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Asymmetric Hydrovinylation of Unactivated Linear 1,3-Dienes

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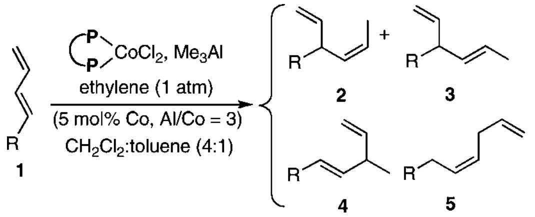
Rhodium-catalyzed linear codimerization of 1,3-butadiene and ethylene is an industrially important process for the synthesis of hexadienes.[1] Related iron[2] and cobalt[3] catalyzed heterodimerizations of substituted 1,3-butadienes and α-olefins have seen a resurgence of activity recently.[4] Impressive 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 Ru-[7] and Ni-catalyzed[8−10] hydrovinylation reactions 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.



(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 Tables 1 and 2. Thus **1a** undergoes hydrovinylation promoted by (dppb)$CoCl_2$ (dppb = 1,4-*bis*-diphenylphosphinobutane) and Me_3Al for 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** was 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).

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.

Table 2. Hydrovinylation of 1,3-Dienes: Scope of Substrates[a]

			product, yield[b]			
no.	alkene/R in **1**	P∼P	**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].

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,

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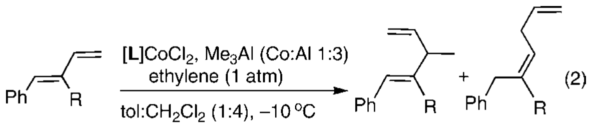
and the latter by a broad triplet at ~δ 2.80. The reaction is compatible with functionalized dienes such as the benzyl ether **1f** and a 1,3-diene carrying a remote trisubstituted double bond (β-myrcene, **6**), which is not affected by the hydrovinylation of the terminal 1,3-diene functionality (entry 7).



8 (R = H)
11 (R = Me)

9 (R = H)
12 (R = Me)

10 (R = H)
13 (R = Me)

8 (R = H)

L	9	10
dppm	83[a]	0
dppp	0	99 (93)
dppb	0	71[a,b]

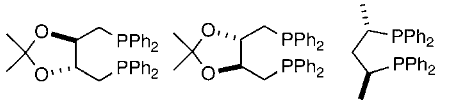
[a] −20 °C, [b] rest sm

11 (R = Me)

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

[b] rest sm

Hydrovinylation of 1-aryl-substituted 1,3-butadienes behaves 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)$_2$CoCl$_2$ and (dppb)$_2$CoCl$_2$ (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 analogues of dppb and dppp that are commercially available, gave the best results (Table 3).

Under the optimized conditions (*E*)-1,3-nonadiene (**1a**) gave (*S*)-(*Z*)-4-vinylnon-2-ene (95% ee) in nearly quantitative yield upon reaction with [(*RR*)-DIOP]CoCl$_2$ and Me$_3$Al (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 reacts sluggishly. Finally, a diene with aryl conjugation (e. g., **11**) gave essentially a racemic product (entry 12).[16]

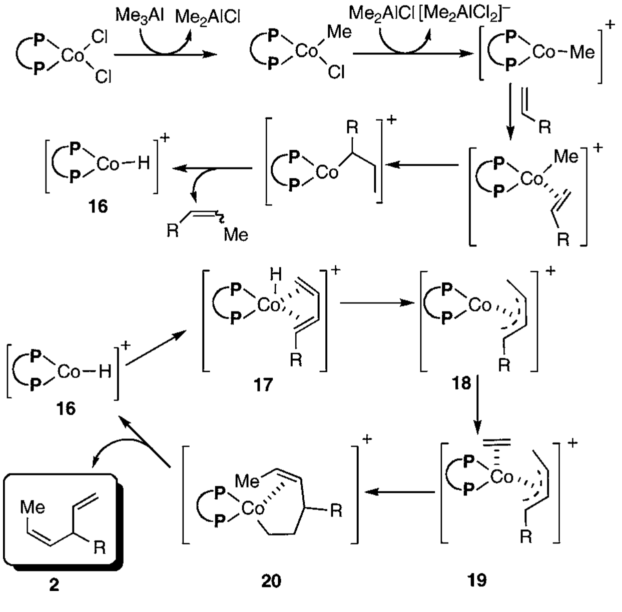
Table 3. Co-Catalyzed Asymmetric Hydrovinylation of 1,3-Dienes[a]

			product	
no.	diene/R in **1**	**P**~**P**	yield (%)[b]	%ee (config.)[c]
1	C$_5$H$_{11}$ (**1a**)	(*RR*)-DIOP	>99 (95)	95.0 (*S*)
2	C$_5$H$_{11}$ (**1a**)	(*SS*)-DIOP	>99 (96)	93.3 (*R*)
3	C$_5$H$_{11}$ (**1a**)	(*SS*)-BDPP	>99 (96)	97.1 (*R*)
4	C$_6$H$_{13}$ (**1b**)	(*RR*)-DIOP	>99 (96)	95.3 (*S*)
5	C$_7$H$_{15}$ (**1c**)	(*RR*)-DIOP	>99 (98)	95.4 (*S*)
6	C$_8$H$_{17}$ (**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$_2$CH$_2$ (**1f**)	(*RR*)-DIOP	(40)[e]	99.0 (*S*)
10	BnOCH$_2$CH$_2$ (**1f**)	(*SS*)-DIOP	(40)[e]	96.0 (*R*)
12	alkene **11** (eq 2)	(*SS*)-BDPP	>99	<5% (−)

[a] See eq 1. 0.05 of equiv of (**P**~**P**)CoCl$_2$, Co:Al 1:3; ethylene (1 atm); solvent (CH$_2$Cl$_2$: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 [α]$_D$) assigned by analogy; see Supporting Information for details. [d] Volatile products. [e] Reaction done at −20 °C, rest starting materials.

The mechanism of the Me$_3$Al-mediated hydrovinylation is currently under investigation. It is conceivable that, under the nonreducing conditions[5] used here (vis-à-vis the Hilt procedures[4b−e] which employ a Co(II) salt with a reducing agent in the presence of a Lewis acid), a [(**L**)Co(II)−H]$^+$ (**16**) is the catalytic species.[17] This species could be formed by metathesis of the Al−Me/Co−Cl bonds and 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 (**18**), 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*)-

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



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.

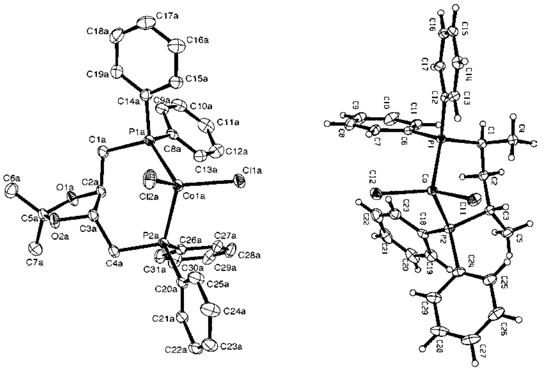


Figure 1. Solid-state structures of precatalysts (*RR*)-[DIOP]$CoCl_2$ and (*SS*)-[BDPP]$CoCl_2$.

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

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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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(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 with (*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. A trimethylaluminum solution (2 M) in toluene (4.3 mg, 30 μl, 0.060 mmol) was added dropwise as the 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 the evolution of fumes was observed. This evolution stopped in typically 3−5 min. The reaction vessel was cooled to−45 °C, (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, 0.1 mL of methanol was introduced into the flask, and stirring was continued for 5 min. 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 the 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 Supporting Information).

(14) For a complete list see Supporting Information.

(15) Assignment of the absolute configuration of **2e** was initially done by comparison of chromatographic behaviors 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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