Asymmetric Hydrogenation

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Chloride-Bridged Dinuclear Rhodium(III) Complexes Bearing Chiral Diphosphine Ligands: Catalyst Precursors for Asymmetric Hydrogenation of Simple Olefins

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Abstract: *Efficient rhodium(III) catalysts were developed for asymmetric hydrogenation of simple olefins. A new series of chloride-bridged dinuclear rhodium(III) complexes* ***1*** *were synthesized from the rhodium(I) precursor [RhCl(cod)]$_2$, chiral diphosphine ligands, and hydrochloric acid. Complexes from the series acted as efficient catalysts for asymmetric hydrogenation of (E)-prop-1-ene-1,2-diyldibenzene and its derivatives without any directing groups, in sharp contrast to widely used rhodium(I) catalytic systems that require a directing group for high enantioselectivity. The catalytic system was applied to asymmetric hydrogenation of allylic alcohols, alkenylboranes, and unsaturated cyclic sulfones. Control experiments support the superiority of dinuclear rhodium(III) complexes* ***1*** *over typical rhodium(I) catalytic systems.*

Asymmetric hydrogenation of olefins is one of the most efficient reactions for generating enantiomerically enriched compounds.[1] A number of chiral transition metal complexes have been used as catalysts for asymmetric hydrogenation of olefins.[2] Among the chiral transition metal catalyst systems used for asymmetric hydrogenation of olefins, chiral rhodium catalysts have attracted particular attention because of their efficiency, enantioselectivity, pressure tolerance, and solvent profiles.[3] However, to achieve high asymmetric induction, rhodium catalysts unavoidably require a coordinating group next to the C=C double bond.[4] Such high enantioselectivity was considered a consequence of the chelating coordination of substrates. A typically proposed intermediate in asymmetric hydrogenation of olefinic substrates bearing a coordinating amide group involves, 1) both the C=C double bond and the coordinating functional group, 2) a dihydride rhodium(III) species generated in situ by the reaction of a rhodium(I) precursor with H_2.[5] Thus, hydrogenation of simple olefins with high enantioselectivity by chiral rhodium systems has remained challenging,[6] despite the tremendous advances in iridium-catalyzed asymmetric hydrogenation of unfunctionalized olefins. In this pioneering work, Pfaltz demonstrated the high catalytic performance of P,N-ligated iridium complexes.[2b, 4, 7, 8] Aiming to develop a rhodium(III) catalytic system, we focused our attention on monohydride rhodium(III) complexes. Our research was based on the reported reactivity of ethene inserted into a Rh–H bond of monohydride rhodium(III) complexes bearing dicyclohexyl(2-methoxyethyl)phosphine.[9] Previously, we developed chloride-bridged dinuclear iridium complexes that dissociated into the corresponding mononuclear monohydride iridium(III) complexes.[10] Asymmetric hydrogenation of heteroaromatics, such as quinolinium salts,[11] quinoxalines,[12] isoquinolinium salts,[13] pyridinium salts,[14] and quinazolinium salts,[15] was accomplished with the latter. Accordingly, we envisioned that rhodium analogues could serve as efficient new catalyst precursors, that could provide monohydride rhodium(III) species capable of catalyzing the asymmetric hydrogenation of simple olefins. We found that chiral chloride-bridged dinuclear rhodium(III) complexes proficiently catalyzed the asymmetric hydrogenation of simple olefins, as well as allylic alcohols, alkenylboranes, and unsaturated cyclic sulfones.

We initially synthesized chloride-bridged dinuclear rhodium(III) complex (*S*)-**1a**, bearing (*S*)-BINAP, by adding 5 equiv of HCl in diethyl ether to a mixture of [RhCl(cod)]$_2$ and 2.05 equiv of (*S*)-BINAP in toluene at room temperature (Scheme 1). The ^{1}H NMR spectrum of (*S*)-**1a** exhibited a hydride signal at −15.9 ppm with two coupling constants ($J_{P\text{-}H}$ of 22.7 and 15.5 Hz), indicating that the hydride was located at a position *cis* with respect to the two phosphines of (*S*)-BINAP. The ^{31}P{^{1}H} NMR spectrum of (*S*)-**1a** displayed a typical doublet of doublets pattern at 48.0 and 36.2 ppm ($J_{Rh\text{-}P}$ = 137 Hz and $J_{P\text{-}P}$ = 27 Hz). Figure 1 shows the cationic part of (*S*)-**1a**, which has a bifacial dinuclear structure with three chloride atoms bridging two rhodium atoms (one outer-sphere chloride anion is omitted for clarity). Application of the same synthetic procedure to a series of chiral atropisomeric diphosphine ligands with an (*S*)-configuration led to successful synthesis of the corresponding dinuclear rhodium complexes (*S*)-**1b–e** in high yields, although (*S*)-**1f** was obtained in only moderate yield because of the steric congestion imposed by the (*S*)-DTBM-SEGPHOS ligand.

We conducted asymmetric hydrogenation of a simple olefin, (*E*)-prop-1-ene-1,2-diyldibenzene (**2a**), using (*S*)-**1a–f** as catalysts. To our delight, **2a** was hydrogenated using (*S*)-**1a** as a catalyst with 30 bar hydrogen pressure in toluene at 100 °C for 20 h, producing (*S*)-propane-1,2-diyldibenzene [(*S*)-**3a**] in 30 % yield with 70 % *ee* (Table 1, entry 1). The catalysts (*S*)-**1b** and (*S*)-**1c**, respectively bearing (*S*)-tol-

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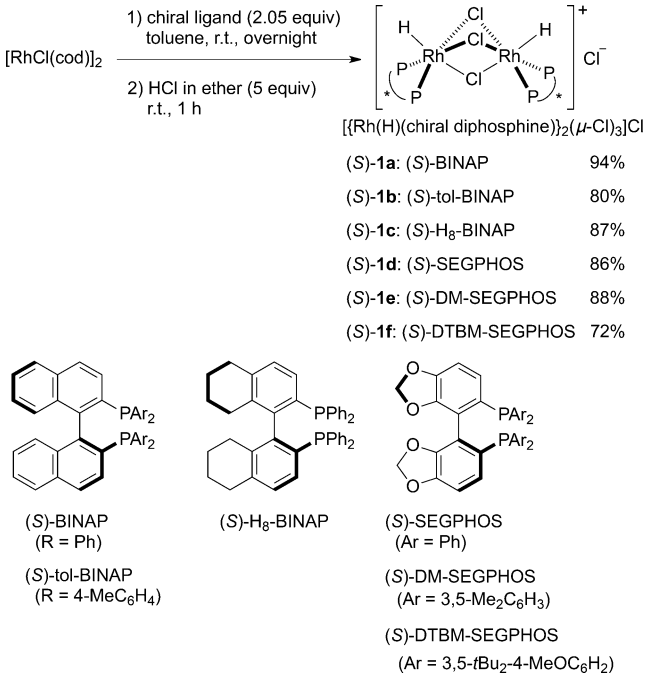


Scheme 1. Synthesis of chloride-bridged dinuclear rhodium complexes.

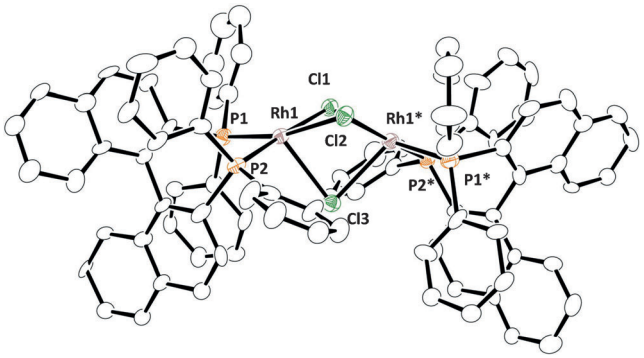
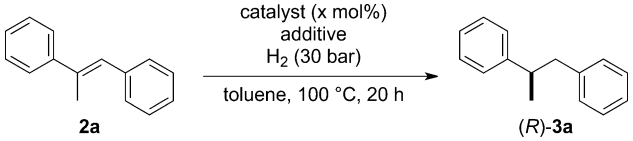


Figure 1. Molecular structure of the cationic part of (*S*)-**1a**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Rh(1)–P(1) = 2.273(3), Rh(1)–P(2) = 2.268(3), Rh(1)–Cl(1) = 2.451(2), Rh(1)–Cl(2) = 2.449(2), Rh(1)–Cl(3) = 2.5743(16); P(1)-Rh(1)-P(2) = 92.27(8), Cl(1)-Rh(1)-Cl(2) = 80.50(7), Cl(1)-Rh(1)-Cl(3) = 79.15(6), Cl(2)-Rh(1)-Cl(3) = 79.11(6), P(1)-Rh(1)-Cl(1) = 91.74(8), P(1)-Rh(1)-Cl(2) = 167.68(7), P(1)-Rh(1)-Cl(3) = 108.99(7).

BINAP and (*S*)-H_8-BINAP, were ineffective (entries 2 and 3). In contrast, (*S*)-SEGPHOS-type ligands showed high catalytic activity and high enantioselectivity: (*S*)-**1d** resulted in a 67% yield of products with 84% *ee* (entry 4), and the reaction using bulkier diphosphines, such as (*S*)-DM-SEGPHOS and (*S*)-DTBM-SEGPHOS, produced (*S*)-**3a** in excellent yields with 91% *ee* and 95% *ee*, respectively (entries 5 and 6).

Toluene was the best among the screened solvents, based on the balance of yield and enantioselectivity (see Supporting Information). The chloride-bridged dinuclear structure is robust; therefore, we examined the effects of adding ammonium chloride to facilitate the dissociation of dinuclear complexes into catalytically active mononuclear complexes.

Table 1: Optimization study.[a]



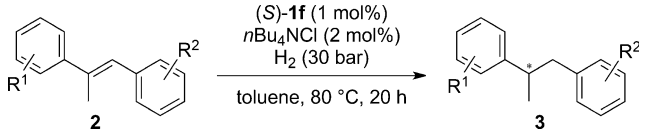
Entry	Catalyst	*x*	Additive	Yield[b] [%]	*ee*[c] [%]
1	(*S*)-**1a**	4	–	30	70
2	(*S*)-**1b**	4	–	48	70
3	(*S*)-**1c**	4	–	24	31
4	(*S*)-**1d**	4	–	67	84
5	(*S*)-**1e**	4	–	>99	91
6	(*S*)-**1f**	4	–	96	95
7	(*S*)-**1f**	2	nBu$_4$NCl (20 mol%)	90	94
8	(*S*)-**1f**	2	nBu$_4$NCl (10 mol%)	93	95
9	(*S*)-**1f**	2	nBu$_4$NCl (5 mol%)	93	95
10[d]	(*S*)-**1f**	1	nBu$_4$NCl (2 mol%)	96 (98)[e]	95
11	[RhCl(cod)]$_2$/ (*S*)-DTBM-SEGPHOS	1	NaBArF (4 mol%)	88	<5
12	[RhCl((*S*)-DM-SEGPHOS)]$_2$	2	–	27	35

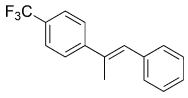
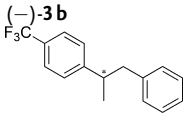
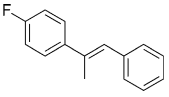
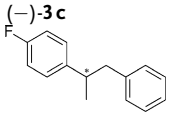
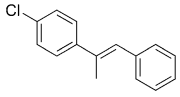
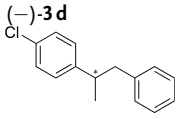
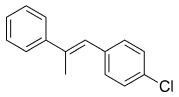
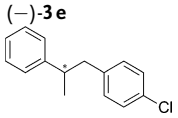
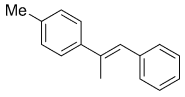
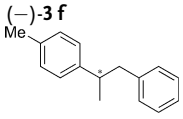
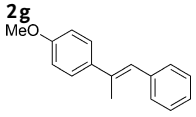
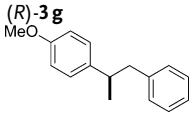
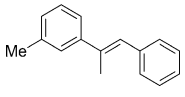
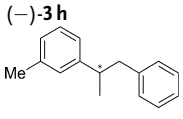
[a] Reaction conditions: a mixture of **2a** (0.20 mmol), rhodium catalyst (2.0 μmol), and toluene (3.0 mL) under H_2 (30 bar) was heated at 100 °C for 20 h. [b] Determined by ^{1}H NMR analysis. [c] Determined by HPLC analysis. [d] Run at 80 °C. [e] Isolated yield of products obtained by a 1 mmol scale reaction at 100 °C.

Development of this method was based on our previous observation that a chloride anion reacted with cationic triply chloride-bridged dinuclear iridium complexes, analogous to **1**, to give the corresponding mononuclear anionic iridium complexes.[13b] In fact, the addition of 20 mol% of nBu$_4$NCl increased catalyst activity, resulting in decreased catalyst loading (2 mol%; entry 7). Decreasing the amount of nBu$_4$NCl led to an increase in the yield of (*R*)-**3a**, reaching 96% using 1 mol% of (*S*)-**1f** and 2 mol% of nBu$_4$NCl, without loss of enantioselectivity (entries 8–10). Finally, we determined that the optimized hydrogenation conditions required 1 mol% (*S*)-**1f**, 2 mol% nBu$_4$NCl in toluene, and 30 bar hydrogen pressure at 80 °C for 20 h. A comparison with typical rhodium catalysis suitable for asymmetric hydrogenation of olefins bearing directing groups was subsequently carried out. Asymmetric hydrogenation of **2a** was performed using [RhCl(cod)]$_2$, (*S*)-DTBM-SEGPHOS, and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBArF), resulting in almost racemic **3a** (entry 11). The poor results obtained using a chiral chelating arylphosphine ligand are consistent with the previous results, in which only chiral chelating alkylphosphine ligands worked well for asymmetric hydrogenation catalyzed by cationic rhodium catalysts.[16] Additionally, asymmetric hydrogenation catalyzed by [RhCl((*S*)-DM-SEGPHOS)]$_2$ furnished **3a** in low yield and low enantioselectivity (entry 12). These findings clearly demonstrate that the activity of dinuclear rhodium complexes **1** differ from that of the typical rhodium(I) catalysts.

With the optimized conditions in hand, we examined the scope of the reaction using a range of alkenes without any directing groups (Table 2). Olefins with differing substituents on the phenyl ring were subjected to asymmetric hydrogenation (entries 1–7). The reaction was compatible with several functional groups, including trifluoromethyl, fluoro, and chloro groups, affording the hydrogenated products in high yield with high enantioselectivity (entries 1–3). Substrates with an electron-donating group, such as a methyl or methoxy group, required higher catalyst loading or a longer reaction time to achieve high conversion, and the corresponding hydrogenated products (*R*)-**3f** and (−)-**3g** were obtained in 87% and 94% *ee*, respectively (entries 5 and 6). As the *meta*-methyl substituent on the phenyl group significantly decreased the yield of (−)-**3h**, we used a more reactive catalyst (*S*)-**1e** to complete conversion to give (−)-**3h** in 98% *ee* (entry 7).

Table 2: Scope of alkenes lacking a directing group.[a]

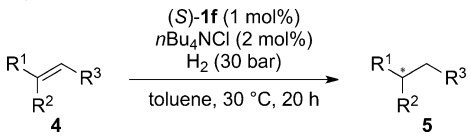


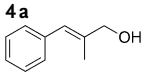
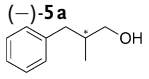
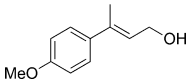
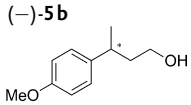
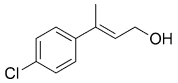
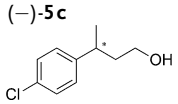
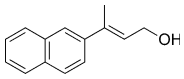
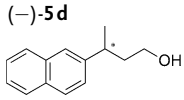
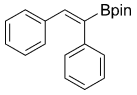
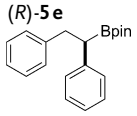
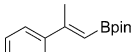
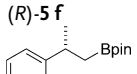
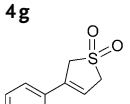
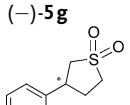
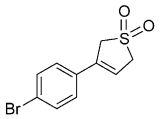
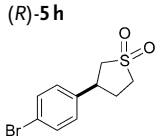
Entry	2	3	Yield[b] [%]	*ee*[c] [%]
1[d]	**2b** 	(−)-**3b** 	94	97(−)
2	**2c** 	(−)-**3c** 	99	98(−)
3	**2d** 	(−)-**3d** 	94	95(−)
4	**2e** 	(−)-**3e** 	98	96(−)
5[e]	**2f** 	(−)-**3f** 	76	87(−)
6[f]	**2g** 	(*R*)-**3g** 	80	94(*R*)
7[d]	**2h** 	(−)-**3h** 	99	98(−)

[a] Reaction conditions: a mixture of **2** (0.20 mmol), (*S*)-**1f** (2.0 μmol), nBu$_4$NCl (4.0 μmol), and toluene (3.0 mL) under H_2 (30 bar) was heated at 80°C for 20 h. [b] Isolated yield of products. [c] Determined by HPLC analysis. [d] (*S*)-**1e** was used as the catalyst. [e] 2 mol% of (*S*)-**1f** was used. [f] Run for 24 h.

The applicability of the rhodium catalyst system for asymmetric hydrogenation of different kinds of alkenes bearing a functional group with rather weak coordination ability is noteworthy (Table 3). Typical allylic alcohols were used as substrates for this catalytic reaction.[17] 3-Phenylmethallyl alcohol (**4a**) was hydrogenated at 30°C to furnish the corresponding product in quantitative yield with 99% *ee* (entry 1). The reaction of 3-aryl substituted 3-methylallyl alcohols proceeded with high enantioselectivity regardless of the substitution pattern on the phenyl ring (entries 2–4). Alkenyl boranes were also suitable substrates, and chiral centers on the α- or β-position of borane were readily introduced (entries 5 and 6). Furthermore, we applied our

Table 3: Scope of alkenes.[a]



Entry	4	5	Yield[b] [%]	*ee*[c] [%]
1[d]	**4a** 	(−)-**5a** 	99	99(−)
2[e]	**4b** 	(−)-**5b** 	99	87(−)
3	**4c** 	(−)-**5c** 	94	96(−)
4	**4d** 	(−)-**5d** 	87	90(−)
5[f]	**4e** 	(*R*)-**5e** 	99	85(*R*)[g]
6[f]	**4f** 	(*R*)-**5f** 	99	93(*R*)[g]
7[h]	**4g** 	(−)-**5g** 	96	95(−)
8[i]	**4h** 	(*R*)-**5h** 	61	94(*R*)

[a] Reaction conditions: a mixture of **4** (0.20 mmol), (*S*)-**1f** (2.0 μmol), nBu$_4$NCl (4.0 μmol), and toluene (3.0 mL) under H_2 (30 bar) was heated at 30°C for 20 h. [b] Isolated yield of products. [c] Determined by HPLC analysis. [d] (*S*)-**1e** was used as the catalyst. [e] Run for 24 h. [f] 2 mol% of (*S*)-**1e** was used. Run at 80°C for 24 h. [g] Determined with the corresponding alcohol obtained after oxidation. [h] Run at 80°C. [i] Run at 100°C. Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl.

system to the hydrogenation of unsaturated cyclic sulfones **4g** and **4h**, which resulted in smooth formation of chiral sulfolanes (−)-**5g** and (*R*)-**5h** with 95% *ee* and 94% *ee*, respectively (entries 7 and 8).

Notably, the catalytic activity of dinuclear rhodium complexes differs from that of well-established rhodium(I) catalysts, including mononuclear cationic rhodium complexes[5,16] and Wilkinson type complexes,[18] which generate dihydride rhodium complexes under hydrogen gas. On this basis, we assumed that the active species was a dichloro-monohydride species derived from the dinuclear rhodium complexes (*S*)-**1**, though we could not detect any defined species in spectral measurements. Dissociation of (*S*)-**1** into dichloro-monohydride complexes can be accelerated by reversible interaction with nBu$_4$NCl. Thus, we propose the following mechanism based on previous reports of dinuclear iridium catalysts for asymmetric hydrogenation.[10–15] Initially, the dinuclear complexes (*S*)-**1** dissociate into the corresponding mononuclear dichloro-monohydride rhodium(III) complexes, in which a Rh−H bond readily adds to a C=C bond. The resulting Rh-alkyl complex subsequently reacts with dihydrogen via a σ-bond metathesis pathway to give a hydrogenated product; regeneration of the dichloro-monohydride rhodium(III) species occurs simultaneously. At this stage, we cannot rule out the possibility that the catalytic reaction proceeds through a monochloro-dihydride rhodium complex[18] generated by reaction of the dichloro-monohydride rhodium complex with H_2.[19]

In summary, we prepared new chiral dinuclear rhodium(III) complexes as active catalysts for asymmetric hydrogenation of simple olefins. These complexes were applied to the asymmetric hydrogenation of allylic alcohols, alkenylboranes, and cyclic unsaturated sulfones. In sharp contrast to the widely used cationic rhodium(I) catalysts, we propose that the monohydride rhodium(III) complex acted as an active species, which incorporates hydride attack of simple olefins as its key step. Further investigations involving the newly developed triply halide-bridged dinuclear rhodium(III) and various types of olefinic substrates are ongoing.

Experimental Section

A glass tube was charged with a rhodium complex (0.010 mmol, 1 mol%) and nBu$_4$NCl (0.020 mmol, 2 mol%) in a glove box. Subsequently, an olefin (1.0 mmol) in toluene (6.0 mL) was added into the glass tube in the stainless autoclave reactor using an inlet. After three vacuum/argon cycles, the reactor was charged with H_2, and hydrogen pressure subsequently increased to 30 bar. The reaction mixture in the reactor was stirred at 80 °C for 20 h. After release of H_2, solvent was removed by evaporation. Enantiomeric excess (*ee*) was determined by HPLC analysis of the crude product. The product was purified by filtration through a short pad of silica gel (eluted with hexane), and analyzed by spectroscopic methods.

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Keywords: asymmetric catalysis · hydrogenation · reaction mechanisms · rhodium

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Communications

Asymmetric Hydrogenation

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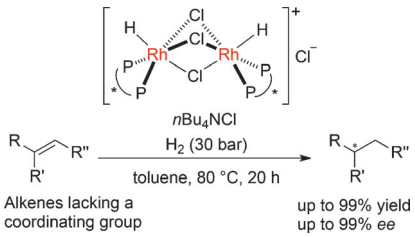
Chloride-Bridged Dinuclear Rhodium(III) Complexes Bearing Chiral Diphosphine Ligands: Catalyst Precursors for Asymmetric Hydrogenation of Simple Olefins



Dinuclear rhodium(III) complexes were highly catalytically active for asymmetric hydrogenation of simple olefins in contrast to widely utilized rhodium(I) catalytic systems.

