

Supporting information

Highly selective cobalt-catalyzed hydrovinylation of styrene

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Chemicals were purchased from Aldrich, Acros or Merck and used as received. (*S,S*)-Dipamp was purchased at Digital Specialty Chemicals. (*1R,2R*)-1,2-Diaminocyclohexane-*N,N'*-bis(2'-diphenylphosphinobenzoyl) and (*S,S*)-DIOP were purchased at Strem. All preparations were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were distilled from sodium/benzophenone (THF, ether, toluene, hexanes and ethanol) or calcium hydride (CH_2Cl_2 and CDCl_3) prior to use. All glassware was dried by heating under vacuum.

Preparation of bis(diphenylphosphino)ethane dichloro cobalt(II), $[\text{Co}(\text{dppe})\text{Cl}_2]$:

Compound Co(3)Cl_2 was prepared according to a modified procedure reported in literature:¹
To a solution of anhydrous cobalt(II)dichloride (130 mg, 1 mmol) in THF (5 mL) was added a solution of bis(diphenylphosphino)ethane (438 mg, 1.1 mmol) in THF (5 mL). The mixture changed color from blue to dark green rapidly and the resulting solution was stirred overnight. After evaporation of all volatiles *in vacuo*, diethylether (10 mL) was added and the green suspension was stirred and subsequently filtrated with a filtering cannula. The remaining volatiles were removed *in vacuo* to yield $[\text{Co}(\text{dppe})\text{Cl}_2]$ as a green powder (498 mg, 0.94 mmol). Yield 94%.

Preparation of bis(diphenylphosphino)methane dichloro cobalt(II), $[\text{Co}(\text{dppm})\text{Cl}_2]$:

Compound Co(2)Cl_2 was prepared according to a modified procedure reported in literature:²
To a solution of anhydrous cobalt(II)dichloride (29.3 mg, 0.22 mmol) in THF (5 mL) was added a solution of bis(diphenylphosphino)methane (95.4 mg, 0.25 mmol) in THF (5 mL). The mixture changed color from blue to dark green rapidly and the resulting solution was stirred overnight. After evaporation of all volatiles *in vacuo*, diethylether (10 mL) was added and the greenish

brown suspension was stirred and subsequently filtrated with a filtering cannula. The remaining volatiles were removed *in vacuo* to yield [Co(dppm)Cl₂] as a green-brown powder (109.8 mg, 0.21 mmol). Yield 95%.

Preparation of bis(diphenylphosphino)propane dichloro cobalt(II), [Co(dppp)Cl₂]:

The compound Co(4)Cl₂ was prepared according to a modified procedure reported in literature:³ To a solution of anhydrous cobalt(II)dichloride (128.4 mg, 0.99 mmol) in THF (5 mL) was added a solution of bis(diphenylphosphino)propane (433.1 mg, 1.05 mmol) in THF (5 mL). The mixture changed color from blue to dark green rapidly and was stirred overnight, resulting in a clear bright blue solution. After evaporation of all volatiles *in vacuo*, diethylether (10 mL) was added and the bright blue suspension was stirred and subsequently filtrated with a filtering cannula. The remaining volatiles were removed *in vacuo* to yield [Co(dppp)Cl₂] as a bright blue powder (527.2 mg, 0.97 mmol). Yield 98%.

Preparation of dichloro bis(triphenylphosphino) cobalt(II), [Co(PPh₃)₂Cl₂]:

Co(PPh₃)₂Cl₂ was prepared according to a modified procedure reported in literature:⁴ To a solution of anhydrous cobalt(II)dichloride (99.2 mg, 0.76 mmol) in THF (5 mL) was added a solution of triphenylphosphine (410.8 mg, 1.57 mmol) in THF (5 mL). The blue mixture was stirred overnight. After evaporation of all volatiles *in vacuo*, diethylether (10 mL) was added and the bright blue suspension was stirred and subsequently filtrated with a filtering cannula. The remaining volatiles were removed *in vacuo* to yield [Co(PPh₃)₂Cl₂] as a bright blue powder (484.8 mg, 0.74 mmol). Yield 97%.

Preparation of 9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene dichloro cobalt(II), [Co(Xantphos)Cl₂]:

To a solution of anhydrous cobalt(II)dichloride (88.0 mg, 0.68 mmol) in THF (5 mL) was added a solution of 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (430.2 mg, 0.74 mmol) in THF (5 mL). The mixture was stirred overnight, resulting in a clear bright blue solution. After evaporation of all volatiles *in vacuo*, diethylether (10 mL) was added and the bright blue suspension was stirred and subsequently filtrated with a filtering cannula. The remaining volatiles were removed *in vacuo* to yield [Co(Xantphos)Cl₂] as a bright blue powder (673.0 mg, 0.65 mmol). Yield 95%. Elemental analysis calcd for C₃₉H₃₂Cl₂CoOP₂: C, 66.12; H, 4.55. Found: C, 65.96; H, 4.50.

Preparation of 1,1-bis[(3-phenylphosphanyl-4-methoxy)phenyl]cyclohexane dichloro cobalt(II), [Co(BPC₆-phos)Cl₂]:

To a solution of anhydrous cobalt(II)dichloride (30.4 mg, 0.24 mmol) in THF (5 mL) was added a solution of 1,1-bis[(3-phenylphosphanyl-4-methoxy)phenyl]cyclohexane (165.5 mg, 0.25 mmol) in THF (5 mL). The blue mixture was stirred overnight. After evaporation of all volatiles *in vacuo*, diethylether (10 mL) was added and the blue suspension was stirred and subsequently filtrated with a filtering cannula. The remaining volatiles were removed *in vacuo* to yield [Co(BPC₆-phos)Cl₂] as a blue powder (180.8 mg, 0.23 mmol). Yield 95%. Elemental analysis calcd for C₄₄H₄₂Cl₂CoO₂P₂: C, 66.51; H, 5.33. Found: C, 65.20; H, 4.86.

Preparation of (4*S*,5*S*)-O-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane dichloro cobalt(II), [Co((*S*,*S*)-DIOP)Cl₂]:

To a solution of anhydrous cobalt(II)dichloride (19.8 mg, 0.15 mmol) in THF (5 mL) was added a solution of (4*S*,5*S*)-O-Isopropylidene-2,3-dihydroxy-1,4-bis(di[phenylphosphino])butane (84.4 mg, 0.17 mmol) in THF (5 mL). The resulting blue solution was stirred overnight. After evaporation of all volatiles *in vacuo*, diethylether (10 mL) was added and the blue suspension was stirred and subsequently filtrated with a filtering cannula. The remaining volatiles were removed *in vacuo* to yield [Co((*S*,*S*)-DIOP)Cl₂] as a bright blue powder (91.9 mg, 0.15 mmol). Yield 96%.

Preparation of (1*R*,2*R*)-Bis[(2-methoxyphenyl)phenylphosphino]ethane dichloro cobalt(II) [Co((*S*,*S*)-Dipamp)Cl₂]:

To a solution of anhydrous cobalt(II)dichloride (33 mg, 0.26 mmol) in THF (5 mL) was added a solution of bis(diphenylphosphino)ethane (118 mg, 0.26 mmol) in THF (5 mL). The mixture changed color from blue to very dark green rapidly and the resulting solution was stirred overnight. After evaporation of all volatiles *in vacuo*, diethylether (10 mL) was added and the green suspension was stirred and subsequently filtrated with a filtering cannula. The remaining volatiles were removed *in vacuo* to yield [Co((*S*,*S*)-Dipamp)Cl₂] as a dark green powder (145 mg, 0.246 mmol). Yield 96%. Elemental analysis calcd for C₂₈H₂₈Cl₂CoO₂P₂: C, 58.29; H, 4.80. Found: C, 58.30; H, 4.39.

Preparation of (1*R*,2*R*)-1,2-Diaminocyclohexane-N,N'-bis(2'-diphenylphosphinobenzoyl) dichloro cobalt(II) [Co((*R*,*R*)-9)Cl₂]:

To a solution of anhydrous cobalt(II)dichloride (92.2 mg, 0.71 mmol) in THF (5 mL) was added a solution of (1*R*,2*R*)-1,2-Diaminocyclohexane-N,N'-bis(2'-diphenylphosphinobenzoyl) (495.7 mg,

0.72 mmol) in THF (5 mL). The resulting solution was stirred overnight. After evaporation of all volatiles *in vacuo*, diethylether (10 mL) was added and the blue suspension was stirred and subsequently filtrated with a filtering cannula. The remaining volatiles were removed *in vacuo* to yield [Co((1*R*,2*R*)-1,2-Diaminocyclohexane-*N,N'*-bis(2'-diphenylphosphinobenzoyl))Cl₂] as a pale blue powder (565.1 mg, 0.69 mmol). Yield 97%. Elemental analysis calcd for C₄₄H₄₀Cl₂CoN₂O₂P₂: C, 64.40; H, 4.91; N, 3.41. Found: C, 64.35; H, 5.00; N, 3.36.

Preparation of N,N-bis[o-(diphenylphosphino)benzylidene]-(1*R*,2*R*)-diiminocyclohexane-dichloro cobalt(II) [Co((*R,R*)-10)Cl₂]:

To a solution of anhydrous cobalt(II)dichloride (25.6 mg, 0.20 mmol) in THF (5 mL) was added a solution of N,N-bis[o-(diphenylphosphino)benzylidene]-(1*R*,2*R*)-diiminocyclohexane **10** (137.6 mg, 0.21 mmol) in THF (5 mL). The mixture changed color from blue to very dark brown and the resulting solution was stirred overnight. After evaporation of all volatiles *in vacuo*, diethylether (10 mL) was added and the brown suspension was stirred and subsequently filtrated with a filtering cannula. The remaining volatiles were removed *in vacuo* to yield [Co((*R,R*)-**10**)Cl₂] as a brown powder (147.7 mg, 0.19 mmol). Yield 94%.

Preparation of N,N-bis[o-(diphenylphosphino)benzylidene]-(1*R*,2*R*)-daminocyclohexane dichloro cobalt(II) [Co((*R,R*)-11)Cl₂]:

To a solution of anhydrous cobalt(II)dichloride (35.2 mg, 0.27 mmol) in THF (5 mL) was added a solution of N,N-bis[o-(diphenylphosphino)benzylidene]-(1*R*,2*R*)-diaminocyclohexane (197.5 mg, 0.30 mmol) in THF (5 mL). The mixture changed color from blue to very dark purple rapidly and the resulting solution was stirred overnight. After evaporation of all volatiles *in vacuo*, diethylether (10 mL) was added and the dark purple/blue suspension was stirred and subsequently filtrated with a filtering cannula. The remaining volatiles were removed *in vacuo* to yield [Co((*R,R*)-**11**)Cl₂] as a dark purple powder (206.5 mg, 0.26 mmol). Yield 96%. Elemental analysis calcd for C₄₄H₄₄Cl₂CoN₂P₂: C, 62.24; H, 5.60; N, 3.53. Found: C, 62.50; H, 5.73; N, 3.12.

Hydrovinylation reaction: A home made stainless steel 75 mL autoclave equipped with a copper mantle and a glass beaker inset was pre-cooled to 0°C with ice and water for 30 min. A cobalt complex, e.g. [Co(dppe)Cl₂] (27.1 mg, 0.05 mmol) was weighed in a 15 mL Schlenk and dichloromethane (5 mL) was added before transfer to the pre-cooled autoclave via syringe. Subsequently, weighed amounts of styrene (4 mL), ethylbenzene (1 mL, int. std.) and DEAC

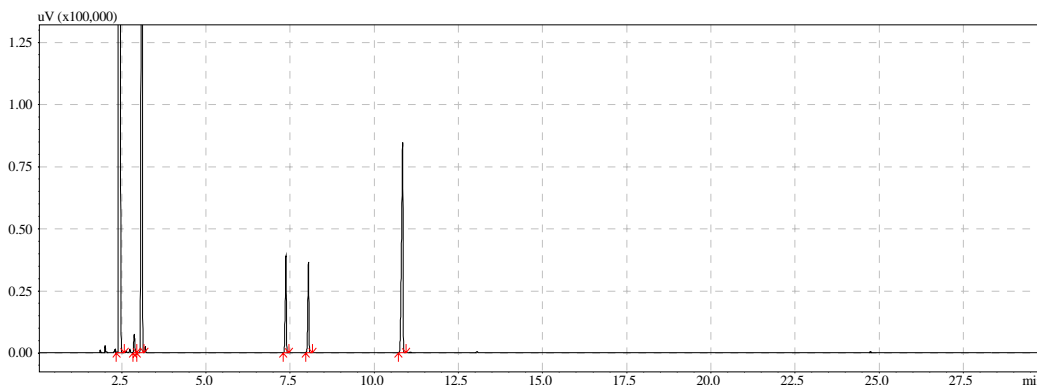
(0.25 mL, 1.0 M in hexanes) were transferred to the autoclave via syringe. After flushing of the ethylene line and the autoclave to remove the protecting Argon atmosphere, the autoclave was pressurized with ethylene to 30 bar initial pressure. After 1.5 h at 0° C the pressure was released and the contents were subjected to flash chromatography over basic alumina before quantitative analysis with GC.

GC Analysis

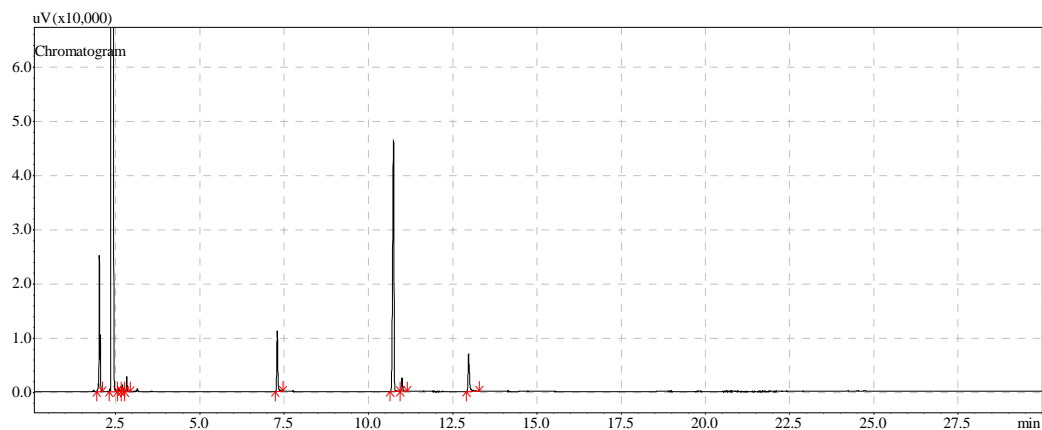
GC: Shimadzu GC 17A
 Column: Ultra 2 (crosslinked 5% Ph Me Siloxane), 25m, innerØ 0.20 mm, film thickness 0.33 µm
 Carrier gas: Helium 102 kPa (total flow 53 mL/min.)
 Temperature program: 50°C (hold: 2 min.), 8°C/min. to 250°C(hold: 5 min.)
 Injector: 270°C
 Detector(FID): 270°C
 Split ratio: 76
 Injection volume: 1 µl

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

Typical chromatogram for a hydrovinylation reaction.



Typical chromatogram for a hydrovinylation reaction where all styrene is consumed:

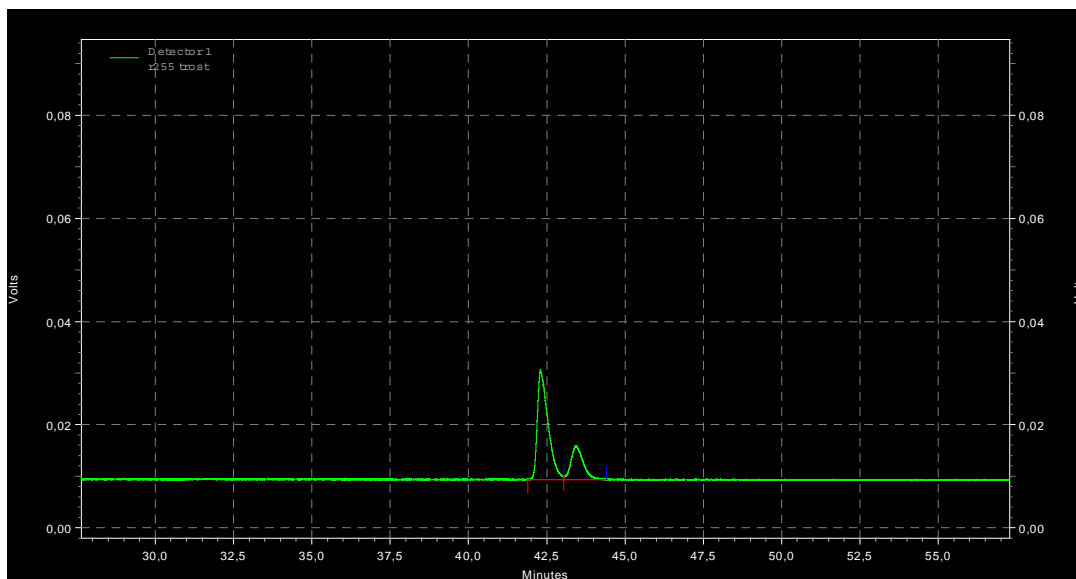


GC Analysis of the enantiomeric excess

GC: Carlo Erba 6000 Vega series 2
Column: FS Cyclodex, 50 m, innerØ 0.25 mm
Carrier gas: Helium 240 kPa
Temperature program: 65 °C (isotherm)
Injector: 200°C
Detector(FID): 250°C
Split ratio: 75
Injection volume: 1 µl

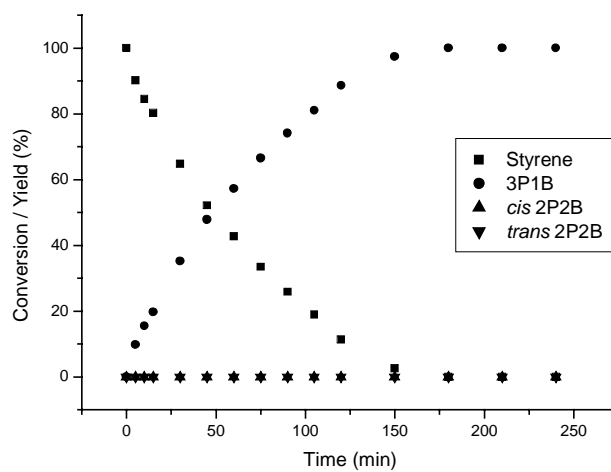
Compound	Retention time (min.)
(<i>R</i>)-3-phenyl-1-butene	42.4
(<i>S</i>)-3-phenyl-1-butene	43.5

Typical chromatogram:



$[\text{Co}(\mathbf{8})\text{Cl}_2]/\text{DEAC}$ catalyst system 47% *ee* (*R*)

When the reaction is monitored in time, a plot like the one depicted below is obtained.
 $[\text{Co}(\text{dppe})\text{Cl}_2]/\text{DEAC}$ catalyst system)



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