Rhodium-catalyzed linear codimerization of 1,3-butadiene and ethylene is an industrially important process for the synthesis of hexadienes.\(^5\) Related iron\(^6\) and cobalt\(^7\) catalyzed heterodimerizations of substituted 1,3-butadienes and \(\alpha\)-olefins have seen a resurgence of activity recently.\(^8\) Impressive advances in Fe- and Co-mediated polymerization reactions of alkene have been made.\(^9\) However, surprisingly little attention has been paid to the Co-catalyzed codimerization of ethylene with other alkene 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)\(^9\) and a recently reported Co-catalyzed (also high pressure) hydrovinylation of styrene (50% ee).\(^6\) Both Ru\(^7\) and Ni-catalyzed\(^10\) 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 \(\textit{unacti-}
ated\) linear 1,3-dienes, a class of readily available substrates for which few asymmetric catalyzed \(C\rightarrow C\) bond-forming reactions are known.\(^10\) In this Communication we report our initial studies on the ligand effects on the Co(II)-catalyzed hydrovinylation of such 1,3-dienes which culminated in the discovery of a surprisingly simple method\(^12\) for an asymmetric variation of this reaction at ambient pressure of ethylene.

![Diagram](image)

Our studies started with an examination of the codimerization of ethylene and \((E)-1,3\)-nonadine (eq 1, 1a, \(R = \text{C}_3\text{H}_7\)) with isolated complexes \(\text{L}_2\text{CoX}_2\) (\(\text{L} = \text{mono and bis-phosphines; } X = \text{halogen}) as catalysts in the presence of Lewis acids such as aluminum alkyls as promoters.\(^12\) Initial scouting experiments revealed that CoCl\(_2\) complexes with \(\alpha,\alpha\)-bis-diphenylphosphino-alkanes \([\text{Ph}_2\text{P}(\text{CH}_2)_n\text{Ph}_2; n = 1\sim 4]\) in the presence of Me\(_3\)Al (Co:Al = 1:3) in a mixture of CH\(_2\)Cl\(_2\) and toluene (4:1) had the most potential as catalysts for this reaction.\(^12\) In view of the previous report that Me\(_3\)Al 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 (dpbb)CoCl\(_2\) (dpbb = 1,4-bis-diphenylphosphino-butane) and Me\(_3\)Al for 93% yield of a 1,4-addition product 2a (\(R = \text{C}_3\text{H}_7\), \(Z\)-isomer) (entry 1). Under these conditions \textit{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 (\(R = \text{C}_3\text{H}_7\)). The product distribution is highly dependent on the \(\text{bis-phosphine employed and the reaction conditions, especially the temperature. As shown in entry 2 (Table 1), (dpdp)CoCl\(_2\) (dpdp = \(\text{bis-diphenylphosphino-}\) methane) at \(-20^\circ C\) gives mostly a mixture of the \((E)-1,4\)-adduct 3a (30%) and a 1,2-adduct 4a (67%). Under these conditions, (dpdp)CoCl\(_2\) (dpdp = \(\text{1,2-bis-diphenylphosphinoethane}\)) and (dpdp)CoCl\(_2\) (dpdp = \(\text{1,3-bis-diphenylphosphinopropane}\)) 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 (dpdp)CoCl\(_2\) 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\(_3\)P)\(_2\)CoCl\(_2\) as the catalyst led to polymerization of the diene (entry 6).

| Table 1. Co-Catalyzed Hydrovinylation of 1a (\(R = \text{C}_3\text{H}_7\))
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<td>3a (1,4-E) (%)</td>
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<tr>
<td>6</td>
<td>2 Ph(_3)P</td>
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\(^a\) 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 \(^\circ C\). \(^f\) Only 1,4-linear product (7) is formed in 78% yield. 7: \((\text{Z})\)-2-methyl-6-(3-propenyl)-octa-2,6-diene.

The optimized reaction conditions using (dpbb)CoCl\(_2\) have broad applicability as shown in Tables 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 hydrovinylation 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 adducts 5.\(^12\) The former is easily identified by the presence of a quintet around \(\delta 2.61,\)

Asymmetric Hydrovinylation of Unactivated Linear 1,3-Dienes

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and the latter by a broad triplet at ∼d 2.80. The reaction is compatible with functionalized dienes such as the benzyl ether $\text{If}$ and a 1,3-diene carrying a remote trisubstituted double bond ($\beta$-myrcene, $\text{6}$), which is not affected by the hydrovinylation of the terminal 1,3-diene functionality (entry 7).

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.$^{13}$ (E)-1-Phenyl-1,3-butadiene ($\text{8}$), a substrate that underwent facile Ni(II)-catalyzed hydrovinylolation to give a 1,2-adduct ($\text{9}$) exclusively,$^{10b}$ gives a linear 1,4-adduct $\text{10}$ with both (dppp)COCl$_2$ and (dppb)COCl$_2$ (eq 2). In sharp contrast, the corresponding dppm complex gives $\text{9}$ as the major HV product. (E)-2-Methyl-1-phenyl-1,3-butadiene ($\text{11}$) gives only a branched product ($\text{12}$) 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.

![Scheme 1](image)

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-diybis(methylene)-bis-diphenylphosphine [(RR)-DIOP,$^{14}$ and (SS)-2,4-bis-diphenylphosphinopentane [(SS)-BDPP,$^{15}$ simplest chiral analogues of dppp and dppb that are commercially available, gave the best results (Table 3).

Under the optimized conditions (E)-1,3-nonadiene ($\text{1a}$) gave (S)-(Z)-4-vinylhynon-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 $\text{2e}$, by comparison of observed$^{12}$ and reported$^{13}$ 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 $\text{If}$ (entries 9, 10) are tolerated in these highly enantioselective reactions. Not unexpectedly, substrate $\text{If}$ carrying a Lewis basic oxygen reacts sluggishly. Finally, a diene with aryl conjugation (e. g., $\text{11}$) gave essentially a racemic product (entry 12).$^{16}$

$\text{1e}$ gives only a single product ($\text{2a}$) which would undergo coupling with ethylene to give $\text{2b}$. Reductive elimination from $\text{2b}$ regenerates the catalyst $\text{1}$.

![Table 3](image)

$^a$ 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; $^c$ Isolated yield in brackets. $^d$ Configuration of $\text{2e}$ assigned by comparison of optical rotation and relative retention times on a $\beta$-cyclodex chiral stationary phase GC column.$^{12,2c}$ Others (all of same sense of (P$_i$O) assigned by analogy; see Supporting Information for details. $^d$ Volatile products. $^e$ Reaction done at −20 °C, rest starting materials.

**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]CoCl2 and (SS)-[BDPP]-CoCl2, 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.

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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.

References


