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Rh(I)-Catalyzed Enantioselective Hydrogenation of α-Substituted Ethenylphosphonic Acids

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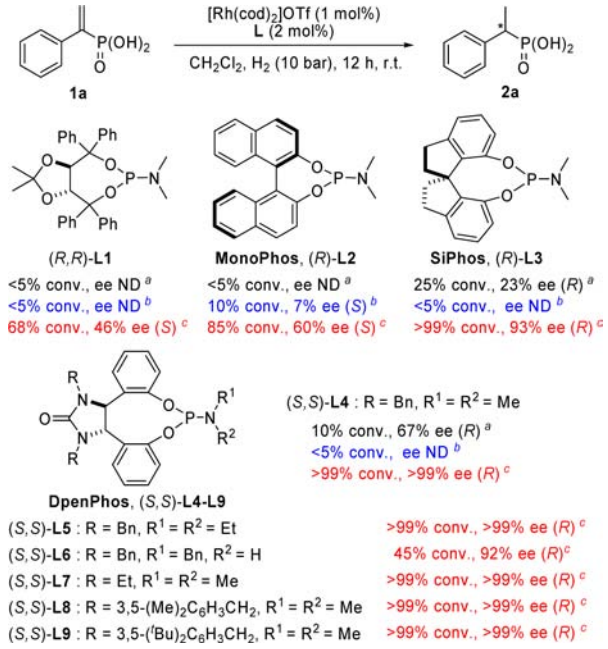
Supporting Information

ABSTRACT: A class of chiral Rh(I) catalysts containing monodentate phosphorous acid diesters tautomerized from the corresponding secondary phosphine oxides was discovered by serendipitous hydrolysis of phosphoramidite ligands. The evolved catalysts demonstrated unprecedented enantioselectivities (98−99% ee) and high catalytic activities (as low as 0.01 mol% catalyst loading) in asymmetric hydrogenations of a wide variety of α-aryl-/alkyl-substituted ethenylphosphonic acids, providing a facile approach to the corresponding enantiopure phosphonic acids with significant biological importance.

Enantiopure α-arylethylphosphonic acids can be considered phosphorus analogues of α-arylpropionic acids, well-known nonsteroid antiphlogistic and analgetic drugs such as naproxen and ibuprofen.[1] α-Aryl-/-alkylphosphonates represent one class of biologically important molecules in the search of new potent drugs.[2] Several methodologies have been developed for their preparation;[3] catalytic asymmetric hydrogenation[4] of the corresponding α-aryl-substituted ethenylphosphonic acids and esters represents the most straightforward approach. Although high enantioselectivities have been achieved for hydrogenation of diethyl α-aryl-substituted ethenylphosphonates with Ir(I) or Rh(I) complexes of bidentate PHOX- or BoPhoz-type ligands,[5] direct hydrogenation of α-aryl substituted ethenylphosphonic acids to afford the corresponding free α-aryl-substituted ethylphosphonic acids remains a challenge in terms of substrate scope, enantioselectivity (≤86% ee), and activity (≥1 mol% catalyst loading) of the catalysis.[6] The use of Rh(I) complexes of readily available monodentate chiral phosphorus ligands as catalysts for hydrogenation of α,β-unsaturated phosphonic acids has not been reported to date, despite their great success in asymmetric hydrogenation of many other types of substrates.[7] Here we report preliminary results on the discovery of a class of Rh(I) catalysts containing chiral monodentate phosphorous acid ester ligands by serendipitous hydrolysis of the corresponding phosphoramidite, DpenPhos.[8] The catalysts show unprecedented enantioselectivity and high catalytic activity in asymmetric hydrogenation of a wide range of α-aryl-/alkyl-substituted ethenylphosphonic acids to give the corresponding enantiopure phosphonic acids with biological importance.

The research was inspired by the excellent performance of well-established chiral phosphoramidite ligands, such as MonoPhos, SiPhos, and DpenPhos, in Rh(I)-catalyzed asymmetric hydrogenation of various olefin substrates.[7−9] We first investigated the viability of Rh(I) complexes of monodentate phosphoramidite ligands **L1**−**L4** as catalysts for the asymmetric hydrogenation of α,β-unsaturated acids with strong acidity using α-phenylethenylphosphonic acid (**1a**) as a model substrate (Scheme 1). The reaction did not occur or proceeded sluggishly with modest activity and enantioselectivity. When **1a** was first treated with 1 equiv of Et_3N and the resultant salt was added to the Rh(I) catalyst prepared with ligand (*R*,*R*)-**L1**, (*R*)-**L2**−**L3**, or (*S*,*S*)-**L4**, no beneficial effect of Et_3N on the catalysis was observed. When substrate **1a** was added to the catalyst Rh(I)/(*S*,*S*)-**L4** in CH_2Cl_2 before Et_3N was introduced to the

Scheme 1. Initial Tests of Monodentate Phosphoramidite Ligands for Rh(I)-Catalyzed Asymmetric Hydrogenation of 1a: Impact of Et_3N and the Phosphonic Acid Additive



ND = not determined. [a]In the absence of Et_3N. [b]**1a** was first reacted with 1 equiv of Et_3N; the resultant salt was added to the Rh(I) catalyst prepared with **L1**−**L4**. [c]**1a** was first mixed with the Rh(I) catalyst prepared with the ligand in CH_2Cl_2 and stirred for 10 min; 1 equiv of Et_3N was introduced into the reaction system.

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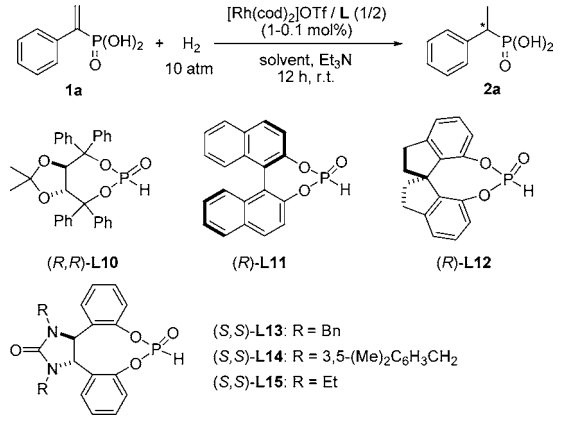
reaction system, complete conversion of **1a** occurred and hydrogenation product **2a** was obtained with >99% ee, clearly showing the critical importance of the acidic substrate addition sequence. When the right substrate addition sequence was followed, catalytic performance of Rh(I)/(*R*)-**L1**−**L3** was also significantly improved. Under the same experimental conditions, analogous catalysts containing (*S*,*S*)-**L5**−**L9** showed good to excellent activity and high enantioselectivity (92−99% ee) in hydrogenation of **1a**. These results indicate that the phosphonic acid substrate effects the evolution of chiral catalyst to form the active species before addition of Et_3N. The strong acidity of the phosphonic acid substrate might facilitate hydrolysis of hemilabile phosphoramidite ligands with adventitious water during catalyst preparation, affording a Rh(I) complex containing a phosphorous acid diester formed by tautomerization from its secondary phosphine oxide [see Scheme S1, Supporting Information (SI)].[10] In fact, addition of other strong acids [e.g., inorganic H_3PO_4 or organic $PhP(O)(OH)_2$] to the Rh(I)/(*S*,*S*)-**L4** complex in CH_2Cl_2 also resulted in formation of an active catalyst that demonstrated comparable enantioselectivities (97% and 98% ee, respectively; see SI) in hydrogenation of the **1a**/Et_3N salt, albeit with relatively lower activities, providing circumstantial evidence for catalyst evolution under acidic conditions.

In comparison with numerous successful applications of monodentate phosphoramidite, phosphite, and phosphonite[7−9] chiral ligands in transition-metal-catalyzed asymmetric reactions, the use of secondary phosphine oxides or their tautomeric phosphorous acid derivatives is less explored.[10,11] With the above observations in mind, we decided to employ the corresponding secondary phosphine oxides directly as the ligands to check their feasibility in the catalysis. Thus, chiral secondary phosphine oxides **L10**−**L15** were prepared by simple hydrolysis of the corresponding phosphorochloridites in a two-step, one-pot manner from readily available enantiopure diols. **L10**−**L13** were first applied to the Rh(I)-catalyzed hydrogenation of **1a**. The reaction proceeded effectively with complete conversion of substrate within 12 h in CH_2Cl_2 in the presence of 1 mol% catalyst and 1 equiv of Et_3N under 10 atm H_2 at rt, affording the corresponding optically active phosphonic acid **2a** with various ee values (Table 1, entries 1−4). Catalyst (*S*,*S*)-**L13** composed of DpenPhos-derived phosphine oxide was the most enantioselective (>99% ee, entry 4) and its asymmetric induction level was essentially same as that previously observed for Rh(I)/(*S*,*S*)-**L4** (Scheme 1). This suggests that *in the catalyst system Rh(I)/(S,S)-**L4**, the phosphoramidite ligand most likely undergoes hydrolysis under acidic conditions to generate phosphine oxide (S,S)-**L13**, and the catalyst evolves into the new and highly efficient species Rh(I)/(S,S)-**L13**′ via tautomerization of (S,S)-**L13*** (Scheme S1). In the absence of Et_3N, the reaction proceeded sluggishly with a significant decrease in enantioselectivity (68% ee; entry 5). In contrast, addition of Et_3N (0.5−2 equiv) to the reaction system resulted in a considerable enhancement in catalytic performance (see SI). Analogous ligands (*S*,*S*)-**L14** and (*S*,*S*)-**L15** with more and less steric hindrance, respectively, due to the substituents on the imidazolidinone backbone also demonstrated excellent catalytic performance (entries 6 and 7). When the catalyst loading of Rh(I)/(*S*,*S*)-**L13** was decreased to 0.1 mol%, hydrogenation of **1a** still proceeded efficiently without deterioration of the enantioselectivity (entry 8 vs 4). Examination of the effect of solvent on catalysis at 0.1 mol% catalyst loading indicated that in addition to CH_2Cl_2, other

Table 1. Enantioselective Hydrogenation of 1a Catalyzed by Rh(I) Complexes of Various Secondary Phosphine Oxides[a]



entry	ligand	s/c	solvent	conv. (%)[b]	ee (%)[c]
1	(*R*,*R*)-**L10**	100	CH_2Cl_2	>99	46 (*S*)
2	(*R*)-**L11**	100	CH_2Cl_2	>99	93 (*S*)
3	(*R*)-**L12**	100	CH_2Cl_2	>99	98 (*R*)
4	(*S*,*S*)-**L13**	100	CH_2Cl_2	>99	>99 (*R*)
5[d]	(*S*,*S*)-**L13**	100	CH_2Cl_2	25	68 (*R*)
6	(*S*,*S*)-**L14**	100	CH_2Cl_2	>99	>99 (*R*)
7	(*S*,*S*)-**L15**	100	CH_2Cl_2	>99	>99 (*R*)
8	(*S*,*S*)-**L13**	1000	CH_2Cl_2	>99	>99 (*R*)
9	(*S*,*S*)-**L13**	1000	DCE	>99	>99 (*R*)
10	(*S*,*S*)-**L13**	1000	$CHCl_3$	>99	>99 (*R*)
11	(*S*,*S*)-**L13**	1000	THF	73	>99 (*R*)
12	(*S*,*S*)-**L13**	1000	Et_2O	>99	>99 (*R*)
13	(*S*,*S*)-**L13**	1000	toluene	87	>99 (*R*)
14	(*S*,*S*)-**L13**	1000	EtOAc	90	>99 (*R*)
15	(*S*,*S*)-**L13**	1000	MeOH	<5	–
16	(*S*,*S*)-**L13**	1000	*i*-PrOH	9	–

[a]Conditions: $[Rh(cod)_2]OTf$/**L** = 1:2, Et_3N (1 equiv), [**1a**] = 0.1 M at a substrate/catalyst ratio (s/c) of 100 and 0.5 M at s/c = 1000. [b]Determined by ^1H NMR analysis. [c]Determined by chiral HPLC. [d]In the absence of Et_3N.

aprotic solvents, such as DCE, $CHCl_3$, THF, Et_2O, toluene, and EtOAc are compatible for catalysis, affording perfect enantioselectivity (>99% ee), albeit with various conversion of **1a** (73−99%) (entries 9−14). In contrast, protic solvents such as CH_3OH and *i*-PrOH inhibited the catalysis under otherwise identical reaction conditions (entries 15 and 16).

Under the optimized reaction conditions, the substrate scope of the catalysis explored (Scheme 2). Catalysis by Rh(I)/(*S*,*S*)-**L13** (1−0.1 mol%) is quite general with substituted ethenylphosphonic acids **1a**−**q**. The reactions were accomplished within 12 h at rt under 10 atm H_2, providing the corresponding optically active phosphonic acids **2a**−**q** with unprecedented 98−99% ee. Neither the electronic properties nor the steric hindrance of the substituent (R^1) had an obvious influence on the enantioselectivity (**2a**−**2p**), although a higher catalyst loading (1 mol%) was necessary for the reaction of sterically hindered aryl- (**1b**−**d**) or alkyl-substituted (**1n**−**p**) ethenylphosphonic acids to realize full substrate conversion. Hydrogenation of a more challenging substrate, α,β-disubstituted vinylphosphonic acid **1q**, in the presence of 1 mol% catalyst afforded the corresponding phosphonic acid **2q** with 98% ee and >99% conversion. Notably, the productivity of the Rh(I)/(*S*,*S*)-**L13** catalyst can be very high under elevated hydrogen pressures. As shown for hydrogenation of **1a** with a

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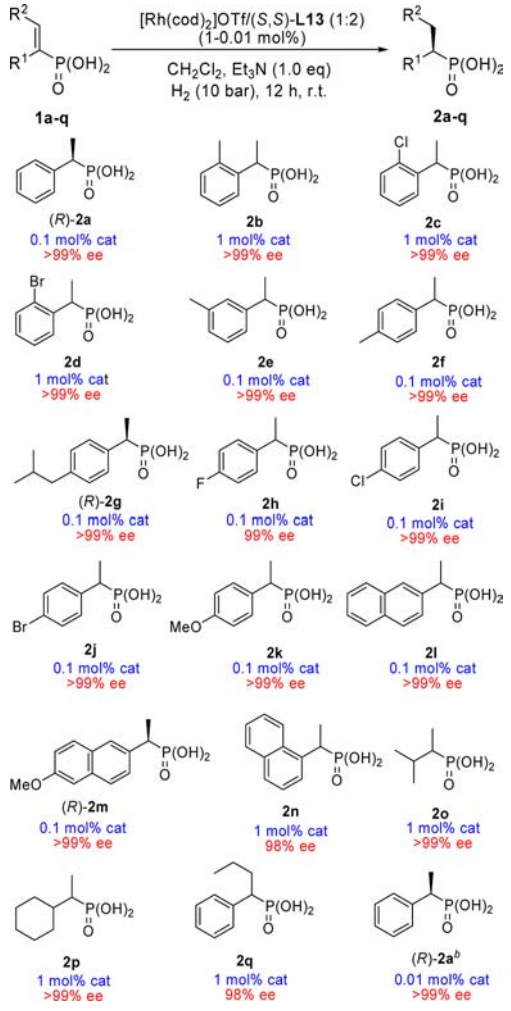
Scheme 2. Rh(I)/(*S*,*S*)-L13-Catalyzed Asymmetric Hydrogenation of Various Substituted Ethenylphosphonic Acids 1a−q[a]



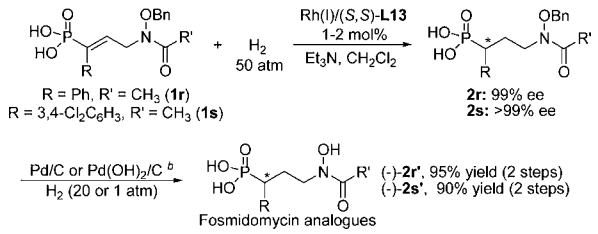
[a]For reaction conditions, see footnote *a* of Table 1. Conversion of all substrates was >99%; ee values of the products were determined by chiral-stationary-phase HPLC or GC after esterification with CH_2N_2. [b]Conditions: $[Rh(cod)_2]OTf/(S,S)$-**L13** =1:2, [**1a**] = 2.0 M; s/c = 10000, P_{H_2} = 50 bar, 24 h. Isolated yield of **2a** was 95%.

catalyst loading of 0.01 mol% (s/c = 10000), (*S*)-**2a** was isolated in high yield (95%) on a gram scale without loss of enantioselectivity (>99% ee) after prolonged reaction (24 h) at 50 bar H_2.

As a synthetic application of present methodology, hydrogenations of **1r** and **1s** were also carried out in the presence of 1−2 mol% Rh(I)/(*S*,*S*)-**L13**, affording the corresponding key *α*-aryl precursors **2r** and **2s** as single enantiomers (99% ee). These products were readily converted to the corresponding chiral fosmidomycin analogues **2r′** and **2s′** with more favorable physicochemical properties and higher activity in inhibiting malaria parasite growth[2] by hydrogenative deprotection of the Bn group in 95 and 90% yield (for two steps), respectively (Scheme 3), highlighting the potential utility of the present method for the synthesis of biologically interesting molecules.

To provide more insights into the mechanism of the present catalytic system, the nonlinear effect (NLE)[12] of the $[Rh(cod)_2]OTf/(S,S)$-**L13**-catalyzed hydrogenation of **1a** was examined using (*S*,*S*)-**L13** with varying ee as the ligand under

Scheme 3. Rh(I)-Catalyzed Asymmetric Hydrogenation in the Synthesis of Fosmidomycin Analogues[a]



[a]For the hydrogenations of **1r** and **1s**, 2 and 1 mol% loadings of $[Rh(cod)_2]OTf/(S,S)$-**L13**, respectively, were employed. [b]**2r**: 10% Pd/C, 20 atm H_2, MeOH. **2s**: 20% $Pd(OH)_2/C$, 1 atm H_2, THF.

the optimized reaction conditions. A weak positive NLE was observed (Figure S2), indicating that the Rh(I) species involved in the catalysis should contain more than one monodentate phosphorous acid derivative within or at the periphery of the catalytic cycle. ^{31}P and ^{1}H NMR studies of the $[Rh(cod)_2]$-$OTf/(S,S)$-**L13** systems generated in situ at Rh/**L** molar ratios of 1:1, 1:2, 1:3, and 1:4 (see SI) indicated exclusive formation of $Rh(I)\{(S,S)\text{-}\mathbf{L13}\}_2$ species. Investigation of the effect of the Rh(I)/**L** ratio (from 1:1 to 1:4) on the reaction rate and enantioselectivity showed that the catalyst system with 1:2 Rh(I)/(*S*,*S*)-**L13** demonstrated optimal performance, suggesting that $[Rh(cod)\{(S,S)\text{-}\mathbf{L13}\}_2]OTf$ is responsible for the catalysis.[8,9,13]

To clarify the structural details of the precatalyst, a single crystal of $[Rh(cod)\{(S,S)\text{-}\mathbf{L13'}\}_2]OTf$ was characterized by X-ray crystallography (Figure 1). The complex contains two

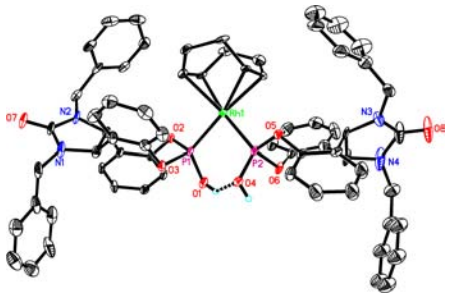


Figure 1. Molecular structure of $[Rh(cod)\{(S,S)\text{-}\mathbf{L13'}\}_2]OTf$. H atoms and the OTf anion have been omitted for clarity.

(*S*,*S*)-**L13′** molecules coordinated to Rh(I) through the P atoms with a square-planar coordination geometry typical for d^8 Rh(I) complexes. The Rh−P bond lengths (2.201 and 2.238 Å) are essentially in keeping with literature values, whereas the P−Rh−P bite angle (88.78°) is obviously smaller than those observed in analogous phosphoramidite complexes (94.78 and 93.78°).[8a,c] Most interestingly, both ligand molecules in the complex are present in the form of the phosphorous acid diester tautomerized from the secondary phosphine oxide, as evidenced by their P−O single bond lengths (1.54−1.63 Å), and thus effectively bring their acidic OH groups near the catalytic metal center with a O(1)···O(4) distance of 3.143 Å, indicating the existence of intermolecular H-bonding between the OH groups of the two (*S*,*S*)-**L13′** ligands. Hydrogenation of **1a** using this isolated complex afforded **2a** in full conversion with >99% ee, identical to the results with the complex prepared in situ, illustrating that $[Rh(cod)\{(S,S)\text{-}\mathbf{L13}\}_2]OTf$ should be the catalyst precursor for the reaction. The ^{31}P NMR

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spectrum of {Rh(cod)[(*S*,*S*)-**L13′**]$_2$OTf was also identical to that of the Rh(I) complex of (*S*,*S*)-**L13** prepared in situ at a 1:2 molar ratio, indicating the clean formation of a single species in solution (see SI). Although we are unable to clarify the exact underlying reason for the outstanding catalytic performance of this type of Rh catalyst presently, the OH group in the tautomerized ligand seems to be important in influencing the electronic and steric scenarios of the Rh(I) center[14] by ligand−ligand or/and ligand−substrate[15] interaction(s) through H-bonding. In fact, the distinct effects of aprotic and protic solvents on the catalytic outcome using [Rh(cod){(*S*,*S*)-**L13′**)}$_2$]OTf observed in Table 1 provide circumstantial evidence for the involvement of H-bonding interactions in the catalysis.

In conclusion, a class of Rh(I) catalysts containing monodentate phosphorous acid diesters tautomerized from the corresponding secondary phosphine oxides has been discovered by serendipitous acidic hydrolysis of phosphoramidite ligands. The evolved catalyst demonstrates excellent enantioselectivity (98−99% ee) and catalytic activity (catalyst loading as low as 0.01 mol%) in asymmetric hydrogenations of a list of α-aryl-/alkyl-substituted ethenylphosphonic acids, challenging olefinic substrate, providing a facile approach to the corresponding enantiopure phosphonic acids with significant biological interest. The OH groups in two adjacent monodentate phosphorous acid diester ligands around the Rh metal center and the related H-bonding interactions might be beneficial in the catalysis, which will provide a useful basis to bridge the gap between mono- and bidentate phosphorus ligands for construction of chiral transition-metal catalysts.[15]

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, spectral and analytical data for all products, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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