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RESEARCH ARTICLE

Monohydride-dichloro Rhodium(III) Complexes with Chiral Diphosphine Ligands as Catalysts for Asymmetric Hydrogenation of Olefinic Substrates

Kosuke Higashida,[a] Fabian Brüning,[b] Nagataka Tsujimoto,[a] Kenya Higashihara,[a] Haruki Nagae,[a] Antonio Togni,*[b] and Kazushi Mashima*[a]

Abstract: We report full details of the synthesis and characterization of monohydride-dichloro rhodium(III) complexes bearing chiral diphosphine ligands, such as (*S*)-BINAP, (*S*)-DM-SEGPHOS, and (*S*)-DTBM-SEGPHOS, producing cationic triply-chloride bridged dinuclear rhodium(III) complexes (**1a**: (*S*)-BINAP; **1b**: (*S*)-DM-SEGPHOS) and a neutral mononuclear monohydride-dichloro rhodium(III) complex (**1c**: (*S*)-DTBM-SEGPHOS) in high yield and high purity. Their solid state structure and solution behavior were determined by crystallographic studies as well as full spectral data, including DOSY NMR spectroscopy. Among these three complexes, **1c** has a rigid pocket surrounded by two chloride atoms bound to the rhodium atom together with one ^{t}Bu group of (*S*)-DTBM-SEGPHOS for fitting to simple olefins without any coordinating functional groups. Complex **1c** exhibited superior catalytic activity and enantioselectivity for asymmetric hydrogenation of *exo*-olefins and olefinic substrates. The catalytic activity of **1c** was compared with that of well-demonstrated dihydride species derived *in situ* from rhodium(I) precursors such as $[Rh(cod)Cl]_2$ and $[Rh(cod)_2]^+BF_4^-$ upon mixing with (*S*)-DTBM-SEGPHOS under dihydrogen.

Introduction

Asymmetric hydrogenation by chiral transition metal complexes is one of the most important and practically applicable reactions for atom-economical and environmentally benign synthesis of chiral organic compounds.[1],[2] Intensive research has focused on the rational design and synthesis of chiral chelating ligands with different chiral skeletons for adjusting targeted asymmetric hydrogenations in combination with standard metal precursors whereas little attention has been paid to metal catalyst precursors. In fact, asymmetric hydrogenation of functionalized olefins such as α,β-unsaturated acids,[3] enamides,[4] enol ester,[5] and so on[6] has been catalyzed by chiral rhodium complexes derived *in situ* by mixing rhodium(I) precursors such as $[Rh(diene)Cl]_2$ and $[Rh(diene)_2]^+X^-$ with suitable chiral chelating diphosphine ligands. Other than the recently reported rhodium(I) complex with a MeO-BIPOP ligand,[7] however, these chiral rhodium(I) catalyst systems do not work well for the asymmetric hydrogenation of non-chelating olefin substrates.[8]

In contrast to the rhodium system, chiral cationic iridium complexes serve as catalysts for the asymmetric hydrogenation of unfunctionalized olefins:[9]-[14] in 1998, Pfaltz *et al.* demonstrated that cationic iridium complexes bearing a phosphanodihydrooxazole ligand (P^N ligand, Figure 1a) were efficient catalysts for the asymmetric hydrogenation of (*E*)-α-methylstilbene derivatives.[9a] Later, not only the Pfaltz group,[9] but also several other groups, independently reported asymmetric hydrogenation of unfunctionalized olefins, such as cyclic olefins and *exo*-olefins, using various chiral P^N ligands.[10],[11] Iridium cationic complexes with bidentate carbene oxazoline ligands[12],[13] and a thioether-phosphite ligands[14] also showed high catalytic activity and enantioselectivity. Recently, cobalt-based catalyst systems were reported:[15],[16] Chirik *et al.* found that cobalt complexes bearing a tridentate C_1-symmetric bis(imino)pyridine ligand (Figure 1b) acted as superior catalyst for the asymmetric hydrogenation of *exo*-olefins[15a] as well as cyclic olefins.[15c]

a) Ir complex with P^N ligand[9a] b) Co catalyst with bis(imino)pyridine ligand[15a]

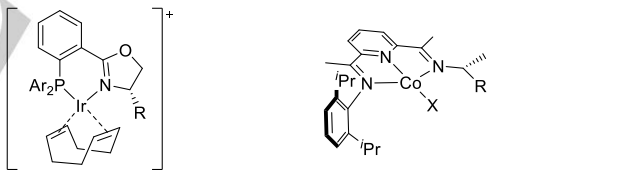

Figure 1. Examples of (a) iridium and (b) cobalt catalysts for asymmetric hydrogenation of unfunctionalized olefins.

In 2016, we have reported that rhodium(III) complexes with commercially available chiral diphosphine ligands (Figure 2), **1a** ((*S*)-BINAP), **1b** ((*S*)-DM-SEGPHOS), and **1c** ((*S*)-DTBM-SEGPHOS), served as highly enantioselective catalysts for asymmetric hydrogenation of both unfunctionalized olefins such as α-methylstilbene and functionalized olefins *e.g.* allylic alcohols. In addition, we determined the bifacial dinuclear structure of cationic triply-chloride bridged complex **1a** by X-ray single crystal analysis.[17a] Herein, we report full details of the preparation and characterization of cationic dinuclear rhodium(III) complex **1b** as well as a neutral mononuclear monohydride-dichloro rhodium(III) complex **1c** which has been assigned as cationic dinuclear complex in previous report.[17a] The solid and solution structures of **1c** were revealed by crystallographic studies and DOSY NMR spectroscopy, respectively. We demonstrated that complex **1c** exhibited a superior catalytic activity and enantioselectivity for the asymmetric hydrogenation of simple olefins and some related olefinic substrates in comparison with those of standard rhodium

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catalyst systems, *i.e.*, a dihydridemonochloro rhodium(III) catalyst and a cationic dihydride rhodium(III) catalyst generated *in situ* by respectively treating rhodium(I) precursors, $[Rh(cod)Cl]_2$ and $[Rh(diene)_2]^+X^-$, with (*S*)-DTBM-SEGPHOS under dihydrogen gas.

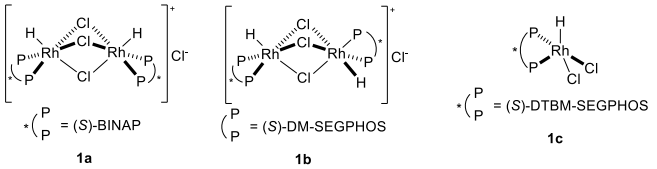

Figure 2. Rhodium(III) monohydride complexes **1a**—**c** as the catalyst for asymmetric hydrogenation of simple olefins.

Results and Discussion

Preparation and Characterization of Monohydride Rhodium(III) Complexes 1a, 1b, and 1c

We previously reported the syntheses of **1a**—**c** by adding ethereal HCl to an *in situ* mixture of $[Rh(cod)Cl]_2$ (COD = 1,5-cyclooctadiene) with two equivalents of the corresponding chiral diphosphine ligands, and confirmed the dinuclear structure of **1a** crystallographically.[17a] A similar dinuclear complex **1b** and a mononuclear complex **1c** were prepared by the same procedure of **1a** (Scheme 1a), and the structures of complexes **1b** and **1c** were determined by single crystal X-ray analyses (Scheme 1b and 1c, *vide infra*). Noteworthy was that the addition of ethereal HCl was essentially required to isolate these rhodium(III) complexes in high yield with high purity.[18] The reaction of $[Rh(cod)Cl]_2$ with two equivalents of (*S*)-DM-SEGPHOS in CD_2Cl_2 at room temperature for 7 minutes afforded a mixture of [{(*S*)-DM-segphos}Rh(μ-Cl)$_2$Rh(cod)] and [Rh(μ-Cl)$_2${(*S*)-DM-segphos}]$_2$ in the ratio of 3:1, and more than 1 hour was required to complete the ligand exchange reaction. Our observation was consistent with the reports by Heller *et al.* that the ligand-exchange reaction of $[Rh(cod)Cl]_2$ and two equivalents of diphosphines, such as BINAP, SEGPHOS, DM-SEGPHOS, and DIFLUORPHOS, proceeded in a stepwise manner to give $[Rh(diphosphine)Cl]_2$ through a mixed ligated dinuclear complex [(diphosphine)Rh(μ-Cl)$_2$Rh(cod)].[19a] They clarified that the second replacement of COD of [(diphosphine)Rh(μ-Cl)$_2$Rh(cod)] was slower than the first replacement of COD of $[Rh(cod)Cl]_2$, presumably due to the extended *trans*-effect in a double square planer geometry connected by two chloride atoms. Furthermore, they reported that a reaction of $[Rh(cod)Cl]_2$ with sterically hindered DTBM-SEGPHOS afforded [(DTBM-segphos)Rh(μ-Cl)$_2$Rh(cod)] as a single product, and the second replacement of COD did not proceed.[19b] Accordingly, the successful preparation of **1a**—**c** in a highly pure form was attributed to avoiding the extended *trans*-effect of dinuclear rhodium(I) d^8 species by generating octahedral rhodium(III) d^6 species, whose COD was labile.

Schematic structures of these three complexes are shown in Scheme 1, and selected bond parameters are summarized in Table 1. Complexes **1a** and **1b** have a cationic triply-chloride bridged bifacial dinuclear rhodium(III) skeleton with different stereochemistry relatively to the hydride position on each rhodium atom, *i.e.*, *syn* for **1a** and *anti* for **1b**, although the outer facial geometry of two phosphorous atoms and one hydrogen atom in each rhodium atom of **1b** is highly twisted compared with that for **1a** owing to the steric bulkiness of (*S*)-DM-SEGPHOS. The *trans* effect of the hydrogen atom significantly elongates the bond distance of Rh—Cl1* (2.5736(10) Å) and its operation-correlated Rh*—Cl1 for **1b**, and the bond distances of Rh1—Cl3 (2.5742(18) Å) and Rh2—Cl3 (2.5699(18) Å) for **1a**. Such a bifacial dinuclear geometry has one hydride ligand on the rhodium atom at the *cis*-position in relation to two phosphine atoms, consistent with the ^{1}H NMR and ^{31}P{^{1}H} NMR spectra of **1a** and **1b**. In the ^{1}H NMR spectra, hydride signals were observed as doublet of triplets at -15.9 ppm ($^1J_{Rh\text{-}H}$ = 22.5 Hz and $^2J_{P\text{-}H}$ = 15.8 Hz) for **1a** and at -16.1 ppm ($^1J_{Rh\text{-}H}$ = 21.8 Hz and $^2J_{P\text{-}H}$ = 16.1 Hz), respectively, for **1b**. In the ^{31}P{^{1}H} NMR spectra, one *dd* signal and one *ddd* signal were observed at 48.6 ($^1J_{Rh\text{-}P}$ = 137 Hz, $^2J_{P\text{-}P}$ = 27 Hz) and 36.1 ppm ($^1J_{Rh\text{-}P}$ = 134 Hz, $^2J_{P\text{-}P}$ = 26 Hz, $^2J_{P\text{-}H}$ = 3 Hz), respectively, for **1a**, and two *ddd* signals were detected at 48.3 ($^1J_{Rh\text{-}P}$ = 135 Hz, $^2J_{P\text{-}P}$ = 26 Hz, and $^2J_{P\text{-}H}$ = 8 Hz) and 41.1 ppm ($^1J_{Rh\text{-}P}$ = 136 Hz, $^2J_{P\text{-}P}$ = 26 Hz, and $^2J_{P\text{-}H}$ = 12 Hz) for **1b**.[20] Accordingly, these two complexes existed in solution as each pure single isomer.

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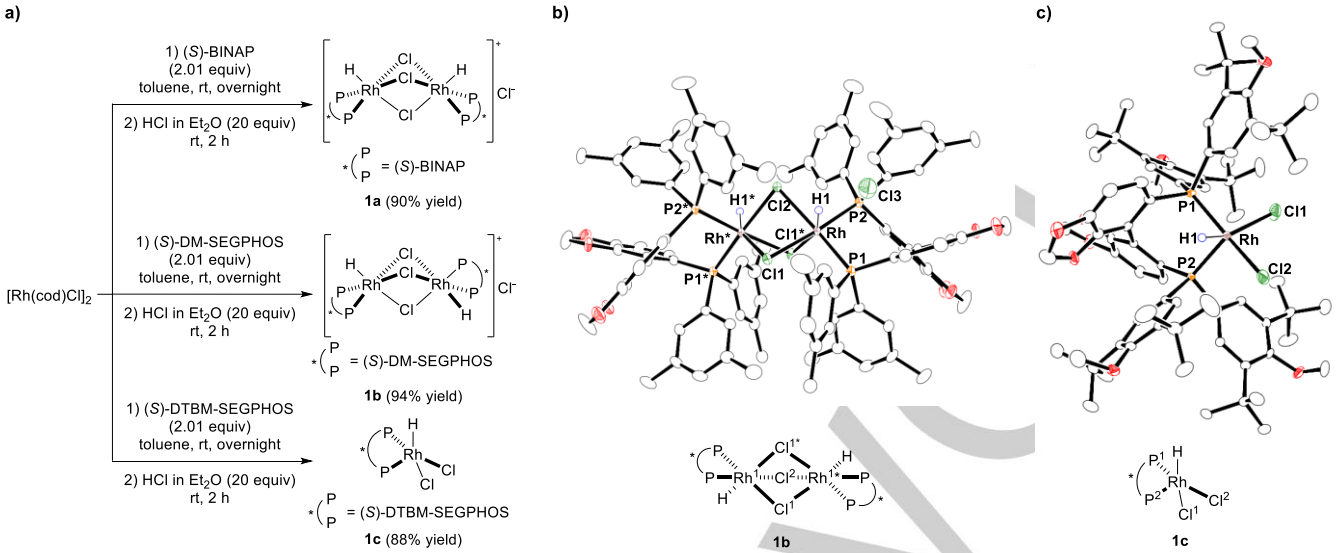

Scheme 1. (a) Preparation of rhodium(III) monohydride complexes **1a**—**c**. Molecular structures and Top views of cationic dinuclear complexes **1b** (b) and **1c** (c). A solvent molecule and all hydrogen atoms on (*S*)-DM-SEGPHOS and (*S*)-DTBM-SEGPHOS are omitted for clarity. Position of hydride atom is located based on calculation.

The increased steric congestion of (*S*)-DTBM-SEGPHOS compared with (*S*)-BINAP and (*S*)-DM-SEGPHOS makes **1c** mononuclear, where the rhodium atom adopts a highly distorted square-pyramidal geometry with one phosphorus atom, two chloride atoms, and one hydrogen atom as four corners of the square and the other phosphine atom at the apical position. The bond distances of Rh—Cl1 (2.3872(12) and Rh—Cl2 (2.3858(13) Å) in **1c** are clearly shorter than these found for **1a** (2.42—2.57 Å) and **1b** (2.44—2.57 Å). In the ^{1}H NMR spectrum of **1c**, a hydride signal was observed as double doublets of doublets at -16.5 ppm ($^{1}J_{Rh\text{-}H}$ = 20.0 Hz, $^{2}J_{P\text{-}H}$ = 12.1 Hz, and $^{2}J_{P\text{-}H}$ = 6.8 Hz), and, in its ^{31}P{^{1}H} NMR spectrum, two phosphorous nuclei were observed as *dd* signal at 62.5 ($^{1}J_{Rh\text{-}P}$ = 138 Hz and $^{2}J_{P\text{-}P}$ = 26 Hz) and *ddd* signal at 32.6 ppm ($^{1}J_{Rh\text{-}P}$ = 130 Hz, $^{2}J_{P\text{-}P}$ = 26 Hz, and $^{2}J_{P\text{-}H}$ = 5 Hz),[20],[21] suggesting that the geometry around the rhodium center of **1c** was rigidly fixed with keeping a mononuclear five coordinated structure that is responsible for the high enantioselectivity of the simple olefin hydrogenation (*vide infra*).

Table 1. Selected Distances and Angles for **1a**,[17a] **1b** and **1c**.

1a				**1b**		**1c**	
Distances (Å)							
Rh1—Cl1	2.4509(19)	Rh2—Cl1	2.4242(18)	Rh—Cl1	2.4408(9)	Rh—Cl1	2.3872(12)
Rh1—Cl2	2.4489(18)	Rh2—Cl2	2.4468(19)	Rh—Cl2	2.4436(9)	Rh—Cl2	2.3858(13)
Rh1—Cl3	2.5742(18)	Rh2—Cl3	2.5699(18)	Rh—Cl1*	2.5736(10)	Rh—P1	2.2467(11)
Rh1—P1	2.273(2)	Rh2—P3	2.2597(19)	Rh—P1	2.2576(9)	Rh—P2	2.1846(11)
Rh1—P2	2.268(2)	Rh2—P4	2.277(2)	Rh—P2	2.2658(9)		
Angles (deg)							
P1—Rh1—P2	92.27(8)	P3—Rh1—P4	91.00(7)	P1—Rh—P2	94.02(3)	P1—Rh—P2	95.07(4)
P1—Rh1—Cl1	91.75(7)	P3—Rh2—Cl1	95.43(7)	P1—Rh—Cl1	90.62(3)	P1—Rh—Cl1	95.55(4)
P2—Rh1—Cl2	95.19(7)	P4—Rh2—Cl2	92.69(7)	P2—Rh—Cl2	92.62(3)	P2—Rh—Cl2	90.62(4)
Cl1—Rh1—Cl2	80.50(6)	Cl1—Rh2—Cl2	81.08(6)	Cl1—Rh—Cl2	82.87(3)	Cl1—Rh—Cl2	92.17(5)
P1—Rh1—Cl2	167.68(7)	P3—Rh2—Cl2	176.26(7)	P1—Rh—Cl2	169.49(3)	P1—Rh—Cl2	163.23(5)
P2—Rh1—Cl1	175.48(7)	P4—Rh2—Cl1	166.60(7)	P2—Rh—Cl1	175.31(3)	P2—Rh—Cl1	132.43(5)
						H—Rh—Cl1	146(2)

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To examine whether complexes **1a**—**c** exist as mono- or dinuclear species in solution, the diffusion coefficients of all complexes and diphosphine ligands were determined by DOSY NMR spectroscopy. The experimental diffusion coefficients were additionally normalized using the solvent signal as an internal reference (Table 2). The normalized coefficients for complexes **1a** and **1b** (D_{1a} = 6.09×10^{-10} m^2/s and D_{1b} = 5.98×10^{-10} m^2/s, respectively) are significantly smaller than those of their corresponding ligands (D_{BINAP} = 8.84×10^{-10} m^2/s and $D_{DM\text{-}SEGPHOS}$ = 8.42×10^{10} m^2/s). In contrast, the normalized coefficients of **1c** ($D_{DTBM\text{-}SEGPHOS}$ = 6.83×10^{-10} m^2/s) and its ligand DTBM-SEGPHOS ($D_{DTBM\text{-}SEGPHOS}$ = 6.81×10^{-10} m^2/s) are almost identical. Since diffusion coefficients decrease as the size of a molecule increases, our results show that **1a** and **1b** are significantly larger than their corresponding ligands, whereas **1c** shows almost the same diffusion behavior as DTBM-SEGPHOS and thus has a similar hydrodynamic volume. Consequently, we conclude that **1a** and **1b** do not exist as mononuclear species in solution, in contrast to complex **1c**.[22] This observation is consistent with their respective mono- and dinuclear structures determined by X-ray single crystal analysis (*vide supra*). A complementary, quantitative approach by comparison of the estimated molecular sizes by the Stokes-Einstein relation indicates that the sizes for **1a** and **1b** are consistent with a dinuclear structure (see SI for details). These observations demonstrate that the rhodium(III) complexes **1a**—**c** are maintained as single species in both solution and solid state without any substrate or hydrogen.

Table 2. Diffusion Coefficients of Chiral Diphosphine Ligands and Complexes **1a**—**c**.

compounds	$D_{normalised}$ [m^2/s]
(*S*)-BINAP	8.84×10^{-10}
(*S*)-DM-SEGPHOS	8.42×10^{-10}
(*S*)-DTBM-SEGPHOS	6.81×10^{-10}
1a	6.09×10^{-10}
1b	5.98×10^{-10}
1c	6.83×10^{-10}

Diffusion coefficients of of diphosphine ligands and rhodium complexes were determined by ^{1}H NMR diffusion experiments of 20 mM solutions in CD_2Cl_2 at 298 K using a diffusion delay Δ = 0.50 ms. Normalised values were calculated according to the formula log D_{norm} = log $D_{ref,\ fix}$ – log $D_{ref,\ measured}$ + log $D_{measured}$[23] using the solvent signal of $CDHCl_2$ as internal reference.

Asymmetric Hydrogenation of Simple Olefinic Substrates

Mononuclear complex **1c** was found to be the best catalyst among the three complexes for asymmetric hydrogenation of α-methylstilbene (**2a**),[17a] whereas a mixture of **1c** and $NaBPh_4$, a neutral mixture of $[Rh(cod)Cl]_2$ and two equivalents of (*S*)-DTBM-SEGPHOS as well as a cationic mixture of $[Rh(cod)_2]^+BF_4^-$ and one equivalent of (*S*)-DTBM-SEGPHOS resulted in lower enantioselectivities (Table 3, entry 1, *vide infra* and Table S1). Figures 3a—d show a space-filling model and topographic steric map[24] of **1c** and those of a cationic rhodium complex, [Rh((*S*)-DTBM-segphos)]$^+$:[25] topographic steric map shows steric bulkiness around the rhodium atom with a warm color. As shown in Figure 3b, it is visible that the *tert*-butyl substitution of (*S*)-DTBM-SEGPHOS in **1c** is the largest sterically hindered group that blocks one potential approach of the olefinic substrate to the rhodium-hydride moiety, and two chloride ligands strictly control the selection of one of the enantio-faces of α-methylstilbene, resulting in high enantioselectivity. In sharp contrast, Figures 3c and 3d show a space-filling model and a topographic steric map of [Rh{(*S*)-DTBM-segphos}]$^+$, where two *tert*-butyl substitutions of (*S*)-DTBM-SEGPHOS in [Rh{(*S*)-DTBM-segphos}]$^+$ become two parallel fences creating two large open sites, leading to low enantioselectivity.

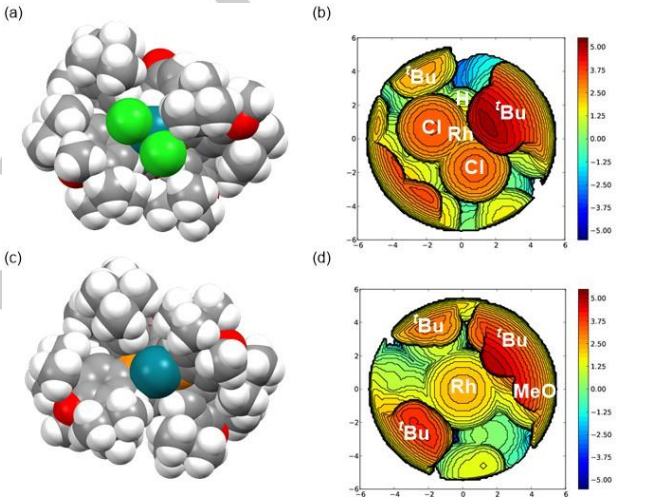

Figure 3. (a) Space-filling model of **1c**, (b) Topographic steric map of **1c**, and (c) Space-filling model of cationic complex without hydride, [Rh((*S*)-DTBM-segphos)]$^+$, (d) Topographic steric map of [Rh((*S*)-DTBM-segphos)]$^+$. The structure of [Rh((*S*)-DTBM-segphos)]$^+$ was optimized by using the B3LYP/def2SVP density-functional theory.

The fitting suitability of α-methylstilbene to the catalyst pocket around a Rh—H bond prompted us to predict that **1c** becomes an efficient catalyst for asymmetric hydrogenation of a non-chelating olefins, not only (*E*)-α-methylstilbene (**(*E*)-2**), which is our previous model substrate,[17a] but also (*E*)-1-benzylidene-2,3-dihydro-1H-indene (**4**) and (*Z*)-3-benzylidene-2,3-dihydrobenzofuran (**6**), which have a similar shape as (*E*)-α-methylstilbene (**2**). The same optimized conditions were employed for the asymmetric hydrogenation experiments as previously reported. Substrate **4** gave (*R*)-1-benzyl-2,3-dihydro-1*H*-indene (**(*R*)-5**) in 96% ee with the same enantio-face selectivity as α-methylstilbene (entry 2). In the case of asymmetric hydrogenation of **6** by complex **1c**, (*R*)-3-benzyl-2,3-dihydrobenzofuran (**(-)-7**) was obtained in quantitative yield and excellent enantioselectivity (entry 3). On the other hand, the use

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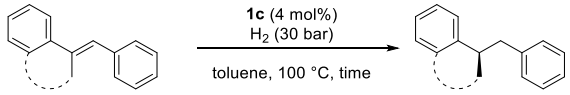
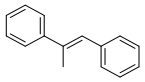
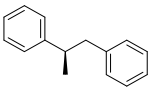
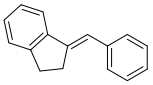
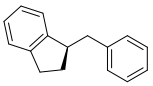
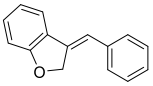
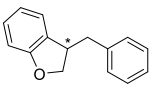
of a mixture of **(*E*)-2** and **(*Z*)-2** (22:78) as substrate afforded the opposite enantiomer **(*S*)-3** in 45% ee.

Table 3. Asymmetric Hydrogenation of Simple Olefins Catalyzed by **1c**.

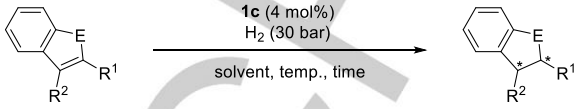


entry	starting material	product	time [h]	yield [%]	ee [%]
1[a]	 **(*E*)-2**	 **(*R*)-3**	20	96	95
2	 **4**	 **(*R*)-5**	18	>99	96
3	 **6**	 **(-)-7**	20	>99	94

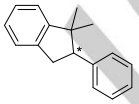
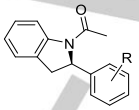
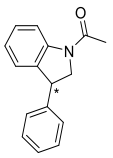
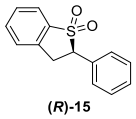
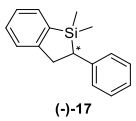
Yield was determined by ^{1}H NMR analysis. Ee was determined by HPLC analysis. [a] Included in our previous report.[17a]

Next, we conducted the hydrogenation of 1,1-dimethyl-2-phenyl-1H-indene (**8**), indoles **10a**—**e** and **12**, 2-phenylbenzo[*b*]thiophene 1,1-dioxide (**14**), and 1,1-dimethyl-2-phenyl-1H-benzo[*b*]silole (**16**), and the results are shown in Table 4. When 1,1-dimethyl-2-phenyl-1H-indene (**8**) was hydrogenated by **1c**, we obtained 1,1-dimethyl-2-phenyl-2,3-dihydro-1H-indene ((-)-**9**) in 97% yield with 95% ee (entry 1). Asymmetric hydrogenation of 1-(2-phenyl-1H-indol-1-yl)ethan-1-one (**10a**), which fits to the rigid pocket of **1c**, also proceeded smoothly to give 1-(2-phenylindolin-1-yl)ethan-1-one (**11a**) as an (*R*)-form in high yield with high enantioselectivity (entry 2). Asymmetric hydrogenation of *N*-acetylindole derivatives **10b**—**e** having a functional group on the Ph group was conducted, and **10b**, **10c**, and **10e**, which have a methoxy or trifluoromethyl group at the *para*- or *meta*- position, respectively, were hydrogenated under the optimized conditions to give the corresponding products **11b**, **11c**, and **11e** in excellent yields and with excellent enantioselectivities (entries 3, 4, and 6). On the other hand, indole **11d**, having a methoxy group at the *ortho*-position of the Ph group did not give the corresponding hydrogenated product (entry 5). When 1-(3-phenyl-1H-indol-1-yl)ethan-1-one (**12**) was used as the substrate for the asymmetric hydrogenation by **1c**, no reaction was observed (entry 7). The asymmetric hydrogenation of heterocyclic compounds such as 2-phenylbenzo[*b*]thiophene 1,1-dioxide (**14**) and 1,1-dimethyl-2-phenyl-1H-benzo[*b*]silole (**16**) afforded the corresponding products **15** and **17** in 96% and 93% yield, respectively, with moderate to high enantioselectivities (entries 8 and 9).

Table 4. Asymmetric Hydrogenation of Cyclic Olefins Catalyzed by Complex **1c**.



E = CMe_2, NAc, SO_2, $SiMe_2$

entry	product	solvent	temp. [°C]	time [h]	yield [%]	ee [%]
1	 **(-)-9**	toluene	100	20	97	95(-)
	 **(*R*)-11**					
2[a]	**(*R*)-11a** R = H	1,4-dioxane	80	18	94	99(+)
3[a]	**(+)-11b** R = *para*-MeO	1,4-dioxane	80	18	86	96(+)
4[a]	**(+)-11c** R = *meta*-MeO	1,4-dioxane	80	18	96	99(+)
5[a]	**11d** R = *ortho*-MeO	1,4-dioxane	80	18	No reaction	-
6[a]	**(+)-11e** R = *para*-CF_3	1,4-dioxane	80	18	96	99(+)
7[a]	 **13**	1,4-dioxane	80	18	No reaction	-
8	 **(*R*)-15**	toluene	100	40	99	77(-)
9	 **(-)-17**	toluene	100	20	93	93(-)

Isolated yield. Ee was determined by HPLC analysis. [a] 2 mol% of **1c** was used.

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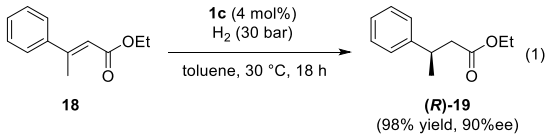
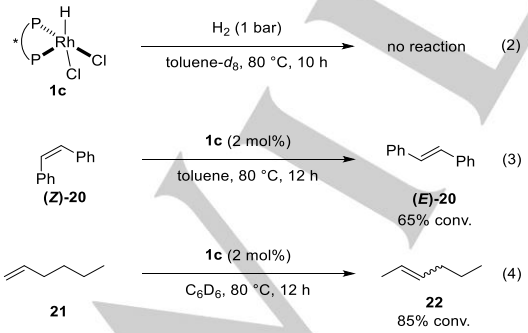
10.1002/chem.202000542

We further investigated the scope of rhodium(III) complex **1c** as the catalyst for asymmetric hydrogenation. The asymmetric hydrogenation of olefins bearing an ester group at the vicinal position is unsuitable for rhodium(I) catalysts because of the low coordinating ability of the conjugated ester group.[26][27] Thus, a specially designed diphosphine ligand was required in order to achieve high enantioselectivity.[28] In contrast, our rhodium(III) complex exhibited high catalytic activity and enantioselectivity toward asymmetric hydrogenation of ethyl (*E*)-3-phenylbut-2-enoate (**18**) to give the corresponding product (*R*)-**19** in 98% yield and 90% ee (eq. 1). This selectivity is higher than that obtained using both the neutral precursor $[Rh(cod)Cl]_2$ and two equivalents of (*S*)-DTBM-SEGPHOS, or the cationic precursor of $[Rh(cod)_2]BF_4$ and one equivalent of (*S*)-DTBM-SEGPHOS (Table S2).



Reaction Mechanism

We conducted some controlled experiments to clarify the reaction mechanism using **1c**. When complex **1c** was exposed to 1 bar of hydrogen gas in toluene-d_8 at 80 °C, **1c** remained intact as evident from ^1H and $^{31}P\{^1H\}$ NMR measurements at 80 °C (eq. 2). The hydride of **1c** (2 mol%) without hydrogen gas reversibly inserted into (*Z*)-stilbene to give a mixture of (*E*)- and (*Z*)-stilbene in a 35:65 ratio (eq. 3) and isomerized 1-hexene to a mixture of (*E*)- and (*Z*)-2-hexene in 85% conversion (eq. 4). In the isomerization of **21**, a first-order rate dependence on the catalyst concentration was observed over 3-fold range (Figure S18). These results suggested that a C=C double bond was easily inserted into Rh—H bond of mononuclear complex **1c**. Hence, the reaction mechanism of asymmetric hydrogenation by **1c** differed from unsaturated mechanism,[29] dihydride mechanism,[30] and cooperative dinuclear mechanism[31] of asymmetric hydrogenation catalyzed by conventional rhodium(I) complexes.



According to these results, we suggested a possible reaction mechanism of asymmetric hydrogenation of olefins by the mononuclear monohydride-dichloro rhodium(III) complex **1c** (Figure 4). Olefins coordinate to **1c** to afford complex **A**, in which the highly rigid pocket of the rhodium(III) species efficiently recognizes the *Re*- or *Si*-face of the substrates without any coordination of the functional groups of substrates. Facile insertion of the coordinated olefin into the Rh—H bond of **A** gives a Rh—alkyl complex **B** reversibly.[32] The resulting Rh—alkyl complex reacts with dihydrogen through a σ-bond metathesis pathway to afford the chiral alkanes along with the regeneration of **1c**. Noteworthy of this mechanism is that oxidative addition to low valent rhodium(I), giving dihydride species, is excluded.

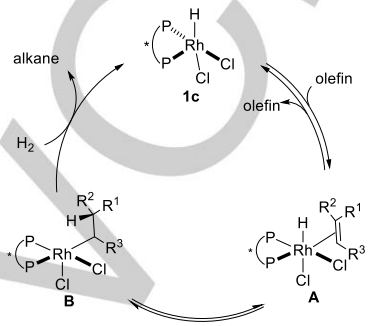


Figure 4. Proposed reaction mechanism.

Conclusion

We demonstrated that the addition of HCl to the isolated dinuclear rhodium(I) complex, $[Rh(\mu\text{-}Cl)(diphosphine)]_2$, and an *in situ* mixture of $[Rh(cod)Cl]_2$, two equivalents of chiral diphosphine ligands, and an excess amount of ethereal HCl proceeded smoothly to produce the corresponding cationic triply-chloride bridged dinuclear rhodium(III) complexes **1a** and **1b** as well as a mononuclear rhodium(III) complex **1c** in high yield and high purity. Complex **1c** exhibited the best catalyst performance for asymmetric hydrogenation of various simple olefins, because the catalyst pocket of the monohydride-dichloro rhodium(III) center is quite rigid and narrow, even in solution as evident from NMR measurements, including DOSY. Therefore, we used a topographic steric map based on the crystal structure of **1c** to expand the substrate scope and predict the selection of one of two enantio-faces.

Experimental Section

All reactions and manipulations involving air- and moisture-sensitive organometallic compounds were operated using the standard Schlenk techniques under argon gas. Monohydride rhodium(III) complexes were prepared by the improved method of previous report.[17a] 1,4-Dioxane was dried and deoxygenated by distillation over sodium benzophenone ketyl under argon atmosphere. Alternatively, CH_2Cl_2 and toluene were dried and deoxygenated by using Grubbs column (Glass Counter Solvent Dispending System, Nikko Hansen & Co, Ltd.).[33] Benzene-d_6 was distilled over CaH_2 and thoroughly degassed by trap-to-trap distillation before use. Compounds **4**,[11e] **6**,[11e] **8**,[34] **14**,[35] **16**[36] were prepared according to the literature. ^1H NMR (400 MHz), $^{13}C\{^1H\}$ NMR (100 MHz), $^{31}P\{^1H\}$ NMR (162 MHz), and $^{19}F\{^1H\}$ NMR (376 MHz) spectra were measured on Bruker Avance III-400 spectrometers. All ^1H NMR chemical shifts were reported in ppm (δ) relative to tetramethylsilane at δ 0.00 or

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solvent residual signal ($CHCl_3$ at δ 7.26 ppm, CH_2Cl_2 at δ 5.32 ppm, C_6D_6 at 7.15 ppm). All $^{13}C\{^1H\}$ NMR chemical shifts were reported in ppm (δ) relative to carbon resonances of $CDCl_3$ at δ 77.16. All $^{31}P\{^1H\}$ NMR chemical shifts were reported in ppm (δ) relative to phosphine resonances in external standard of phosphoric acid at δ 0.00. All $^{19}F\{^1H\}$ NMR chemical shifts were reported in ppm (δ) relative to fluorine resonances in external standard of α,α,α-trifluorotoluene at δ -63.90. Diffusion experiments were measured on Bruker AVANCE III HD 500 MHz spectrometer. HPLC spectra were recorded on a JASCO UV-4075. Optical rotation values were recorded on Anton Paar MCP100 polarimeter at 589 nm (sodium lamp) and are given in 10^{-1} deg cm^2 g^{-1}. High resolution mass spectra were obtained on JEOL JMS-700 and Thermo Fisher Scientific Orbitrap XL. All melting points were recorded on BUCHI Melting Point M-565. Flash column chromatography was performed using silica gel 60 (0.040-0.0663 nm, 230-400 mesh ASTM) with hexane (>95 %, KANTO CHEMICAL CO., INC.) and EtOAc (>99 %, NACALAI TESQUE, INC.). Hydrogenation reaction was conducted using Biotage Endeavor® or TAIATSU stainless autoclave.

General Procedure for Rhodium Catalyzed Asymmetric Hydrogenation

An olefinic substrate (0.20 mmol) was added to a glass tube in an autoclave, and the autoclave was charged with argon gas. A rhodium catalyst (8.0 μmol, 4.0 mol%) was dissolved in dry solvent (3 mL) under argon atmosphere, and the solution was transferred to the glass tube in the autoclave. When the mixture of rhodium(I) pre-catalyst and chiral diphosphine ligand were used as a catalyst system, the solution was stirred for 30 minutes before injection to the autoclave. Then, the autoclave was charged with H_2 gas, and the pressure was increased to 30 bar. The reaction mixture was stirred for periodic time. After the reaction, H_2 gas was released, and phenanthrene was added to the reaction mixture as an internal standard. All volatiles were removed under reduced pressure. The yield was determined by ^1H NMR analysis, and the enantiomeric excess was determined by HPLC analysis.

Diffusion Experiments

All diffusion experiments were acquired on a Bruker AVANCE III HD 500 MHz spectrometer using a double stimulated echo pulse sequence according to Mueller *et al*,[37],[38] with alternative phase cycling as described by G. Morris.[39] All experiments were ^1H NMR measurements and performed at 298 K with samples of 20 mM concentration in CD_2Cl_2. A maximum gradient strength of g = 50 G/cm was used and each experiment was acquired with 32 gradient steps with varying gradient strength from 2% to 98%. To gain insight systematic errors caused by convection of the CD_2Cl_2, all diffusion experiments were performed twice using two different diffusion delays Δ = 1.00 s and Δ = 0.50 s. The diffusion coefficients for the remaining solvent signal in CD_2Cl_2 were then determined for each experiment separately and the mean values from all experiments of $29.49(64) \cdot 10^{-10}$ m^2s^{-1} (for Δ = 1.00 ms) and $29.84(70) \cdot 10^{-10}$ m^2s^{-1} (for Δ = 0.50 ms) reveal a small, but systematic error of in comparison to the literature[39] value of $31.7 \cdot 10^{-10}$ m^2s^{-1}. Consequently, the obtained diffusion coefficients for the solute for each value of Δ (0.50 or 1.00 s) are directly comparable, whereas absolute coefficient values should be used with care. Data analysis and determination of the diffusion coefficients by curve fitting according to $I = I_0\, e^{-D\gamma^2 g^2 \delta^2 (\Delta - \frac{\delta}{3})}$ was done using the Topspin Bruker T1/T2 software using integral areas. For each compound, three separate integral regions were defined and three diffusion coefficients from each experiment and the corresponding mean values plus standard deviation are given below, for both Δ. The normalized diffusion coefficients were obtained using the empirically derived formula:[23]

$$\log D_{norm} = \log D_{ref,\ fix} - \log D_{ref,\ measured} + \log D_{measured} \quad (5)$$

Volume ratios complex/ligand in Table S3 was calculated according to Stokes-Einstein assuming spherical geometries by the dividing the ratios of $(1/D_{norm})^3$ of the corresponding ligands and complexes.

X-ray Analysis

The crystals of **1b** and **1c** were mounted on the CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 113(2) K. A measurement was made on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Mo-Ka (0.71075 Å) radiation with CrystalClear program.[40] Crystal data and structure refinement parameters are in Table S4. The structure of complex **1b** was solved by SHELXT-2014[41a] and refined on F^2 by full matrix least-squares method, using SHELXL-2015[41] in the Olex2 program.[42] The structure was solved by SIR 92[43] and refined on F^2 by full-matrix least-squares method, using SHELXL-2016[41] in the Crystal Structure Analysis Package.[44] Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\Sigma w(Fo^2 - Fc^2)^2]$ ($w = 1 / [\sigma^2 (Fo^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(Fo^2,0) + 2Fc^2) / 3$ with $\sigma^2(Fo^2)$ from counting statistics. The function $R1$ and $wR2$ were $(\Sigma||Fo| - |Fc||) / \Sigma|Fo|$ and $[\Sigma w(Fo^2 - Fc^2)^2 / \Sigma(wFo^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecule.[45]

Preparation of rhodium(III) complexes 1

These complexes were prepared by modified method of the reported procedure.[17a] $[Rh(cod)Cl]_2$ (222 mg, 0.450 mmol) was dissolved in toluene (10 mL) under argon atmosphere. A solution of chiral diphosphine ligand (0.91 mmol, 2.01 equiv) in toluene (20 mL) was added to the solution of $[Rh(cod)Cl]_2$, and the resulting mixture was stirred overnight at room temperature. 2.0 M HCl/Et_2O (4.5 mL, 9.0 mmol, 20 equiv, purchased from SIGMA-ALDRICH with Sure/Seal bottle) was added to the mixture. After stirring for 2 hours at room temperature, all volatiles were removed under reduced pressure. The crude residue was purified by reprecipitation with DCM/hexane (1/20) twice to afford the corresponding complex.

[{Rh(H)((*S*)-binap)}$_2$(μ-Cl)$_3$]Cl (1a): Brown solid. IR (KBr): ν(Rh-H): 2136 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz, 30 °C): δ 8.08 (t, *J* = 9.1 Hz, 2H), 8.00 (d, *J* = 8.3 Hz, 2H), 7.85-7.70 (m, 8H), 7.61-7.46 (m, 8H), 7.44-7.21 (m, 20 H), 7.08 (t, *J* = 7.9 Hz, 2H), 7.03 (t, *J* = 7.9 Hz, 2H), 6.98 (brs, 4H), 6.91 (t, *J* = 7.8 Hz, 2H), 6.82 (t, *J* = 7.1 Hz, 2H), 6.70-6.54 (m, 10H), 6.31 (d, *J* = 8.8 Hz, 2H), -15.9 (dt, *J* = 22.5,15.8 Hz, 1H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162 MHz, 30 °C): δ 48.6 (dd, *J* = 137, 27 Hz), 36.1 (ddd, *J* = 134, 26 Hz, 3 Hz).

[{Rh(H)((*S*)-DM-segphos)}$_2$(μ-Cl)$_3$]Cl (1b): White solid. IR (KBr): ν(Rh-H) 2123 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz, 30 °C): δ 7.34 (d, *J* = 12.1 Hz, 6H), 7.21 (s, 4 H), 7.10-6.96 (m, 12H), 6.56 (d, *J* = 8.3 Hz, 4H), 6.37-6.28 (m, 4H), 5.85 (d, *J* = 12.8 Hz, 6H), 5.50 (s, 2H), 5.33 (m, 2H), 2.37 (s, 24H), 2.28 (s, 12H), 1.94 (s, 12H), -16.1 ppm (dt, *J* = 21.8, 16.1 Hz, 1H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162 MHz, 30 °C): δ 48.3 (ddd, *J* = 135, 26, 8 Hz), 41.1 (ddd, *J* = 136, 26, 12 Hz).

Rh((*S*)-DTBM-segphos)HCl$_2$ (1c): Orange solid. IR (KBr): ν(Rh-H) 2007 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz, 30 °C): δ 7.82 (d, *J* = 13.4 Hz, 3H), 7.74 (d, *J* = 11.6 Hz, 3H), 6.56 (d, *J* = 7.9 Hz, 1H), 6.48-6.38 (m, 3 H), 5.82 (s, 1H), 5.73 (s, 1H), 5.67 (d, *J* = 5.5 Hz, 2H), 5.36 (d, *J* = 4.6 Hz, 2H), 3.77 (s, 3H), 3.75 (s, 3H), 3.70 (s, 3H), 3.67 (s, 3H), 1.43 (s, 36H), 1.38 (s, 36H), –16.5 (ddd, *J* = 20.0, 12.1, 6.8 Hz, 1H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162 MHz, 30 °C): δ 62.5 (dd, *J* = 138, 26 Hz), 32.6 (ddd, *J* = 130, 26, 5 Hz).

***(R)*-1-benzyl-2,3-dihydro-1H-indene ((*R*)-5):** Colourless oil. ^1H NMR ($CDCl_3$, 400 MHz, 30 ºC): δ 7.33-7.25 (m, 2H), 7.25-7.18 (m, 4H), 7.18-7.07 (m, 3H), 3.44 (quint, *J* = 7.3 Hz, 1H), 3.13 (dd, *J* = 13.6, 5.8 Hz, 1H), 2.93-2.73 (m, 2H), 2.69 (dd, *J* = 13.5, 9.2 Hz, 1H), 2.20-2.07 (m, 1H), 1.83-1.70 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, 30 °C): δ 147.0, 144.3, 141.0, 129.2, 128.4, 126.6, 126.1_4, 126.0_8, 124.7, 123.9, 46.6, 41.6, 32.1, 31.3; HPLC (Daicel OJ-H, temperature: 30 °C, hexane : ^{i}PrOH = 95 : 5, detector : 215 nm, flow rate 0.5 mL/min, t_1(-) = 9.5 min, t_2(+) = 10.6 min). $[\alpha]^{20}_D$ =

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+7.2 (c = 0.57, $CHCl_3$) (for an ee of 96%). The absolute configuration was determined by the optical rotation in comparison with literature.[11e]

3-benzyl-2,3-dihydrobenzofuran ((-)-7): Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz, 30 °C): δ 7.35 (t, *J* = 7.3 Hz, 2H), 7.28 (m, 1H), 7.22 (d, *J* = 7.3 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 7.3 Hz, 1H), 6.91-6.77 (m, 2H), 4.56 (t, *J* = 9.0 Hz, 1H), 4.29 (dd, *J* = 9.0, 5.9 Hz, 1H), 3.82-3.70 (m, 1H), 3.08 (dd, *J* = 13.9, 6.4 Hz, 1H), 2.86 (dd, *J* = 13.9, 8.9 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 30 °C): δ 160.1, 139.3, 130.4, 129.1, 128.7, 128.5, 126.6, 124.7, 120.4, 109.8, 76.5, 43.6, 41.2; HPLC (Daicel OJ-3, temperature: 30 °C, hexane : ^{i}PrOH = 95 : 5, detector : 215 nm, flow rate 1.0 mL/min, t_1(+) = 9.4 min, t_2(-) = 9.8 min); $[\alpha]^{20}_D$ = -34.8 (c = 0.65, $CHCl_3$) (for an ee of 94%). The absolute configuration was determined by the HPLC measurement in comparison with literature.[11e]

1,1-dimethyl-2-phenyl-2,3-dihydro-1H-indene ((-)-9): White solid. mp 54.9-61.2 °C (2 °C/min); IR (KBr, ν /cm^{-1}): 3066 w, 3031 w, 2958 s, 2938 m, 2883 m, 2849 m, 1602 w, 1582 w, 1494 m, 1477 s, 1453 s, 1381 w, 1361 m, 1290 w, 1262 w, 1227 w, 1185 w, 1109 w, 1082 m, 1026 w, 775 m, 763 s, 732 m, 707 s; ^1H NMR ($CDCl_3$, 400 MHz, 30 °C): δ 7.42-7.19 (m, 9H, *Ar*, *Ph*), 3.46-3.33 (m, 2H, PhC*H*, ArC*H*), 3.27-3.14 (m, 1H, ArC*H*), 1.42 (s, 3H, CH_3), 0.87 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 30 °C): δ 152.2, 141.5, 141.0, 129.0, 128.1, 126.8, 126.7, 126.5, 124.6, 122.5, 57.6, 47.3, 36.0, 27.3, 24.9; HPLC (Daicel OJ-H, temperature: 30 °C, hexane : ^{i}PrOH = 95 : 5, detector : 215 nm, flow rate 0.5 mL/min, t_1(+) = 9.6, t_2(-) = 16.3; $[\alpha]^{20}_D$ = -155.4 (c = 0.24, $CHCl_3$) (for an ee of 95%); HRMS (ESI) (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{18}$, 223.1481; found, 223.1477.

1-(2-phenylindolin-1-yl)ethan-1-one ((*R*)-11a): Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz, 30 °C): δ 8.33 (d, *J* = 7.2 Hz, 1H), 7.37-7.05 (m, 7 H), 7.05-7.00 (m, 1H), 5.34 (d, *J* = 9.2 Hz, 1H), 3.75 (dd, *J* = 15.4, 10.4 Hz, 1H), 2.94 (dd, *J* = 16.1, 1.9 Hz, 1H) 2.01 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 30 °C): δ 169.5, 143.4, 143.2, 129.2, 127.8, 127.7, 125.0, 124.9, 124.1, 117.0, 63.5, 38.9, 24.2; HPLC (Daicel AD-H, temperature: 30 °C, hexane : ^{i}PrOH = 90 : 10, detector : 215 nm, flow rate 1.0 mL/min, t_1(-) = 11.6 min, t_2(+) = 15.9 min). $[\alpha]^{20}_D$ = +147.6 (c = 0.95, $CHCl_3$) (for an ee of 99%). The absolute configuration was determined by the optical rotation in comparison with literature after deprotection of an acetyl group.[46]

1-(2-(4-methoxyphenyl)indolin-1-yl)ethan-1-one ((+)-11b): Colorless oil. ^1H NMR ($CDCl_3$, 400 MHz, 30 °C): δ 8.34 (brs, 1H), 7.31-7.25 (m, 1H), 7.16-7.00 (m, 4H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.34 (d, *J* = 8.7 Hz, 1H), 3.80-3.69 (m, 4H), 2.96 (d, *J* = 16.1 Hz, 1H), 2.06 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 30 °C): δ 169.6, 159.1, 143.3, 135.3, 129.3, 127.7, 126.2, 124.9, 124.0, 117.0, 114.5, 63.1, 55.3, 39.1, 24.1; HPLC (Daicel AD-H, temperature: 30 °C, hexane : ^{i}PrOH = 90 : 10, detector : 215 nm, flow rate 1.0 mL/min, t_1(-) = 18.9 min, t_2(+) = 25.0 min); $[\alpha]^{20}_D$ = +98.0 (c = 0.96, $CHCl_3$) (for an ee of 96%).[47]

1-(2-(3-methoxyphenyl)indolin-1-yl)ethan-1-one ((+)-11c): White solid. ^1H NMR ($CDCl_3$, 400 MHz, 30 °C): δ 8.36 (d, *J* = 7.0 Hz, 1H), 7.30-7.18 (m, 2H), 7.16-7.10 (m, 1H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.81-6.67 (m, 3H), 5.36 (d, *J* = 9.3 Hz, 1H), 3.83-3.69 (m, 4H), 2.99 (d, *J* = 16.0 Hz, 1H), 2.07 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 30 °C): δ 169.5, 160.2, 144.8, 143.4, 130.3, 129.2, 127.7, 124.8, 124.0, 117.2, 116.9, 112.6, 111.0, 63.4, 55.2, 38.8, 24.1. HPLC (Daicel AD-H, temperature: 30 °C, hexane : ^{i}PrOH = 90 : 10, detector : 215 nm, flow rate 1.0 mL/min, t_1(+) = 11.2 min, t_2(-) = 17.0 min); $[\alpha]^{20}_D$ = +164.1 (c = 0.82, $CHCl_3$) (for an ee of 99%).[48]

1-(2-(4-(trifluoromethyl)phenyl)indolin-1-yl)ethan-1-one ((+)-11e): Colorless oil. IR (KBr, ν /cm^{-1}): 3449 br, 3070 w, 3048 w, 2955 w, 2858 w, 1664 s, 1620 m, 1599 m, 1481 s, 1463 m, 1394 s, 1326 s, 1275 m, 1167 m, 1124 s, 1111 s, 1067 s, 1017 m, 755 m; ^1H NMR ($CDCl_3$, 400 MHz, 55 °C): δ 8.26 (brs, 1H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.34-7.23 (m, 3H), 7.17-7.08 (m, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 5.49 (brs, 1H), 3.78 (dd, *J* = 15.0, 10.6 Hz, 1H), 2.93 (d, *J* = 16.0 Hz, 1H), 2.07 (brs, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 30 °C): δ 169.3, 147.1, 143.2, 128.6, 128.1, 126.4, 125.6, 125.1, 124.5, 122.7, 117.2, 63.2, 38.9, 24.2; C-F coupling constants could not be determined by $^{13}C\{^1H\}$ NMR analysis due to broad signals. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 376 MHz, 30 °C): δ -63.8; HPLC (Daicel AD-H, temperature: 30 °C, hexane : ^{i}PrOH = 90 : 10, detector : 215 nm, flow rate 1.0 mL/min, t_1(-) = 9.3 min, t_2(+) = 10.5 min); $[\alpha]^{20}D$ = +155.8 (c = 0.94, $CHCl_3$) (for an *ee* of >99%). HRMS (FAB$^+$) *m/z* calcd. for $C_{17}H_{15}ONF_3$ 306.1106 found 306.1105.

2-phenyl-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide ((*R*)-15): Pale brown solid. ^1H NMR ($CDCl_3$, 400 MHz, 30 °C): δ 7.80 (d, *J* =7.7 Hz, 1H), 7.62 (td, *J* = 7.6, *J* = 1.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.49-7.40 (m, 6H), 4.68 (t, *J* = 8.4 Hz, 1H), 3.65 (d, *J* = 8.4 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 30 °C): δ 138.6, 136.5, 133.6, 130.3, 129.6, 129.5, 129.2, 129,1, 127.2, 122.5, 67.6, 33.0; HPLC (Daicel AS-H, temperature: 30 °C, hexane : ^{i}PrOH = 70 : 30, detector : 215 nm, flow rate 1.0 mL/min, t_1(-) = 16.5 min, t_2(+) = 18.4 min); $[\alpha]^{20}_D$ = -77.9 (c = 0.57, $CHCl_3$) (for an ee of 77%). The absolute configuration was determined by the optical rotation in comparison with literature.[49]

1,1-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[*b*]silole ((-)-17): Colorless oil. ^1H NMR ($CDCl_3$, 400 MHz, 30 °C): δ 7.52 (d, *J* = 7.0 Hz, 1 H), 7.39-7.29 (m, 2H), 7.26-7.19 (m, 3H), 7.13-7.04 (m, 3H), 3.51 (dd, *J* = 16.5, 8.3 Hz, 1H), 3.37 (dd, *J* = 16.5, 7.5 Hz, 1H), 2.83 (t, *J* = 7.9 Hz, 1H), 0.39 (s, 3H), -0.03 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 30 °C): δ 151.8, 144.6, 138.7, 132.5, 129.8, 128.5, 126.6, 126.3, 125.6, 124.5, 39.4, 35.6, -1.9, -3.9; HPLC (Daicel OJ-3, temperature: 30 °C, hexane : ^{i}PrOH = 95 : 5, detector : 215 nm, flow rate 1.0 mL/min, t_1(+) = 6.9 min, t_2(+) = 35.5 min); $[\alpha]^{20}_D$ =-151.6 (c = 0.82 , $CHCl_3$) (for an ee of 93%).[50]

Ethyl 3-phenylbutanoate ((*R*)-19): Colorless oil. ^1H NMR ($CDCl_3$, 400 MHz, 30 °C): δ 7.32-7.26 (m, 2H), 7.23-7.16 (m, 3H), 4.07 (q, *J* = 7.2 Hz, 2H), 3.27 (sext, *J* = 7.8 Hz, 1H), 2.57 (qd, *J* = 15.6, 8.1 Hz, 1H), 1.30 (d, *J* = 7.0 Hz, 3H), 1.17 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 30 °C): δ 172.5, 145.9, 128.6, 126.9, 126.5, 60.4, 43.1, 36.7, 21.9, 14.3; HPLC (Daicel OD-H, temperature: 30 °C, hexane : ^{i}PrOH = 98 : 2, detector : 215 nm, flow rate 0.5 mL/min, t_1(-) = 9.2 min, t_2(+) = 11.3 min). $[\alpha]^{20}_D$ = -23.7 (c = 1.08, $CHCl_3$) (for an ee of 89%). The absolute configuration was determined by the optical rotation in comparison with literature.[28]

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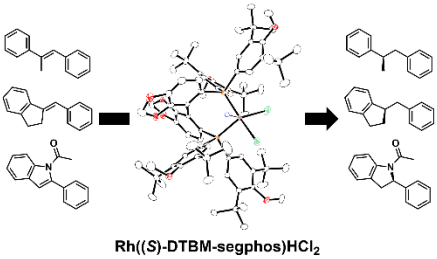

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