DOI: 10.1002/adsc.200900261

Highly Selective Cobalt-Catalyzed Hydrovinylation of Styrene

Michiel M. P. Grutters,[a] Jarl Ivar van der Vlugt,[a,d] Yuxin Pei,[c] Allison M. Mills,[b] Martin Lutz,[b] Anthony L. Spek,[b] Christian Müller,[a] Christina Moberg,[c] and Dieter Vogt[a,]*

[a] Schuit Institute of Catalysis, Laboratory of Homogeneous Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
Fax: (+31)-(0)40-245-5054; phone: (+31)-(0)40-247-2483; e-mail: d.vogt@tue.nl
[b] Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, 3584 CH Utrecht, The Netherlands
[c] Department of Organic Chemistry, Royal Institute of Technology (KTH), Stockholm, Sweden
[d] Current address: van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, the Netherlands

Received: April 15, 2009; Published online: August 24, 2009

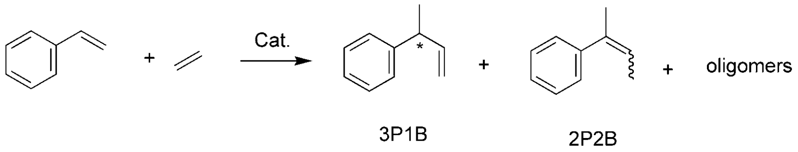
Abstract: Phosphine complexes of cobalt halide salts activated by diethylaluminum chloride are shown to yield highly active catalysts in the hydrovinylation of styrene, with unprecedented high selectivity to the desired product 3-phenyl-1-butene (3P1B). Double-bond isomerization, a common problem in codimerization reactions, only occurs after full conversion with these catalyst systems, even at elevated temperature. The most active catalysts are based on cobalt halide species combined with either C_1- or C_2-bridged diphosphines, heterodonor P,N or P,O ligands, flexible bidentate phosphine ligands or monodentate phosphine ligands. Kinetic investigations show an order >1 in catalyst, which indicates either the involvement of dinuclear species in the catalytic cycle or partial catalyst decomposition *via* a bimolecular pathway.

Keywords: cobalt; dimerization; homogeneous catalysis; hydrovinylation; phosphine ligands; regioselectivity

Introduction

The codimerization of ethene and alkenes, also known as the hydrovinylation reaction, is the addition of the elements of ethene (vinyl and hydrogen) across the double bond of a second alkene. The codimerization of vinylarenes and ethene[1,2] has attracted a lot of attention (Scheme 1), particularly in an asymmetric fashion.[3] Enantiomerically enriched 3-aryl-1-butenes are potential monomers for the production of very high-melting syndiotactic polymers[4] and intermediates in the production of optically active anti-inflammatory 2-arylpropionic acids such as Naproxen and Ibuprofen.[5]

Cobalt-based systems as catalysts for codimerization reactions have been studied only scarcely, and have been applied mainly in the codimerization of 1,3-butadiene and ethene and in the addition of ethene to norbornadiene.[6] Consequently, little is known about the factors governing the cobalt-catalyzed hydrovinylation of ethene and vinylarenes. We have recently demonstrated the first successful application of Co catalysts in the asymmetric hydrovinylation of sytrene and ethene with diphosphine ligands, yielding up to 47% *ee* under non-optimized conditions when applying the *(S,S)*-Trost ligand.[7] With these results in hand, a further exploration of the scope and limitations of Co-catalyzed codimerization of styrene and ethene is justified.[8]



Scheme 1. Codimerization of vinylarenes and ethene.

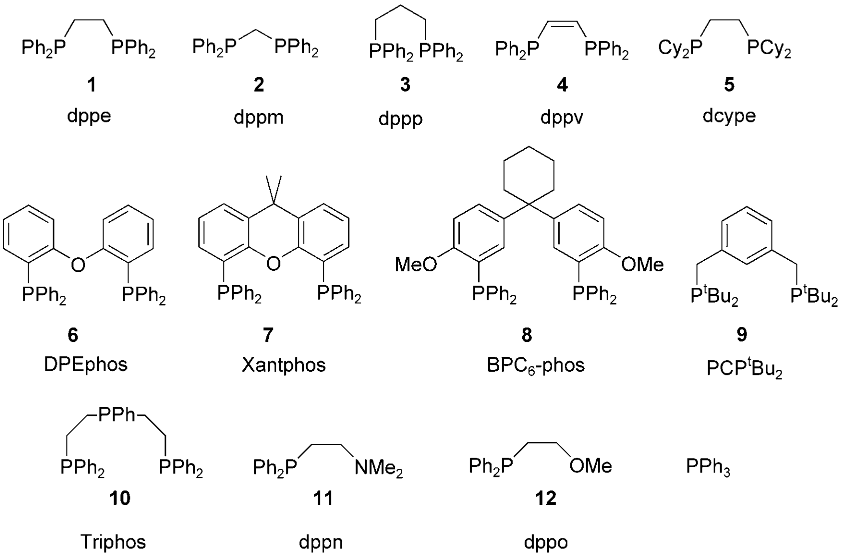


Figure 1. Structures of the diphosphine ligands used in the screening study.

Results and Discussion

Ligand Screening

The use of monodentate or hemilabile ligands has proven very crucial for a successful approach to codimerize ethene and styrene with a variety of transition metals, including Ni and Pd as prominent examples.[9] To test if this paradigm would also hold for a Co-based catalytic system, several diphosphine ligands with varying bite angles were screened (Figure 1). Besides a number of common alkyl-bridged diphosphines (ligands **1**–**5**), including dppe, well-established wide bite angle ligands such as DPEphos (**6**) and Xantphos (**7**) have been studied.

Furthermore, as heterodonor P,O ligands with potential hemilabile coordination[10] to a metal center have been applied succesfully in Pd-catalyzed hydrovinylation,[11] also two heterodonor analogues of dppe, namely dppn (**11**)[12] and dppo (**12**)[13] were tested in the Co-catalyzed hydrovinylation of styrene. For comparison, the reaction was also performed with 2 equivalents of PPh_3. The results of these hydrovinylation experiments are listed in Table 1.

The use of $CoCl_2$ without any additional ligand resulted in poor catalytic activity. Moreover, the main product proved to be oligomeric species (entry 1). The most active catalyst in the series of diphosphines is based on dppm (**2**) (entry 3). This system performs slightly better than the dppe system Co(**1**)Cl_2 (entry 2) and significantly better than dppp (**3**), as the activity dropped dramatically to only 15% (entry 4). Notably, dppm (**2**), when coordinated to $CoCl_2$, was shown to exist as a dimeric species in the solid state, whereas ESR studies indicated that mononuclear (distorted) tetrahedral species were present in solution.[14] Introduction of the rigid ethene backbone (dppv, **4**) also results in low activity (entry 5), probably related to geometric constraints upon coordination of styrene and/or ethene during catalysis. Finally, sterically more demanding and electron-donating cyclohexyl substituents on the phosphorus donor atoms (dcype, **5**) accounted for a decrease in activity as well (entry 6). Notably, all systems showed high selectivity towards 3P1B, with the exception of **2**, which is solely due to the very high activity of this catalytic system, with unwanted isomerization to 2-phenyl-2-butene (2P2B) after 100% conversion was reached. Formation of higher oligomers was not detected for any of these reactions catalyzed by cobalt complexes bearing phosphine ligands.

With respect to the activity of the wide bite angle diphosphine systems, the flexible BPC_6-phos ligand[15] (**8**) yielded the most active catalyst (entry 9). Two possible coordination modes for this ligand are mononuclear P,P-coordination or dinuclear bridging P,P-coordination. X-ray crystallographic studies reveal that in the solid state BPC_6-phos (**8**) coordinates in a bridging dimeric fashion in complexes of $PdCl_2$, $PtCl_2$ and Rh(CO)Cl.[16] DPEphos (**6**) and Xantphos (**7**) led to significantly lower activities, as the conversion reached only 24 and 9% conversion, respectively, after 90 min of reaction time (entries 7 and 8). Cobalt complexes bearing the heterodonor ligands dppn and dppo perform even better than Co(**1**)Cl_2, with Co(**12**)Cl_2 being slightly more active than Co(**11**)Cl_2, giving 100% conversion after 30 min (entry 14). The selectivity toward codimers is excellent, whereas the selectivity toward 3P1B suffers with prolonged reaction time, due to subsequent isomerization of 3P1B to 2P2B.

Table 1. Co(**L$_n$**)Cl$_2$-catalyzed hydrovinylation of styrene with different diphosphine and monophosphine ligands.[a]

Entry	Ligand	Conv. [%][b]	S$_{(codim.)}$ [%]	S$_{(3P1B)}$ [%][c]	S$_{(2P2B)}$ [%][d]
1	–	10	10[e]	100	–
2	dppe **1**	93	>99	100	–
3	dppm **2**	100	>99	87	13
4	dppp **3**	15	>99	100	–
5	dppv **4**	16	>99	100	–
6	dcype **5**	12	>99	100	–
7	DPEphos **6**	24	>99	100	–
8	Xantphos **7**	9	>99	100	–
9	BPC$_6$phos **8**	100	>99	95	5
10	PCP(tBu)$_2$ **9**	2	>99	100	–
11	Triphos **10**	75	>99	98	2
12	dppn[f] **11**	94	>99	100	–
13	dppn **11**	100	>99	96	4
14	dppo[f] **12**	100	>99	100	–
15	dppo **12**	100	>99	89	11
16	PPh$_3$ (2 equiv.)	100	>99	65	35
17	PPh$_3$ (1 equiv.)[f,g]	20	>99	100	–
18	PPh$_3$ (2 equiv)[f,g]	73	>99	100	–
19	PPh$_3$ (3 equiv.)[f,g]	50	>99	100	–
20	PPh$_3$ (4 equiv.)[f,g]	22	>99	100	–

[a] *Conditions:* CH$_2$Cl$_2$, $T=0\,°C$, $t=90$ min, $p=30$ bar ethene, S/C=750, 5 equiv. DEAC (1.0 M in hexanes).

[b] Determined by GC analysis with an Ultra-2 column.

[c] Selectivity to 3P1B within the codimers fraction.

[d] Isomerization only occurs after 100% conversion.

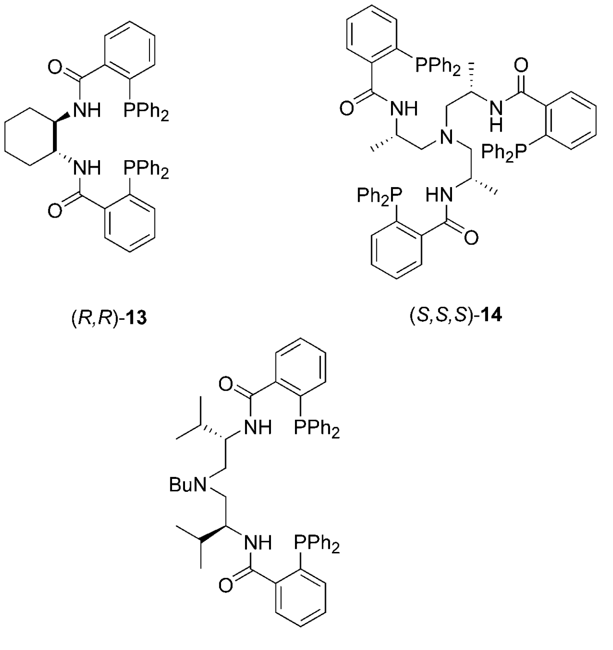
[e] Oligomerization (90%) was the main reaction observed.

[f] 30 min reaction time.

[g] S/C=1500.

Co(PPh$_3$)$_2$Cl$_2$ proved to be the most active catalyst system, with the same excellent selectivity as observed with the diphosphine ligands (entry 16). Upon addition of more than two equivalents of ligand the activity decreases significantly but the selectivity remains high. The possibility of the two monodentate ligands to allow maximum flexibility during the catalytic cycle could be responsible for the very high activity.

Based on our initial results in the asymmetric cobalt-catalyzed hydrovinylation of ethene and styrene,[7] using Trost's bis(phosphine-amide) ligand (R,R)-**13**, which was originally designed for the palladium-catalyzed allylic amination,[17] we decided to do a preliminary screening with two other ligands incorporating this amide-phosphine scaffold, i.e., the C_3-symmetrical tris(phosphine-amide) ligand (S,S,S)-**14** as well as the diphosphine analogue (S,S)-**15** (Figure 2).



(R,R)-**13** (S,S,S)-**14** (S,S)-**15**

Figure 2. Chiral amido-phosphine ligands used for screening in the asymmetric hydrovinylation.

We have communicated that Co((R,R)-**13**)Cl$_2$ performed surprisingly well, with up to 70% conversion and 47% enantiomeric excess.[7] It is believed that the nitrogen donor atoms do not coordinate to the cobalt metal center. If this would be the case, a decrease in activity is expected. It should be noted that this catalyst shows a trace of isomerization before the styrene substrate is fully consumed. When the cobalt dichloride catalyst precursor bearing the C_3-symmetrical (S,S,S)-**14**[18] was employed, only 5% of conversion was detected by GC, whereas the enantiomeric excess

Table 2. $Co(\overset{\frown}{\mathbf{PP}})Cl_2$-catalyzed hydrovinylation of styrene with chiral amido-phosphine ligands.

Entry	Ligand	Conv. [%][b]	$S_{(codim.)}$ [%]	$S_{(3P1B)}$ [%]	$S_{(oligomers)}$ [%][c]	*ee* [%][d]
1	(*R,R*)-**13**	74	>99	100	n.d.	47 (*R*)
2	(*S,S,S*)-**14**	5	>99	100	n.d.	50 (*S*)
3	(*S,S*)-**15**	80	>99	100	n.d.	50 (*S*)

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

turned out to be 50% to (*S*)-3-phenyl-1-butene (Table 2). It is argued that one of the three equivalent phosphine-amide moieties has to dissociate from the metal center in order to create a free coordination site for substrate binding, leading to low catalytic turnover. This has been confirmed by employing ligand (*S,S*)-**15**.[18] With the same stereoselectivity of up to 50% *ee* this catalyst accounts for a high conversion of 80% due to the fact that there are only two phosphorus donor atoms available for coordination. To date, Co[(*R,R*)-**13**]Cl_2 and Co[(*S,S*)-**15**]Cl_2 prove to be the best performing catalysts in the asymmetric cobalt-catalyzed hydrovinylation of styrene, combining good activity and excellent regioselectivity with enantioselectivities of up to 50%.

X-Ray Crystal Structures of Co(6)Cl_2 and Co(7)Cl_2

Especially the rigid structures imposed by DPEphos (**6**), Xantphos (**7**) and the PCP(*t*-Bu)$_2$-pincer ligand **9** seemed to inhibit the reaction. However, the average bite angles for these ligands are primarily based on square-planar coordination in Rh, Pt, and Pd complexes. We were therefore interested in the molecular structure of the complexes Co(**6**)Cl_2 and Co(**7**)Cl_2 (unfortunately no suitable crystals could be obtained for the complex with ligand **9**). In both cases, blue crystals were grown by slow diffusion of diethyl ether into a solution in dichloromethane (for DPEphos an interface layer of toluene was used), which proved to be suitable for X-ray diffraction. ORTEP representations of the molecular structures obtained for the complexes are depicted in Figure 3.

The 15-electron cobalt(II) centers in Co(**6**)Cl_2 and Co(**7**)Cl_2 both show slightly distorted tetrahedral geometry with subtle differences, as is mainly evident from the bite angles P1–Co1–P2 of 104.81(2)° and 114.54(2)°, respectively (Table 3). Concerning the diphosphine derivative, the typical P–M–P angle in a *cis* palladium complex is 104.6° [Pd(**7**)(TECN)][19] while for [$PtCl_2$(**7**)] the angle is 99.17°.[20] However, it is known that the weak interaction with the bridgehead oxygen atom can give rise to pseudo-terdentate coordination and hence to very large bite angles.[21] The P–Co bond lengths of ~2.3–2.4 Å are in the typical range observed for Co(II)-phosphine complexes.[22] The Xantphos ligand backbone is close to planar, significantly different as observed in various other metal complexes bearing this particular ligand scaffold.[23] The Co–O distances of ~2.9–3.0 Å are considerably shorter than the sum of the ionic radii (3.55 Å), which might suggest some weak bonding interaction with the oxygen atom, while this does not lead to a very large P–Co–P angle. However, the out of plane position of the Co ion with respect to the DPE and xanthene backbone seems to disfavor any true cobalt-oxygen coordination (see side view, Figure 3).

The Role of the Activator, Solvent, and Temperature

Nickel-based hydrovinylation pre-catalysts need alkylaluminum compounds to generate a cationic nickel complex, which then reacts with ethene to form a nickel hydride upon β-hydrogen elimination, which is thought to be the active species.[3] For the cationic palladium catalysts; the allylpalladium species reacts directly with ethene to subsequently form a Pd-hydrido complex through β-hydrogen elimination. With the present cobalt complexes, activation by alkylaluminium species is also needed to generate an active catalyst. The results of the Co(**1**)Cl_2-catalyzed reaction using different activators compared to the 'standard' diethylaluminum chloride (DEAC) are given in Table 4.

Activation of Co(**1**)Cl_2 by aluminum species other than diethylaluminum chloride (DEAC) was only moderately successful with triisobutylaluminum (TIBA, entry 5). Activation with ethylaluminum dichloride (EADC) gave full conversion but a very low selectivity towards 3P1B. Next to traces of codimers, oligomerization was the major observed reaction. Reactions activated with trimethylaluminum (TMA), triethylaluminum (TEA), diisobutylaluminum hydride (DIBALH) or methylaluminoxane (MAO) suffered from very low conversions although selectivities were good in most cases (entries 2–4, 6).

A screening of solvent effects, using DEAC as activator, revealed that THF completely inhibited catalyt-

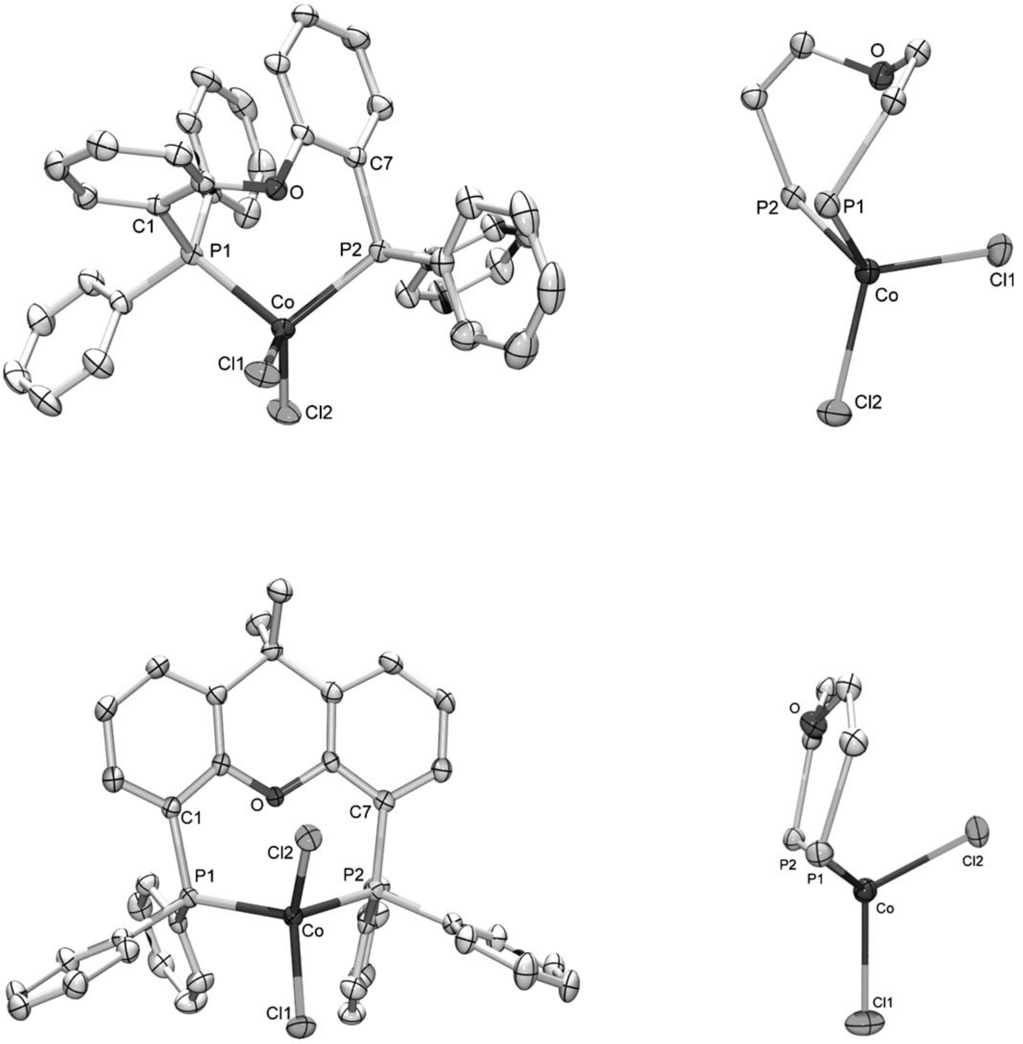


Figure 3. ORTEP representations of Co(**6**)Cl$_2$ (*top*) and Co(**7**)Cl$_2$ (*bottom*) at 50% probability level (*left*) and side-view of selected atoms (*right*). For Co(**6**)Cl$_2$ the disordered solvent molecules are not depicted. For Co(**7**)Cl$_2$ only one of the two independent molecules in the unit-cell is depicted. Hydrogen atoms are omitted for clarity.

Table 3. Selected atom distances (Å) and angles (°) for complexes Co(**6**)Cl$_2$ and Co(**7**)Cl$_2$.

	Co(**6**)Cl$_2$	Co(**7**)Cl$_2$		Co(**6**)Cl$_2$	Co(**7**)Cl$_2$
Bond lengths (Å)					
Co−P1	2.3703(6)	2.3858(7)	Co−P2	2.4031(6)	2.3800(6)
Co−Cl1	2.2143(5)	2.2030(6)	Co−Cl2	2.2266(6)	2.2413(6)
P1−C1	1.824(2)	1.819(2)	P2−C7	1.821(2)	1.824(2)
Co···O	3.0277(14)	2.9024(16)			
Bond angles (°)					
P1−Co−P2	104.81(2)	114.54(2)	Cl1−Co−Cl2	112.84(2)	115.41(3)
P1−Co−Cl1	106.88(2)	107.97(3)	P1−Co−Cl2	105.56(2)	107.02(2)

ic activity.[24] In toluene, the conversion reached 40%, which is significantly lower than for the reaction performed in CH$_2$Cl$_2$, whereas the selectivity towards 3P1B remained very high at >99%. The moderate solubility of Co(dppe)Cl$_2$ in toluene could cause the lower activity of the catalyst system. For the 'solvent-free' reaction run in neat styrene, it was observed that the high substrate to catalyst ratios of ~2600 did not negatively affect the selectivity toward 3P1B. The conversion was determined at 12%, which results in a relatively low turnover frequency of 200 h^{-1} compared to 590 h^{-1} in CH$_2$Cl$_2$.[25]

Table 4. Co(**1**)Cl_2-catalyzed hydrovinylation of styrene using different activators and different temperatures (for DEAC only).[a]

Entry	Activator	Temp (°C)	Conv. [%][b]	$S_{(codim.)}$ [%]	$S_{(3P1B)}$ [%]	$S_{(oligomers)}$ [%][c]
1	EADC	0	100	<5	–	>95
2	TMA	0	3	>99	100	n.d.
3	TEA	0	0	–	–	–
4	DIBALH	0	2	>99	100	n.d.
5	TIBA	0	60	80	100	20
6	MAO	0	3	>99	100	n.d.
7	DEAC	0	93	>99	100	n.d.
8	DEAC	25	100	>99	96	n.d.
9	DEAC[d]	60	100	>99	85	n.d.

[a] *Conditions:* CH_2Cl_2, $T = 0\,°C$, $t = 90$ min, $p = 30$ bar ethene, S/C = 750.
[b] Determined by GC analysis with an Ultra-2 column.
[c] n.d. = not detected.
[d] Reaction time = 30 min.

For the hydrovinylation of styrene and ethene using Co(**1**)Cl_2/DEAC the benchmark temperature is 0 °C, whereas especially Ni-catalyzed reactions have to be run at −60 °C to prevent isomerization and oligomerization. The extremely high selectivity to 3P1B of the cobalt system is preserved even at 60 °C (Table 4, entry 9). A consequence of the fast reaction at 60 °C is complete consumption of styrene with subsequent isomerization. However, the total absence of other side products and oligomerization products further underlines the excellent selectivity.

Isomerization

The absence of isomerization to 2-phenyl-2-butene prior to full conversion is perhaps the most striking feature of the cobalt-catalyzed hydrovinylation and a great step to achieve an atom-efficient process at ambient temperature. Concentration profiles of both substrates and products were monitored in time for two catalyst systems and it was thereby confirmed that isomerization only occurs after full conversion of styrene (Figure 4).

The reaction catalyzed by $Co(PPh_3)_2Cl_2$ (Figure 4, *left*) reached full conversion in ~40 min, while with Co(**1**)Cl_2 as catalyst (Figure 4, *right*) this took 150 min. Isomerization of 3P1B to *cis*- and *trans*-2P2B could be detected in the case of $Co(PPh_3)_2Cl_2$ after approximately 120 min.

Kinetic and Mechanistic Considerations

The question arises whether the cobalt active species is a mononuclear complex or that dinuclear cobalt complexes are required to perform the reaction. The rate of the overall reaction can be expressed as Eq. (1), where *a*, *b* and *c* are the orders in styrene, ethene and catalyst, respectively.

Performing a series of reactions while varying only the catalyst concentration reduces this equation to Eq. (2), from which the order in catalyst can be deduced.

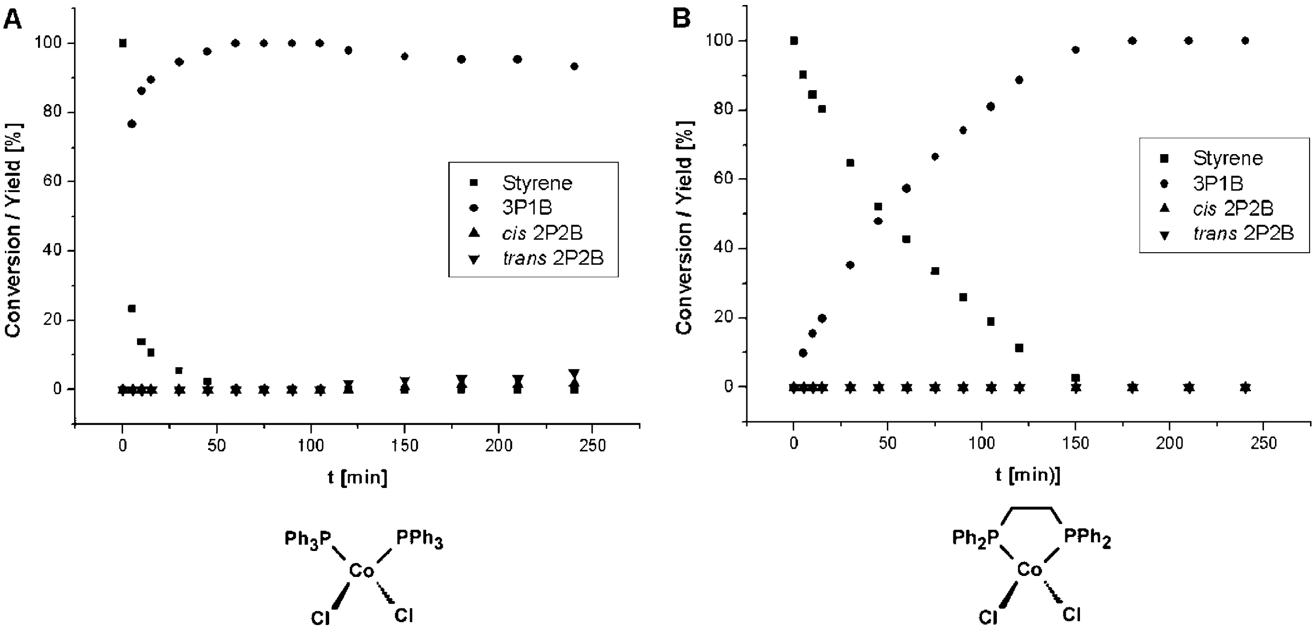


Figure 4. Conversion (substrate)/yield (products) *vs.* time in the hydrovinylation of styrene catalyzed by $Co(PPh_3)_2Cl_2$ (*left*) and Co(**1**)Cl_2 (*right*).

$$r = -\frac{d[Styrene]}{dt} = -\frac{d[Ethene]}{dt} = \frac{d[products]}{dt} = k[Styrene]^a[Ethene]^b[Cat]^c \qquad (1)$$

$$r = k'[Cat]^c \qquad \ln r = \ln k' + c\ln[Cat] \qquad (2)$$

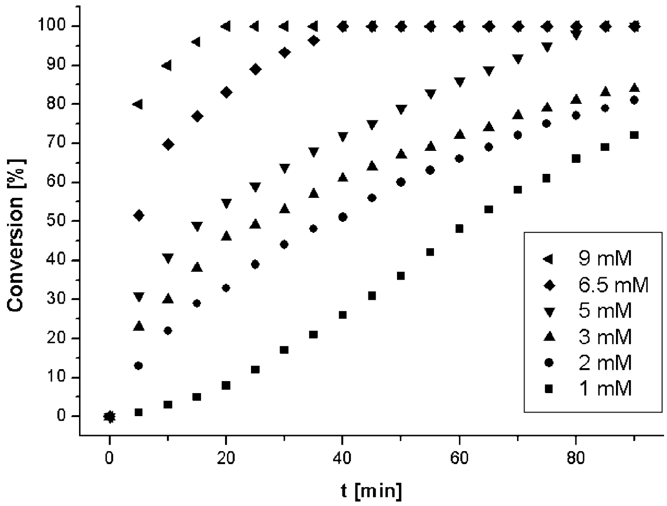


Figure 5. 3P1B yield *vs.* time at various Co(dppe)Cl_2 concentrations. *Conditions:* 20 mL CH_2Cl_2, $T = 0\,°C$, $p = 30$ bar ethene, 5 equiv. DEAC (1.0 M in hexanes).

Figure 5 displays the results obtained from a series of catalytic runs, in which the catalyst concentration is varied between 1 and 9 mM.

Obviously the catalyst concentration has a large influence on the rate of the reaction. The time required for 50% conversion varies from less than 5 min (9 mM) to more than 60 min (1 mM). All curves show a high initial rate followed by a more constant rate, except for the reaction with 1 mM catalyst concentration, which displayed also an induction period. Initial rates for all have been determined and are summarized in Figure 6.

From these data the order in catalyst concentration was calculated to be 1.4, which indicates mixed-order kinetics in catalyst and thus suggests either i) interplay or exchange between a monomeric catalytically active species and the involvement of two cobalt metal centers in the rate-determining step of the catalytic cycle, ii) partial catalyst decomposition to e.g., Co(0) species *via* a bimolecular disproportion or reductive elimination pathway. We have no definite proof for either possibility at this moment.

Conclusion and Outlook

We have described here a highly active and selective catalyst system for the hydrovinylation of vinylarenes with ethene based on phosphino-cobalt dihalide complexes. Excellent selectivities to the desired codimer were obtained. Double-bond isomerization, a common problem in codimerization reactions, only occurred after full conversion of the substrate to the primary product was reached, even at elevated temperature. The most active catalysts are based on cobalt halide species combined with either C_1- or C_2-bridged diphosphines, heterodonor P,N or P,O ligands, flexible bidentate phosphine ligands or monodentate phosphine ligands. The system exhibits great tolerance to temperature from at least 0 to 60 °C. Kinetic studies indicate an order in catalyst higher than 1, which suggests that dinuclear Co species are involved in the rate-determining step of the catalytic cycle. The unprecedented high selectivity and high activity transform this atom-efficient codimerization catalyst

Entry	Catalyst concentrations (mM)	Rate (mol·l^{-1}·h^{-1})
1	1	1.0[a]
2	2	2.5
3	3	4.5
4	5	6.6
5	6.5	12.6
6	9	23.8

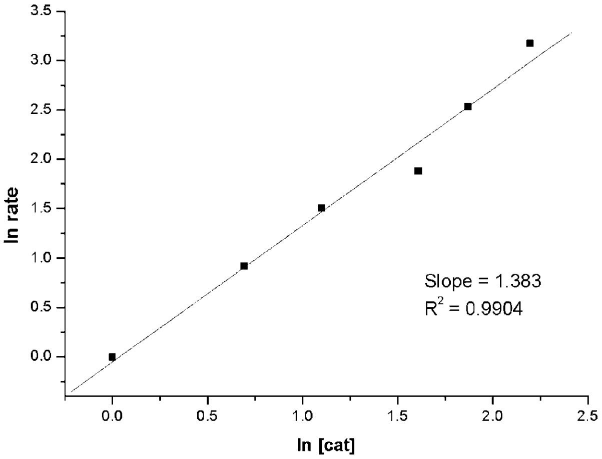


Figure 6. Initial rates at various catalyst concentrations and plot of ln(rate) *vs.* ln([catalyst]).

system into an ideal candidate for new enantioselective catalysts. Current research is directed toward a detailed understanding of the mechanism operative for this catalytic reaction, including characterization of the presumed active catalytic species involved and explanation of the broken order in catalyst. We also want to examine the scope of the substrates and expand on the asymmetric hydrovinylation, based on our current results.

Experimental Section

Chemicals were purchased from Aldrich, Acros or Merck and used as received unless stated otherwise. All preparations were carried out under an argon atmosphere using standard Schlenk techniques. Glassware was dried by heating under vacuum. Solvents were taken from custom-made solvent purification columns filled with Al_2O_3. Styrene was distilled from CaH_2 and stored at −20 °C. Ethylbenzene was distilled from CaH_2. Ethene was purchased from Hoek Loos with a purity of 3.5 and used as received. 1,1-Bis(3-diphenylphosphino-4-methoxyphenyl)cyclohexane (**8**, BPC$_6$-phos),[15] 3,5-bis[(di-*tert*-butylphosphino)methyl]benzene (**9**, PCP-pincer),[26] 1-(diphenylphosphino)-2-dimethylaminoethane (**11**, dppn),[12] 1-(diphenylphosphino)-2-methoxyethane (**12**, dppo),[13] and amidophosphines **14** and **15**[18] were synthesized according to literature procedures. Cobalt complexes were prepared as previously described by us.[7] IR spectra were recorded on a Shimadzu 7300 FT-IR spectrometer. Elemental analyses were obtained using a Perkin–Elmer 240 apparatus.

Preparation of Co(DPEphos)Cl$_2$, Complex Co(6)Cl$_2$[27]

To a solution of anhydrous cobalt(II) dichloride (75.0 mg, 0.58 mmol) in THF (5 mL) was added a solution of DPEphos [2,2′-bis(diphenylphosphino)diphenyl ether] (311.1 mg, 0.58 mmol) in THF (5 mL). The mixture was stirred overnight, resulting in a clear bright blue solution. After evaporation of all volatiles, the bright blue solid was washed with diethyl ether (10 mL), filtered and then dried to leave Co(**6**)Cl$_2$ as a bright blue powder; yield: 355.2 mg (0.53 mmol, 92%). Recrystallization by slow diffusion of diethyl ether into a solution of the Co(**6**)Cl$_2$ in CH_2Cl_2, layered with toluene, yielded deep-blue single crystals suitable for X-ray crystallographic analysis. Anal. calcd. for $C_{36}H_{28}Cl_2CoOP_2$: C 64.69, H 4.22; found: C 65.01, H 4.19.

Hydrovinylation Reaction

A home-made stainless steel 75-mL autoclave equipped with a copper mantle for rapid heat exchange and a glass beaker insert was pre-cooled to 0 °C with ice and water for 30 min. The appropriate cobalt complex (0.05 mmol) was weighed in a 15-mL Schlenk tube and dichloromethane (5 mL) was added before transfer to the pre-cooled autoclave *via* syringe. Subsequently, weighed amounts of styrene (4 mL) and ethylbenzene (1 mL, internal standard) were transferred to the autoclave *via* syringe. After flushing of the autoclave with ethene to remove the protecting argon atmosphere, DEAC (0.25 mL, 1.0 M in hexanes) was added to the magnetically stirred autoclave and it was pressurized to 30 bar initial pressure. After 1.5 h at 0 °C the pressure was released and the contents were subjected to flash chromatography over basic alumina before quantitative GC analysis.

GC Analysis Details

GC: Shimadzu GC 17 A; column: Ultra 2 (cross-linked 5% Ph-Me-siloxane), 25 m, i.d. 0.20 mm, film thickness 0.33 μm; carrier gas: helium 102 kPa (total flow 53 mL/min); temperature program: 50 °C (hold: 2 min.), 8 °C/min. to 250 °C (hold: 5 min.); injector temperature: 270 °C; detector temperature (FID): 270 °C; split ratio: 76; injection volume: 1 μL; retention times, see Table 5.

Table 5. Selected retention times of various substrates and products.

Compound	Retention time (min)
ethylbenzene	7.4
styrene	8.1
3-phenyl-1-butene	10.8
cis-2-phenyl-2-butene	11.1
trans-2-phenyl-2-butene	13.1

Crystal Structure Determination of Co(6)Cl$_2$ and Co(7)Cl$_2$

X-ray reflections were measured with Mo-K$_\alpha$ radiation (λ = 0.71073 Å) on a Nonius KappaCCD diffractometer with rotating anode at a temperature of 150 K. The reflections were integrated with the program HKL2000.[28] The structures were solved with automated Patterson methods (program DIRDIF99).[29] Refinement was performed with SHELXL97[30] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were introduced in calculated positions and refined with a riding model. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[31]

Co(6)Cl$_2$: $C_{36}H_{28}Cl_2CoOP_2$ + disordered solvent, MW = 668.35 g mol^{-1},[33] blue plates, 0.36 × 0.24 × 0.06 mm^3, triclinic, $P\bar{1}$ (no. 2), a = 10.0706(1), b = 11.2715(2), c = 17.6931(3) Å, α = 78.9337(6), β = 74.0765(7), γ = 76.6650(8)°, V = 1861.37(5) Å^3, Z = 2, D_x = 1.192 g cm^{-3},[33], μ = 0.715 mm^{-1}.[33] 34773 reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. The reflections were corrected for absorption on the basis of multiple measured reflections with the program SADABS[32] (0.68–0.96 correction range). 8494 reflections were unique (R_{int} = 0.0434) and 6682 reflections were observed [$I > 2\sigma(I)$]. The crystal contained large voids (434 Å^3/unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the routine SQUEEZE of the program PLATON[31] resulting in 45 electrons/unit cell. 379 parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0389/0.1171. R1/wR2 [all refl.]: 0.0537/0.1229. S = 1.157. Residual electron density between −0.41 and 0.38 e Å^3.

Co(7)Cl$_2$: $C_{39}H_{32}Cl_2CoOP_2$, MW = 708.42 g mol^{-1}, blue plates, 0.30 × 0.30 × 0.09 mm^3, monoclinic, $P2_1/c$ (no. 14), a = 16.9077(1), b = 10.5145(1), c = 40.3113(3) Å, β = 111.2220(3)°, V = 6680.39(9) Å^3, Z = 8, D_x = 1.409 g cm^{-3}, μ = 0.801 mm^{-1}. 56974 reflections were measured up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.62 Å^{-1}. The reflections were corrected for absorption using the routine DELABS of the program PLATON[31] (0.62–0.93 correction range). 13107 reflections were unique (R_{int} = 0.0435) and 9535 reflections were observed [I > 2σ(I)]. 811 parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0339/0.0728. R1/wR2 [all refl.]: 0.0583/0.0832. S = 1.032. Residual electron density between −0.38 and 0.37 e Å^3. CCDC 701657 [compound Co(**6**)Cl$_2$] and CCDC 701658 [compound Co(**7**)Cl$_2$] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Acknowledgements

*We thank Eindhoven University of Technology, the National Research School Combination on Catalysis (NRSC-C) and The Netherlands Organization for Scientific Research (NWO-CW) for financial support. Funding by the EC (HPRN-CT-2001-00187, **AC3S**) is kindly acknowledged.*

References

[1] H. Olivier-Bourbigou, L. Saussine, in: *Applied Homogeneous Catalysis with Organometallic Compounds*, (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, New York, **2002**, Vol. 1, p 253.

[2] P. W. Jolly, G. Wilke, in: *Applied Homogeneous Catalysis with Organometallic Compounds*, (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, New York, **2002**, Vol. 3, p 1164.

[3] T. V. RajanBabu, *Chem. Rev.* **2003**, *103*, 2845.

[4] G. Wilke, *Angew. Chem.* **1988**, *100*, 189; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 185.

[5] H. R. Sonawane, N. S. Bellur, J. R. Ahuja, D. G. Kulkarni, *Tetrahedron: Asymmetry* **1992**, *3*, 163.

[6] a) M. Iwamoto, S. Yuguchi, U.S. Patent 3,548,022, **1970**; b) R. J. Harder, (to Du Pont), U.S. Patent 3,574,139, **1971**; c) S. M. Pillai, G. L. Tembe, M. Ravindranathan, *J. Mol. Catal.* **1993**, *84*, 77.

[7] M. M. P. Grutters, C. Müller, D. Vogt, *J. Am. Chem. Soc.* **2006**, *128*, 7414.

[8] For Co-catalyzed hydrovinylation of 1,3-dienes, see: G. Hilt, S. Lüers, *Synthesis* **2002**, 609.

[9] See ref.[4] and: a) N. Nomura, J. Jin, H. Park, T. V. RajanBabu, *J. Am. Chem. Soc.* **1998**, *120*, 459; b) T. V. RajanBabu, N. Nomura, J. Jin, M. Nandi, H. Park, X. Sun, *J. Org. Chem.* **2003**, *68*, 8431; c) M. Nandi, J. Jin, T. V. RajanBabu, *J. Am. Chem. Soc.* **1999**, *121*, 9899; d) T. V. RajanBabu, N. Nomura, J. Jin, B. Radetich, H. Park, M. Nandi, *Chem. Eur. J.* **1999**, *5*, 1963; e) H. Park, T. V. RajanBabu, *J. Am. Chem. Soc.* **2002**, *124*, 734; f) G. Franciò, F. Faraone, W. Leitner, *J. Am. Chem. Soc.* **2002**, *124*, 736; g) R. Bayersdörfer, B. Ganter, U. Englert, W. Keim, D. Vogt, *J. Organomet. Chem.* **1998**, *552*, 187; h) J. Albert, J. M. Cadena, J. Granell, G. Muller, J. I. Ordinas, D. Panyella, C. Puerta, C. Sañudo, P. Valerga, *Organometallics* **1999**, *18*, 3511; i) U. Englert, R. Haerter, D. Vasen, A. Salzer, E. B. Eggeling, D. Vogt, *Organometallics* **1999**, *18*, 4390.

[10] a) J. C. Jeffrey, T. B. Rauchfuss, *Inorg. Chem.* **1979**, *18*, 2658; b) P. Braunstein, F. Naud, *Angew. Chem.* **2001**, *113*, 702; *Angew. Chem. Int. Ed.* **2001**, *40*, 680.

[11] a) G. J. P. Britovsek, W. Keim, S. Mecking, D. Sainz, T. Wagner, *J. Chem. Soc. Chem. Commun.* **1993**, 1632; b) N. J. Hovestad, E. B. Eggeling, H. J. Heidbüchel, J. T. B. H. Jastrzebski, U. Kragl, W. Keim, D. Vogt, G. van Koten, *Angew. Chem.* **1999**, *111*, 1763; *Angew. Chem. Int. Ed.* **1999**, *38*, 1655; c) E. B. Eggeling, N. J. Hovestad, J. T. B. H. Jastrzebski, D. Vogt, G. van Koten, *J. Org. Chem.* **2000**, *65*, 8857.

[12] a) G. K. Anderson, R. Kumar, *Inorg. Chem.* **1984**, *23*, 4064; b) J. Zimmermann, I. Tkatchenko, P. Wasserscheid, *Adv. Synth. Catal.* **2003**, *345*, 402.

[13] a) W. E. McEwen, A. B. Janes, J. W. Knapczyk, V. L. Kyllingstad, W.-I. Shiau, S. Shore, J. H. Smith, *J. Am. Chem. Soc.* **1978**, *100*, 7304; b) E. Lindner, S. Meyer, P. Wegner, B. Karle, B. Sickinger, B. Steger, *J. Organomet. Chem.* **1987**, *335*, 59.

[14] K. K. Chow, C. A. McAuliffe, *Inorg. Chim. Acta* **1975**, *14*, 121.

[15] J. I. van der Vlugt, J. M. Bonet, A. M. Mills, A. L. Spek, D. Vogt, *Tetrahedron Lett.* **2003**, *44*, 4389.

[16] J. I. van der Vlugt, M. M. P. Grutters, A. M. Mills, H. Kooijman, A. L. Spek, D. Vogt, *Eur. J. Inorg. Chem.* **2003**, *24*, 4361.

[17] a) B. M. Trost, D. L. van Vranken, *Angew. Chem.* **1992**, *104*, 194–196; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 228–230; b) B. M. Trost, D. L. van Vranken, *Chem. Rev.* **1996**, *96*, 395–422; c) B. M. Trost, *Acc. Chem. Res.* **1996**, *29*, 355–364.

[18] a) E. Brulé, Y. Pei, F. Lake, F. Rahm, C. Moberg, *Mendeleev Commun.*, **2004**, *14*, 276; b) Y. Pei, E. Brulé, C. Moberg, *Org. Biomol. Chem.* **2006**, *4*, 544.

[19] M. A. Zuideveld, B. H. G. Swennenhuis, M. D. K. Boele, Y. Guari, G. P. F. van Strijdonck, J. N. H. Reek, P. C. J. Kamer, K. Goubitz, J. Fraanje, M. Lutz, A. L. Spek, P. W. N. M. van Leeuwen, *J. Chem. Soc. Dalton Trans.* **2002**, 2308.

[20] R. van Duren, J. I van der Vlugt, H. Kooijman, A. L. Spek, D. Vogt, *Dalton Trans.* **2007**, 1053.

[21] a) P. Dierkes, P. W. N. M. van Leeuwen, *J. Chem. Soc. Dalton Trans.* **1999**, 1519; b) A. J. Sandee, L. A. van der Veen, J. N. H. Reek, P. C. J. Kamer, M. Lutz, A. L. Spek, P. W. N. M. van Leeuwen, *Angew. Chem.* **1999**, *111*, 3428; *Angew. Chem. Int. Ed.* **1999**, *38*, 3231; c) P. Nieczypor, P. W. N. M. van Leeuwen, J. C. Mol, M. Lutz, A. L. Spek, *J. Organomet. Chem.* **2001**, *625*, 58; d) J. Yin, S. L. Buchwald, *J. Am. Chem. Soc.* **2002**, *124*, 6043.

[22] See for recent examples: a) K. Heinze, G. Huttner, L. Zsolnai, P. Schober, *Inorg. Chem.* **1997**, *36*, 5457;

b) P. R. Meehan, E. C. Alyea, R. P. Shakya, G. Ferguson, *Polyhedron* **1998**, *17*, 11; c) R. Rupp, G. Huttner, P. Kircher, R. Soltek, M. Büchner, *Eur. J. Inorg. Chem.* **2000**, 1745; d) G. Müller, M. Klinga, M. Leskelä, B. Rieger, *Z. Anorg. Allg. Chem.* **2002**, *628*, 2839; e) C. E. Kriley, M. M. Majireck, J. M. Tobolewski, L. E. Kelvington, S. H. Cummings, S. J. Hershberger, J. D. Link, A. L. Silverio, P. E. Fanwick, I. P. Rothwell, *Inorg. Chim. Acta* **2005**, *358*, 57; f) T. Suzuki, T. Tsukuda, M. Kiki, S. Kaizaki, K. Isobe, H. D. Takagi, K. Kashiwabara, *Inorg. Chim. Acta* **2005**, *358*, 2501.

[23] For crystal structures of metal complexes of diphosphonite ligands derived from the xanthene framework, featuring the out-of-plane folding of the metal center and non-planar geometry of the xanthene fragment, see: a) W. Goertz, P. C. J. Kamer, P. W. N. M. van Leeuwen, D. Vogt, *Chem. Eur. J.* **2001**, *7*, 1614; b) J. I. van der Vlugt, R. Sablong, A. M. Mills, H. Kooijman, A. L. Spek, A. Meetsma, D. Vogt, *Dalton Trans.* **2003**, 4690; c) J. I. van der Vlugt, R. Sablong, P. C. M. M. Magusin, A. M. Mills, A. L. Spek, D. Vogt, *Organometallics* **2004**, *23*, 3177; d) J. I. van der Vlugt, A. C. Hewat, S. Neto, R. Sablong, A. M. Mills, A. L. Spek, C. Müller, D. Vogt, *Adv. Synth. Catal.* **2004**, *346*, 993; e) J. I. van der Vlugt, J. M. J. Paulusse, E. J. Zijp, J. A. Tijmensen, A. M. Mills, A. L. Spek, C. Claver, D. Vogt, *Eur. J. Inorg. Chem.* **2004**, 4193; f) R. van Duren, L. J. J. M. Cornelissen, J. I. van der Vlugt, J. P. J. Huibers, A. M. Mills, A. L. Spek, C. Müller, D. Vogt, *Helv. Chim. Acta* **2006**, *89*, 1547.

[24] Although Ni- and Pd-catalyzed reactions are predominantly performed in CH_2Cl_2, good results have also been reported using MeOH (see: K. Kawamoto, A. Tatani, T. Imanaka, S. Teranishi, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1239) and THF (see: R. Ceder, G. Muller, J. I. Ordinas, *J. Mol. Catal.* **1994**, *92*, 127).

[25] Additional factors that could play a role are i) the solubility of Co(dppe)Cl_2 in styrene compared to dichloromethane and ii) the significantly higher styrene to ethene ratio (factor 3.5, assuming the solubility of ethene in styrene and dichloromethane is approximately the same), leading to considerably different substrate concentrations.

[26] D. G. Gusev, M. Madott, F. M. Dolgushin, K. A. Lyssenko, A. M. Yu, *Organometallics* **2000**, *19*, 1734.

[27] See also ref.[7] Modification of procedure reported by: a) ref.[22a]; b) F. P. Alt, W. Heitz, *Macromol. Chem. Phys.* **1998**, *199*, 1951; c) W. D. Horrocks Jr. , G. R. van Hecke, D. D. Hall, *Inorg. Chem.* **1967**, *6*, 694.

[28] Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307.

[29] P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, C. Smykalla, *The DIRDIF99 program system*, **1999**, University of Nijmegen, The Netherlands.

[30] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.

[31] A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7.

[32] G. M. Sheldrick, *SADABS: Area-Detector Absorption Correction*, v2.10, **1999**, Universität Göttingen, Germany.

[33] Derived parameters do not contain the contribution of the disordered solvent.