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Highly Selective Cobalt-Catalyzed Hydrovinylation of Styrene

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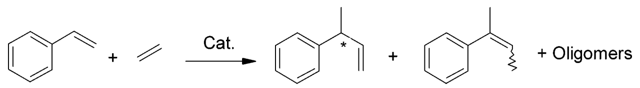
Transition-metal-mediated C−C coupling reactions have attracted considerable interest and continue to gain importance due to the demand for atom-efficient syntheses. The hydrovinylation reaction, for example, exhibits great potential in fine chemicals as well as the pharmaceutical industry because it can generate optically active products. This codimerization reaction, usually catalyzed by either nickel or palladium complexes, is depicted in eq 1 for styrene and ethene as starting materials.[1]



However, the main problems in the hydrovinylation reaction are isomerization of the desired product (3-phenyl-1-butene to 2-phenyl-2-butene) and oligomerization of ethene or styrene.

In addition to various catalysts based on nickel[2] and palladium,[3] complexes of ruthenium,[4] rhodium,[5] cobalt,[6] and iridium[7] have been used as catalysts in the hydrovinylation, as well, although with moderate success. The most active catalysts are still nickel systems bearing a monodentate phosphorus ligand and palladium-based catalysts bearing a hemilabile P,O donor ligand. To increase the regio- and stereoselective control as well as complex stability, the use of bidentate and tridentate ligands was taken into consideration. However, these ligands cannot be applied for nickel or palladium because a free coordination site at the metal center, which is required for monomer coordination during the catalytic cycle, is blocked by the additional donor atom and the corresponding chelate effect. Triggered by the simultaneous discovery of highly active iron and cobalt catalysts bearing bis(imine)pyridine ligands for the oligo- and polymerization of ethene,[8,9] we decided to explore the potential of iron- and cobalt-based catalysts in the hydrovinylation of styrene. These transition metal centers can usually exhibit higher coordination numbers compared to those of nickel and palladium.

In a first approach, $FeCl_2$ and $CoCl_2$ were reacted with a bidentate phosphorus ligand (dppe, **3**) and the tridentate nitrogen-based ligand **1**. After activation with either Bu_4NBH_4 or DEAC (diethylaluminumchloride), these eight different species were applied in the hydrovinylation of styrene. However, $[Co(dppe)Cl_2]$ activated by DEAC proved to be the only system which showed catalytic activity. Consequently, a range of different phosphine ligands (Figure 1) was used in the cobalt-catalyzed hydrovinylation of styrene. The results are depicted in Table 1.[10]

Several highly active catalysts have been discovered and investigated, including $CoCl_2$ bearing the narrow bite-angle ligand dppm (**2**) (entry 2), the monodentate PPh_3 ligand (entry 6), and the flexible BPC_6-phos ligand (**6**) (entry 7). Simple diphosphines display lower activities in combination with $CoCl_2$ upon an enlarged ligand backbone (entries 2−4). However, this trend cannot be extrapolated to other types of diphosphine ligands exhibiting wide bite-angles: while the rigid Xantphos ligand (**5**) shows low activity (entry 5), the cobalt catalyst bearing the flexible BPC_6-phos ligand shows high activity (entry 7). This could be explained by the coordination mode of the latter ligand toward the cobalt center; we assume that BPC_6-phos bridges two metal centers, rather than acting as a chelating ligand. In fact, X-ray crystal structure analysis reveals that this diphosphine forms dimeric species in the solid state in the analogous reaction with $PdCl_2$, $PtCl_2$, and $[Rh(CO)_2(\mu\text{-}Cl)]_2$.[11] It therefore acts as a monodentate ligand per metal center, such as PPh_3. The dppm ligand, however, also forms dimeric bridging species in the solid state but is believed to form monomers in solution.[12] We can conclude that the most active catalysts contain either a narrow bite-angle diphosphine or a monodentate phosphine ligand (including bridging ligands). At this time, it is not possible to discard the partial dissociation of a bidentate phosphine.

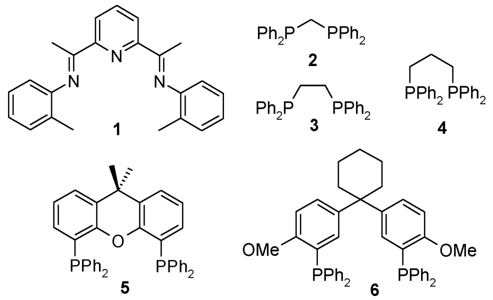


Figure 1. Achiral ligands applied in the cobalt-catalyzed hydrovinylation.

Table 1. Cobalt-Catalyzed Hydrovinylation of Styrene with Different Phosphine Ligands[a]

entry	ligand	conv.[b] (%)	$S_{(codim.)}$ (%)	$S_{(3P1B)}$ (%)	$S_{(oligomers)}$ (%)
1		10	10	100	90
2	**2**	100	>99	87	n.d.
3	**3**	93	>99	100	n.d.
4	**4**	15	>99	100	n.d.
5	**5**	9	>99	100	n.d.
6	2 PPh_3	100	>99	65	n.d.
7	**6**	100	>99	95	n.d.

[a] Conditions: CH_2Cl_2, $T = 0$ °C, $t = 90$ min, $p = 30$ bar ethylene, $S/C = 750$, 5 equiv of DEAC (1.0 M in hexanes). [b] Determined by GC analysis with an Ultra-2 column. n.d.: not detected.

Furthermore, the lower selectivity of the systems $[Co(\mathbf{2})Cl_2]$, $[Co(PPh_3)_2Cl_2]$, and $[Co(\mathbf{6})Cl_2]$ toward 3-phenyl-1-butene compared to those of $[Co(\mathbf{3})Cl_2]$, $[Co(\mathbf{4})Cl_2]$, and $[Co(\mathbf{5})Cl_2]$ might be attributed to their high catalytic activity, although it should be kept in mind that selectivity and activity cannot always be related to one another. Complete conversion of the substrate styrene is reached within the 90 min of reaction time, and subsequent isomerization will thus take place. When the reaction is monitored in time, it was confirmed that isomerization does not occur prior to complete consumption of the substrate styrene.[10] This offers great opportunities with respect to environmentally benign processes and atom-efficient syntheses.

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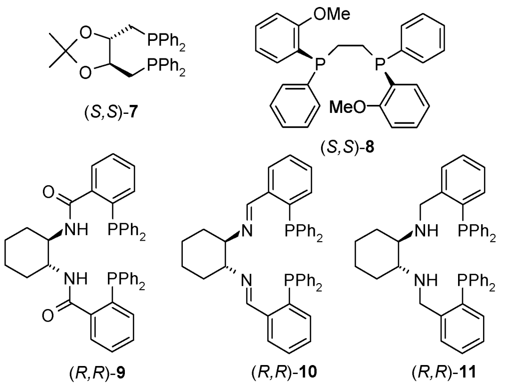

(*S*,*S*)-**7** (*S*,*S*)-**8** (*R*,*R*)-**9** (*R*,*R*)-**10** (*R*,*R*)-**11**

Figure 2. Chiral ligands applied in the cobalt-catalyzed hydrovinylation.

Table 2. Cobalt-Catalyzed Hydrovinylation of Styrene with Different Chiral Phosphine Ligands[a]

entry	ligand	conv.[b] (%)	$S_{(codim.)}$ (%)	$S_{(3P1B)}$ (%)	ee[c] (%)
1	(*S*,*S*)-**7**	8	>99	100	14 (*R*)
2	(*S*,*S*)-**8**	30	>99	100	26 (*R*)
3	(*R*,*R*)-**9**	74	>99	100	47 (*R*)
4	(*R*,*R*)-**10**	2	>99	100	
5	(*R*,*R*)-**11**	0			

[a] Conditions: CH_2Cl_2, $T = 0$ °C, $t = 90$ min, $p = 30$ bar ethylene, $S/C = 750$, 5 equiv of DEAC (1.0 M in hexanes). [b] Determined by GC analysis with an Ultra-2 column. [c] Determined by GC analysis with a β-cyclodextrin column.

It should be noted that the reaction is performed at $T = 0$ °C, whereas the nickel-catalyzed reactions usually have to be cooled to $T = -60$ °C to prevent isomerization and oligomerization reactions. Interestingly, the system [Co(dppe)Cl_2] yields very selectively 3-phenyl-1-butene even at $T = +60$ °C, and no formation of oligomers was observed. The absence of any isomerization to 2-phenyl-2-butene is perhaps the most important feature of the cobalt-catalyzed hydrovinylation.

Activation of [Co(dppe)Cl_2] with aluminum containing species other than Et_2AlCl was not promising. Activation with $EtAlCl_2$ gave, for example, full conversion but a very low selectivity toward the desired 3-phenyl-1-butene, and oligomerization proved to be the major reaction. $AlMe_3$- and MAO-activated reactions showed low conversions and moderate selectivities. In addition to excellent product selectivity, high enantioselectivities of the desired product are also required. For the first time, enantioselective Co-catalyzed hydrovinylation of styrene was achieved using a Co-based system bearing chiral ligands, as depicted in Table 2.

Well-known chiral diphosphines, such as DIOP[13] **7** and DIPAMP[14] **8** (see Figure 2), show moderate activities in combination with $CoCl_2$ and an activator and also low enantioselectivities (entries 1 and 2). Various other chiral diphosphine ligands showed similar results in terms of activity and enantioselectivity. Very promising results were obtained with the bis(phosphine)amide ligand ((*R*,*R*)-**9**) employed in combination with $CoCl_2$ and DEAC (entry 3). This ligand was originally designed for palladium-catalyzed allylic alkylation reactions.[15] An excellent activity as well as a promising enantioselectivity with an enantiomeric excess of 47% was observed. The corresponding systems based on the imine ((*R*,*R*)-**10**) and amine ((*R*,*R*)-**11**) analogues of (*R*,*R*)-**9**, however, are catalytically inactive in combination with $CoCl_2$ (entries 4 and 5). On the basis of the comparison between these ligand systems, it is assumed that the amide nitrogen atoms do not coordinate to the metal center during catalysis or play the role of a hemilabile donor group. In contrast, it is anticipated that in the imine and amine analogues the nitrogen atoms occupy the required free coordination site at the metal center and therefore inhibit the catalytic reaction. Moreover, in combination with the alkylaluminum activator species, the amide functionalities could play an important role in the induction of the stereogenic information.

In conclusion, we have investigated a new series of catalysts for the hydrovinylation of styrene based on $CoCl_2$ combined with a mono- or diphosphine ligand and an aluminum-based activator. A virtually 100% chemoselectivity has been achieved, even at elevated temperatures. Isomerization of the desired product does not occur prior to full consumption of the styrene substrate. In addition, the first enantioselective Co-catalyzed hydrovinylation has been described using $CoCl_2$ equipped with bis(phosphine)amide ligands. Promising enantioselectivities of up to 47% have been achieved.

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Supporting Information Available: A listing of experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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