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J Am Chem Soc. Author manuscript; available in PMC 2011 March 17.

Published in final edited form as:
J Am Chem Soc. 2010 March 17; 132(10): 3295–3297. doi:10.1021/ja1004703.

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Asymmetric Hydrovinylation of Unactivated Linear 1,3-Dienes

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Abstract

Monosubstituted acyclic (*E*)-1,3-dienes undergo efficient hydrovinylation giving (*Z*)-3-alkylhexa-1,4-dienes upon treatment with catalytic amounts of bidentate phosphine-$CoCl_2$ complexes {[**P~P**]($CoCl_2$)} and Me_3Al in an atmosphere of ethylene. The regioselectivity of the reaction (i.e., 1,4- or 1,2-addition) depends on the nature of the ligand and temperature at which the reaction is carried out. Complexes derived from (*RR*)-DIOP and (*SS*)-BDDP at −45 °C give very high enantioselectivities for several prototypical 1,3-dienes. In sharp contrast to the corresponding Ni(II)-catalyzed hydrovinylation, 1-aryl-substituted 1,3-dienes give almost exclusively achiral linear 1,4-addition products, unless the 2-position is also substituted. Solid-state structures of the precatalysts are presented.

Rhodium-catalyzed linear codimerization of 1,3-butadiene and ethylene is an industrially important process for the synthesis of hexadienes.[1] Related iron2 and cobalt3 catalyzed heterodimerizations of substituted 1,3-butadienes and α-olefins have seen a resurgence of activity recently.4 Impressive advances in Fe- and Co-mediated polymerization reactions of alkenes have also been made.[5] However, surprisingly little attention has been paid to the Co-catalyzed codimerization of ethylene with other alkenes in which chiral branched products are formed. Only reported examples pertain to the high-pressure Fe(0)-catalyzed heterodimerization of ethylene (hydrovinylation) with (*E*)-1,3-pentadiene (37% ee) and 2-methyl-1,3-pentadiene (31% ee)[2c] and a recently reported Co-catalyzed (also high pressure) hydrovinylation of styrene (50% ee).6 Both Ru7 and Ni-catalyzed8−10 hydrovinylation reaction of 1,3-dienes have been reported, even though high enantioselectivity has been realized only for very limited substrates.[9,10] Conspicuously absent among these reports are synthetically useful asymmetric hydrovinylation reactions of *unactivated linear 1,3-dienes*, a class of readily available substrates for which few asymmetric catalyzed C-C bond-forming reactions are known.10b,[11] In this Communication we report our initial studies on the ligand effects on the Co(II)-catalyzed hydrovinylations of such 1,3-dienes which culminated in the discovery of a surprisingly simple method[12],13 for an asymmetric variation of this reaction at ambient pressure of ethylene.

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Supporting Information Available: Full experimental details for the preparation of complexes and hydrovinylation reactions, spectroscopic and chromatographic data for characterization of all compounds, Crystallographic Information File for the Co-complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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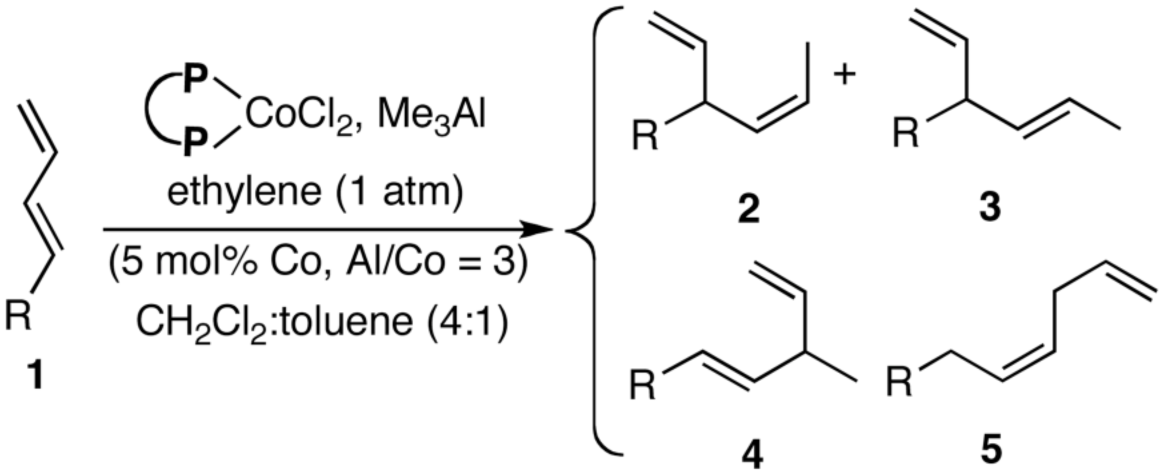
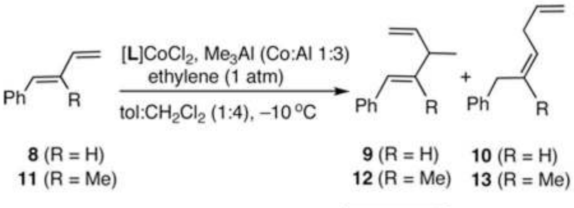


(1)

Our studies started with an examination of the codimerization of ethylene and (*E*)-1,3-nonadiene (Eq 1, **1a**, R = C_5H_{11}) with isolated complexes $\mathbf{L}_nCoX_2$ (**L** = mono and bis-phosphines; X = halogen) as catalysts in the presence of Lewis acids such as aluminum alkyls as promoters.[1c] Initial scouting experiments revealed that $CoCl_2$ complexes with α,ω-*bis*-diphenylphosphinoalkanes [$Ph_2P\ (CH_2)_nPPh_2$; n = 1–4] in the presence of Me_3Al (Co:Al = 1:3) in a mixture of CH_2Cl_2 and toluene (4:1) had the most potential as catalysts for this reaction.[12] In view of the previous report that Me_3Al was ineffective in the hydrovinylation of styrene,[6] we were surprised to find that under the optimal reaction conditions excellent yield and selectivity in the hydrovinylation of **1a** and a number of other substrates can be realized as shown in Table 1 and Table 2. Thus **1a** undergoes hydrovinylation promoted by (dppb) $CoCl_2$ (dppb = 1,4-*bis*-diphenylphosphinobutane) and Me_3Al to yield 93% yield of a 1,4-addition product **2a** (R = C_5H_{11}, *Z*-isomer) (entry 1). Under these conditions *no trace* of a 1,2-adduct **4a** or any linear dimerization product **5a** were formed as ascertained by NMR and gas chromatography.[12] The only contaminant (~7%) has been identified as the (*E*)-1,4-adduct, **3a** (R = C_5H_{11}). The product distribution is highly dependent on the *bis*-phosphine employed and the reaction conditions, especially the temperature. As shown in entry 2 (Table 1), (dppm) $CoCl_2$ (dppm = *bis*-diphenylphosphinomethane) at −20 °C gives mostly a mixture of the (*E*)-1,4-adduct **3a** (30%) and a 1,2-adduct **4a** (67%). Under these conditions, (dppe)$CoCl_2$, (dppe = 1,2-*bis*-diphenylphosphinoethane) and (dppp)$CoCl_2$ (dppp = 1,3-*bis*-diphenylphosphinopropane) give the (*Z*)-1,4-adduct **2a** as the major product in 70% and 75% yields, contaminated with what appears to be a linear dimer **5a** (entries 3 and 4). At room temperature $(dppp)_2CoCl_2$ gives very little of **2a**; instead a mixture of **3a** [(*E*)-1,4-prdduct] and **4a** [(*E*)-1,2-adduct] was formed (entry 5), suggesting that **2a** might be a kinetic product. Similar reaction conditions using $(Ph_3P)_2CoCl_2$ as the catalyst led to polymerization of the diene (entry 6).

The optimized reaction conditions using (dppb)$CoCl_2$ have broad applicability as shown in Table 2 and Eq 2. Terminally substituted *E*-1,3-dienes (entries 1–5, Table 2) including (*E*)-1,3-pentadiene are excellent substrates for the Co-mediated hydrovinylations giving almost exclusively the (*Z*)-1,4-adducts (**2**) in yields exceeding 90%. A minor product in these reactions has been tentatively identified as the geometrical isomer **3** or a linear HV adduct **5**.[12] The former is easily identified by the presence of a quintet around ~ δ 2.61 and, the latter by a broad triplet at ~ δ 2.80. The reaction is compatible with functionalized dienes such as the benzyl ether **1f**, and a 1,3-diene carrying a remote trisubstituted double bond (β-myrcene, **6**), which is not affected by the hydrovinylation of the terminal 1,3-diene functionality (entry 7).



8 (R = H)

L	9	10
dppm	83^a	0
dppp	0	99 (93)
dppb	0	$71^{a,b}$

^{a} −20 °C, ^{b} rest sm

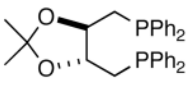
11 (R = Me)

L	12	13
dppm	99 (92)	0
dppp	62^b	0
dppb	0	0

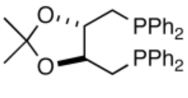
^{b} rest sm

(2)

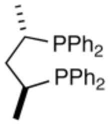
Hydrovinylation of 1-aryl-substituted 1,3-butadienes behave differently, and parallels the trend recently seen in the dimerization of such dienes with terminal alkenes.[4d] (*E*)-1-Phenyl-1,3-butadiene (**8**), a substrate that underwent facile Ni(II)-catalyzed hydrovinylation to give a 1,2-adduct (**9**) exclusively,[10a] gives a linear 1,4-adduct **10** with both $(dppp)_2CoCl_2$ and $(dppb)_2CoCl_2$ (Eq 2). In sharp contrast, the corresponding dppm-complex gives **9** as the major HV product. (*E*)-2-Methyl-1-phenyl-1,3-butadiene (**11**) gives only a branched product (**12**) arising from a 1,2-addition at the less substituted double bond, irrespective of the Co complex used, even though it appears that ligands with larger bite angles retard the reaction.



14 (*RR*)-DIOP



ent-**14** (*SS*)-DIOP



15 (*SS*)-BDPP

Having realized synthetically useful chemo- regio- and diastereoselectivity in the hydrovinylations of simple 1,3-dienes using dppp and dppb, we turned our attention to the asymmetric reaction. Among the limited set of ligands that were explored,[14] (*RR*)-(2,2-dimethyl-1,3-dioxalane-4,5-diylbismethylene) *bis*-diphenylphosphine [(*RR*)-DIOP, **14**] and (*SS*)-2,4-*bis*-diphenylphosphinopentane [(*SS*)-BDPP, **15**], simplest chiral analogs of dppb and dppp that are commercially available, gave the best results (Table 3).

Under the optimized conditions (*E*)-1,3-nonadiene (**1a**) gave nearly quantitative yield of (*R*)-(*Z*)-4-vinylnon-2-ene (95% ee) upon reaction with $[(RR)\text{-DIOP}]CoCl_2$ and Me_3Al (Table 3, entry 1). At −45 °C where these reactions are carried out < 2% of isomeric products are observed. The identities of the hydrovinylation products were rigorously established by spectroscopic methods, and, in the case of **2e**, by comparison of observed[12] and reported[15] properties.

The reaction appears to be quite general for dienes (entries 1–8) including (*E*)-1,3-pentadiene. Substrates with functional groups such as a benzyl ether **1f** (entries 9, 10) are tolerated in these highly enantioselective reactions. Not unexpectedly, substrate **1f** carrying a Lewis basic oxygen

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reacts sluggishly. Finally, a diene with aryl conjugation (e.g., **11**) gave essentially a racemic product (entry 12).[16]

Mechanism of the Me_3Al-mediated hydrovinylation is currently under investigation. It is conceivable that under the non-reducing conditions5 used here (vis-à-vis the Hilt procedures4b–e which employ a Co(II)-salt with a reducing agent in the presence of a Lewis acid), a $[(\mathbf{L})Co(II)\text{-}H]^+$ (**16**) is the catalytic species.[17] This species could be formed by metathesis of the Al-Me/Co-Cl bonds, migratory insertion of an alkene into Co-Me bond, followed by reductive elimination (Scheme 1). Addition of the Co-H via an η^4-diene complex **17** would produce a *syn-anti*-(allyl)Co-species **18** which would undergo coupling with ethylene to give **20**. Reductive elimination from **20** regenerates the catalyst giving the major product **2**.[18] Intermediacy of the η^3-allylic intermediate (**19**), which is capable of syn/anti isomerization,[19] would also explain the temperature dependence of the product distribution (entries 4 and 5 in Table 1). Note that none of the product **2a**, which is the major component at −20 °C formed from the *syn-anti*-allyl intermediate **18**, is observed at 23 °C (entry 5). At low temperature where the asymmetric catalyzed reactions are carried out **18** must be configurationally stable to give the high selectivities observed. Consistent with the intermediacy of an η^4-diene complex **17**, in preliminary studies with a mixture of (*E*)-and (*Z*)-penta-1,3-diene, we have observed that the *Z*-isomer, which is expected to form this species slower, indeed turns over at a slower rate.[12]

As a prelude to further studies we have obtained solid state structures of the complexes (*RR*)-[DIOP]$CoCl_2$ and (*SS*)-[BDPP]$CoCl_2$, which are shown in Figure 1. These tetrahedral complexes with the bidentate ligands appear to overcome one of the serious limitations of catalysis by Ni(II)-complexes, where only monodentate ligands have been successful.[20] Cobalt with the possibility of higher coordination numbers can support more flexible geometries for the intermediates in the catalytic cycle.

Further studies to expand the scope of the reaction and to clarify its mechanism are currently underway.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We thank Dr. Judith Gallucci for determination of the crystal structures shown in Fig 1. Financial assistance for this research by NSF (CHE-0610349) and NIH (General Medical Sciences, R01 GM075107) is gratefully acknowledged.

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11. For example, see: (a) Cyclopropanation: Doyle, M. In Catalytic Asymmetric Synthesis. Ojima, I., editor. New York: Wiley-VCH; 2000. (b) In *Advances in Cycloaddition*; Davies, HML., editor. Vol. Vol. 5. Greenwich: JAI Press; 1998. p. 119-164. (c) Ene reaction: Terada M, Mikami K. J. Chem. Soc., Chem. Commun 1995:2391. (d) Hydroformylation: Horiuchi T, Ohta T, Shirakawa E, Nozaki K, Takaya H. Tetrahedron 1997;53:7795. (e) Hydrocyanation: Saha B, RajanBabu TV. Org. Lett 2006;8:4657. [PubMed: 16986974]
12. See Supporting Information for the details of experimental procedures.
13. **Typical procedure for Co-catalyzed asymmetric hydrovinylation**. An oven-dried 10 mL round-bottom flask with a sidearm, was charged (*RR*)-[DIOP]$CoCl_2$ (12.6 mg, 0.0201 mmol) under argon in a mixture of degassed dichloromethane (2.0 mL) and toluene (0.5 mL), at 0 °C. Trimethylaluminum solution (2M) in toluene (4.3 mg, 30 μl, 0.060 mmol) was added dropwise as color of the solution changed from deep blue to red-brown with the formation of white fumes over the solution. When all the fumes disappeared (typically in 5–10 min), the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The filled balloon was used to maintain the ethylene atmosphere, while a vigorous reaction with evolution of fumes was observed. This evolution stopped in typically 3–5 min. The reaction vessel was cooled to − 45 °C and (3*E*)-nona-1,3-diene (50 mg, 0.40 mmol) was added under ethylene and the mixture was stirred for 6 h (color of the reaction solution turned blue again at the end of the reaction). The ethylene balloon was removed and 0.1 mL of methanol was introduced into the flask and stirring was continued for 5 minutes. The solution was warmed to room temperature and was subsequently passed through a silica plug. The plug was washed with pentane. Concentration and removal of last traces of solvent yielded the product as a colorless oil (58 mg, 95%). Isomeric compositions were determined by gas chromatography and NMR spectroscopy (See attached chromatograms and spectra).
14. For a complete list see Supporting Information.
15. Assignment of the absolute configuration of **2e** was initially done by comparison of chromatographic behavior on a cyclodex-B column. It is known that for this hydrocarbon, the levorotatory (S) isomer has a longer retention time.[2c] Configurations of other similar compounds (**2**) were assigned by analogy. All major enantiomers obtained from (*RR*)-DIOP have the same sense of rotation (−). See Supporting Information.
16. Under these conditions hydrovinylation of 4-methylstyrene {using (*RR*)-[DIOP]$CoCl_2$} gave 3-(4-methylphenyl)-1-butene in 18% ee (R).
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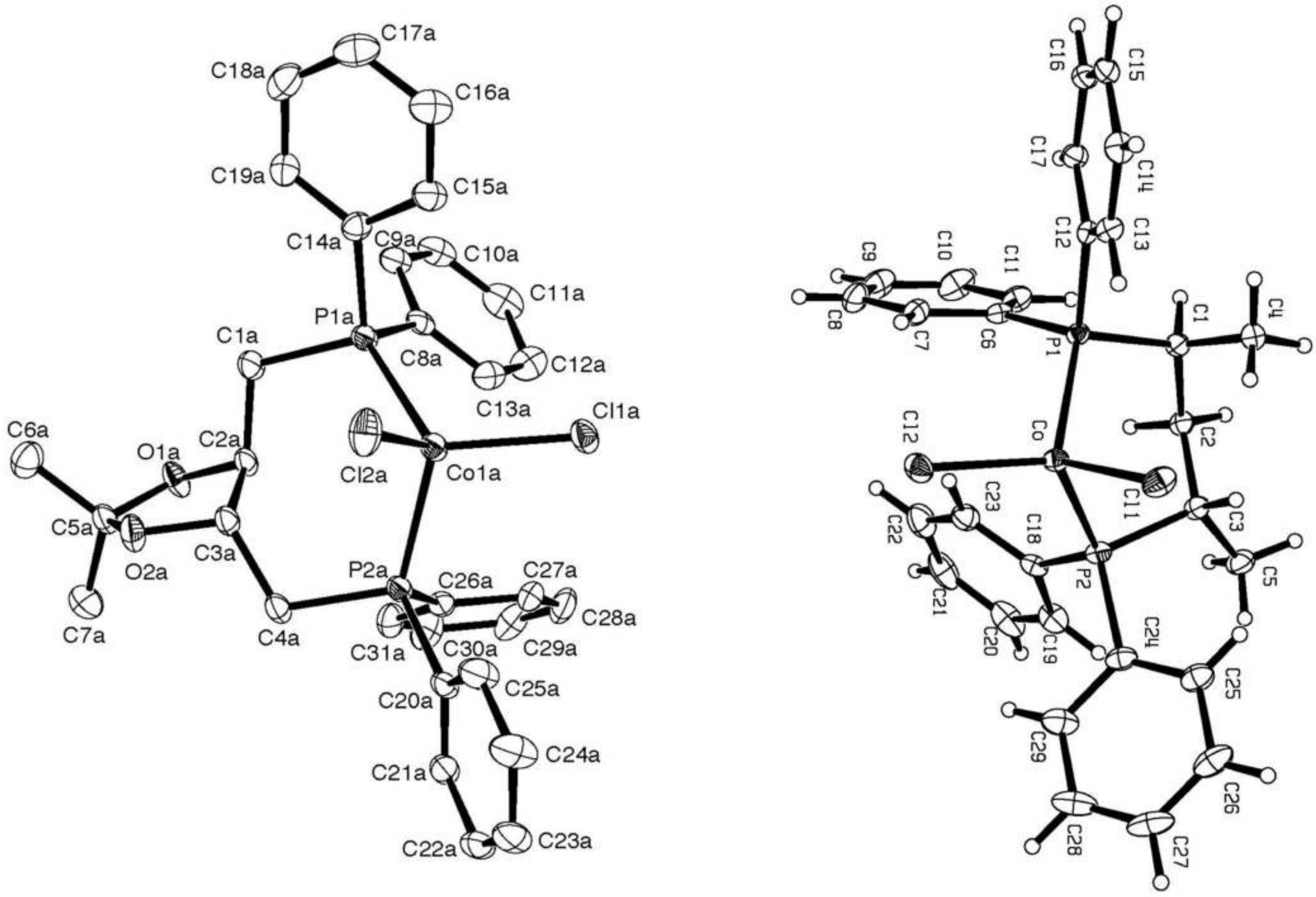

Figure 1.

Solid-state structures of Precatalysts (*RR*)-[DIOP]$CoCl_2$ and (*SS*)-[BDPP]$CoCl_2$

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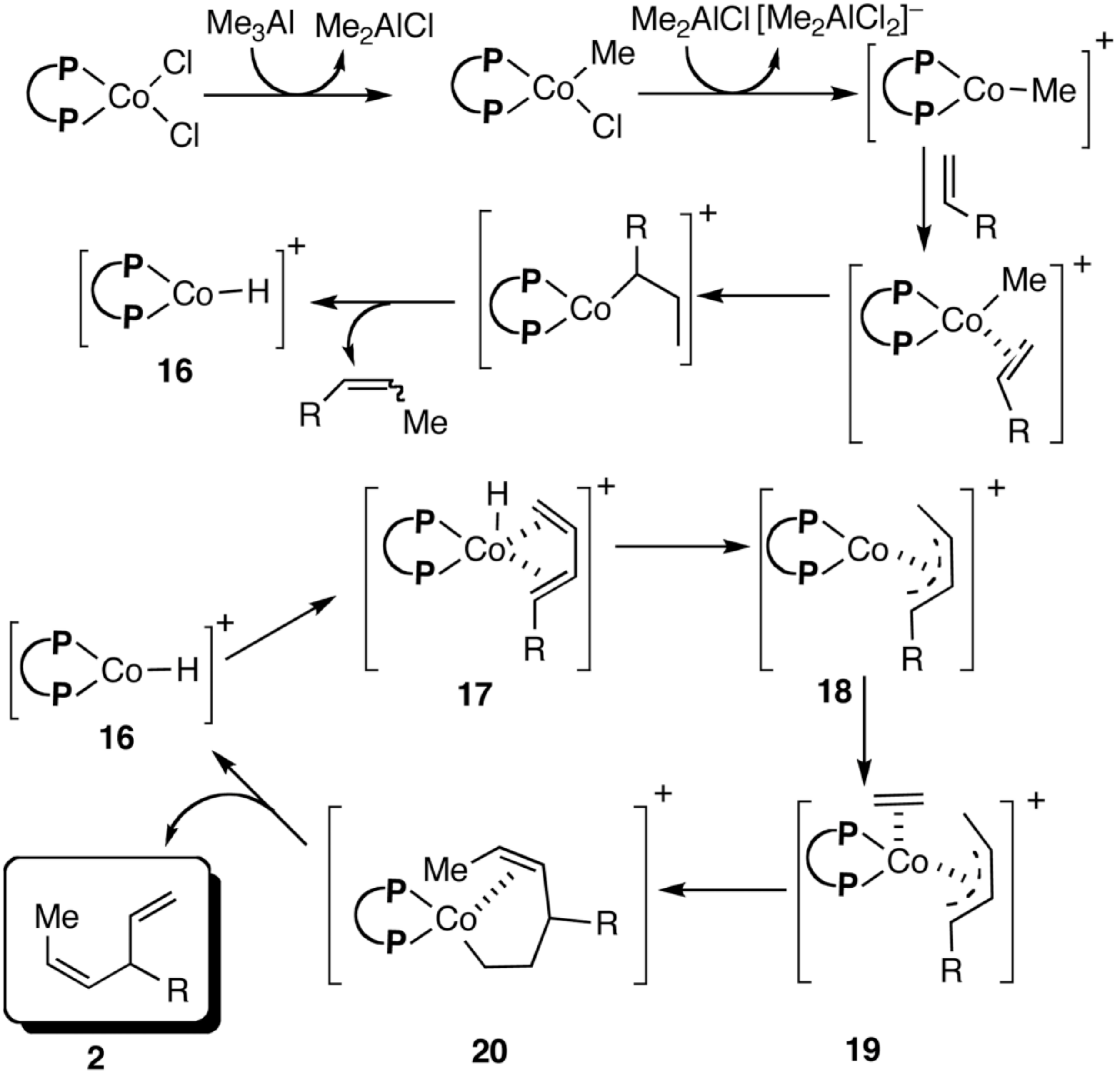

Scheme 1.
A Possible Mechanism of Co(II)-Catalyzed Hydrovinylation of 1,3-Dienes

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Table 1

Co-Catalyzed Hydrovinylation of **1a** (R= C_5H_{11})[a]

			product, yield (%)[b]			
no.	**P~P**	***T*** **°C**	**2a (1,4-*Z*)**	**3a (1,4-*E*)**	**4a (1,2-*E*)**	**5a (1,4-linear)**
1.	dppb	−10	93	7	0	0
2.	dppm	−20	<2	30	67	<2
3.[c]	dppe	−10	70	0	0	10
4.[c]	dppp	−20	75	0	0	14
5.[c]	dppp	23	0	26	65	<4
6.	2 Ph_3P	−10	--		--	--

[a] See Eq 1 and Supporting Information for details.

[b] Estimated by GC and NMR.

[c] In addition to the products the rest is starting material.

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Table 2

Hydrovinylation of 1,3-Dienes. Scope of Substrates[a]

no.	alkene/R in 1	P~P	product, yield[b]			
			2	**3**	**4**	**5**
1.	C_5H_{11} (**1a**)	dppb	93 (>93)	7	0	0
2.	C_6H_{13} (**1b**)	dppb	95 (>99)	0	0	<2
3.	C_7H_{15} (**1c**)	dppb	95 (>99)	0	0	<2
4.	C_8H_{17} (**1d**)	dppb	95 (>99)	<1	0	0
5.	CH_3 (**1e**)	dppb	(>95)[c]	(<5)	_[d]	0
6.	$BnOCH_2CH_2$ (**1f**)	dppb	78[e]	0	0	0
7.	β-myrcene (**6**)	dppb	0	0	0	_[f]

[a] See Eq 1 and Supporting Information for details.

[b] Isolated yield (in brackets are yields estimated by GC and NMR).

[c] Volatile products.

[d] same as **3**.

[e] At 0 °C.

[f] Only 1,4-linear product (**7**) is formed in 78% yield. **7**: [(*Z*)-2-methyl-6-(3-propenyl)-octa-2,6-diene].

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Table 3

Co-Catalyzed Asymmetric Hydrovinylation of 1,3-Dienes[a]

no.	diene/R in 1	P~P	product yield (%)[b]	product %ee (config.)[c]
1.	C_5H_{11} (**1a**)	(*RR*)-DIOP	>99 (95)	95.0 (*S*)
2.	C_5H_{11} (**1a**)	(*SS*)-DIOP	>99 (96)	93.3 (*R*)
3.	C_5H_{11} (**1a**)	(*SS*)-BDPP	>99 (96)	97.1 (*R*)
4.	C_6H_{13} (**1b**)	(*RR*)-DIOP	>99 (96)	95.3 (*S*)
5.	C_7H_{15} (**1c**)	(*RR*)-DIOP	>99 (98)	95.4 (*S*)
6.	C_8H_{17} (**1d**)	(*RR*)-DIOP	>99 (95)	96.1 (*S*)
7.	CH_3 (**1e**)	(*RR*)-DIOP	>90[d]	90.1 (*S*)
8.	CH_3 (**1e**)	(*SS*)-DIOP	>90[d]	89.1 (*R*)
9.	$BnOCH_2CH_2$ (**1f**)	(*RR*)-DIOP	(40)[e]	99.0 (*S*)
10.	$BnOCH_2CH_2$ (**1f**)	(*SS*)-DIOP	(40)[e]	96.0 (*R*)
12.	alkene **11** (Eq 2)	(*SS*)-BDPP	>99	<5% (−)

[a] See Eq 1. 0.05 equiv. (**P~P**)$CoCl_2$, Co:Al 1:3; ethylene (1 atm); solvent (CH_2Cl_2:tol = 4:1); −45 °C; 6 h.

[b] Determined by GC; isolated yield in brackets.

[c] Configuration of **2e** assigned by comparison of optical rotation and relative retention times on a β-cyclodex chiral stationary phase GC column.12,2c Others (all of same sense of $[\alpha]_D$) assigned by analogy; see Supporting Information for details.

[d] Volatile products.

[e] Reaction done at −20 °C, rest starting materials.