers (up to 78 : 22 in the former case and up to 79 : 21 in the latter case),[17] although the products are formed as mixtures of 2- (**5**) and 3-formylated hexanes (**6**).

† Compound **6**, the product of carbonylation at the allylic position, does not refer directly to the Markovnikov rule, since the reaction proceeds *via* an π-allylic complex.

Scheme 9



Structures L^9, L^{10}



R = Ph, 2-MeC_6H_4, 4-$MeOC_6H_4$, 4-$Me_2NC_6H_4$, 3,5-$F_2C_6H_3$

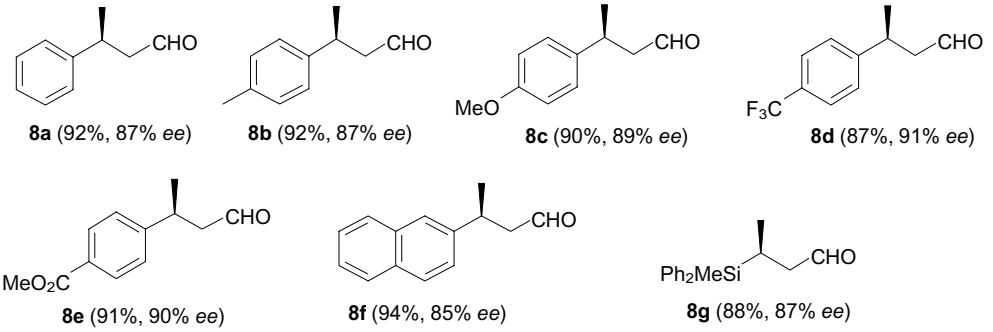
Phanopoulos and Nozaki[18] proposed a new type of ligand, Azatriphos (**L**[9]): hydroformylation of hex-1-ene in the presence of this ligand provided a high branched to linear product ratio (b : l = 5.46) at low temperature (50 °C), but relatively low conversion of the substrate. In all other cases, the ratio of isomers was close to 1.

The use of bulky ligands, including 10,10′-[2,7-di-*tert*-butyl-9,9-dimethyl-9*H*-xanthene-4,5-diyl]bis-(10*H*-phenoxaphosphinine) (**L**[10]) sharply increases the proportion of anti-Markovnikov aldehydes: for the reaction of oct-1-ene, the l : b ratio is 3.1 in the presence of Ph_3P and 68 in the presence of **L**[10].[19]

α-Substituted styrenes were previously studied in the asymmetric hydroformylation catalyzed by platinum[20] and rhodium[21] complexes, but the substrate conversion and enantiomeric excess (*ee*) of the product were low. This result does not seem surprising, because the absence of functional groups capable of coordination to the catalyst and induction of remote optical activity are not favourable for high values for the above characteristics.

However, recently, having tested quite a few chemically different chiral ligands, Zhang and co-workers[22] found the ligand **L**[11], which made it possible to prepare a set of chiral aldehydes **8a** – **g** (anti-Markovnikov isomers) in high yields and with high enantioselectivity (Scheme 10).

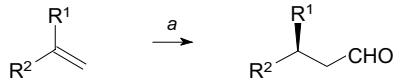
Structures 8



8a (92%, 87% *ee*) **8b** (92%, 87% *ee*) **8c** (90%, 89% *ee*) **8d** (87%, 91% *ee*)

8e (91%, 90% *ee*) **8f** (94%, 85% *ee*) **8g** (88%, 87% *ee*)

Scheme 10

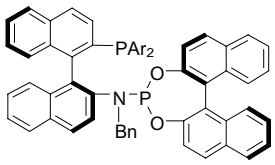


R^1 = Alk;
R^2 = Ar, Alk, $SiMePh_2$

8a – g (77% – 93% *ee*, TON up to 1720)

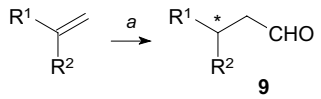
(*a*) H_2 (2.5 bar), CO (2.5 bar), Rh(acac)$(CO)_2$ – **L[11]**, PhMe, 80 °C;

L[11] =



(Ar = 3,5-$Bu^t_2C_6H_3$)

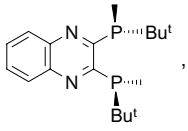
Scheme 11



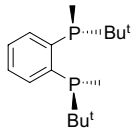
9

(*a*) H_2, CO, [Rh], **L[12]** or **L[13]**;

L[12] =



, **L[13]** =

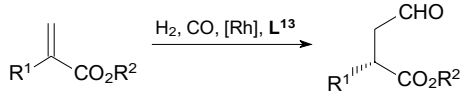


[(*R*,*R*)-QuinoxP*] [(*R*,*R*)-BenzP*]

Wang and Buchwald[23] performed asymmetric hydroformylation of 1,1-disubstituted alkenes (Scheme 11).

β-Chiral linear aldehyde **9a** (R^1 = Bn, R^2 = CO_2Et) was successfully synthesized after studying a wide range of chiral ligands. Phosphines — (*R*,*R*)-(−)-2,3-bis(*tert*-butylmethylphosphino)quinoxaline [(*R*,*R*)-QuinoxP*, **L**[12]] and (*R*,*R*)-(+)-1,2-bis(*tert*-butylmethylphosphino)benzene [(*R*,*R*)-BenzP*, **L**[13]] — were the ligands of choice, furnishing the product in a moderate yield, but with rather high (considering the complexity of the problem and a temperature of 100°C) enantioselectivity (75% and 82% *ee*, respectively). In the case of hydroformylation of acrylates with R^1 = Pr^i, cyclo-C_5H_9, cyclo-C_6H_{11} under the same conditions in the presence of **L**[13], the yields of products **9** were 84% – 91% and *ee* were 92% – 94% (Scheme 12).

Scheme 12



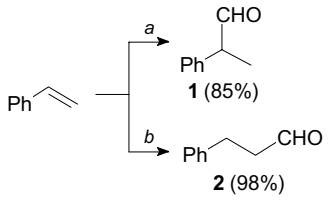
9

R^1 = Alk, cyclo-Alk, $(CH_2)_3OTBDMS$; R^2 = Me, Et;
TBDMS is *tert*-butyldimethylsilyl

Using the extensive published data on the hydroformylation of diverse olefins, it is possible to compose divergent pairs in which either of two isomers is formed regioselectively owing to the control performed by varying the nature of the ligand.

For example, styrene hydroformylation (Scheme 13) catalyzed by a Rh complex with the NHC-ligand **L**[14] (NHC is N-heterocyclic carbene) gives Markovnikov isomer **1** in a good yield and with high regioselectivity

Scheme 13

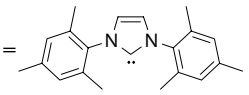


1 (85%)

2 (98%)

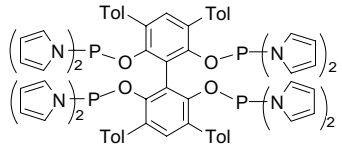
(*a*) H_2 + CO (34 atm), Rh(Cl)$(PPh_3)_2$ – **L[14]** (1 mol.%), PhH, 60 °C;
(*b*) H_2 + CO (5 atm), Rh(acac)$(CO)_2$ (0.1 mol.%), **L[15]** (0.3 mol.%), PhMe, 80 °C; Tol is *p*-methylphenyl (tolyl);

L[14] =



,

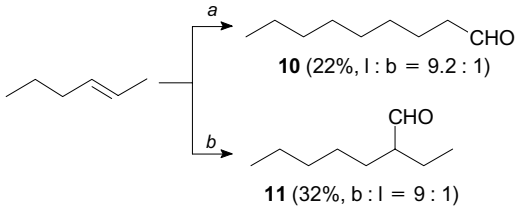
L[15] =



(b : l = 96 : 4).[12] However, the use of bulky phosphine ligand **L**[15] suppresses the formation of this product, giving linear (anti-Markovnikov) isomer **2** in a high yield and with unique regioselectivity attained for the first time (l : b = 95.5 : 4.5).[24]

Like with styrenes, for reactions of internal alkenes, various authors reported cases of predominant formation of one particular isomer. It is natural that the anti-Markovnikov aldehyde is produced upon fast isomerization of the double bond. In the presence of a Rh complex with bulky 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos) derivative **L**[10], linear aldehyde **10** is formed,[19] while Markovnikov isomer **11** is obtained in the case of rhodium encapsulated in a self-assembled system of a Zn porphyrin complex with tris(3-pyridyl)phosphine (**L**[16]), which suppresses isomerization (Scheme 14).[25]

Scheme 14

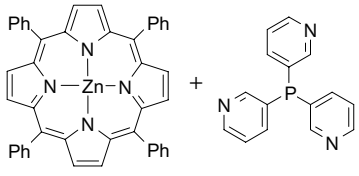


10 (22%, l : b = 9.2 : 1)

11 (32%, b : l = 9 : 1)

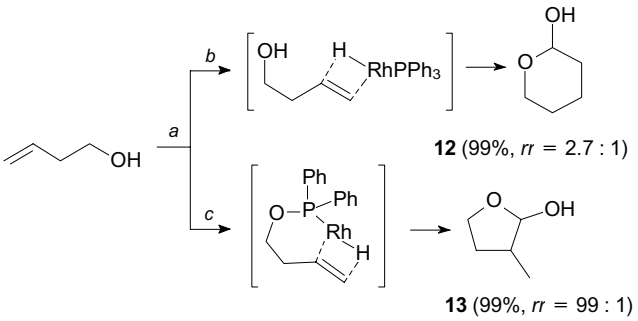
(*a*) H_2 + CO (2 bar), Rh ($Bu^tC(=O)CH=C(Bu^t)O)(CO)_2$ (0.15 mol.%), **L[10]** (1.5 mol.%), PhMe, 120 °C; (*b*) H_2 + CO (10 bar), Rh(acac)$(CO)_2$ (0.1 mol.%), **L[16]** (0.9 mol.%), PhMe, rt;
rt is room temperature;

L[16] =



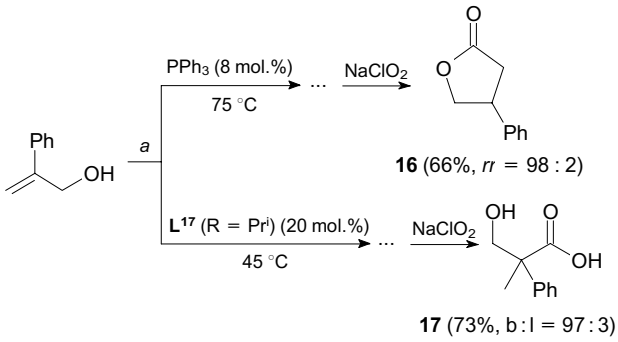
Tan and co-workers[26] and Grünanger and Breit[27] independently described the effect of ligands on the hydroformylation of homoallylic alcohols. Depending on the nature of the ligand, this reaction gives different Rh intermediates, the acetalization of which affords five- or

Scheme 15



(*a*) H_2 + CO (20 bar), $Rh(acac)(CO)_2$ (1 mol.%); (*b*) PPh_3 (10 mol.%), PhMe, 40 °C; (*c*) Ph_2POMe (10 mol.%), THF, 40 °C; *rr* is regioselectivity ratio (ratio of regioisomers)

Scheme 17

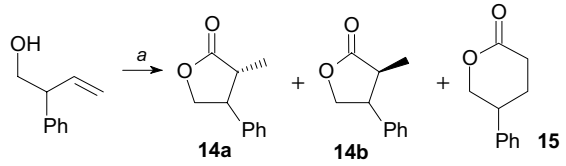


(*a*) H_2 + CO (27 atm), $Rh(acac)(CO)_2$ (4 mol.%), TsOH (0.2 mol.%), PhH; TsOH is *p*-toluenesulfonic acid

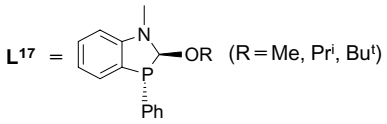
six-membered lactols. Grünanger and Breit[27] reported the formation of δ-lactol **12** for Ph_3P used as the ligand and γ-lactol **13** for the Ph_2POMe ligand (Scheme 15). Both reactions give products in high yields and with good (in some cases very high) regioselectivity.

Tan and co-workers[26,28] carried out hydroformylation of substituted homoallylic alcohol using Ph_3P and the chiral ligand $\mathbf{L}^{17}$ (Scheme 16). Like in the study mentioned above,[27] this reaction gave a mixture of lactones **14a**,**b** and **15**, but in the presence of PPh_3, δ-lactone **15** was formed predominantly, while in the case of chiral $\mathbf{L}^{17}$ (R = Me), a mixture of diasteromeric γ-lactones **14a**,**b** considerably predominated among the products.[26]

Scheme 16



(*a*) 1) H_2, CO, $Rh(acac)(CO)_2$, $\mathbf{L}^{17}$; 2) PCC, NaOAc; PCC is pyridinium chlorochromate;

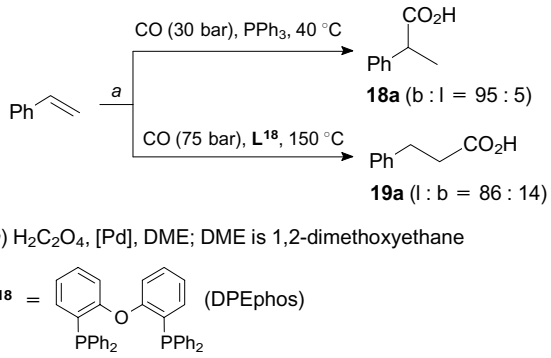


Pronounced regiodivergence was also observed for substituted allyl alcohol (Scheme 17): when PPh_3 was replaced by $\mathbf{L}^{17}$ (R = Pr^i),[28] the site of attack on the molecule by rhodium changed and, after oxidation, the reaction gave γ-butyrolactone **16** (anti-Markovnikov product) and β-hydroxy-α-phenylpropionic acid **17** (Markovnikov product).

Examples of divergent regioselectivity are also known among alkoxy- and aminocarbonylation reactions.

In the palladium-catalyzed hydroxy(methoxy)carbonylation of styrene, the ratio of the resulting Markovnikov to anti-Markovnikov isomers is determined, first of all, by the nature of the ligand. In the case of Pd complexes with 1,1′-bis(diphenylphosphino)metallocene[29] or N_3P-ligands,[30] a linear (anti-Markovnikov) isomer is formed predominantly. However, when palladium with a soluble TPPTS ligand is used as the catalyst, the l : b ratio depends on the pressure and temperature; the Markovnikov isomer predominates at high pressure and low temperature. Van Leeuwen and co-workers[31] demonstrated that in the case of the monophosphine ligand, hydroxycarbonylation of styrene gives mainly Markovnikov isomer **18a**, while the use of bidentate bis-phosphine ligands {*e.g.*, bis[(2-diphenylphosphino)-phenyl] ether (DPEphos, $\mathbf{L}^{18}$)} results in anti-Markovnikov isomer **19a** (Scheme 18).

Scheme 18



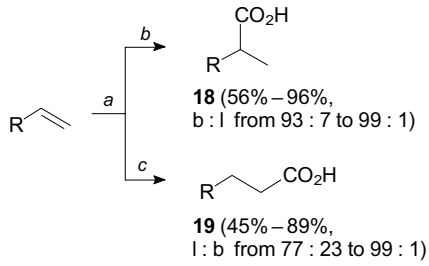
(*a*) $H_2C_2O_4$, [Pd], DME; DME is 1,2-dimethoxyethane

However, apart from the ligand nature, the reaction pathway depends on other factors such as pressure, temperature and ligand : Pd and substrate : Pd ratios.

Clarke and co-workers[32] prepared a series of new bidentate phosphanes by carrying out the reaction in the presence of TsOH and LiCl (130 °C, 50 bar); the Markovnikov isomer predominated among the products under these conditions.

Beller and co-workers[33] demonstrated that alkoxycarbonylation catalyzed by $PdCl_2$ with the 2-(dicyclohexylphosphino)-1-(2-methoxyphenyl)-1*H*-pyrrole ligand follows the Markovnikov rule and gives the branched isomer, although most reactions of terminal alkenes result in the formation of linear products due to steric effects. Exceptions are provided by reactions of styrenes, vinyl acetate and allenes in which the branched (Markovnikov) isomer is also the major or the only product. If Pd catalysis is performed in the presence of a co-catalyst, a Fe^{3+} salt, the reaction outcome depends on the counter-ion in the FeX_3 salt (Scheme 19): the use of $FeCl_3$ produces Markovnikov isomer **18**, while the use of $Fe(OTf)_3$ leads to linear

Scheme 19



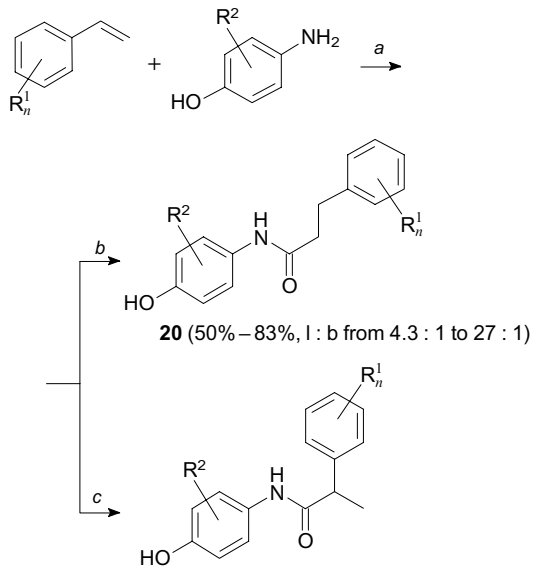
(*a*) $Pd(OAc)_2$ (1 mol.%), PPh_3 (3 – 6 mol.%), 1,4-dioxane, 80 – 120 °C; (*b*) CO (50 bar), H_2O (2 equiv.), $FeCl_3$ (2 mol.%); (*c*) CO (10 bar), H_2O (2 equiv.), $Fe(OTf)_3$ (5 mol.%); Tf is trifluoromethanesulfonyl (triflyl); R = Ar, Alk

acid **19** (anti-Markovnikov isomer). Thus, the regiodivergence is controlled by the anion of the co-catalyst.[34]

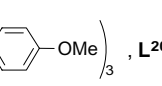
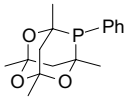
According to density functional theory (DFT) calculation for styrene,[34] the energy of addition of $[L_nPdH]Cl$ is lower for the branched isomer, while the addition energy of $[L_nPdH]^+$ is lower for the linear isomer.

The regiodivergency of the aminocarbonylation of styrenes with aminophenol catalyzed by palladium complexes was described by Alper and co-workers[35] (Scheme 20). The use of an ionic palladium complex with the tri(anisyl)phosphine (**L**[19]) ligand as the catalyst gave linear amide **20** (anti-Markovnikov isomer) as the major product, whereas in the presence of the $PdCl_2 - \mathbf{L}^{20}$ system, branched amide **21** (Markovnikov isomer) was predominantly formed.

Scheme 20

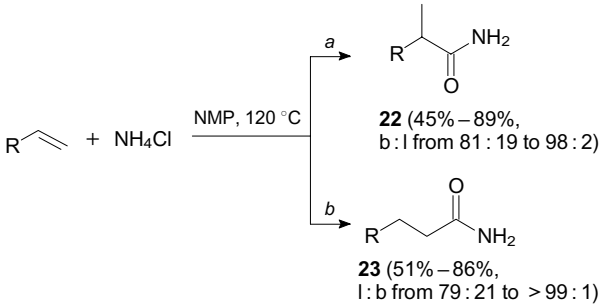


(*a*) CO (20 bar), $B(OH)_3$ (10 mol.%), 2-OH-5-$ClC_6H_3CO_2H$ (20 mol.%), 120 °C; (*b*) $Pd(MeCN)_4(BF_4)_2$ (5 mol.%), **L**[19] (10 mol.%), MeCN; (*c*) $PdCl_2$ (5 mol.%), **L**[20] (10 mol.%), EtC(O)Me; R^1_n = H, 4-Me, 2,4-Me_2, 4-Br, 4-F, 4-CO_2Me; R^2 = H, 3-Me, 2-F, 3-F, 2-CO_2Me;

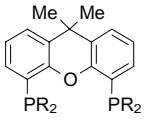
L[19] =  , **L**[20] = 

Recently, control over reaction regioselectivity *via* variation of ligands was reported by Huang and co-workers.[36] In the alkene aminocarbonylation, the authors used ammonium chloride instead of ammonia and demonstrated that with $Pd(PBu^t_3)_2$ as the catalyst, styrene is mainly converted to Markovnikov isomer **22** (R = Ph), while catalysis by the complex PdI_2 – Xantphos (**L**[21]) leads to conversion of any alkenes to anti-Markovnikov linear isomers **23** (Scheme 21). In the former case, the formation of a benzyl intermediate is assumed, while in the latter case (involving a bidentate bulky phosphine), the formation of linear isomers is attributed to steric hindrance.

Scheme 21

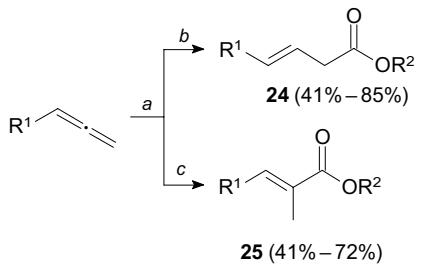


(*a*) for R = Ar: CO (30 atm), $Pd(PBu^t_3)_2$ (5 mol.%); (*b*) CO (30 atm), PdI_2 (2 mol.%), **L**[21] (2.5 mol.%); R = Alk, Ar; NMP is *N*-methyl-2-pyrrolidone;

L[21] =  (Xantphos)

Ligand-controlled Pd-catalyzed regiodivergent alkoxycarbonylation of terminal allenes has been reported.[37] The linear isomer (β,γ-unsaturated ester **24**) was obtained using the Xantphos ligand (**L**[21]) and *p*-toluenesulfonic acid, while branched α,β-unsaturated isomer **25** was formed in the presence of PPh_2Py (Py is 4-pyridyl) and trifluoroacetic acid (TFA) (Scheme 22).

Scheme 22



(*a*) CO (40 bar), R^2OH, $Pd(OAc)_2$ (1 mol.%), PhMe, 110 °C; (*b*) **L**[21] (2 mol.%), $TsOH \cdot H_2O$ (4 mol.%); (*c*) PPh_2Py (6 mol.%), TFA (10 mol.%); R^1 = Alk, Ar, CO_2Et; R^2OH = AlkOH, cholesterol, borneol

3. Hydrosilylation

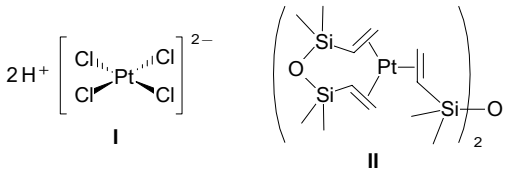
Along with hydroformylation, hydrosilylation of unsaturated compounds is an important reaction that is implemented in industry and employs homogeneous catalysis on

a large scale. Hydrosilylation catalyzed by transition metal complexes is the simplest and most convenient synthetic route to silanes and, especially, vinylsilanes.[38–41]

The literature on hydrosilylation is very extensive, because in this case, the outcome of reactions is affected by not only the nature of the starting compound, the type of the catalyst and conditions, but also the nature of silane, whether it is mono-, di- or trisubstituted, contains aliphatic, aromatic, alkoxyl or mixed substituents. It is quite obvious that the reactivities of, for example, trialkyl- and trichlorosilanes are considerably different.

The most popular hydrosilylation catalysts, especially for industrial processes, are platinum compounds, first of all, Speier (**I**)[42,43] and Karstedt (**II**)[44] catalysts.

Structures I, II



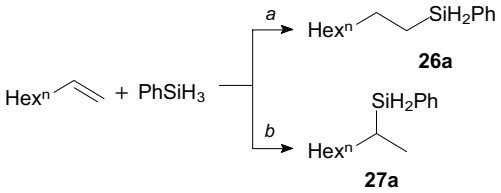
In the last decades, the range of Pt catalysts was considerably expanded to include not only platinum salts, but also complexes containing various ligands.[45–50] In view of high cost of platinum and its large consumption when used in industry, hydrosilylation was studied in the presence of recyclable catalysts based on platinum supported on various materials (MgO, SiO_2, TiO_2)[51–54] and Pt nanoparticles in the presence of stabilizers.[55] Some known reactions are catalyzed by early transition metal complexes[56] and Main Group metal (Ca, Sr) derivatives.[57] Lanthanide complexes are good catalysts of hydrosilylation.[58–61]

Rhodium[62–64] and palladium[65–69] complexes are widely used along with platinum; lately, less expensive Ni complexes[70–72] and also readily available and relatively non-toxic cobalt[73,74] and iron[75–77] complexes have been utilized.

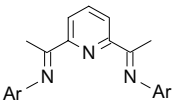
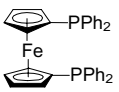
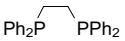
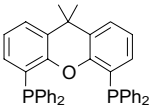
Metal-catalyzed hydrosilylation of ordinary terminal alkenes results in the formation of 1-silylalkanes (anti-Markovnikov isomers) and is often highly selective.[30,78] Reactions catalyzed by cobalt complexes can be considered as examples. The ability of Co complexes to promote hydrosilylation of alkenes has been known since the publication of Harrod and Chalk[79] (1965), who obtained the anti-Markovnikov product. Subsequently, regioselectivity with the formation of the anti-Markovnikov isomer required for industry was demonstrated for reactions catalyzed by cobalt complexes with a variety of ligands.

Ge and co-workers,[80] who studied hydrosilylation of oct-1-ene catalyzed by a Co complex in the presence of ligands $\mathbf{L}^{21}$ – $\mathbf{L}^{24}$, demonstrated the possibility of preparing either of the isomers by varying the nature of the ligand. In the case of Xantphos ($\mathbf{L}^{21}$), 1,1′-bis(diphenylphosphino)ferrocene (dppf, $\mathbf{L}^{23}$) or 1,2-bis(diphenylphosphino)ethane (dppe, $\mathbf{L}^{24}$), the reaction gives anti-Markovnikov product **26a**, whereas in the case of the pyridine-2,6-diimine ligand (^{Mes}PDI, $\mathbf{L}^{22}$), Markovnikov isomer **27a** was isolated in a high yield (Scheme 23). Thus, the researchers presented a vivid example of a divergent hydrosilylation reaction of alkenes. Presumably, the reaction mechanism changes upon variation of the ligand, and olefin insertion into the Co – H bond (Chark – Harrod mechanism)[81] is replaced by the insertion into the Co – Si bond (modified Chark – Harrod mechanism).[30,78]

Scheme 23



(*a*) $Co(acac)_2$ (2 mol.%), $\mathbf{L}^{21}$, or $\mathbf{L}^{23}$, or $\mathbf{L}^{24}$ (2 mol.%), THF, rt, 3 h; (*b*) $Co(acac)_2$ (3 mol.%), $\mathbf{L}^{22}$ (3 mol.%), PhMe, 60 °C, 24 h; Hex^n is n-hexyl, Mes is mesityl (2,4-6-trimethylphenyl)

Ligand	Structure	I : b ratio (**26a** : **27a**)
$\mathbf{L}^{22}$ (Ar = Mes)		2 : 96
$\mathbf{L}^{23}$		91 : 2
$\mathbf{L}^{24}$		87 : 2
$\mathbf{L}^{21}$		95 : 2

Using the ligand $\mathbf{L}^{22}$, a series of Markovnikov isomers **27** was obtained in high yields *via* the appropriate hydrosilylation reactions (Fig. 1).

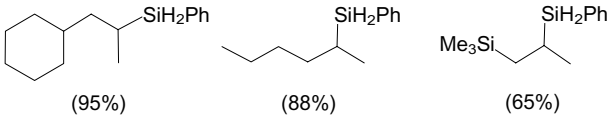
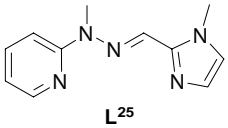


Figure 1. Markovnikov addition products formed in the presence of the ligand $\mathbf{L}^{22}$.

Hydrosilylation of styrenes catalyzed by the Co^{II} complex (*E*)-2-{1-methyl-2-[(1-methyl-1*H*-imidazol-2-yl)methylidene]hydrazinyl}pyridine ($\mathbf{L}^{25}$) as the ligand in the presence of $NaBHEt_3$ as a reducing agent affords the linear (anti-Markovnikov) isomer in a high yield.[82]

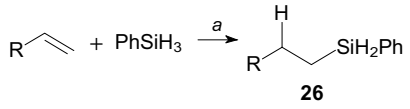
Structure $\mathbf{L}^{25}$



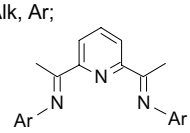
$\mathbf{L}^{25}$

Unlike the reaction catalyzed by the Co^{II} complex, which gives the Markovnikov isomer when the ligand $\mathbf{L}^{22}$ is used (see Scheme 23), the reaction catalyzed by a low-valent iron complex formed upon the reduction of iron(II)

Scheme 24



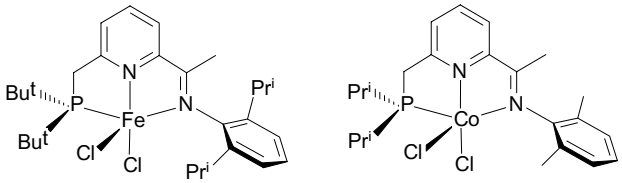
(*a*) $FeCl_2$ (1 mol.%), **L**[26] (1 mol.%), EtMgBr (2 mol.%), THF, rt, 1 h; R = Alk, Ar;

L[26] =  (Ar = 2,6-$Et_2C_6H_3$)

chloride with ethylmagnesium bromide with a similar pyridine-2,6-diimine ligand **L**[26] (Scheme 24) furnishes anti-Markovnikov linear isomers **26** even in the case of styrene.[83]

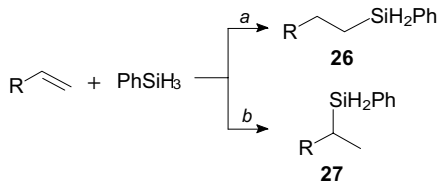
Huang and co-workers[84] prepared Fe^{II} and Co^{II} complexes with hybrid phosphine-iminopyridine ligands (structures **III** and **IV**) and demonstrated that these catalysts show divergent behaviour in the hydrosilylation of various olefins on treatment with Ph_3SiH. Catalysis by the cobalt complex results in the formation of Markovnikov isomer **27** in a high yield, whereas the iron complex gives anti-Markovnikov product **26** also in a high yield (Scheme 25, Table 1).

Structures III, IV



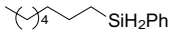
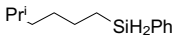
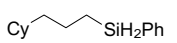
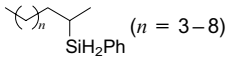
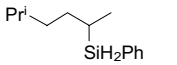
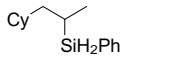
III **IV**

Scheme 25

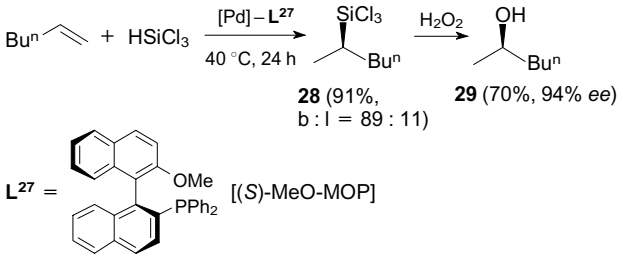


(*a*) [Fe] (**III**) (0.5 mol.%), $NaBHEt_3$ (1 mol.%), THF, rt, 24 h;
(*b*) [Co] (**IV**) (0.5 mol.%), THF, 60 °C, 24 h; R = Alk, Ar, *etc*.

Table 1. Products of reactions of alkenes with phenylsilane (see Scheme 25).[84]

Product	Conditions	Yield (%)	l : b ratio
Anti-Markovnikov products **26**			
	*a*	89	> 99 : 1
	*a*	87	> 99 : 1
	*a*	92	> 99 : 1
Markovnikov products **27**			
	*b*	90 – 94	< 1 : 99
	*b*	88	2 : 98
	*b*	98	4 : 96

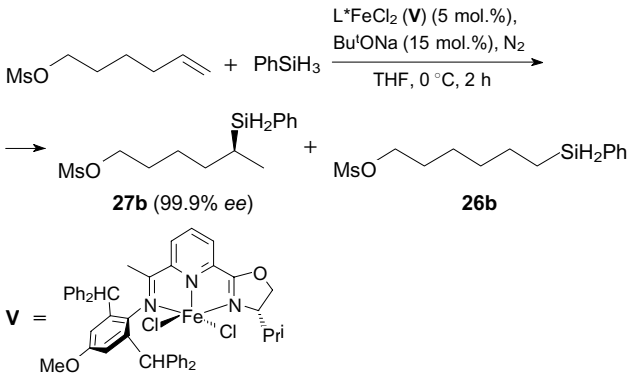
Scheme 26



28 (91%, b : l = 89 : 11) **29** (70%, 94% *ee*)

L[27] = [(*S*)-MeO-MOP]

Scheme 27



For aliphatic alkenes, the synthesis of Markovnikov isomers in enantiomerically pure form is a complicated task, which was solved so far only for a limited range of substrates and often with a moderate regioselectivity.

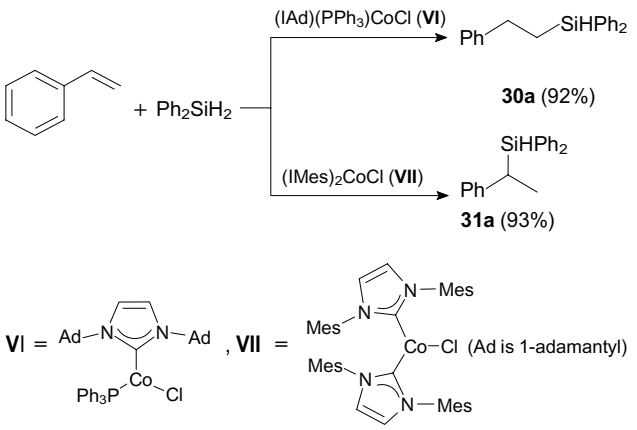
Uozumi and Hayashi[85] were the first to prepare Markovnikov isomer **28** in high yields and with high enantioselectivity (for alcohol **29**) *via* hydrosilylation of aliphatic alkenes using the monophosphine ligand (*S*)-2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl [(*S*)-MeO-MOP, **L**[27]] proposed by Hayashi (Scheme 26). However, this reaction was carried out only with active silicochloroform.

In 2018, Lu co-workers[76] isolated Markovnikov isomer **26b** with an exceptional enantioselectivity upon alkene hydrosilylation with $PhSiH_3$ catalyzed by chiral iron complex **V** (Scheme 27). The yield of isomers **26b** and **27b** was 99% and the b : l ratio was 96 : 4.

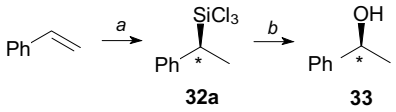
Recently, Deng and co-workers[86] demonstrated that the use of Co^{I} complexes in the reaction of styrene with Ph_2SiH_2 can selectively give either an anti-Markovnikov (**30a**) or an Markovnikov (**31a**) isomer depending on the nature of the *N*-heterocyclic carbene ligand — 1,3-bis(1-adamantyl)imidazol-2-ylidene (IAd) or 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes). Thus, the authors accomplished ligand-controlled divergent regioselectivity of silane addition, with each isomer being formed in a high yield (Scheme 28).

In the Pd-catalyzed reaction of styrene with trichlorosilane, the use of the 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) ligand induces a high Markovnikov selectivity and high enantioselectivity of formation of silane **32a**, which can be oxidized to chiral alcohol **33** (Scheme 29).[87]

Scheme 28



Scheme 29

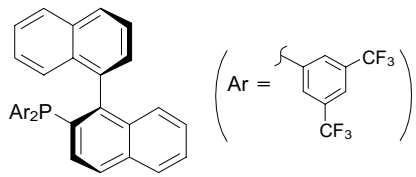


(*a*) $HSiCl_3$, (*S*)- or (*R*)-BINAP–Pd; (*b*) H_2O_2, KF, $KHCO_3$

This reaction can proceed not only at room temperature, but also at 0 °C, thus providing high enantioselectivity of the product (up to 95% *ee*), although according to Uozumi *et al.*,[88] palladium complexes with bidentate ligands do not catalyze this reaction at all.

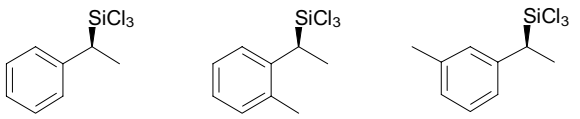
Excellent results were attained in the enantioselective Pd-catalyzed hydrosilylation using monodentate phosphine (MOP) ligands. Reactions involving various alkenes resulted in the isolation of Markovnikov isomers in high yields and with high enantioselectivity.[85,89–91] For example, in the presence of efficient MOP ligand **L**[28] in toluene, products of styrene hydrosilylation **32a–c** were obtained under mild conditions (temperature from −20 to 0 °C); their yields and *ee* values are presented below.[90]

Structure L[28]



L[28]

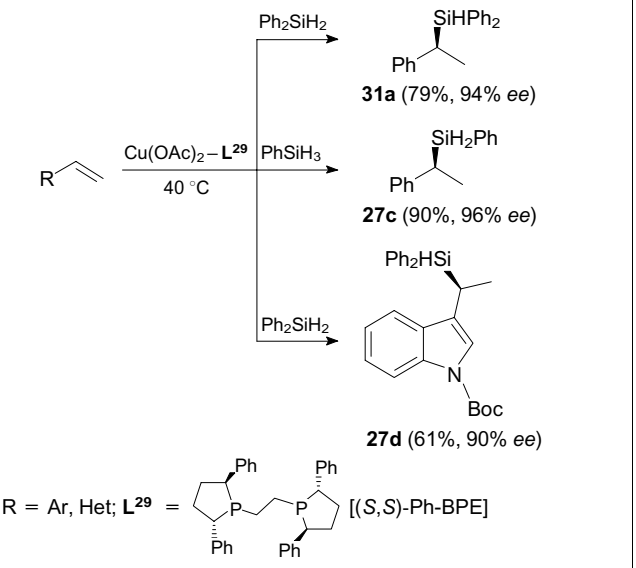
Structures 32



32a (93%, 97% *ee*) **32b** (96%, 96% *ee*) **32c** (91%, 97% *ee*)

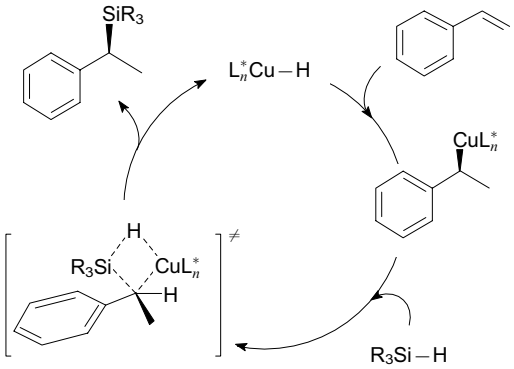
Buchwald and co-workers[92] investigated hydrosilylation of vinylarenes and vinylheteroarenes catalyzed by Cu^{II} salt with a chiral ligand — (+)-1,2-bis[(2*S*,5*S*)-2,5-diphenylphospholano]ethane [(*S*,*S*)-Ph-BPE, **L**[29]]. The reactions occur to give Markovnikov isomers (*e.g.*, compounds **27c**,**d** and **31a**) with high enantioselectivity (Scheme 30).

Scheme 30



The reaction mechanism includes the addition of the L_n^*CuH complex to the double bond and metathesis of the C–Cu and Si–H bonds (Scheme 31).

Scheme 31

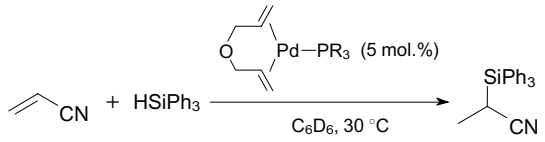


The hydrosilylation of electron-deficient alkenes, for example, acrylonitrile catalyzed by a diallylpalladium complex with the monophosphine ligand was described by Komine *et al.*[69] The reaction gives Markovnikov isomer **34a** (Scheme 32). The yields of analogous hydrosilylation products **34b–d** obtained for R = Me in the phosphine molecule vary from 50% to 100%.

Other examples of regiodivergence, involved in the hydrosilylation of styrenes and aliphatic alkenes and controlled by varying the catalyst, are still few in number.

For example, the reaction of styrene with Ph_2SiH_2 catalyzed by zirconium complexes generated *in situ* from Cp_2ZrCl_2 (Cp is cyclopentadienyl) and Bu^nLi gives high yields of different regioisomers, depending on the Bu^nLi : Zr ratio (Scheme 33).[56] The ratio of isomers **30a** and **31a** depends also on the order of addition of the reactants. This was attributed to the fact that different zirconium complexes, $Cp_2Zr(\eta^2$-styrene) or $(Cp_2ZrBu^n)Li$, can participate in the reaction.

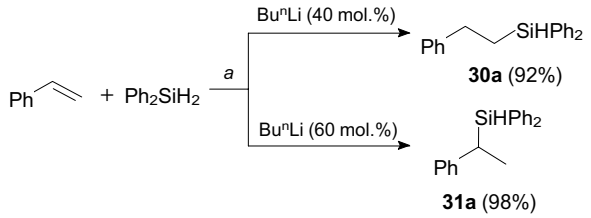
Scheme 32



R = Me, Cy, Ph

Product	Structure	Time /h	Yield (%)
34a	$SiPh_3$, CN	1	97
34b	$SiPh_3$, C(O)Me	1	93
34c	$SiPh_3$, CO_2Me	2	100
34d	$SiPh_3$, $C(O)NMe_2$	5	50

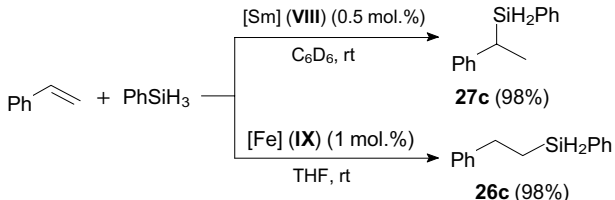
Scheme 33



(*a*) Cp_2ZrCl_2 (20 mol.%), THF, −78 °C → rt

A crucial role in the formation of a desired regioisomer is played by the nature of the metal. Whereas samarium complex **VIII**, like Karstedt and Speier catalysts,[42–44] leads to the formation of Markovnikov isomer **27c** in the reaction of styrene with phenylsilane,[75,83] iron complex **IX** with pyridine-2,6-diimine ligands gives rise to anti-Markovnikov isomer **26c** in an equally high yield (Scheme 34).[58]

Scheme 34

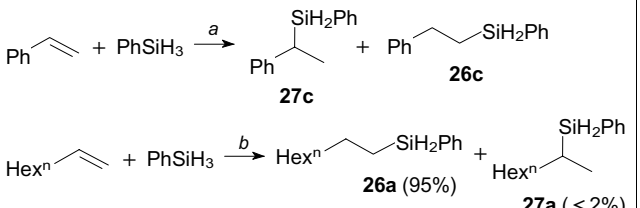


VIII = Me_2Si (Sm—$CH(TMS)_2$), **IX** = Ar, N, Fe, N_2, N_2, Ar

TMS is trimethylsilyl

Previously, it was shown that in the Co-catalyzed hydrosilylation reactions, the formation of either Markovnikov or anti-Markovnikov isomers is controlled by the ligands; however, this control may be different for styrenes and aliphatic alkenes. In the case of styrene, the use of a Co complex with the Xantphos ligand ($\mathbf{L}^{21}$) affords the branched isomer (conversion > 98%, b:l = 97:3), while in the reaction of oct-1-ene, the same complex gives predominantly the linear isomer with an equally high selectivity (Scheme 35).[80]

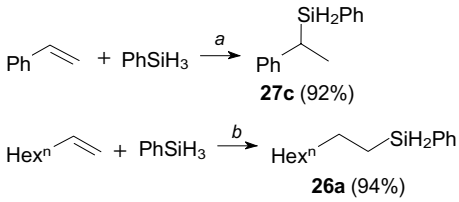
Scheme 35



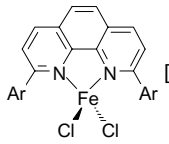
(*a*) $Co(acac)_2$ (1 mol.%), $\mathbf{L}^{21}$ (1 mol.%), THF, rt, 6 h;
(*b*) $Co(acac)_2$ (2 mol.%), $\mathbf{L}^{21}$ (2 mol.%), THF, rt, 3 h

A similar result was obtained with the use of iron complexes **X** and **XI** prepared from $FeCl_2$ and 2,9-diaryl-substituted 1,10-phenanthrolines in the presence of EtMgBr as the reducing agent.[93] The reaction of phenylsilane with various styrenes carried out under mild conditions affords Markovnikov products (*e.g.*, compound **27c** with a regioselectivity > 98%) in a high yield, while the reactions of non-activated alkenes give anti-Markovnikov products (*e.g.*, compound **26a** with a regioselectivity of 100%) (Scheme 36).

Scheme 36



(*a*) **X** (2 mol.%), EtMgBr (4.4 mol.%), THF, 30 – 35 °C, 10 h;
(*b*) **XI** (2 mol.%), EtMgBr (4.4 mol.%), PhMe, 30 – 35 °C, 24 h

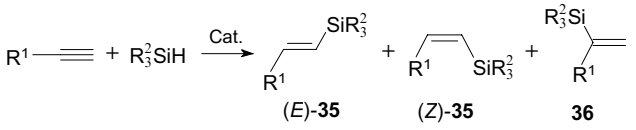
X, **XI** =  [Ar = 3,5-$Bu^t_2C_6H_3$ (**X**), 2,4,6-$Pr^i_3C_6H_2$ (**XI**)]

Hence, for both styrenes and non-activated alkenes, it is possible to find catalytic systems that ensure the synthesis of either anti-Markovnikov or Markovnikov isomers.

The hydrosilylation of terminal alkynes is the most direct and atom-economic route to the synthesis of vinylsilanes,[94] which attract considerable attention as useful intermediates in organic synthesis and in the manufacture of various materials.[39,95]

The hydrosilylation of terminal alkynes can, in principle, give three isomers (Scheme 37) — the products of addition at the β- [(*E*)-**35** and (*Z*)-**35**] and α-positions (**36**). The ratio of the products is determined by the natures of the catalyst, alkyne and silane and by reaction conditions. Mechanisms of formation of β-addition products for different double bond configurations were proposed, in particular, Chalk – Harrod mechanism for isomer (*E*)-**35** (M = Pt, Co, Ni, Pd)[39,81] and Crabtre – Ojima mechanism for isomer (*Z*)-**35** (M = Rh, Ir, Ru, Zr, Y, Ti).[96–99]

Scheme 37



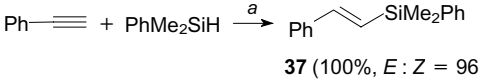
(*E*)-**35** (*Z*)-**35** **36**

Various platinum-based catalysts lead to the predominant formation of linear vinylsilanes. Platinum-catalyzed hydrosilylation tends to proceed as *syn*-addition, which affords *trans*-vinylsilanes.[39] In the presence of the platinum complex Pt(DVDS)–$Bu^nN(CH_2PPh_2)_2$ (DVDS is 1,3-divinyl-1,1,3,3-tetramethyldisiloxane), the reaction of terminal acetylenes in water proceeds at room temperature to give the anti-Markovnikov isomer with the *trans*-configuration in a high yield.[100]

The iron hydride complex $FeH(CO)(RO)(PPh_3)_2$ was efficient towards the addition to internal alkynes, with the reaction stereoselectivity (formation of *E*- or *Z*-form) being dependent on the nature of substituents in silane.[101]

Heterogeneous catalysis is rarely used for hydrosilylation because of insufficient catalytic activity and low regio- and stereoselectivity. However, there are examples of advanced versions. Palladium nanoparticles (NPs) supported on N,O-doped porous carbon (N,O-carbon) in the presence of tetra-n-butylammonium iodide (TBAI) ensure 100% conversion of phenylacetylene to anti-Markovnikov isomer **37** with high *E*-selectivity on treatment with $PhMe_2SiH$ (Scheme 38).[102]

Scheme 38



37 (100%, *E* : *Z* = 96 : 2)

(*a*) Pd-NP/N,O-carbon, TBAI, THF, 20 °C, 2 h

However, in the case of Et_3SiH, the ratio of *E* : *Z* isomeric products becomes 89 : 11, while silanes Ph_3SiH and $PhSiH_3$ do not react with phenylacetylene under these conditions. Nevertheless, it is important that this catalyst was recycled without significant loss of activity over six cycles.[102]

When Pt-NPs supported on mesoporous SBA-15 silica gel were used to catalyze the reaction of phenylacetylene with Et_3SiH, the catalyst activity and selectivity were found to depend on the nanoparticle size.[103]

Anti-Markovnikov β-isomers (*E*)-**35** C were obtained in high yield *via* hydrosilylation of alkynes catalyzed by Pt/TiO_2 (see Scheme 37).[54] Although the β-(*E*)-product usually predominates, Markovnikov isomer **36** was also detected among the products. Depending on the nature of the substituent in the terminal alkyne and the nature of the substituent R in R_3SiH, the l : b ratio varied from 94 : 6 to 52 : 48. When the $PtO/PtO_2–Fe_3O_4$ system was used as the catalyst, this ratio varied from 3.5 : 1 to 2.3 : 1.[104]

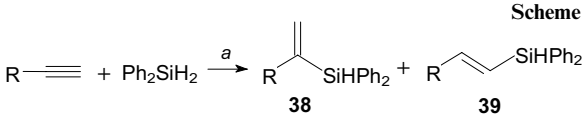
In the presence of the heterogeneous bimetallic Pd/Cu catalyst supported on SiO_2, hydrosilylation of aromatic and aliphatic alkynes gives predominantly (up to 100%) the *E*-configured β-isomer.[68] The catalyst may be reused five times.

The same product is obtained in gold-catalyzed reactions. Recent studies describe hydrosilylation of aromatic and aliphatic alkynes catalyzed by Au-NPs on various substrates (C, Al_2O_3 , CeO_2, TiO_2, Fe_2O_3, ZrO_2, *etc.*) and on the glass surface.[105–110] Some of the mentioned catalysts proved to be highly efficient, which allowed the use of low gold concentrations and mild reaction conditions. The reaction selectivity was always in favour of the β-(*E*)-isomer.

The Ir-catalyzed hydrosilylation of alkynes also predominantly gives the anti-Markovnikov product, but mainly its *Z*-isomer.[96] The *Z* : *E* isomer ratio of the products considerably depends on the nature of silane and alkyne. Whereas this ratio is 94 : 6 in the reaction of phenylacetylene with Et_3SiH, the ratio changes to 60 : 40 upon the replacement of silane by $(MeO)_3SiH$. In the reaction of cyclohexylacetylene with Et_3SiH, the β-(*Z*)- to β-(*E*)-isomer ratio is close to 1.

Recently, Guo and Lu[111] showed that the reaction between terminal acetylenes and diphenylsilane catalyzed by low-valent cobalt complexes **XII** has very high regioselectivity towards the Markovnikov isomer: for R = Ph, the b : l (**38** : **39**) ratio reaches 97 : 3 with the total yield being 90% (Scheme 39).

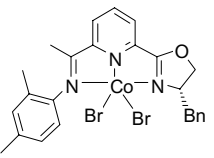
Scheme 39



38 **39**

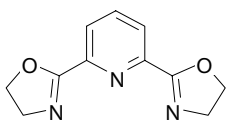
(*a*) **XII** (2 mol.%), $NaBHEt_3$, THF, rt, 5 min; R = Ar, Het, CH_2OBn, TMS

XII =

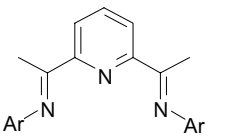


Ma and Han[112] reported computer investigation of the hydrosilylation of phenylacetylene with SiH_4 catalyzed by cobalt complexes with tridentate nitrogen-containing ligands: Pybox type ligand $\mathbf{L}^{30}$ [Pybox is 2,6-bis(oxazolin-2-yl)pyridine], diiminopyridine $\mathbf{L}^{31}$ and unsymmetrical combined ligand $\mathbf{L}^{32}$. For all of these ligands, the reaction pathway involving the formation of Co^0 was the energetically most favourable. According to the results, the reaction of phenylacetylene with Ph_2SiH_2 catalyzed by cobalt(0) leads to the Markovnikov isomer, which is in line with the data of Huang and co-workers,[113] while the Co^I-catalyzed reaction gives the anti-Markovnikov product.[114] The calculations also showed that the electronic effects in the ligand

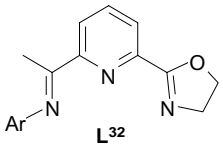
Structures $\mathbf{L}^{30}$–$\mathbf{L}^{32}$



$\mathbf{L}^{30}$ (Pybox)



$\mathbf{L}^{31}$ (Ar = Ph, 2,6-$Pr^i_2C_6H_3$)

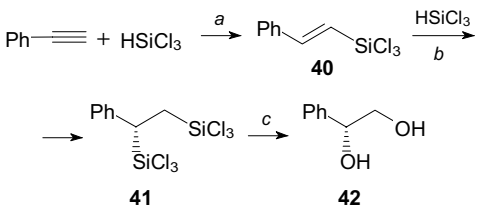


$\mathbf{L}^{32}$

are more important for the reaction pathway than the steric factors.[112]

Consider an example reported by Hayashi and co-workers,[115] who studied the addition of $HSiCl_3$ to arylacetylenes for the synthesis of chiral diols. In this cascade process, the first step catalyzed by a Pt complex gives anti-Markovnikov isomer **40**, the second step is the Markovnikov addition in the presence of a chiral Pd catalyst, and the subsequent oxidation of product **41** furnishes chiral diol **42** (Scheme 40).

Scheme 40

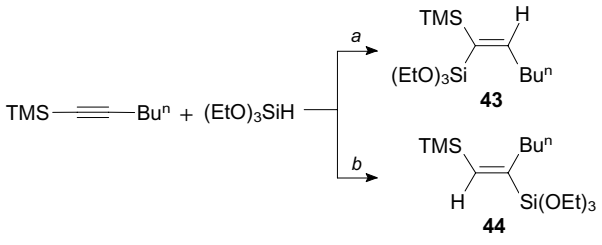


(*a*) $[PtCl_2(C_2H_4)]_2$ (0.01 mol.%); (*b*) $[PdCl(C_3H_5)]_2$–**L**[28] (0.3 mol.%); (*c*) H_2O_2, KF, $KHCO_3$

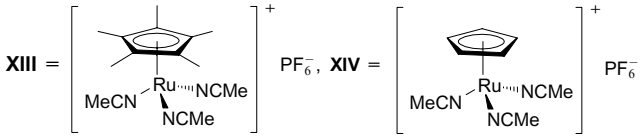
The reactions of internal alkynes were also studied with various platinum[5, 55, 104] and rhodium[64, 116–118] complexes as catalysts.

While attempting to overcome the difficulties related to regio- and stereoselectivity, which are especially pronounced in the case of asymmetric internal alkynes,[116, 119] Ding *et al.*[120] investigated the reactions of $(EtO)_3SiH$ with n-butyltrimethylsilylacetylene catalyzed by ruthenium complexes. They discovered a curious example of divergent regioselectivity with a simultaneous change in the stereoselectivity as a result of a relatively small change in the ligand structure. It was found that the use of catalyst **XIII** with the Cp* ligand (Cp* is pentamethylcyclopentadienyl) gives isomer **43**, while complex **XIV** with the Cp ligand provides the formation of isomer **44** (Scheme 41).

Scheme 41



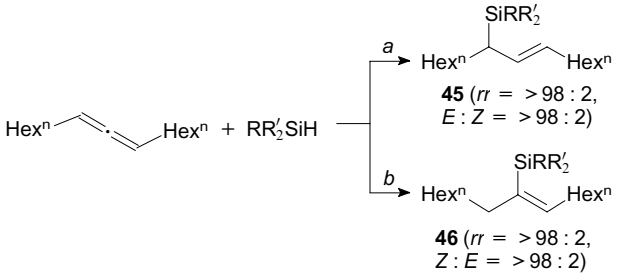
(*a*) **XIII** (2 mol.%), CH_2Cl_2, rt, 24 h; (*b*) **XIV** (2 mol.%), CH_2Cl_2, rt, 24 h;



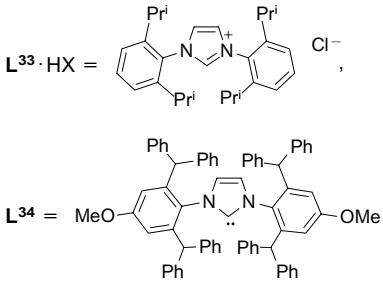
Both reactions proceed quantitatively and have high selectivity. In the electrophilic iodination of alkenes **43** and **44** with *N*-iodosuccinimide, the trimethylsilyl group is replaced by a iodine atom, giving rise to iodinated anti-Markovnikov and Markovnikov isomers. According to DFT calculations, the crucial role in the described silylation reactions[120] is played by the steric factor. Note that silanes devoid of electron-withdrawing groups react only when the reaction is catalyzed by complexes with the Cp* ligand (see Scheme 41).

Although hydrosilylation of allenes is much less popular than this reaction of alkynes, some examples of regiodivergent reactions involving allenes are still known. Montgomery and co-workers[121] showed that the hydrosilylation of internal allenes catalyzed by the palladium carbene complex in the presence of the ligand **L**[33] as hydrochloride gives allylsilanes **45**, while the use of nickel complex with the ligand **L**[34] for catalysis affords vinylsilanes **46** (Scheme 42).

Scheme 42



(*a*) $Pd_2(dba)_3$, **L**[33]·HX, $KOBu^t$, THF, rt; (*b*) $Ni(cod)_2$, **L**[34], THF, rt; R = Ph, Bn; R′ = Me; dba is dibenzylideneacetone;

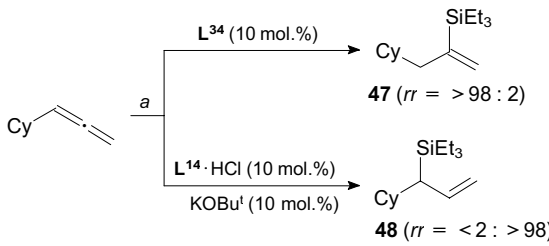


A similar result was obtained for unsymmetrical cyclohexylallene.[122]

The 1,2- and 2,1-addition mechanism with insertion into the M–H or M–SiR_3 bond proposed by the authors was confirmed by DFT calculations.[123]

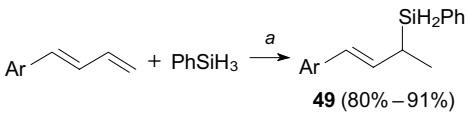
It was found that the size of the *N*-heterocyclic carbene ligand used in the palladium-catalyzed hydrosilylation of terminal allenes may influence the regioselectivity, with the

Scheme 43



(*a*) Et_3SiH, $Pd_2(dba)_3$, THF, rt

Scheme 44



(*a*) $Co(acac)_2$ (1 mol.%), **L**[21] (1 mol.%), THF, rt, 4 h; Ar = Ph, 2-$MeOC_6H_4$, 4-MeC_6H_4

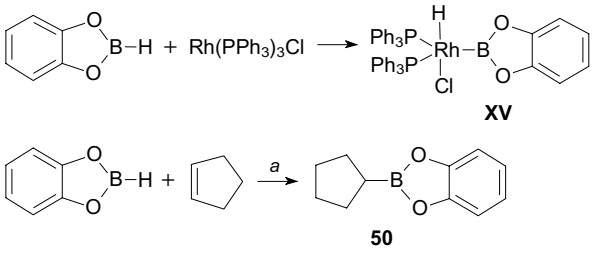
ratio of vinyl (**47**) to allyl (**48**) derivatives being nearly reversed (Scheme 43).[124]

Ge and co-workers[125] performed 1,2-hydrosilylation of 1,3-conhugated dienes in the presence of the Co^{II}– Xantphos (**L**[21]) system (Scheme 44). The yields of products **49** were high and the selectivity was >95% towards the Markovnikov isomer.

4. Hydroboration

The addition of boranes *via* H–B bond to unsaturated compounds was discovered in 1956 by Herbert Charles Brown, who was awarded the Nobel Prize in chemistry for this discovery in 1979. However, hydroboration in the presence of metal complexes has been pioneered almost 20 years later, when Kono *et al.*[126] reported that the reaction of catecholborane with the Wilkinson complex affords complex **XV** with the Rh–B bond (Scheme 45). After more ten years, Männig and Nöth[127] found that the Wilkinson complex catalyzes the reaction of catecholborane with cyclopentene (see Scheme 45). This reaction became highly popular, since the insertion of the H–B bond occurs as *syn*-addition (highly desired for the synthesis of natural products) and the resulting organoboron compounds can be converted to alcohols, acids, amines, *etc*.

Scheme 45

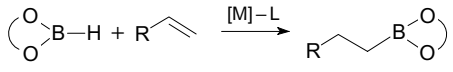


(*a*) [Rh] (0.05 mol.%), PhH, rt

Later it was found that, like other addition reactions, hydroboration can be catalyzed by early[128–130] and late[131–134] transition metals and lanthanides.[135,136] Naturally, in the catalysis by lanthanides (in which the metal oxidation state is retained), the reaction mechanism changes, and 'protonolysis' (σ-bond metathesis) takes place instead of reductive elimination. However, in general, the catalytic cycles of these processes are similar and include the formation of a π-complex (after ligand dissociation) and a σ-complex, which determines the regioselectivity.

Usually, the addition of borane to a non-activated terminal alkene gives the anti-Markovnikov product (Scheme 46).[137,138]

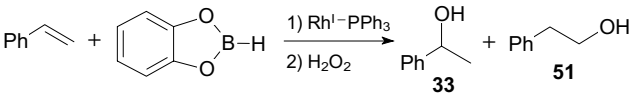
Scheme 46



However, the electronic and steric properties of the alkene and, certainly, the nature of the catalyst can change the regioselectivity of the reaction.[139,140]

The regioselectivity also changes on going to styrenes; in this case, a non-catalyzed or Rh^{III}-catalyzed reaction gives predominantly the anti-Markovnikov product,[141] while catalysis by Rh^{I} complexes with a bulky ligand results in the Markovnikov isomer [after oxidation, the ratio of α-methylbenzyl (**33**) to phenethyl (**51**) alcohols is 99 : 1] (Scheme 47).[142]

Scheme 47



Since hydroboration of styrenes catalyzed by Rh complexes gives predominantly, with rare exceptions, α-isomers (in the presence of a cationic rhodium complex, the b : l ratio reaches 99 : 1), it is this reaction that was used to study numerous chiral ligands. The pioneering studies of Burgess and Ohlmeyer,[143] Suzuki and co-workers[144] and Hayashi *et al.*,[145] who used bidentate phosphine ligands — BINAP, (+)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP), 2,3-bis(diphenylphosphino)-butane (CHIRAPHOS) and *R*-(*R**,*S**)]-1-[1-(dimethylamino)ethyl]-1′,2-bis(diphenylphosphino)ferrocene [(*S*,*R*)-BPPFA] — with axial and planar chirality, were followed by studying a variety of hybrid ligands; the enantiomeric purity of the obtained products varied over wide limits and, in some cases, it could be as high as 99%.

Actually, this reaction triggered the creation of remarkable series of chiral ligands that have become available for asymmetric synthesis.

The chiral di(aminophosphine) ligands were used to carry out successful catalytic hydroboration of norbornene with catecholboranes; however, the *ee* values were moderate.[146]

The reaction of substituted cyclopropene with pinacolborane catalyzed by Rh-NORPhos {NORPhos is 2,3-bis(diphenylphosphino)bicyclo[2.2.1]hept-5-ene} had a remarkable enantioselectivity (99% *ee*) and very high *cis*-stereoselectivity.[147]

The asymmetric Rh-catalyzed hydroboration of the double bond, as a key step of multistep transformations, found use in the synthesis of natural and biologically active compounds. Special mention should be made of the application of this strategy to prepare non-steroidal anti-inflammatory drugs, ibuprofen and naproxen (for the formula, see above),[148–150] and the antidepressant sertraline (Fig. 2).[151]

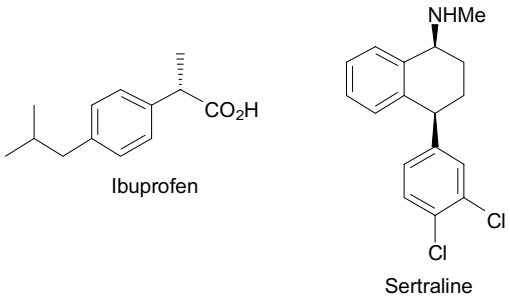
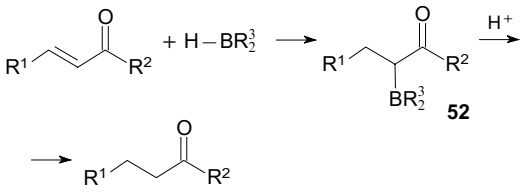


Figure 2. Medications produced by hydroboration.

Hydroboration of α,β-unsaturated carbonyl compounds usually affords α-borylated product **52** (Scheme 48).[152–155]

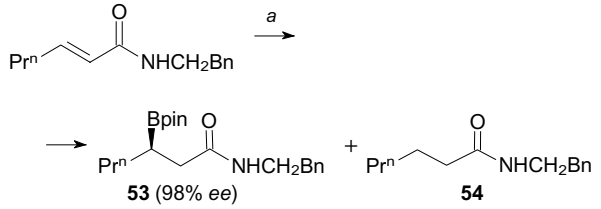
In 2019, this reaction was performed enantioselectively and with unusual regioselectivity for the first time.[156] Owing to minor changes in the ligand structure, that is, by using

Scheme 48

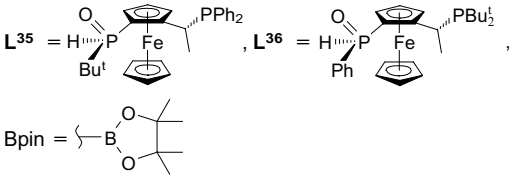


(S_P)-1-[(*R*)-*tert*-butylphosphinoyl]-2-[(*R*)-1-(diphenylphosphino)ethyl]ferrocene (Jospophos, **L**[35]), instead of its analogue **L**[36], with the Rh^I complex, the authors prepared boron derivative **53** with high *ee* value and amide **54** as a by-product (Scheme 49).

Scheme 49



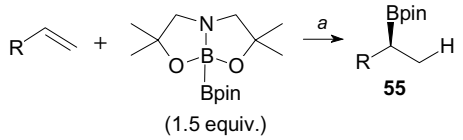
(*a*) HBpin (2 equiv.), $Rh(cod)_2OTf$ (3 mol.%), **L**[35] (3 mol.%), $CHCl_3$, rt, 12 h;



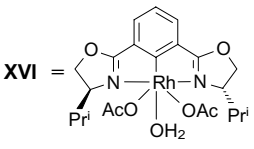
Ligand	Yield of **53** (%)	Yield of **54** (%)
L[35]	74	< 5
L[36]	21	43

In 2017, Aggarwal and co-workers [157] reported the first example of enantioselective hydroboration of non-activated terminal alkenes catalyzed by Rh^{III} complex **XVI** (Scheme 50). The reaction included asymmetric diboration

Scheme 50



(*a*) **XVI** (5 mol.%), H_2O (6 equiv.), heptane (1 mol L^{-1}), 40 °C, 16 h; R = Alk, A, *etc.*;



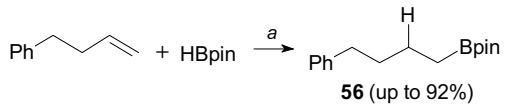
Product	R	Yield (%)	b : l	*er*
55a	$Ph(CH_2)_2$	76	98 : 2	90 : 10
55b	$n\text{-}C_8H_{17}$	61	97 : 3	90 : 10
55c	$Cl(CH_2)_4$	63	98 : 2	88 : 12

catalyzed by chiral Rh^{III} complex [158] and protodemetallation, resulting in the predominant formation of products **55**. For compounds **55a** – **c**, high regio- and enantioselectivity of the reactions were demonstrated.

Crucial changes in the application of and insight into hydroboration reactions were brought about by the use of other metal-containing catalysts. Ritter, Chirick, Huang and other authors (see Refs 159 – 169) demonstrated that expensive platinum and rhodium complexes can be replaced by cheap and accessible iron-, cobalt- and copper-based catalysts. This opened up fundamentally new prospects for hydroboration as a synthetically important reaction. We will consider some examples of these transformations.

Greenhalgh and Thomas [170] studied the reactions of pinacolborane catalyzed by iron complexes, which resulted in the synthesis of alkylboronic esters **56** in high yield (Scheme 51). Reactions of alkynes proceed in a similar way.

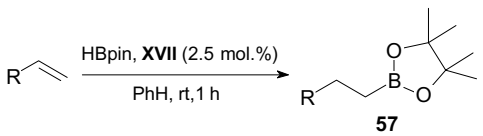
Scheme 51



(*a*) $FeCl_2$ – **L**[25], activating agent (RMgX or Bu^nLi), THF or PhMe, rt

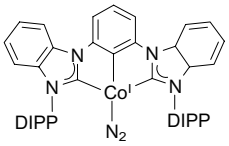
Fout and co-workers [171] carried out hydroboration of alkenes and nitriles catalyzed by cobalt complex **XVII** (Scheme 52). All substrates, including styrenes, were converted to anti-Markovnikov isomers **57** in good to high yields.

Scheme 52



R = Ar , Hex^n, CH_2OPh, CH_2NHPh, $(CH_2)_2CN$, $(CH_2)_2CO_2Me$, $(CH_2)_2Ac$, *etc.*; DIPP is 2,6-diisopropylphenyl

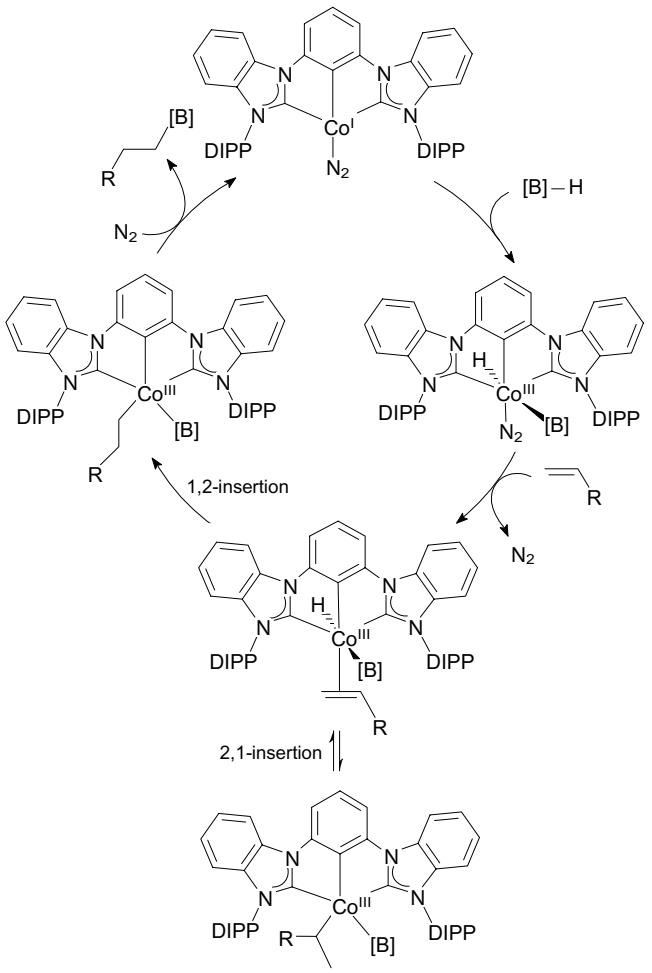
XVII =



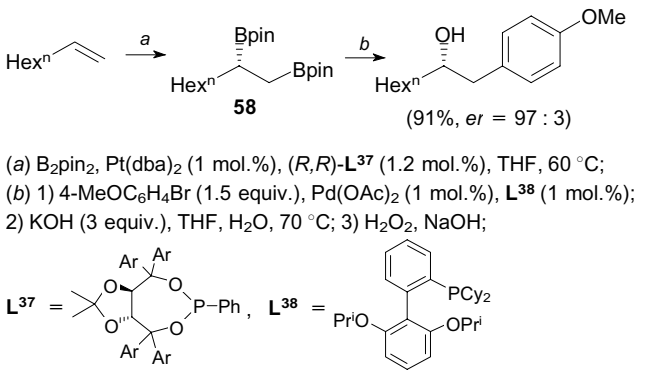
The reactions with nitriles afford diboration products — $RCH_2NB_2pin_2$. The authors proposed a mechanism involving $Co^I - Co^{III}$ complexes in the catalytic cycle and 1,2-insertion of alkene into the Co – H bond (Scheme 53).

An interesting reaction catalyzed by two complexes (Pt and Pd) was reported by Morken and co-workers [172] in the diboration – cross-coupling tandem (Scheme 54). This two-step process includes diboration of a non-functionalized alkene with 1,2-dibronate (B_2pin_2) catalyzed by a chiral platinum complex with (3a*R*,8a*R*)-(-)-4,4,8,8-tetrakis[3,5-di(isopropyl)phenyl]tetrahydro-2,2-dimethyl-6-phenyl-1,3-dioxolo[4,5-*e*]dioxaphosphepin (TADDOlPPh, **L**[37]) as a co-ligand (the product enantioselectivity was > 90%) and the subsequent cross-coupling of intermediate **58** with, for example, 4-methoxybromobenzene catalyzed by a Pd complex with the 2-dicyclohexylphosphino-2′,6′-di(isopropoxy)-biphenyl ligand (RuPhos, **L**[38]) and involving the terminal

Scheme 53



Scheme 54

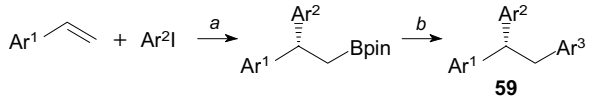


(*a*) B_2pin_2, $Pt(dba)_2$ (1 mol.%), (*R,R*)-**L**^{37} (1.2 mol.%), THF, 60 °C; (*b*) 1) 4-$MeOC_6H_4Br$ (1.5 equiv.), $Pd(OAc)_2$ (1 mol.%), **L**^{38} (1 mol.%); 2) KOH (3 equiv.), THF, H_2O, 70 °C; 3) H_2O_2, NaOH;

boron atom. It is beyond doubt that this reaction can find extensive use in organic synthesis.

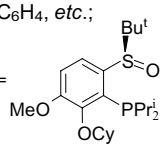
One more example of catalysis by two complexes of different metals acting independently was reported by Liao and co-workers,[173] whose study was devoted to the synthesis of enantioenriched 1,1,2-triarylethanes representing an important structural moiety of various biologically active compounds. The three-component reaction of vinylarenes with B_2pin_2 and RX was catalyzed by the CuCl – (*R*)-[6-(*tert*-butylsulfinyl)-2-cyclohexyloxy-3-methoxyphenyl]diisopropylphosphine system [(*R*)-SOP, **L**^{39}] and the complex $Pd(dppf)Cl_2$ (Scheme 55). The formation of the

Scheme 55



(*a*) B_2pin_2, CuCl (10 mol.%), $Pd(dppf)Cl_2$ (5 mol.%), **L**^{39} (12 mol.%), KOH, 2-MeTHF, 0 °C, 36 h; (*b*) Ar^3Br, $Pd(OAc)_2$, *rac*-BINAP (15 mol.%), KOH, THF – H_2O (10 : 1), 100 °C, 12 h; Ar^1 = Ph, 2-MeC_6H_4, *etc.*;

L^{39} =

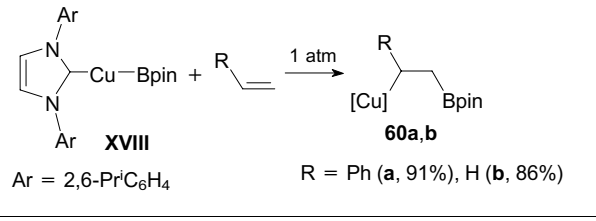


Ar^1	Ar^2	Ar^3	Yield of **59** (%)	*ee* (%)
2-MeC_6H_4	Ph	Ph	90	94
2-MeC_6H_4	Ph	4-MeC_6H_4	82	96
2-MeC_6H_4	Ph	4-ClC_6H_4	90	97
2-MeC_6H_4	Ph	4-$F_3COC_6H_4$	91	95
Ph	4-MeC_6H_4	Ph	83	95
Ph	4-NCC_6H_4	Ph	88	95
Ph	4-FC_6H_4	Ph	90	92

anti-Markovnikov boration product is due to the regioselective addition of the Cu – Bpin-bonded intermediate formed *in situ* to the alkene. The subsequent cross-coupling leads to the target triarylethane **59**.

Stoichiometric preparation of boranes *via* the reaction of copper boryl complex **XVIII** [(IPr)CuBpin, IPr is 1,3-bis(isopropyl)imidazol-2-ylidene] with ethylene, styrene and stilbenes has been studied.[174] The alkene insertion into the Cu – B bond of the carbene complex results in the generation of the anti-Markovnikov isomers, for example, compounds **60a**,**b** (Scheme 56).[175]

Scheme 56



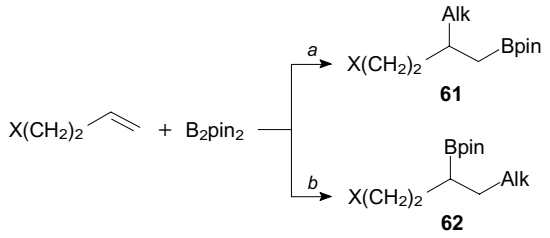
Ar = 2,6-$Pr^i C_6H_3$

The three-component condensation involving a terminal alkene, bis(pinacolyl)borane and alkyl halide catalyzed by CuCl complexes allows regioselective synthesis of either of the isomeric products of alkylborylation, compound **61** or **62**, *via* some changes in the ligand structure [R = Ph (**L**^{21}) or Cy (Cy-Xantphos, **L**^{40})]. In this case, the regiodivergence of the reaction is controlled by the ligand (Scheme 57).[140]

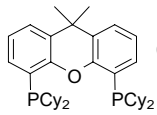
Ligand-controlled regiodivergence was also demonstrated for the aminoborylation reaction by Miura and coworkers.[139] They carried out three-component condensation of terminal alkenes with diboranes and *O*-benzoyl-*N*,*N*-dibenzylhydroxylamine using copper complexes with various ligands as catalysts (Scheme 58).

The use of the copper complex with a carbene ligand results in isomer **63** with the boron atom in an internal position, while in the case of Xantphos, isomer **64** with a terminal position of boron is formed. However, high regio-

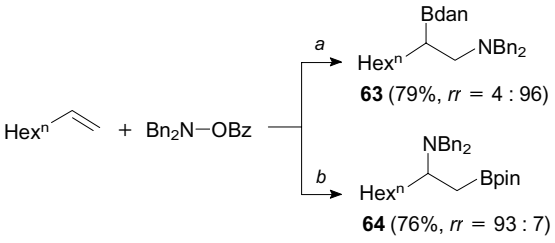
Scheme 57



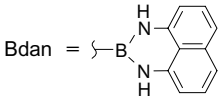
(*a*) AlkI, CuCl, **L[21]**, LiOBu^t, DMA, argon, 60 °C; (*b*) AlkBr, CuCl, **L[40]**, LiOBu^t, DMA, argon, 60 °C; Alk = Pr^n, n-C_5H_{11}, $(CH_2)_4CO_2Et$, $(CH_2)_2Ph$, $(CH_2)_5OTBDMS$; X = ONaph, OPMP, NBn_2, SC_6H_4Me-4, NMePh; DMS is dimethylacetamide, PMP is *p*-methoxyphenyl;

L[40] =  (Cy-Xantphos)

Scheme 58



(*a*) pinB–Bdan, IPrCuBr, LiOBu^t, THF, rt; (*b*) B_2pin_2, Cu(Xantphos)Cl, NaOBu^t, THF, rt; dan is 2-(2,3-dihydro-1*H*-naphtho[1,8-*d*,*e*][1,3,2]diazaborinine)

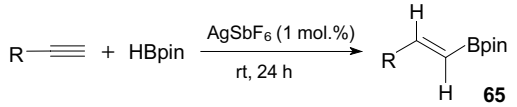
Bdan = 

selectivity combined with a good yield of the product in the case of the carbene complex is attained if an unsymmetrical diborane is used.

Hydroboration of terminal alkynes is important for the preparation of vinylboranes to be used in organic and polymer chemistry and in agrochemistry.[176] Conduction of these reactions regio- and stereoselectively is a challenging task, which is addressed in a large body of literature.[177–187]

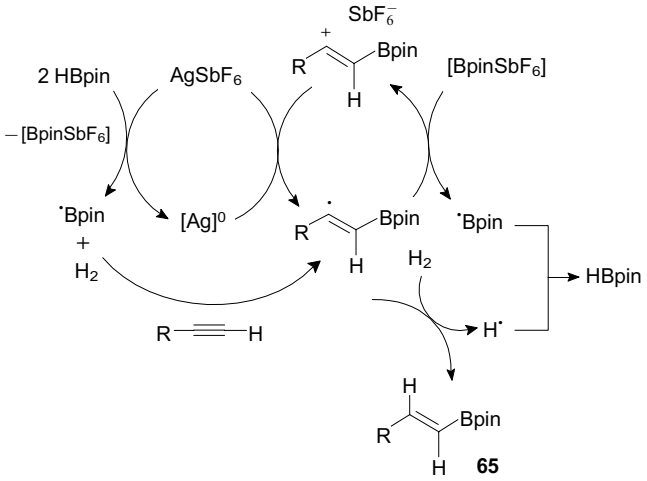
Currently, these studies are in progress. For example, in 2019, Rit and co-workers [188] demonstrated (Scheme 59) that in the presence of the cationic silver salt $AgSbF_6$, arylacetylenes react with HBpin at room temperature without a solvent giving only *E*-isomer **65** (*syn*-addition) in high yield. Previously these compounds were obtained by treatment of alkynes with B_2pin_2 and the Ag-NHC complex at 50 °C (Bu^{t}OK, MeOH), *i.e.*, by the reaction in which half of the organoboron compound was lost and which required a solvent, a base and an expensive ligand.[189]

Scheme 59



R = Alk, Ar, Het

Scheme 60



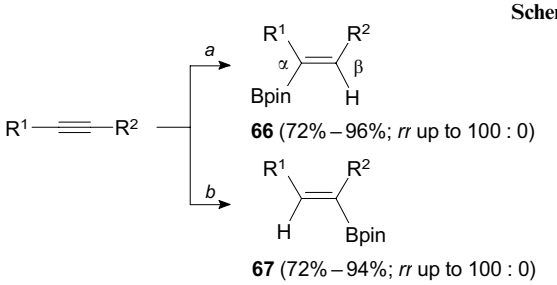
A radical mechanism (Scheme 60), which was confirmed using radical scavengers, was proposed for this reaction and a catalytic cycle involving pinB$^•$ radical, the $pinBSbF_6$ complex and Ag^0 was proposed (evolution of H_2 was detected by ^1H NMR spectroscopy).[188]

In the case of internal unsymmetrical alkynes and Rh or Ir complexes as catalysts, a mixture of isomers is usually formed. An unusual solution to the problem of selectivity was proposed by Tsuji and co-workers.[190] They showed that, by varying the hydroborating agent and by using copper salts with definite ligands, it is possible to generate *in situ* different catalytic species: CuH in the case of HBpin and Cu-Bpin in the case of B_2pin_2. Exactly these species control the regioselectivity of the reaction and, hence, allow selective preparation of each isomer. The reaction with the participation of HBpin affords α-isomer **66**, while in the case of B_2pin_2, β-isomer **67** was isolated (Scheme 61). Both isomers are formed with high regioselectivity (up to 100%).

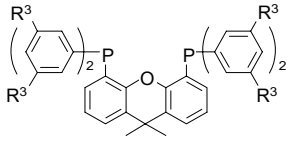
The catalytic cycles for both reactions are presented in Scheme 62.[191]

Armstrong and Lalic [192] performed a three-component reaction of terminal acetylenes with aryl halide and pinacolborane catalyzed by complexes of two metals, copper (**XIX**) and palladium (**XX**) (Scheme 63). This strategy was

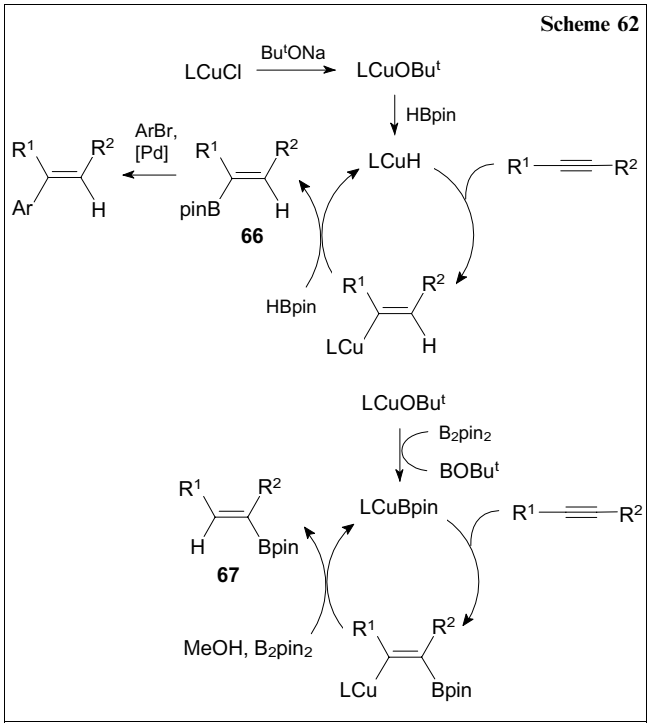
Scheme 61



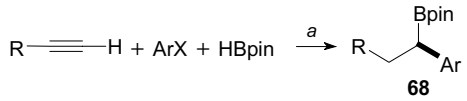
(*a*) HBpin, CuCl, **L[41]**, NaOBu^t, PhMe; (*b*) B_2pin_2, CuCl, **L[42]**, NaOBu^t, MeOH, PhMe; R^1 = Ar, ester, amide, CH_2OAlk, CH_2CH_2OAlk, CH_2NH_2; R^2 = Alk, TMS;

L[41], **L[42]** =  [R^3 = Me (MeArXan, **L[41]**), CF_3 (CF_3ArXan, **L[42]**)]

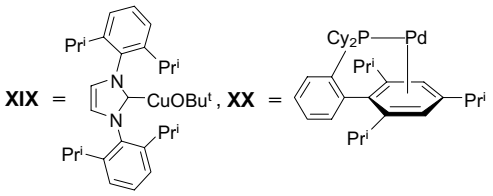
Scheme 62



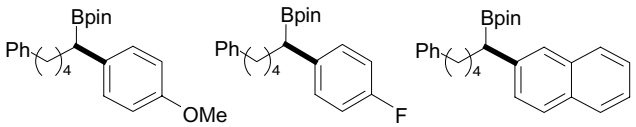
Scheme 63



(*a*) [Cu] (**XIX**), [Pd] (**XX**), KOBu^t, PhMe, 45 °C; R = Bu^t, Cy, $(CH_2)_4Ph$, $(CH_2)_4OPh$, $(CH_2)_5Cl$, $(CH_2)_6Br$, $(CH_2)_5OTBDMS$, $(CH_2)_4CN$ и др.; Ar = 4-XC_6H_4 (X = OMe, CF_3, F), 2-Naph, 2-Fu, 2-Th, *etc.*; Fu is furyl, Th is thienyl;



Structures 68



68a (85%) **68b** (93%) **68c** (81%)

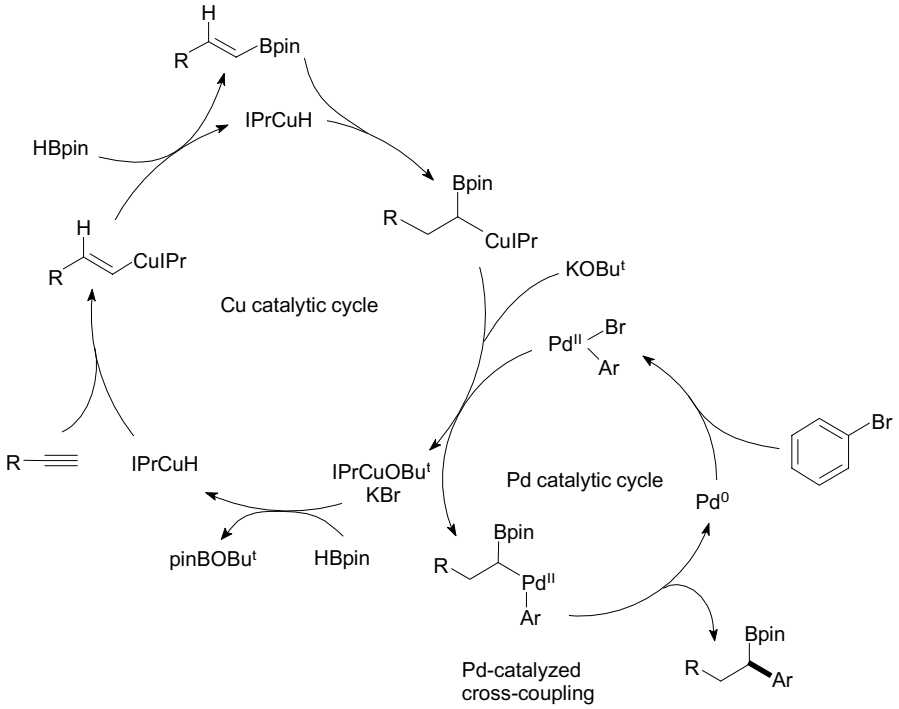
used to prepare a large series of α-aryl(heteryl)boranes in high yields, for example, compounds **68a** – **c**.

A reaction mechanism comprising two catalytic cycles was proposed (Scheme 64).

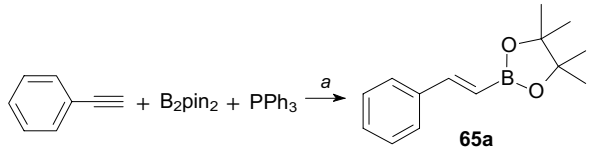
According to the modern trends, heterogeneous hydroboration of arylacetylenes with B_2pin_2 in the presence of PPh_3 was studied using Cu_2O particles of different morphology as catalysts. Copper oxide shaped as rhombic dodecahedra proved to be the most efficient (Scheme 65, Table 2). Since copper was not washed out into the solution, the catalyst was once recycled (the authors did not consider it necessary because of its low cost). As usual, catalysis by copper compounds resulted in the formation of β-addition products (anti-Markovnikov isomers) with *E*-configuration, for example, compound **65a**.[193]

The intramolecular trifunctionalization of alkynes catalyzed by CuI in the absence of a ligand was reported by Zhang and co-workers.[194] The CuI-catalyzed reaction of 2-ynamides **69** with B_2pin_2 proceeded as cyclization and diboration and gave rise to complex molecules **70** with two geminal borate groups (Scheme 66; the positions of substituents in the initial compound are indicated).

Scheme 64



Scheme 65



(*a*) Cu_2O (crystals), 1,4-dioxane, 60 °C, 5 h

Table 2. Hydroboration of phenylacetylene catalyzed by Cu_2O particles with different morphology (see Scheme 65).

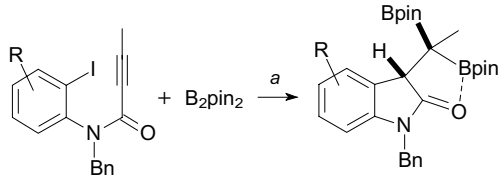
Catalyst	Amount /mg	Yield of **65a** (%)
Cu_2O cubes	1	62
Cu_2O octahedra	5	73
Cu_2O rhombic dodecahedra	2	99

The authors proposed a possible catalytic cycle (Scheme 67).

Studies of the catalytic hydroboration of allenes were started rather recently. In principle, monosubstituted allenes can form up to six regio- and stereoisomeric allyl- and alkenylboranes used in organic synthesis.[195] Miyaura and co-workers[196] performed hydroboration by treatment with HBpin and with platinum complexes as catalysts, which resulted in a mixture of allyl- and alkenylboranes. Yuan and Ma[197] carried out a similar reaction with B_2pin_2 and copper complexes as catalysts and also obtained alkenyl and allyl boron derivatives.

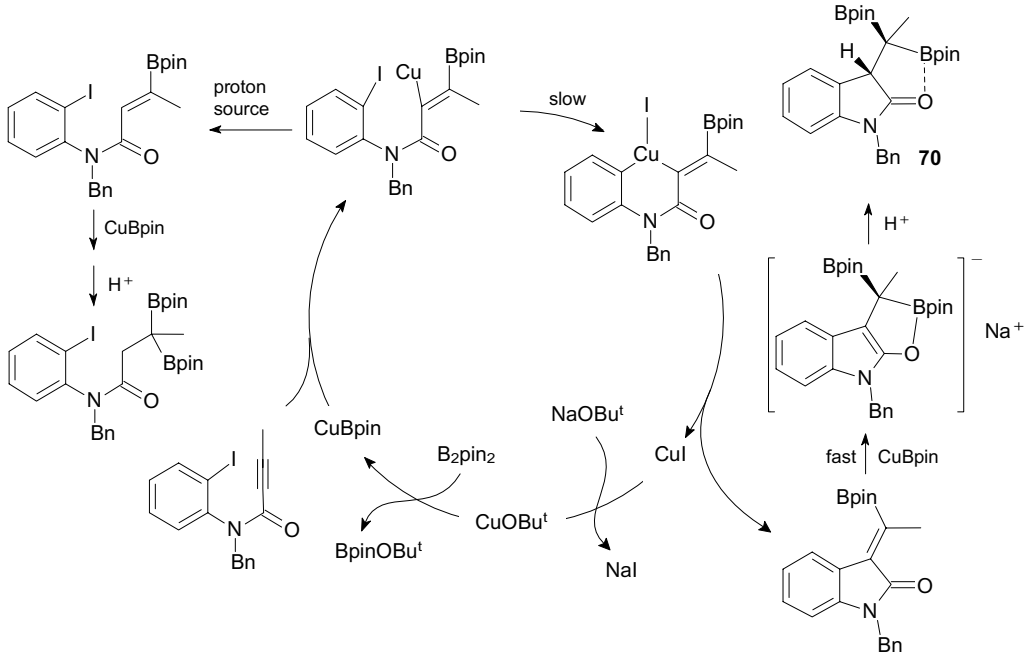
Tsuji and co-workers[198] utilized their method developed for alkynes by separately implementing hydrocupration and borylcupration followed by treatment with

Scheme 66

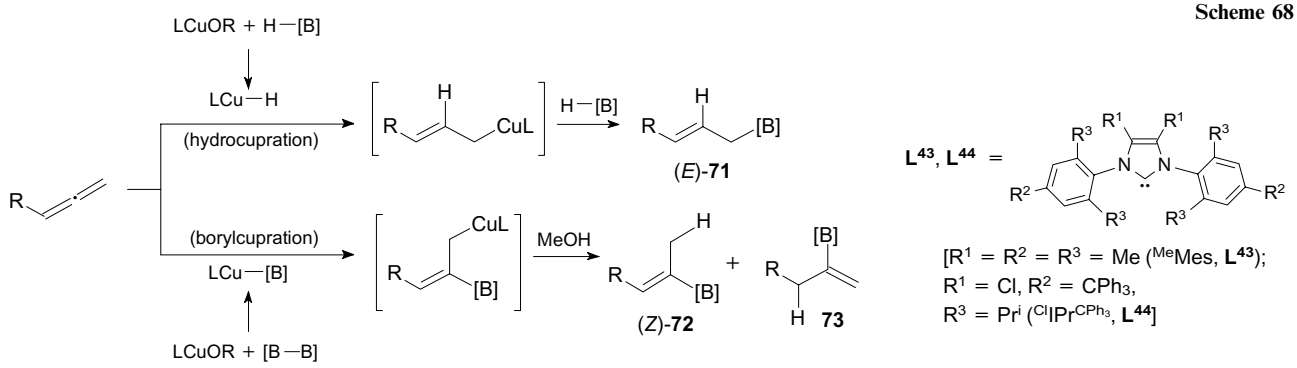


(*a*) CuI (5 mol.%), $NaOBu^t$, PhMe, rt, 24 h; R = 6-Br, 5-Br, 3-Br, 4-Me, 4-F, 4-Cl, 4-CF_3, 4-CO_2Et, 4-NO_2, *etc*.

Scheme 67



Scheme 68

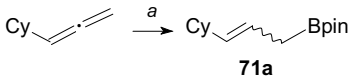


H – [B] = HBpin, [B – B] = B_2pin_2; R = $Ph(CH_2)_2$, $TBDMSO(CH_2)_2$, 4-$MeOC_6H_4$, 4-ClC_6H_4, *etc*.

methanol in the presence of copper complexes with the ligands $\mathbf{L}^{21}$, $\mathbf{L}^{42}-\mathbf{L}^{44}$ (Scheme 68). In the former case, (*E*)-allylboranes **71** were obtained, while in the latter reaction, a mixture of alkenylboranes **72** and **73** was formed.

According to a particular example presented in this publication, hydroboration of cyclohexylallene with the participation of HBpin affords allylboranes **71a**, with the best results being attained upon the addition of CuCl in the presence of Xantphos ($\mathbf{L}^{21}$): $E:Z = >99:1$ (85% total yield). When the ligand $\mathbf{L}^{42}$ is used, the product yield increases to 99% (the isolated yield is 78%), but the $E-Z$ selectivity decreases to $>95:5$ (Scheme 69).

Scheme 69

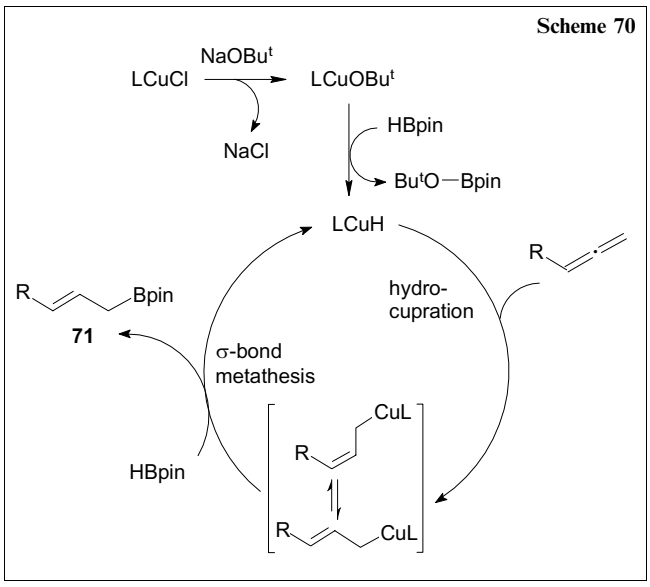


71a

(*a*) HBpin, CuCl, $\mathbf{L}^{21}$ or $\mathbf{L}^{42}$ (5 mol.%), NaOBu^t (12 mol.%), 1,4-dioxane, 28 °C, 2 h

The catalytic cycle of this reaction includes the formation of CuH and insertion of the allene terminal bond followed by metathesis of H–B and C–Cu σ-bonds (Scheme 70).

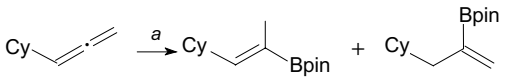
Scheme 70



In the case of B_2pin_2, two alkenylboranes, (*Z*)-**72a** and **73a**, were isolated (Scheme 71). The ratio of these products varies from 99 : 1 (in the presence of $\mathbf{L}^{43}$) to 1 : 99 (for $\mathbf{L}^{44}$ in toluene). Hence, each isomer can be selectively obtained in a high yield (conditions *a* or *b*), depending on the chosen carbene ligand (Table 3).

According to Tsuji and co-workers,[198] the regioselectivity of hydroboration of 1,3-dienes catalyzed by copper complexes and resulting in allyl- and homoallylboranes

Scheme 71



(*Z*)-**72a** **73a**

(*a*) B_2pin_2 , CuCl, $\mathbf{L}^{43}$ or $\mathbf{L}^{44}$ (2 mol.%), NaOBu^t (12 mol.%), MeOH, PhMe, 28 °C, 2 h

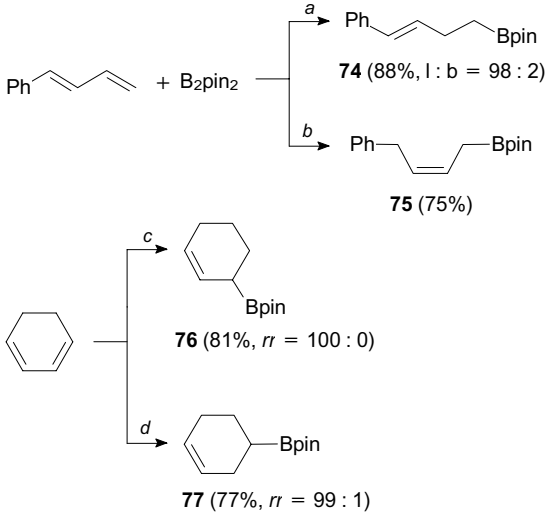
Table 3. Vinylboranes obtained by borylcupration of allenes under various conditions (see Scheme 68).

R	Yield of (*Z*)-**72** (%)	Yield of **73** (%)	Selectivity (*Z*)-**72** : **73**
	Conditions a		
Cy	99	–	99 : 1
$Ph(CH_2)_2$	90	–	93 : 7
Ph	83		95 : 5
	Conditions b		
Cy	–	99	2 : 98
$Ph(CH_2)_2$	–	88	3 : 97
Ph	–	82	2 : 98

Note. Conditions *a*: B_2pin_2 (1.1 equiv.), $\mathbf{L}^{43}$CuCl, MeOH (8 equiv.), PhMe, −20 °C; conditions *b:* B_2pin_2 (1.1 equiv.), $\mathbf{L}^{44}$CuCl, MeOH (2 equiv.), PhMe or THF, 28 °C.

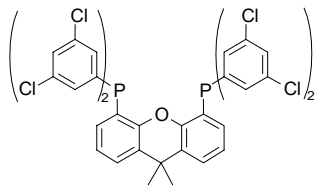
also depends on the nature of the ligand and the source of boron atom used. The reaction of 1-phenylbuta-1,3-diene involving B_2pin_2 may result in the formation of homoallylborane **74** *via* 1,2-addition or in the formation of allylborane **75** *via* predominant 1,4-addition (the ratio of 1,4- to 1,2-addition products is 99 : 1) (Scheme 72). In this divergent

Scheme 72



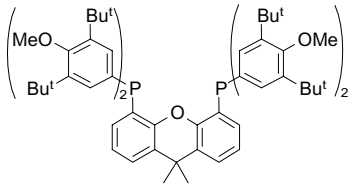
(*a*) CuCl (2 mol.%), $\mathbf{L}^{45}$ (2 mol.%), NaOBu^t, MeOH, PhMe, rt; (*b*) $\mathbf{L}^{14}$CuCl (1 mol.%), NaOBu^t, Bu^{t}OH, THF, rt; (*c*) HBpin, CuCl (1 mol.%), $\mathbf{L}^{46}$, THF, rt; (*d*) B_2pin_2, CuCl (2 mol.%), $\mathbf{L}^{45}$ (2 mol.%), MeOH, THF, 60 °C;

$\mathbf{L}^{45}$ =



(ClAr-Xan),

$\mathbf{L}^{46}$ =

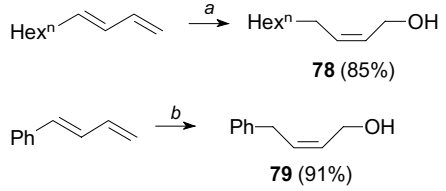


(DTBMAr-Xan)

pair, the reaction pathway is controlled by the ligands. The use of HBpin as the source of boron in the reaction with cyclohexa-1,3-dienes gives Markovnikov isomer **76** in high yield and with high selectivity. A change in the nature of the borating reagent and a minor modification of substituents in the ligand structure [ClAr-Xan (**L**[45]) instead of DTBMAr-Xan (**L**[46])] results in the formation of a different isomer, compound **77** (see Scheme 72).

The nickel complex with donor phosphine ligands such as PCy_3 and $P(NMe_2)_3$ controls the regio- and stereoselective 1,4-addition of HBpin to 1,3-dienes, which gives, for example, *cis*-alkenes **78** and **79** in high yield (Scheme 73).[199]

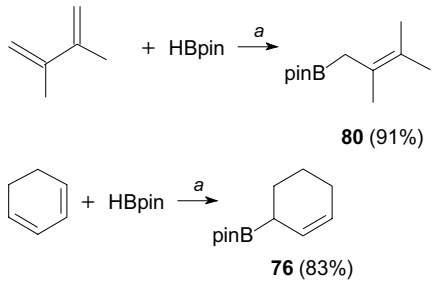
Scheme 73



(*a*) 1) HBpin (1.05 equiv.), $Ni(cod)_2$ (2.5 mol.%), PCy_3 (2.5 mol.%), PhMe, rt, 3 h; 2) H_2O_2, NaOH, THF; (*b*) 1) HBpin (1.05 equiv.), $Ni(cod)_2$ (1 mol.%), PCy_3 (1 mol.%), PhMe, rt, 3 h; 2) H_2O_2, NaOH, THF

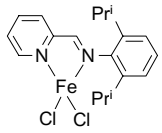
There are known examples of addition of pinacolboranes to 1,3-dienes catalyzed by Fe^{II} complexes **XXI**,[200] in which the 1,4-addition[201] produces anti-Markovnikov products **76** and **80** (Scheme 74).

Scheme 74



(*a*) **XXI** (5 mol.%), Mg (10 mol.%), Et_2O, 23 °C

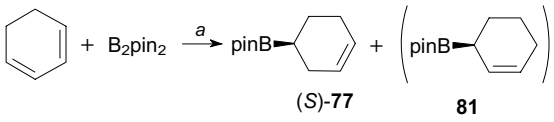
XXI =



The asymmetric hydroboration of 1,3-dienes on treatment with B_2pin_2 catalyzed by copper alkoxides with chiral ligands (Scheme 75) gives 1,2-addition products (homoallyl derivatives). When (−)-1,2-bis[(2*R*,5*R*)-2,5-dimethylphospholano]benzene [(*R*,*R*)-Me-DuPhos, **L**[47]] was used as the ligand at −20 °C, product (*S*)-**77** was formed with high enantioselectivity (94% *ee*), yield (92%) and regioselectivity (**77** : **81** = ⩾99 : 1).[202]

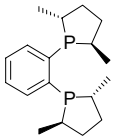
A publication of 2019[203] describes the regio- and enantioselective 1,2-hydroboration of substituted 1,3-dienes catalyzed by reduced cobalt complexes with chiral (P−N)*- and (P−P)*-ligands — phosphinooxazoline (PHOX, **L**[48]) and (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane (BDPP, **L**[49]) (Scheme 76). For alkene **82a**, the substrate conversion

Scheme 75



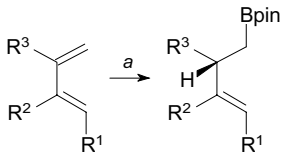
(*a*) CuOBu^t (5 mol.%), **L**[47] (5 mol.%), THF, MeOH, −20 °C;

L[47] =



[(*R*,*R*)-Me-DuPhos]

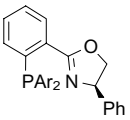
Scheme 76



82 (*er* up to 98 : 2)

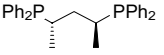
(*a*) HBpin, (**L**[48] or **L**[49])$CoHal_2$ (0.05 equiv.), Zn (1 equiv.), NaBARF (0.1 equiv.), rt; R^2 = H: R^1 = Bu^n, n-C_5H_{11}, $(CH_2)_4OX$ (X = TBDMS, Bn, Ts, Phth), *etc.*; R^1-R^2 = $(CH_2)_n$; R^3 = Me, Et, Pr^i, Cy, *etc.*; BARF is tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, Phth is phthalimido;

L[48] =

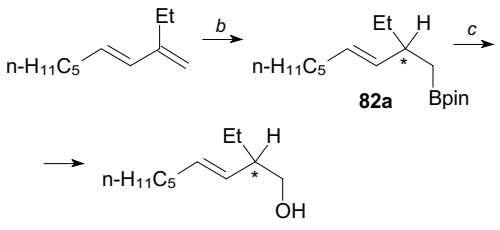


[PHOX (P-N)*],

L[49] =



[BDPP (P-P)*]



(*S*)-**83** (*er* = 93 : 7)

(*b*) HBpin (1.05 equiv.), (**L**[48] or **L**[49])$CoHal_2$ (0.05 equiv.), Zn (1 equiv.), NaBARF (0.1 equiv.), Et_2O or CH_2Cl_2; (*c*) H_2O_2, NaOH, H_2O

is 100%. In the case of alkyl substituents, 1,2-addition products **82b**–**d** are formed with high regio- and enantioselectivity (Table 4). Borane derivative **82a** is then converted to alcohol **83**.

Thus, a change in the nature of the catalyst allows the synthesis of either a Markovnikov or anti-Markovnikov isomer in the same reaction.

Table 4. Products of enantioselective 1,2-hydroboration of substituted 1,3-dienes (see Scheme 76; R^2 = H).

Compound **82**	R^1	R^3	Yield (%)	*rr*	*er*
b	n-C_5H_{11}	Pr^i	84	94 : 6	96 : 4
c	n-C_5H_{11}	Cy	88	95 : 5	96 : 4
d	Bu^n	Me	61	93 : 7	96 : 4

5. Conclusion

This review is dedicated to the memory of V.V.Markovnikov, a the great Russian chemist, on the occasion of celebration of the 150th anniversary of his famous rule. It is known that this rule has been criticized in English-language publications and that it was even proposed to stop teaching this rule in educational institutions due to its ambiguous interpretation. Some adherers of this rule proposed to modify it. Without intending to participate in this discussion, we would like to inform the readers that the merits of V.V.Markovnikov in organic chemistry are much broader. The phenomenon of isomerism he discovered not only validated A.M.Butlerov's theory. The existence of isomers raised an issue of selectivity of chemical reactions, in this particular case, regioselectivity. Thus, it follows that the addition reactions, which are commonly considered to be atom-economic and efficient, can be really economic and efficient only in the case where a single isomer is formed selectively. In relation to important reactions implemented in industry, that is, hydroformylation, hydrosilylation and hydroboration, we demonstrated that catalysis of these processes not only ensures regioselective preparation of the products. Also, a change in the catalytic system can lead to divergent regioselectivity, *i.e.*, to the selective formation of another isomer. In the next part of the review we will continue consideration of the problem of selectivity in relation to hydroamination, hydrothiolation, hydrophosphorylation and hydrophosphination.

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