Rhodium-Catalyzed Asymmetric Dehydrocoupling: Enantioselective Synthesis of a P-Stereogenic Diphospholane with Mistake-Correcting Diastereoselectivity

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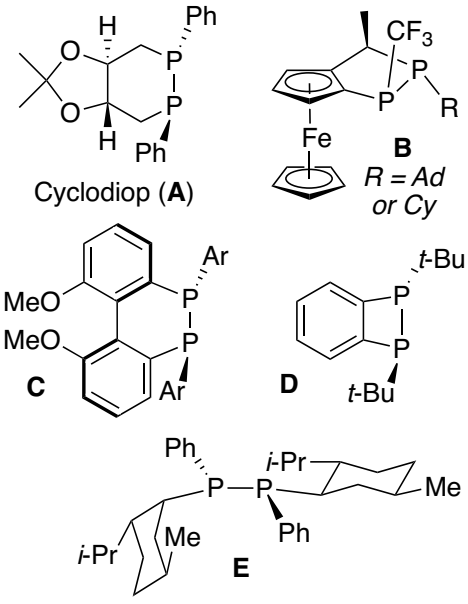
ABSTRACT: Catalytic asymmetric dehydrocoupling of secondary phosphines is a potentially valuable route to enantiomerically enriched P-stereogenic diphosphines for use as ligands or building blocks for chiral bis(phosphines). Rh(diphos*) catalyst precursors converted a racemic/*meso* mixture of PhHP(CH_2)$_3$PHPh (**1**) to the C_2-symmetric P-stereogenic *anti*-diphospholane PhP(CH_2)$_3$PPh (**2**) in up to 58:42 enantiomeric ratio (er) with complete diastereoselectivity via catalyst-mediated isomerization of the intermediate *syn*-diphospholane **3** to **2** (mistake correction by conversion of the diastereomer *meso*-**3** to chiral C_2-**2**). NMR studies of catalytic reactions identified the resting state Rh((*R,R*)-*i*-Pr-DuPhos)(PhHP(CH_2)$_3$PPh) (**4**) and suggested a proposed mechanism for stereocontrolled P-P bond formation via oxidative addition and reductive elimination steps.

P-stereogenic phosphines, whose high inversion barriers (29-36 kcal/mol) ensure configurational stability at room temperature,[1] are important ligands in asymmetric catalysis.[2] Although inversion barriers in P-stereogenic diphosphines[3] RR'P–PRR' are not much lower (22-26 kcal/mol),[4] enantiomerically enriched derivatives (Chart 1) are rare and have found few catalytic applications.[5] However, Cyclodiop (**A**) formed rhodium complexes which were active in asymmetric hydrogenation,[6] and chiral diphosphines **B** and **D** could be converted into P-stereogenic bis(phosphines) by P-alkylation with methyl triflate, followed by nucleophilic cleavage of the P–P bond.[5b-c]

Chart 1. Enantiomerically Enriched P-Stereogenic Diphosphines

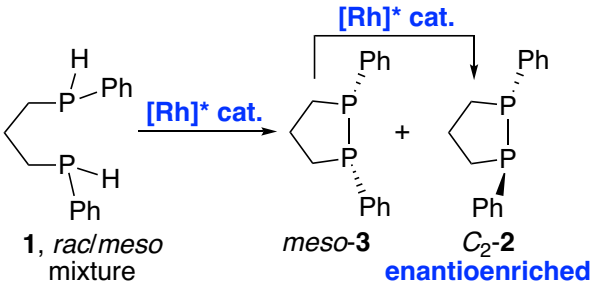


Improved synthetic methods would be valuable for further development of chiral diphosphines as ligands or building blocks for asymmetric catalysis. **A**-**E** were prepared using stoichiometric amounts of chiral reagents via asymmetric synthesis or separation processes.[5] Instead, catalytic asymmetric routes would be more efficient.[7] Catalytic homo-dehydrocoupling of element-hydrogen bonds (2 E–H ⟶ E–E + H_2) is a valuable method for formation of P–P and

other E–E bonds,[8] but asymmetric versions have not yet been developed.[9]

Here, we report the first such process, rhodium-catalyzed asymmetric dehydrocoupling of the bis(secondary phosphine) PhHP(CH$_2$)$_3$PHPh (**1**, *rac*/*meso* mixture) to give enantiomerically enriched P-stereogenic C_2-symmetric *anti*-diphospholane **2** via stereocontrolled P–P bond formation (Scheme 1).[10] Notably, the diastereoselectivity increased over time, as the catalyst corrected its mistakes by converting the unwanted diastereomer *meso*-**3** to the desired chiral C_2-**2**.

Scheme 1. Rh-Catalyzed Asymmetric Synthesis of C_2-2 from 1, with Formation and Disappearance of Intermediate *meso*-3



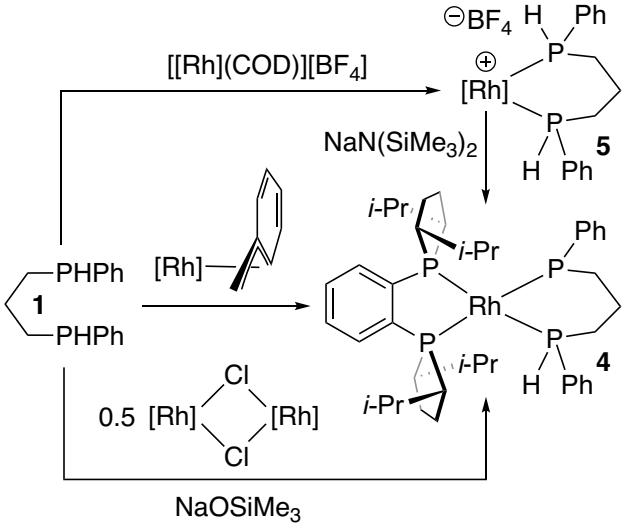
Several catalyst precursors, including Rh(COD)(η^3-CH$_2$Ph)[11] and the analogues Rh(diphos*)(η^3-CH$_2$Ph) generated by addition of chiral bis(phosphines),[12] or [Rh(diphos*)(COD)][BF$_4$] in the presence of NaN(SiMe$_3$)$_2$, converted **1** into C_2-**2** at room temperature (Scheme 1 and Tables S2-S3 in the Supporting Information (SI)).[13] As expected, this process was challenging because the substrate can chelate rhodium and displace the chiral diphos* ligand. Indeed, several ligands including BPE derivatives, DIOP, and Me-FerroLANE were observed in the reaction mixtures. However, modest enantioselectivity was observed in screening experiments, up to 58:42 enantiomeric ratio (er) for the rigid bis(phospholanes) (*R*,*R*)-Et-BPE and (*R*,*R*)-Me-DuPhos. Under these mild conditions, the cyclization was slower than reported Rh-catalyzed phosphine dehydrocouplings,[14] which occurred at higher temperatures. As expected, heating these reaction mixtures resulted in faster conversion, but lower enantioselectivity. Related processes are promoted by hydrogen acceptors,[8d] but cyclooctadiene liberated from the catalyst precursors was not hydrogenated.

The *meso*-diphospholane **3** was observed as a transient intermediate in the cyclization (Scheme 1). Formation of isomers C_2-**2** and *meso*-**3** was competitive early in the reaction, but *meso*-**3** eventually all disappeared. A mixture of **2** and **3**, isolated by chromatography from catalytic reactions before isomerization was complete, remained unchanged at room temperature. These observations are consistent with the computed energy difference between the isomers (0.8 kcal/mol, favoring C_2-**2**), and the barrier to the pyramidal inversion process which interconverts them (28 kcal/mol, M06/6-311G**++).[15] Although C_2-**2** has been reported several times since its first synthesis in 1961,[10] its *meso* isomer **3** was unknown. We identified these diphospholanes and their stereochemistry by NMR spectroscopy and by formation of the known bis(phosphine sulfide) of C_2-**2**,[16] and their bimetallic complexes with two W(CO)$_5$,[17] AuCl, and (*S*)-Pd(C$_6$H$_4$NMe$_2$)(Cl) fragments (see the SI).

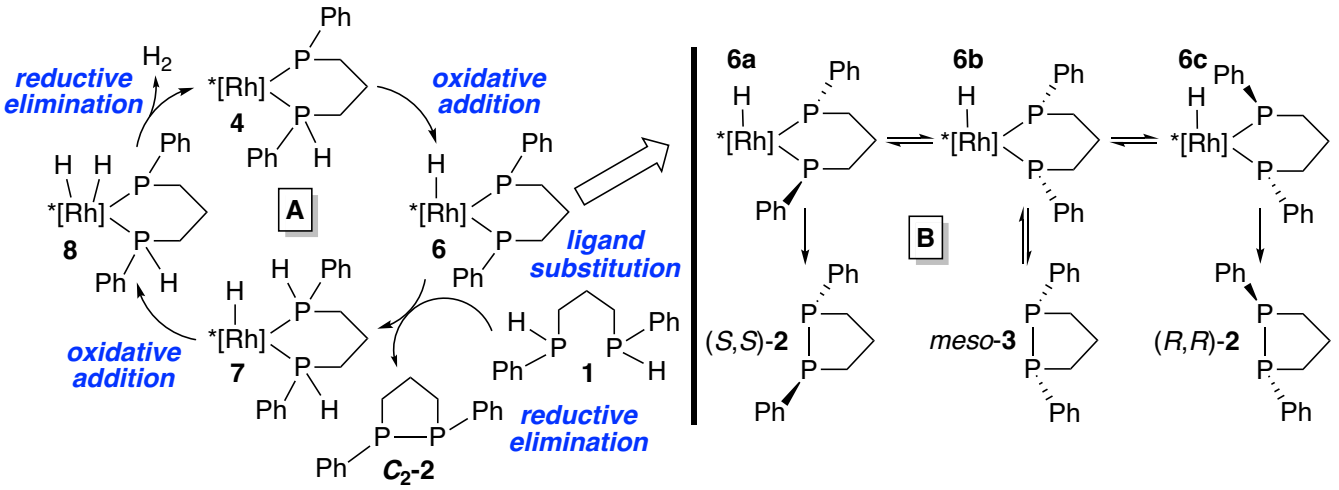
In contrast to the catalyst-mediated isomerization of *meso*-**3**, C_2-**2** was configurationally stable under the reaction conditions, as shown by two complementary experiments. In dehydrocoupling of **1** mediated by the precursor [Rh((*R*,*R*)-*i*-Pr-DuPhos)(Cl)]$_2$ and NaOSiMe$_3$, the enantiopurity of C_2-**2** remained the same, within experimental error, over the course of the reaction.[18a] Similarly, an active catalytic reaction of 0.1 mmol of **1** initiated by [Rh((*S*,*S*)-*i*-Pr-DuPhos)(Cl)]$_2$ and NaOSiMe$_3$ was treated with 0.2 mmol of isolated C_2-**2** (1:0.8 er) which had been prepared with the enantiomeric catalyst precursor [Rh((*R*,*R*)-*i*-Pr-DuPhos)(Cl)]$_2$. Once all of **1** had been consumed, the er of C_2-**2** was as expected for a 1:2 mixture formed by two enantiomeric catalysts; the (*S*,*S*)-catalyst did not affect the configuration of the added diphospholane.[18b]

We chose the especially robust *i*-Pr-DuPhos complexes for mechanistic studies. Monitoring Rh((*R*,*R*)-*i*-Pr-DuPhos)-catalyzed reactions by ^{31}P{^{1}H} NMR spectroscopy showed that the resting state was the phosphine-phosphido complex Rh((*R*,*R*)-*i*-Pr-DuPhos)(PhHP(CH$_2$)$_3$PPh) (**4**), which was also generated by deprotonation of the cation [Rh((*R*,*R*)-*i*-Pr-DuPhos)(PhHP(CH$_2$)$_3$PHPh)][BF$_4$] (**5**) with NaN(SiMe$_3$)$_2$, or from [Rh((*R*,*R*)-*i*-Pr-DuPhos)(Cl)]$_2$, bis(secondary phosphine) **1**, and NaOSiMe$_3$ (Scheme 2). Complex **4** could exist as a mixture of four diastereomers which differ in the P-configurations of the secondary phosphine and phosphido groups, but only two sets of signals were observed by ^{31}P{^{1}H} NMR spectroscopy. This is consistent with rapid interconversion on the NMR time scale of pairs of diastereomers which share the same Rh-PHPh(R) phosphine configuration and differ in their Rh-PPh(R) phosphido configuration, by the fast pyramidal inversion typical of metal-phosphido complexes.[19] We were unable to freeze out this dynamic process at low temperature.

Scheme 2. Generation of the Resting State Phosphine-Phosphido Complex Rh((*R*,*R*)-*i*-Pr-DuPhos)(PhHP(CH$_2$)$_3$PPh) (4, [Rh] = Rh((*R*,*R*)-*i*-Pr-DuPhos)) from Bis(Secondary Phosphine) 1



Scheme 3. Proposed Mechanism of Rh-Catalyzed Asymmetric Dehydrocoupling of 1 to Yield C_2-2 (A) and Curtin-Hammett Control of Selectivity in P–P Reductive Elimination from Rapidly Interconverting Phosphido Diastereomers 6a-c (B, *[Rh] = Rh(diphos*))

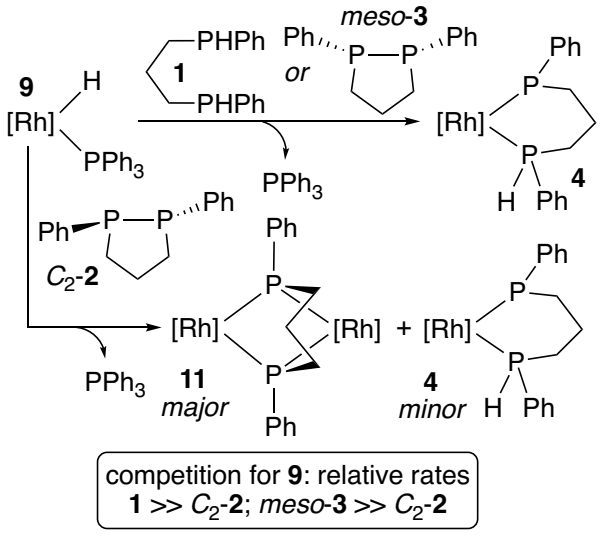


We propose the simplified mechanism in Scheme 3A to explain these observations.[14] After P–H oxidative addition[20] in phosphine-phosphido complex **4** yields Rh(III)-bis(phosphido) hydride **6**, P–P reductive elimination gives diphospholane **2** (or **3**, see Scheme 3B) and ligand substitution by substrate **1** yields **7**. Another P–H activation gives **8**, and reductive elimination of H_2 then regenerates **4**. As we suggested earlier,[21] diastereoselectivity and enantioselectivity could occur via Curtin-Hammett control in Rh(III) hydride intermediate **6** (Scheme 3B).[22] Its three diastereomers **6a-c** should interconvert rapidly by pyramidal inversion at phosphorus.[19] If these equilibria were faster than P–P reductive elimination, the product ratio would depend on the speciation of diastereomers **6a-c** and their relative rates of P–P bond formation.[23] The constant enantioselectivity in formation of C_2-**2** and the increase in diastereoselectivity (C_2-**2**/*meso*-**3** ratio) with time could occur if P–P reductive elimination to form **2** and **3** were irreversible and reversible, respectively. Increased strain in **3** due to lone pair-lone pair repulsion, as well as reduced steric hindrance with the *syn* Ph groups, could promote its oxidative addition to the Rh(diphos*)(H) fragment.[24]

To test the kinetic competence of proposed, but unobserved, rhodium hydride intermediates **6**-**8**, we tried to generate them by ligand substitution on an isolated Rh-H complex bearing a bulky PPh_3 leaving group. Treatment of Rh((*R,R*)-*i*-Pr-DuPhos)(PPh_3)(H) (**9**) with a stoichiometric amount of substrate **1** gave PPh_3 and phosphine-phosphido resting state **4** (Scheme 4), presumably via initial ligand substitution to give **7** and conversion to **4** via **8**, which remained unobserved. With excess substrate **1**, PPh_3 and resting state **4** were again formed, and catalytic formation of intermediate *meso*-**3** and product C_2-**2** proceeded. Reaction of Rh-hydride **9** with *meso*-**3** (in a mixture with C_2-**2**, see below) also gave **4**, consistent with the proposed mechanism for reversible formation of the *meso*-diphospholane.

Surprisingly, treatment of hydride **9** with C_2-**2** also resulted in P–P cleavage to yield the red dinuclear μ-phosphido complex **11** (Scheme 4, Figure 1),[25] plus a small amount of phosphine-phosphido complex **4**; presumably H_2 was also formed.[26] This process occurred whether the Rh-diphospholane ratio was 1:1 (with unreacted **2**) or 2:1. However, dinuclear **11** was not observed in catalytic reactions. A competition experiment (Scheme 4) demonstrated that hydride **9** reacted faster with bis(secondary phosphine) substrate **1** to yield **4** than it did with C_2-**2**. Similarly, treating **9** with a mixture of C_2-**2** and *meso*-**3** resulted in selective reaction of **3**, to give **4**. Therefore, during catalysis, C_2-**2** may be out-competed for coordination to Rh by **1** and **3**, preventing formation of **11**. However, we cannot rule out the possibility that **11** is formed, then converted to on-cycle intermediates. Alternatively, coordination of **1**, **2** or **3** to hydride **6** in an octahedral Rh(III) bis(phosphido) hydride intermediate may be required to trigger P-P reductive elimination, so that the diphospholane complex Rh((*R,R*)-*i*-Pr-DuPhos)(H)(C_2-**2**), which might lead to **11**, is not formed directly from **6**. Similarly, P-H oxidative addition in **4** might be promoted by ligand coordination.[14d]

Scheme 4. Reactions of Bis(Secondary Phosphine) 1 and Diphospholanes C_2-2 and *meso*-3 with Rhodium Hydride Complex 9 ([Rh] = Rh((*R,R*)-*i*-Pr-DuPhos))



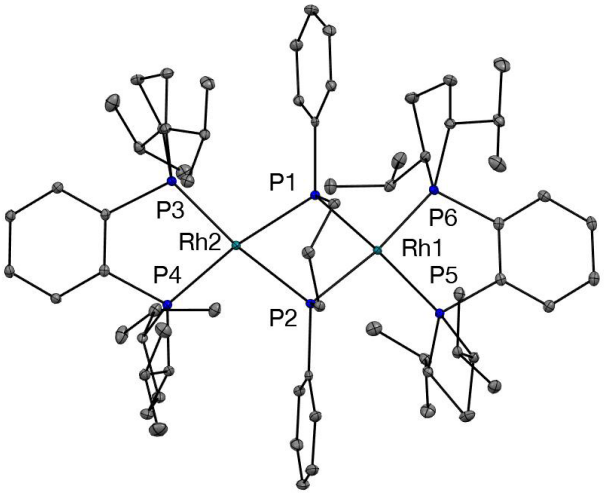


Figure 1. ORTEP Diagram of Dinuclear Bis(μ-phosphido) Complex **11**

We have reported catalytic asymmetric synthesis of a C_2-symmetric P-stereogenic diphospholane, a rare example of a chiral diphosphine, via a novel asymmetric dehydrocoupling. This approach could be more generally useful for enantioselective synthesis of element-element bonds, although we expect intermolecular coupling to yield acyclic products will be more challenging than the intramolecular analogue. Here it occurs via an unusual process in which the catalyst corrects its initial mistakes, increasing the diastereoselectivity over time by converting undesired *meso*-**3** to C_2-**2**. Such proofreading and error correction steps are common in DNA polymerases,[27] but rare with synthetic catalysts. Mistake correction is distinct from "minor enantiomer recycling," where an added catalyst transforms an unwanted product to starting material,[28] and from "editing" processes where the minor enantiomer is converted to a separate product.[29] In all of these examples, unwanted isomers (an enantiomer, or, in this manuscript, a diastereomer) are destroyed by catalyst-mediated processes. Deliberately incorporating such steps into catalytic cycles could be a more general route to increase selectivity.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Additional experimental and computational details and NMR spectra (PDF)
X-ray crystallographic details (CIF)
Computed coordinates (xyz)

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The authors declare no competing financial interests.

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15. Consistent with the calculated lower free energy of C_2-**2**, *meso*-**3** was completely converted to C_2-**2** under catalytic conditions, within the limits of detection by $^{31}P\{^1H\}$ NMR spectroscopy.

16. (a) ref 10a (b) Lee, J. D. The P–P bond length in 1,2-diphenyl-1,2-diphospholane-1,2-disulphide compared with that in other compounds. *J. Organomet. Chem.* **1977**, *137*, 193-198. (c) Lee, J. D.; Boloorizadeh, A. H. The crystal and molecular structure of 1,2-diphenyl-1,2-diphospholane-1,2-disulphide. *J. Organomet. Chem.* **1978**, *152*, 305-310.

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18. (a) See the SI (Table S4 and Figures S46-S56) for details. The reaction was monitored over time with NMR yields of C_2-**2** ranging from 6% to >95%, with er values from 1:0.99 to 1:0.87 (average (standard deviation) = 1:0.93±0.06). (b). See the SI (Figures S57-S60) for details. The expected er of C_2-**2** should be 1(0.8:1) (from the (*S,S*)-catalyst) + 2(1:0.8) (from added C_2-**2** prepared with the (*R,R*)-catalyst) = 2.8:2.6 = 1.08:1, consistent with the experimental observation (1.05:1).

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25. For related $[Rh(diphos)(\mu\text{-}PR_2)]_2$ dinuclear μ-phosphido complexes, see ref 14b.

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