Oxidative Addition of RCO_2H and HX to Chiral Diphosphine Complexes of Iridium(I): Convenient Synthesis of Mononuclear Halo-Carboxylate Iridium(III) Complexes and Cationic Dinuclear Triply Halogen-Bridged Iridium(III) Complexes and Their Catalytic Performance in Asymmetric Hydrogenation of Cyclic Imines and 2-Phenylquinoline

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Received December 14, 2005

Mononuclear iridium(III) complexes of general formula IrX(H)(O_2CR)[(*S*)-binap] (**2**, R = CH_3; **3**, R = Ph; **4**, R = $C_6H_4CH_3$-p; **a**, X = Cl; **b**, X = Br; **c**, X = I) were prepared by one-pot reaction of [Ir(μ-X)(cod)]$_2$ with 2 equiv of (*S*)-BINAP [=2,2′-bis(diphenylphosphino)-1,1′-binaphthyl] and an excess of the corresponding carboxylic acid in toluene. The structure of (*S*)-**2**−**4** bearing an (*S*)-BINAP was confirmed to be *OC*-6−23-*A* (Λ-conformation) by X-ray analysis of (*S*)-**4a**−**c**. In this reaction, the iridium(I) complex {Ir(μ-Cl)[(*S*)-binap]}$_2$ [(*S*)-**5a**] and pentacoordinated iridium(I) complexes IrX(cod)[(*S*)-binap] [(*S*)-**7b**, X = Br; (*S*)-**7c**, X = I] were generated prior to the oxidative addition of carboxylic acid. Cationic dinuclear iridium(III) complexes of general formula [{Ir(H)[(*S*)-binap]}$_2$(μ-X)$_3$]X [(*S*)-**8**: **a**, X = Cl; **b**, X = Br; **c**, X = I] were prepared, and their cationic bifacial octahedral dinuclear structure was characterized by spectral data and combustion analysis. The anionic portion of these complexes could be replaced by $NaPF_6$, leading to the corresponding PF_6 salts [{Ir(H)[(*S*)-binap]}$_2$(μ-X)$_3$]PF_6 [(*S*)-**8**: **d**, X = Cl; **e**, X = Br; **f**, X = I]. Iodo-acetate complexes of *p*-TolBINAP (=2,2′-bis(di-4-tolylphosphino)-1,1′-binaphthyl) [(*S*)-**9c**] and SYNPHOS [=2,2′,3,3′-tetrahydro(5,5′-bi-1,4-benzodioxin)-6,6′-diyl]bis(diphenylphosphine)] [(*S*)-**10c**] were also prepared according to the method used for the BINAP complex (*S*)-**2c** and were characterized spectroscopically. Cationic dinuclear complexes of *p*-TolBINAP [(*S*)-**11c**] and SYNPHOS [(*S*)-**12c**] were also generated. Using these complexes, the effect of halide variation was studied by asymmetric hydrogenation of 2-phenylpyrrolidine (**13**) and 2-phenyl-4,5,6,7-tetrahydro-3*H*-azepine (**15**) along with 2-phenylquinoline (**16**), and the results indicated that iodide complexes were better catalyst precursors for catalytic activity than the corresponding chloride and bromide complexes, but were not superior in enantioselectivity.

Introduction

Practical and efficient catalysts for asymmetric hydrogenation of unsaturated organic compounds have been extensively developed by making the coordination environment around the transition metal center chiral, not only through the design and synthesis of chiral ligands but also via rational combination with auxiliary ligands on the transition metal center.[1] Iridium complexes with chiral diphosphine ligands have attracted much interest because they serve as highly active catalysts for asymmetric hydrogenation of the C═N bond of imines to form chiral amines. The most remarkable feature of the iridium-diphosphine catalyst system is that the addition of an iodide anion source or iodine to the catalyst systems significantly enhances their catalytic activity and, in some cases, enantioselectivity. A halide effect[2] has been reported for asymmetric reactions assisted by halide complexes of ruthenium,[3−5] rhodium,[6] and iridium[7−17] bearing various chiral diphosphine

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10.1021/om051065j CCC: $33.50

ligands. We are interested in catalyst systems based on iridium(III) complexes because of their higher tolerance to air oxidation compared with iridium(I) complexes. Although iridium(III) species are considered key intermediates, there are only a few iridium(III) catalyst precursors. Osborn and co-workers reported that (1) neutral double iodine-bridged dinuclear hydride complexes of iridium(III), $[IrHI_2(diphosphine)]_2$ [diphosphine: BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, DIOP, NORPHOS, etc.], could be prepared by treating cationic mononuclear iridium(I) complexes $[Ir(diphosphine)(cod)]BF_4$ with excess amounts of LiI[7a] and (2) that a metathesis reaction of $[IrHI_2(diphosphine)]_2$ with 1 equiv of AgOAc leads to Ir(I)-(H)(O_2CCH_3)(diphosphine).[7b] Another iridium(III) system is the iridium(III)-xyliphos-carboxylate complex {(*S*)-xyliphos = (*S*)-1-[(*R*)-2-(diphenylphosphanyl)ferrocenyl]ethyldi(3,5-xylyl)phosphane}, which was generated in situ by treating a cationic iridium(I) complex bearing a xyliphos ligand with tetrabutylammonium iodide and acetic acid. This complex showed catalytic activity for asymmetric hydrogenation of imines with an extremely high turnover frequency and moderate enantioselectivity.[11] Additionally, several iridium(III) complexes bearing xyliphos were recently reported.[17] Here, we report the synthesis of mononuclear halide-carboxylate and cationic triply halogen-bridged dinuclear iridium(III) complexes of BINAP and its derivatives and discuss their catalytic performance in the asymmetric hydrogenation of cyclic imines and 2-phenylquinoline.[16]

Results and Discussion

Synthesis and Characterization of Mononuclear Halide-Carboxylate BINAP-Iridium(III) Complexes. A simple one-pot reaction of $[Ir(\mu\text{-}Cl)(cod)]_2$ (**1a**) with 2 equiv of (*S*)-BINAP and 10 equiv of acetic acid in toluene afforded in modest yield a mononuclear iridium(III) complex, IrCl(H)(O_2CCH_3)[(*S*)-binap] [(*S*)-**2a**], as a mixture of major (>95%) and minor (<5%) isomers (eq 1). Bromide [(*S*)-**2b**] and iodide [(*S*)-**2c**] derivatives of (*S*)-**2a** were prepared by the same one-pot reactions, giving a mixture of two isomers (eq 1). Benzoate [(*S*)-**3a**−**c**] and 4-methylbenzoate [(*S*)-**4a**−**c**] iridium(III) complexes of (*S*)-BINAP were similarly prepared as only one isomer. This synthetic method is much easier than the reported metathesis reaction of $[IrHI_2((R)\text{-binap})]_2$ with AgOAc, leading to Ir(I)-(H)(O_2CCH_3)[(*R*)-binap] [(*R*)-**2c**].[7b] The (*S*)-**2**−**4** complexes were characterized by spectral data together with X-ray analyses of 4-methylbenzoate complexes (*S*)-**4a**−**c**. The IR spectra of these complexes demonstrated a typical absorption band assignable to ν_{Ir-H} in the range 2264−2280 cm^{-1}. The ^1H NMR spectra of both isomers of (*S*)-**2** together with (*S*)-**3** and (*S*)-**4** displayed a hydride signal around δ −25, whose coupling pattern (doublet of doublets) and two coupling constants of J_{P-H} placed the hydride atom at a position *cis* to both phosphorus atoms. The $^{31}P\{^1H\}$ NMR spectra of both isomers of (*S*)-**2** together with (*S*)-**3** and (*S*)-**4** showed two doublets with an AB pattern due to the two magnetically nonequivalent phosphorus atoms of the BINAP ligand. These spectral data clearly indicated that both BINAP and carboxylate acted as bidentate ligands, suggesting that these complexes should have a Δ or Λ geometry; however, the *trans*-geometry was ruled out because of the observation of two isomers for (*S*)-**2**. Structures of the major isomer of (*S*)-**2** together with (*S*)-**3** and (*S*)-**4** bearing (*S*)-BINAP were determined to be *OC*-6−23-*A* (Λ-conformation) by X-ray analyses for (*S*)-**4a**−**c**. Thus, the minor isomer of (*S*)-**2** was assigned the Δ-conformation.

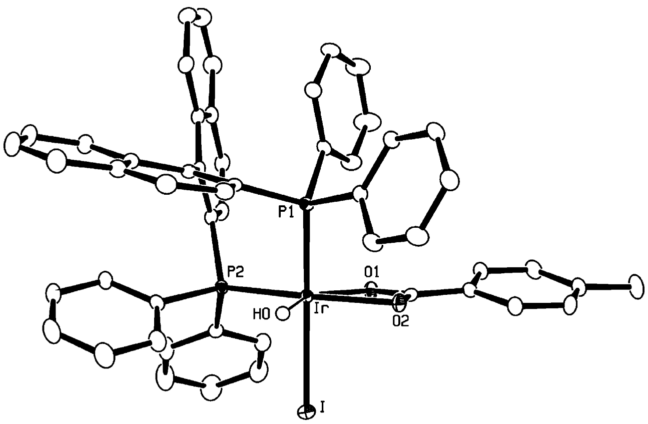
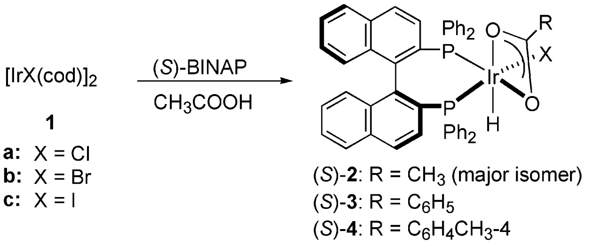


Figure 1. Crystal structure of **2c** with numbering scheme. Hydrogen atoms are omitted for clarity.



(1)

Figure 1 shows the crystal structure of (*S*)-**4c**. The (*S*)-**4a** and (*S*)-**4b** complexes are isomorphic and are depicted in the Supporting Information. The selected bond distances and angles for (*S*)-**4a**−**c** are summarized in Table 1. The iridium(III) center adopts a distorted octahedral geometry, where BINAP and 4-methylbenzoate are bidentate ligands, and a hydride atom is placed at a position *cis* to the two phosphorus atoms. For (*S*)-**4c**, the distance of Ir−P(1) [2.2505(9) Å] is slightly larger than that of Ir−P(2) [2.2353(9) Å], while the distance of Ir−O(1) [2.273(2) Å] is significantly larger than that of Ir−O(2) [2.191(2) Å] because the oxygen atom O(1) is *trans* to the hydride atom. The distances of Ir−O(1) and Ir−O(2) in the iodide complex (*S*)-**4c** are much larger than those in the chloride and bromide complexes, whereas there is no clear difference between the Ir−P distances. Although the bond distance of Ir−X increased in the order of the covalent radii of the halogen atoms,

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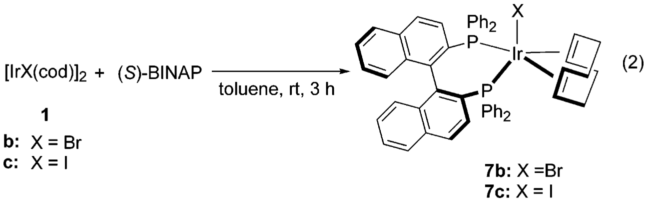
Table 1. Selected Bond Lengths (Å) and Angles (deg) of 4a, 4b, and 4c

	4a (X = Cl)	**4b** (X = Br)	**4c** (X = I)
Ir−P1	2.2483(6)	2.2517(9)	2.2504(9)
Ir−P2	2.2333(6)	2.2355(10)	2.2358(9)
Ir−O1	2.2564(16)	2.2581(17)	2.2736(18)
Ir−O2	2.1736(16)	2.1791(17)	2.1912(18)
Ir−X	2.3990(5)	2.5321(8)	2.7041(7)
Ir−H0	1.62(3)	1.605	1.668
O2−Ir−P2	167.71(4)	167.60(4)	167.25(4)
O2−Ir−P1	90.53(4)	90.06(5)	90.03(5)
P2−Ir−P1	93.26(2)	93.24(3)	92.51(3)
O2−Ir−O1	59.48(6)	59.40(6)	58.77(6)
P2−Ir−O1	108.26(4)	108.20(5)	108.48(5)
P1−Ir−O1	101.40(5)	101.82(5)	100.66(5)
O2−Ir−X	84.56(4)	84.73(5)	86.71(5)
P2−Ir−X	94.31(2)	94.93(3)	94.29(3)
P1−Ir−X	165.87(2)	164.60(2)	163.26(2)
O1−Ir−X	87.52(5)	87.99(5)	91.66(5)
O1−Ir−H0	163.6(12)	152.47(4)	161.74(4)
λ^a	69.88(5)	70.19(5)	70.73(6)

^{a} λ is the dihedral angle between the least-squares planes through the two naphthyl rings.

the structural features of these three complexes are almost the same. The bis(pivalate)ruthenium complex with (*S*)-BINAP complexes also forms the same Λ-configuration.[18] The dihedral angle of the two naphthyl planes of (*S*)-**4** is in the range 69.88(5)−70.72(6)°, a higher range than that for Ru(OCOCMe$_3$)$_2$[(*R*)-binap] (65.47°)[18] and Ir(I)(cod)[(*S*)-binap] [66.84(6)°] (vide infra), but smaller than that for {Ir(μ-Cl)[(*S*)-binap]}$_2$ [(*S*)-**5a**] (74.06° and 76.83°)[19] and [Ir$_2$(μ-Cl)(OMe)$_2$[(*S*)-binap]$_2$]$^+$Cl$^-$ [81.4(1)°].[20]

The reaction outlined in eq 1 involved the formation of Ir(I)-BINAP complexes prior to the oxidative addition of acetic acid. Iridium(I) complex {Ir(μ-Cl)[(*S*)-binap]}$_2$ [(*S*)-**5a**], which was readily obtained from the reaction of **1a** or [Ir(μ-Cl)(cyclooctene)$_2$]$_2$ (**6a**) with 2 equiv of (*S*)-BINAP,[19] reacted with excess acetic acid in toluene to give (*S*)-**2a** quantitatively. In contrast, reactions of **1b** and **1c** with (*S*)-BINAP in toluene at room temperature led to the formation of the pentacoordinated Ir(I) complexes IrX(cod)[(*S*)-binap] [(*S*)-**7b**, X = Br; (*S*)-**6c**, X = I] (eq 2), to which acetic acid was oxidatively added to give (*S*)-**2b** and (*S*)-**2c**, respectively. The stereochemistry of (*S*)-**2**−**4** was thus determined by the oxidative addition of acid to the idirium(I) complexes. The ^{1}H NMR spectra of (*S*)-**7b** and (*S*)-**7c** displayed signals due to protons of the coordinated COD and those of BINAP in an exact 1:1 integral ratio, and there was no hydride signal. The ^{31}P{^{1}H} NMR spectra of (*S*)-**7b** and (*S*)-**7c** showed AB*q* (J_{P-P} = 38 Hz) due to the two dissymmetric phosphorus atoms of the BINAP ligand.



Although two structures, i.e., trigonal bipyramidal and square pyramidal, are possible for the pentacoordinated iridium(I) compounds, the spectral data suggested that (*S*)-**7b** and (*S*)-**7c** adopted a square pyramidal structure, which was revealed by single-crystal X-ray analysis of the complex (*S*)-**7c**. The structure of (*S*)-**7c** is shown in Figure 2, and selected bond distances and angles are summarized in Table 2. The structural features are the same as those of the pentacoordinated iridium(I) complex Ir(I)(cod)[(*S*)-xyliphos].[17] The iodide atom occupies the apical position of the square pyramid, and the iridium atom is thus deformed by 0.4335 Å out of the best plane defined by the two phosphines of BINAP and the centroid of the C=C bonds of the COD ligand. Such deformation was greater than that formed for Ir(cod)(I)[(*S*)-xyliphos] [+0.3536 Å],[17] Ir(Cl)(cod)[bis(μ_2-diphenylphosphino)iron] [0.3542 Å],[21] and Ir(cod)(I)[1,3-bis(diphenylphosphino)propane] [0.3113 Å].[22] The Ir−I distance of (*S*)-**7c** [2.8905(3) Å] is significantly larger than that of the iridium(III) complex (*S*)-**2c** [2.7041(7) Å], but was comparable to that of the pentacoordinated idirium(I) complex Ir(cod)(I)[(*S*)-xyliphos], which was 2.888(4) Å.[17]

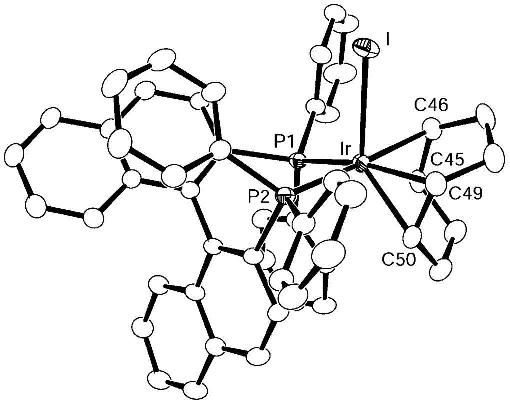


Figure 2. Crystal structure of **7c** with numbering scheme. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for (*S*)-7c^a

Ir−C49	2.183(4)
Ir−C50	2.194(3)
Ir−C46	2.231(3)
Ir−C45	2.245(3)
Ir−P2	2.3248(8)
Ir−P1	2.3297(8)
Ir−I	2.8905(3)
P2−Ir−P1	87.12(3)
P2−Ir−I	93.26(2)
P1−Ir−I	108.53(2)
I−Ir−Cen1	100.84
I−Ir−Cen2	103.14
P1−Ir−Cen1	88.87
P1−Ir−Cen2	148.29
P2−Ir−Cen1	165.89
P2−Ir−Cen2	92.49
Cen1−Ir−Cen2	83.86
λ^b	66.84(6)

^{a} Cen1: centroid of C45 and C46, Cen2: centroid of C49 and C50. ^{b} λ is the dihedral angle between the least-squares planes through the two naphthyl rings.

Synthesis and Characterization of Cationic Dinuclear Triply Halogen-Bridged Iridium(III)-BINAP Complexes.

The cationic dinuclear complex [{Ir(H)[(*S*)-binap]}$_2$(μ-Cl)$_3$]Cl [(*S*)-**8a**] was prepared by adding excess aqueous HCl to a mixture of **6a** and 2 equiv of (*S*)-BINAP in toluene at room temperature (eq 3). The cationic bifacial octahedral dinuclear

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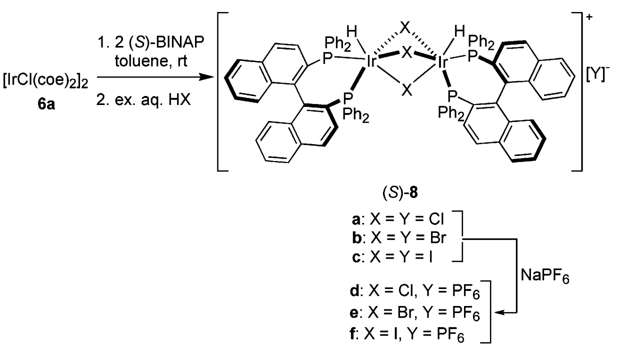
structure was determined by spectral data and combustion analysis. The ^{1}H NMR spectrum of (*S*)-**8a** showed a hydride signal at δ −22.70 with two coupling constants, $J_{\mathrm{P-H}}$ of 15 and 21 Hz, indicating that the hydride was located at a position *cis* to the two phosphines of BINAP. The stretching frequency of Ir−H appeared at 2269 cm^{-1}. The ^{31}P{^{1}H} NMR spectrum of (*S*)-**8a** displayed a typical AA′BB′pattern. It is well established that iridium(III) fragments "Ir$^{\mathrm{III}}$(X)(chiral diphosphine)"[23]as well as isoelectronic ruthenium(II) fragments "Ru$^{\mathrm{II}}$(X)(chiral diphosphine)"[24] form stable triply anionic ligand-bridged bifacial octahedral dinuclear complexes, in which the AA′BB′ pattern due to two chiral diphosphine ligands is observed by ^{31}P{^{1}H} NMR spectroscopy. FAB-MS afforded a parent peak (M$^+$ = 1738) due to the cationic fragment $\{\mathrm{Ir_2H_2Cl_3}[(S)\text{-binap}]_2\}^+$, in accordance with the cationic dimeric structure of (*S*)-**8a**, which was further confirmed by solution conductivity.



(3)

(*S*)-**8**

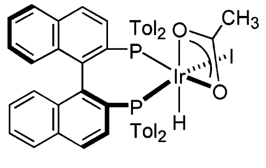
a: X = Y = Cl
b: X = Y = Br
c: X = Y = I
d: X = Cl, Y = PF$_6$
e: X = Br, Y = PF$_6$
f: X = I, Y = PF$_6$

Similar treatment of a mixture of **6a** and 2 equiv of (*S*)-BINAP in toluene with excess aqueous HBr or aqueous HI afforded the corresponding bromide and iodide complexes (*S*)-**8b** and (*S*)-**8c**, whose structures were also revealed by spectral data and combustion analysis together with EDAX measurement, which confirmed the complete replacement of all the chloride ions by bromide or iodide ions. The simple addition of excess amounts of aqueous HBr or aqueous HI resulted in the complete replacement of chloride during the oxidative reaction, because the synthesis of **1b** and **1c** somewhat reduced the chemical yield due to mechanical loss during the metathesis reaction of chloride ions of **1a** using NaX salts.[7b] The anions of these complexes could be replaced using NaPF$_6$, leading to the corresponding PF$_6$ salts (*S*)-**8d**−**f**. Complex (*S*)-**8c** was additionally obtained by adding aqueous HI to the carboxylate complex (*S*)-**2a** in toluene (eq 4) or by treatment of (*S*)-**8a** with excess NaI in dichloromethane (eq 5). The spectral data of (*S*)-**8b** were quite similar to those for (*S*)-**8a**, while (*S*)-**8c** gave spectral data similar to those for (*S*)-**8a**, along with signals due to small amounts of unidentified compounds. Osborn and Chan reported a neutral dinuclear complex, $\{\mathrm{IrHI_2}[(R)\text{-binap}]\}_2$, which has the same chemical formula as the cationic dinuclear complex (*S*)-**8c**.[7a]

$$(S)\text{-}\mathbf{2a} + \text{ex. aq. HI} \xrightarrow{\text{toulene, rt}} (S)\text{-}\mathbf{8c} \qquad (4)$$

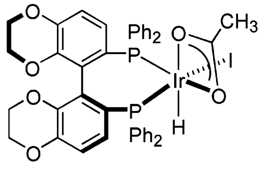
$$(S)\text{-}\mathbf{8a} + \text{ex. aq. NaI} \xrightarrow{\mathrm{CH_2Cl_2},\ \text{rt}} (S)\text{-}\mathbf{8c} \qquad (5)$$

Synthesis and Characterization of Iodide Iridium(III) Complexes Bearing *p*-TolBINAP and SYNPHOS. Iodo-acetate complexes of *p*-TolBINAP [=2,2′-bis(di-4-tolylphosphino)-1,1′-binaphthyl] [(*S*)-**9c**] and SYNPHOS [=2,2′,3,3′-tetrahydro(5,5′-bi-1,4-benzodioxin)-6,6′-diyl]bis(diphenylphosphine)][25] [(*S*)-**10c**] were prepared according to the method used for synthesis of the BINAP complex (*S*)-**2c** and were characterized spectroscopically. Cationic complex (*S*)-**11c** was prepared by adding aqueous HI to a solution of the chloride complex (*S*)-**9a** in toluene, which was prepared by the procedure described for (*S*)-**9c**. Cationic complex (*S*)-**12c** was prepared by adding aqueous HI to (*S*)-**10c**. Though these cationic dinuclear complexes (*S*)-**11c** and (*S*)-**12c** contain some impurities, we used them as catalyst precursors for asymmetric hydrogenation of imines without purification and, in some cases, an situ mixture of the acetate complex and an excess of aqueous HI.

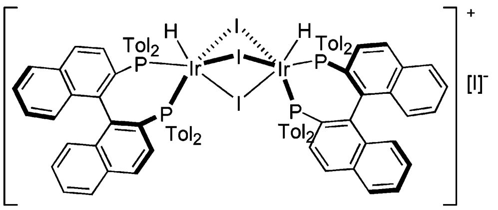


(*S*)-**9c**

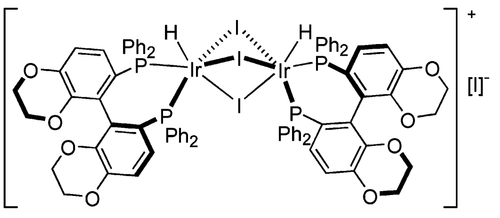
Tol = C$_6$H$_4$CH$_3$-4



(*S*)-**10c**



(*S*)-**11c**



(*S*)-**12c**

Effect of Halide Ligand Bound to Iridium(III)-BINAP Complexes for Asymmetric Hydrogenation of Cyclic Imines. The effect of halide variation in catalytic performance was studied by asymmetric hydrogenation of 2-phenylpyrrolidine (**13**) and 2-phenyl-4,5,6,7-tetrahydro-3*H*-azepine (**15**), using acetate BINAP complexes (*S*)-**2a**−**c.** As expected on the basis of the reported tendency of halide effects for iridium catalyst systems,[7−18] the iodide complex (*S*)-**2c** was a better catalyst precursor in terms of catalytic activity among the tested catalysts (*S*)-**2a**−**c** (Table 3, entries 1−3 and 12−14), though halogen atoms bound to the iridium(III) center did not clearly affect enantioselectivity. Asymmetric hydrogenation of 2-phenylpiperidine (**14**) was catalyzed by iodide complexes (*S*)-**2c**, (*S*)-**3c**, and (*S*)-**4c** with different carboxylate ligands (entries 8−10) with the same activity and enantioselectivity, indicating that the

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[23] (a) Tani, K.; Iseki, A.; Yamagata, T. *Angew. Chem., Int. Ed.* **1998**, *37*, 3381. (b) Dorta, R.; Togni, A. *Organometallics* **1998**, *17*, 3423.

[24] Mashima, K.; Nakamura, T.; Matsuo, Y.; Tani, K. *J. Organomet. Chem.* **2000**, *607*, 51. Ohta, T.; Tonomura, Y.; Nozaki, K.; Takaya, H.; Mashima, K. *Organometallics* **1996**, *15*, 1521.

[25] For SYNPHOS see: (a) Duprat de Paule, S.; Champion, N.; Ratovelomanana-Vidal, V.; Genet, J.-P.; Dellis, P French patent 0112499; PCT FR02/03146, W003029259. (b) Duprat de Paule, S.; Jeulin, S.; Ratovelomanana-Vidal, V.; Genet, J.-P.; Champion, N.; Dellis, P. *Tetrahedron Lett.* **2003**, *44*, 823. (c) Duprat de Paule, S.; Jeulin, S.; Ratovelomanana-Vidal, V.; Genet, J.-P.; Champion, N.; Dellis, P. *Eur. J. Org. Chem.* **2003**, 1931. (d) Duprat de Paule, S.; Jeulin, S.; Ratovelomanana-Vidal, V.; Genet, J.-P.; Champion, N.; Deschaux, G.; Dellis, P. *Org. Process. Res. Dev.* **2003**, *7*, 399.

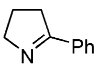
Table 3. Asymmetric Hydrogenation of 2-Phenylpyrrolidine (13), 2-Phenylpiperidine (14), and 2-Phenyl-4,5,6,7-tetrahydro-3*H*-azepine (15) Catalyzed by Iridium(III)-BINAP Complexes[a]

entry	substrate	cat.	S/C[b]	time (h)	yield (%)	% ee[c,d]
1	**13**	(*S*)-**2a**	100	18	21	85 (*S*)
2	**13**	(*S*)-**2b**	100	18	38	89 (*S*)
3	**13**	(*S*)-**2c**	100	18	47	86 (*S*)
4	**13**	(*S*)-**8a**	200	18	15	82 (*S*)
5	**13**	(*S*)-**8b**	210	18	24	82 (*S*)
6	**13**	(*S*)-**8c**	220	19	82	83 (*S*)
7	**14**	(*S*)-**2c**	100	1	99	90 (*S*)
8	**14**	(*S*)-**2c**	1000	40	99	91 (*S*)
9	**14**	(*S*)-**3c**	1000	41	99	91 (*S*)
10	**14**	(*S*)-**4c**	1000	41	99	91 (*S*)
11	**14**	(*S*)-**8c**	1000	3	99	91 (*S*)
12	**15**	(*S*)-**2a**	100	18	99	69 (*S*)
13	**15**	(*S*)-**2b**	100	18	96	60 (*S*)
14	**15**	(*S*)-**2c**	100	18	99	67 (*S*)

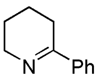
[a] Hydrogenation was carried out in toluene solution charged into an autoclave under an initial hydrogen pressure of 60 atm at 20 °C. [b] Ratio of substrate and catalyst. [c] Enantiomeric excess (ee) of the product. [d] The absolute configuration is given in parentheses.

catalytically active species did not involve the carboxylate ligand during hydrogenation.

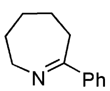
The bis(carboxylate)ruthenium(II) complexes of BINAP are reportedly less active than the corresponding halide complexes for asymmetric hydrogenation of ketonic substrates.[3] Thus, we conducted an asymmetric hydrogenation of **13** using (*S*)-**8a**−**c**, which did not contain a carboxylate ligand. Among the tested complexes, (*S*)-**8a**−**c** (entries 4−6), the iodide complex (*S*)-**8c** was the most active catalyst for asymmetric hydrogenation of **13** despite the fact that (*S*)-**8c** exhibited less enantioselectivity than the carboxylate complexes (*S*)-**2a**−**c**. In addition, (*S*)-**8c** catalyzed the asymmetric hydrogenation of **14** much faster than complexes (*S*)-**2c**, (*S*)-**3c**, and (*S*)-**4c** (entry 11). The superiority of (*S*)-**8c** might be due to the cleavage of the Ir−N bond of the intermediate by HI. A similar additive effect of aqueous HX was reported for the hydrogenation of α-ketoester using ruthenium-halogen complexes of BINAP.[3d] For asymmetric hydrogenation of cyclic imines **13**, **14**, and **15**, hydrosilylation based on chiral oxazolinyl-phosphine complexes of ruthenium, rhodium, and iridium (up to 88% ee for **13**; 25% ee for **14**), as well as hydrogenation or hydrosilylation using chiral ansa-type titanocene/$PhSiH_3$ systems (up to 99% ee for **13** and **14**; 98% ee for **15**), have been reported.[26]



13



14



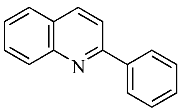
15

Asymmetic Hydrogenation of 2-Phenylquinoline by Iridium(III) Complexes of BINAP, *p*-TolBINAP, and SYNPHOS. On the basis of the hydrogenation of cyclic imines, we used iodide iridium(III) complexes (*S*)-**2c** and (*S*)-**8c** of BINAP as catalyst precursors for asymmetric hydrogenation of 2-phenylquinoline (**16**) with I_2 as an additive,[16] giving (*S*)-**17** (Table 4, entries 1 and 2). The complexes (*S*)-**2c** and (*S*)-**8c** were active catalysts, but the enantioselectivity was not satisfactory. To optimize the chiral phosphine ligand (BINAP, *p*-TolBINAP, and SYNPHOS), asymmetric hydrogenation of **16** using *p*-TolBINAP complexes (*S*)-**9c** and (*S*)-**11c** and SYNPHOS complexes (*S*)-**10c** and (*S*)-**12c** was performed (Table 4, entries 3−6). The results consistently revealed that cationic halogen-bridged dinuclear complexes (*S*)-**10c** and (*S*)-**12c** had better enantioselectivity than the corresponding carboxylate complexes and BINAP catalysts, though the catalytic activity of (*S*)-**10c** and (*S*)-**12c** was lower. Asymmetric hydrogenation of **16** using the $[IrCl(cod)]_2$/(*R*)-MeO-biphep/I_2 system afforded an enantioselectivity of 72%,[16] a better value than that obtained using our system based on BINAP and its derivatives.

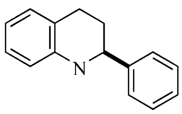
Table 4. Asymmetric Hydrogenation of 2-Phenylquinoline (16) Catalyzed by Iodo-Dinuclear Iridium(III) Complexes[a]

entry	cat.	S/C	temp (°C)	time (h)	yield (%)	% ee[b,c]
1	(*S*)-**2c**	100	30	24	>99	50 (*S*)
2	(*S*)-**8c**	100	30	24	>99	31 (*S*)
3	(*S*)-**9c**	100	30	24	>99	52 (*S*)
4	(*S*)-**10c**	200	30	45	42	64 (*S*)
5	(*S*)-**11c**	100	30	24	>99	49 (*S*)
6	(*S*)-**12c**	100	30	24	46	60 (*S*)

[a] Hydrogenation was carried out in THF solution charged into an autoclave under an initial hydrogen pressure of 50 atm unless otherwise noted. [b] Enantiomeric excess (ee) of the product was determined by HPLC analysis with a Chiralcel AS-H column. [c] The absolute configuration is given in parentheses.



16



(*S*)-17

Conclusion

We developed a new and convenient one-pot reaction to prepare mononuclear halide-carboxylate iridium(III) complexes and cationic triply halogen-bridged dinuclear idirium(III) complexes of BINAP, *p*-TolBINAP, and SYNPHOS. These iridium(III) complexes were tested as catalyst precursors for asymmetric hydrogenation of cyclic imines **13**−**15** and 2-phenylquinoline (**16**). The halide ligand remained intact and the carboxylate ligand was eliminated during the catalytic reaction. Catalytic activity of the cationic iodo-dinuclear BINAP complex **8c** was higher than that of the corresponding chloride and bromide BINAP complexes and superior to all carboxylate complexes, though the enantioselectivity was decreased. Cationic iodo-dinuclear *p*-TolBINAP (*S*)-**10c** and SYNPHOS (*S*)-**12c** complexes had better enantioselectivity for asymmetric hydrogenation of **16** among the tested iridium(III) complexes. Our studies of the catalytic application of these iridium(III) complexes as well as application of our synthetic method to the preparation of other Ir catalysts continue.

Experimental Section

General Procedures. All reactions and manipulations were performed under argon by use of standard vacuum line and Schlenk tube techniques. ^{1}H NMR spectra were recorded on a Varian Mercury 300, and chemical shifts are reported in ppm (δ) relative to tetramethylsilane or referenced to the chemical shifts of residual solvent resonances ($CHCl_3$, C_6H_6, and CH_2Cl_2 were used as internal standards, δ 7.26, 7.20, and 5.32, respectively). $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Varian Mercury 300 at 121.49 MHz, and chemical shifts were referenced to external 85% H_3PO_4. ^{19}F NMR spectra were recorded on a Varian Mercury 300 at 282.34 MHz; chemical shifts were referenced to external α,α,α-trifluorotoluene (−67.73 ppm). Infrared spectra were recorded on a JASCO FT/IR-230; mass spectra on a JEOL JMS DX-303HF spectrometer;

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(26) (a) Takei, I.; Nishibayashi, Y.; Arikawa, Y.; Uemura S.; Hidai, M. *Organometallics* **1999**, *18*, 2271. (b) Willoughby, C. A.; Buchwald, S. L. *J. Org. Chem.* **1993**, *58*, 7627. (c) Verdaguer, X.; Lange, U. E. D.; Reding, M. T.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 6784. (d) Beagley, P.; Davies, P. J.; Blacker, A. J.; White, C. *Organometallics* **2002**, *21*, 5852.

GC analyses on a Shimadzu GC-14A gas chromatograph with a Shimadzu C-R3A Chromatopac; and HPLC on a JASCO UV-970 and PU-980 with a Shimadzu C-R16A Chromatopac. Elemental analyses were recorded on a Perkin-Elmer 2400 at the Faculty of Engineering Science, Osaka University. All melting points were recorded on a Yanaco MP-52982 and are not corrected.

Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Dichloromethane (<0.003%) was degassed. Tetrahydrofuran, toluene, hexane, and diethyl ether were distilled over sodium benzophenone ketyl under argon prior to use. [Ir(μ-Cl)(coe)]$_2$ (**6a**) (COE: cyclooctene),[27] [Ir(μ-Cl)(cod)]$_2$ (**1a**) (COD: 1,5-cyclooctadiene),[27] and [Ir(μ-Cl){(*S*)-binap}]$_2$ [(*S*)-**5a**][19] were prepared according to the literature methods. 2-Phenyl-1-pyrroline (**13**), 2-phenyl-3,4,5,6-tetrahydropyridine (**14**), and 2-phenyl-4,5,6,7-tetrahydro-3*H*-azepine (**15**) were prepared according to the literature.[28,29]

Preparation of [Ir(μ-Br)(cod)]$_2$ (1b). Complex **1b** was prepared according to the modified literature method.[30] To a Schlenk flask were added Na_2IrBr_6 (2.11 g, 2.94 mmol), H_2O (20 mL), 2-propanol (9.0 mL), and COD (2.9 mL, 24 mmol). The mixture was then refluxed for 12 h. After the reaction mixture was cooled to room temperature, a dark yellow suspension was obtained. All volatiles were removed under reduced pressure. The residue was extracted with toluene (20 mL × 3). The combined toluene extract was washed with H_2O (20 mL) and ethanol (20 mL × 2), and then the toluene solution was concentrated in vacuo to afford **1b** (1.28 g, 57%) as a deep red solid. The purity was satisfactory in the following reaction. Recrystallization from THF afforded an analytically pure product of **1b**, mp 196−198 °C (dec). ^{1}H NMR ($CDCl_3$, 35 °C): δ 4.35 (m, 8H, =C*H*), 2.20−2.24 (m, 8H, −C*H*H−), 1.40−1.50 (m, 8H, −CH*H*−). Anal. Calcd for $C_{16}H_{24}Br_2Ir_2$: C, 25.27; H, 3.18. Found: C, 25.22; H, 2.83. The structure of **1b** was confirmed by X-ray analysis. A drawing and crystallographic data are deposited as Supporting Information.

Preparation of [Ir(μ-I)(cod)]$_2$ (1c). The mixture of [Ir(μ-Cl)(cod)]$_2$ (**1a**) (0.429 g, 0.639 mmol) and NaI (1.33 g, 8.86 mmol) in ether (50 mL) was stirred at ambient temperature for 12 h. All volatiles were removed under reduced pressure, and the resulting residue was washed with H_2O (15 mL × 5) and ethanol (10 mL), leaving **1c** (0.441 g, 81%) as a deep red solid. The purity was satisfactory in the following reaction, but recrystallization from THF afforded an analytically pure product of **1c**, mp 249−254 °C (dec). ^{1}H NMR ($CDCl_3$, 35 °C): δ 4.43−4.44 (m, 8H, =C*H*), 2.10−2.14 (m, 8H, −C*H*H−), 1.13−1.36 (m, 8H, −CH*H*−). Anal. Calcd for $C_{16}H_{24}I_2Ir_2$: C, 22.49; H, 2.83. Found: C, 22.82; H, 2.86. The structure of **1c** was confirmed by X-ray analysis. A drawing and crystallographic data are deposited as Supporting Information.

Preparation of Hydrido(carboxylato)iridium(III) Complexes IrX(H)(O$_2$CR)[(*S*)-binap] (R = CH$_3$, Ph, C$_6$H$_4$CH$_3$-4; X = Cl, Br, I). Typical Procedure. A mixture of [Ir(μ-I)(cod)]$_2$ (**1c**) (102 mg, 0.119 mol) and (*S*)-BINAP (151 mg, 0.242 mol) in toluene (15 mL) was stirred for 6 h at room temperature. Acetic acid (0.069 mL, 1.2 mmol) was added to the solution. After the solution was stirred for 15 h, the orange solution finally turned to pale yellow. All volatiles were removed under reduced pressure, and the residue was dissolved in dichloromethane. Addition of hexane resulted in the precipitation of IrI(H)(O_2CCH_3)[(*S*)-binap] [(*S*)-**2c**] as a pale yellow solid (183 mg, 80% yield), mp 105 °C (dec); major:minor = 95:5. Major isomer (Λ-isomer): ^{1}H NMR (C_6D_6, 35 °C): δ 6.34−8.24 (m, 32H, *Ph* + *naphthyl*), 1.55 (s, 3H, O$_2$CC*H*$_3$), −24.94 (dd, $^2J_{H-P}$ = 23 and 17 Hz, 1H, Ir−*H*). ^{31}P{^{1}H} NMR (C_6D_6, 35 °C): δ −0.7 (d, $^2J_{P-P}$ = 15 Hz), −1.5 (d, $^2J_{P-P}$ = 15 Hz). Minor isomer (Δ-isomer): a hydride signal was observed in the ^{1}H NMR (C_6D_6, 35 °C): δ −24.8 (dd, $^2J_{H-P}$ = 23 and 17 Hz, 1H, Ir−*H*). IR (KBr tablet): 2270 cm^{-1} (Ir−H). Anal. Calcd for $C_{46}H_{36}IIrP_2O_2$: C, 55.15; H, 3.62. Found: C, 55.40; H, 3.88.

IrCl(H)(O$_2$CCH$_3$)[(*S*)-binap] [(*S*)-2a]. Although the complex (*S*)-**2a** was obtained by the same procedure as (*S*)-**2c**, modification by using [Ir(μ-Cl)(coe)]$_2$ (**6a**) instead of [Ir(μ-Cl)(cod)]$_2$ (**1a**) as a starting material was conducted to give (*S*)-**2a** in 97% yield, mp 142 °C (dec); major:minor = 96:4. Spectral data were superimposed with that reported in the literature.[7b] Major isomer (Λ-isomer): ^{1}H NMR ($CDCl_3$, 35 °C): δ 6.62−7.79 (m, 32H, *Ph* + *naphthyl*), 1.71 (s, 3H, O$_2$CC*H*$_3$), −26.26 (dd, $^2J_{H-P}$ = 20, 23 Hz, 1H, Ir−*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 35 °C): δ 0.7 (d, $^2J_{P-P}$ = 19 Hz), −2.1 (d). Minor isomer (Δ-isomer): a hydride signal was observed in the ^{1}H NMR (C_6D_6, 35 °C): δ −24.3 (dd, $^2J_{H-P}$ = 23 and 17 Hz, 1H, Ir−*H*). IR (KBr tablet): 2264 cm^{-1} (Ir−H).

IrBr(H)(O$_2$CCH$_3$)[(*S*)-binap] [(*S*)-2b]: 66% yield, mp 120 °C (dec); major:minor = 96:4. Major isomer (Λ-isomer): ^{1}H NMR ($CDCl_3$, 35 °C): δ 6.34−8.25 (m, 32H, *Ph* + *naphthyl*), 1.59 (s, 3H, O$_2$CC*H*$_3$), −25.19 (dd, $^2J_{H-P}$ = 23, 19 Hz, 1H, Ir−*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 35 °C): δ 1.3 (d, $^2J_{P-P}$ = 17 Hz), −1.9 (d). Minor isomer (Δ-isomer): a hydride signal was observed in the ^{1}H NMR (C_6D_6, 35 °C): δ −24.84 (dd, $^2J_{H-P}$ = 23 and 17 Hz, 1H, Ir−*H*). IR (KBr tablet): 2268 cm^{-1} (Ir−H). Anal. Calcd for $C_{46}H_{36}BrIrP_2O_2$: C, 57.86; H, 3.80. Found: C, 57.52; H, 3.91.

IrCl(H)(O$_2$CPh)[(*S*)-binap] [(*S*)-3a]: 74% yield, mp 135 °C (dec). ^{1}H NMR ($CDCl_3$, 35 °C): δ 6.34−8.24 (m, 37H, *Ph* + *naphthyl* + *Ph*CO$_2$), −26.48 (dd, $^2J_{H-P}$ = 23, 21 Hz, 1H, Ir−*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 35 °C): δ −1.3 (d, $^2J_{P-P}$ = 18 Hz), −2.2 (d). IR (KBr tablet): 2279 cm^{-1} (Ir−H).

IrBr(H)(O$_2$CPh)[(*S*)-binap] [(*S*)-3b]: 67% yield, mp 175 °C (dec). ^{1}H NMR (CD_2Cl_2, 35 °C): δ 6.50−8.09 (m, 37H, *Ph* + *naphthyl* + *Ph*CO$_2$), −26.24 (dd, $^2J_{H-P}$ = 23, 19 Hz, 1H, Ir−*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2, 35 °C): δ 0.1 (d, $^2J_{P-P}$ = 16 Hz), −3.6 (d). IR (KBr tablet): 2279 cm^{-1} (Ir−H). Anal. Calcd for $C_{51}H_{38}BrIrP_2O_2$: C, 60.24; H, 3.77. Found: C, 59.98; H, 3.94.

IrI(H)(O$_2$CPh)[(*S*)-binap] [(*S*)-3c]: 77% yield, mp 148 °C (dec). ^{1}H NMR (CD_2Cl_2, 35 °C): δ 6.57−8.03 (m, 37H, *Ph* + *naphthyl* + *Ph*CO$_2$), −25.91 (dd, $^2J_{H-P}$ = 22, 17 Hz, 1H, Ir−*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2, 35 °C): δ 1.7 (d, $^2J_{P-P}$ = 16 Hz), −2.7 (d). IR (KBr tablet): 2279 cm^{-1} (Ir−H). Anal. Calcd for $C_{51}H_{38}IIrP_2O_2 \cdot 0.25(CH_2Cl_2)$: C, 56.72; H, 3.58. Found: C, 56.47; H, 3.76.

IrCl(H)(O$_2$CC$_6$H$_4$CH$_3$-4)[(*S*)-binap] [(*S*)-4a]: 96% yield, mp 147 °C (dec). ^{1}H NMR ($CDCl_3$, 35 °C): δ 6.56−7.87 (m, 36H, *Ph* + *naphthyl* + CH$_3$C$_6$*H*$_4$CO$_2$), 2.29 (s, 3H, C*H*$_3$C$_6$H$_4$), −26.44 (dd, $^2J_{H-P}$ = 20, 23 Hz, 1H, Ir−*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 35 °C): δ 0.9 (d, $^2J_{P-P}$ = 19 Hz), −2.7 (d). IR (KBr tablet): 2280 cm^{-1} (Ir−H). Anal. Calcd for $C_{52}H_{40}ClIrP_2O_2$: C, 63.31; H, 4.09. Found: C, 63.22; H, 3.86.

IrBr(H)(O$_2$CC$_6$H$_4$CH$_3$-4)(H)[(*S*)-binap] [(*S*)-4b]: 54% yield, mp 168 °C (dec). ^{1}H NMR (CD_2Cl_2, 35 °C): δ 6.46−7.90 (m, 36H, *Ph* + *naphthyl* + CH$_3$C$_6$*H*$_4$CO$_2$), 2.34 (s, 3H, C*H*$_3$C$_6$H$_4$), −26.28 (dd, $^2J_{H-P}$ = 23, 19 Hz, 1H, Ir−*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2, 35 °C): δ −0.1 (d, $^2J_{P-P}$ = 18 Hz), −3.5 (d). IR (KBr tablet): 2279 (Ir−H). Anal. Calcd for $C_{52}H_{40}BrIrP_2O_2 \cdot 0.25(CH_2Cl_2)$: C, 59.64; H, 3.88. Found: C, 59.69; H, 4.01.

IrI(H)(O$_2$CC$_6$H$_4$CH$_3$-4)[(*S*)-binap] [(*S*)-4c]: 60% yield, mp 155 °C (dec). ^{1}H NMR (CD_2Cl_2, 35 °C): δ 6.47−7.90 (m, 36H, *Ph* + *naphthyl* + CH$_3$C$_6$*H*$_4$CO$_2$), 2.40 (s, 3H, C*H*$_3$C$_6$H$_4$), −25.95 (dd, $^2J_{H-P}$ = 22, 17 Hz, 1H, Ir−*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2, 35 °C): δ −1.8 (d, $^2J_{P-P}$ = 17 Hz), −3.0 (d). IR (KBr tablet): 2270 cm^{-1}

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(Ir−H). Anal. Calcd for $C_{52}H_{40}IIrP_2O_2{\cdot}CH_2Cl_2$: C, 54.74; H, 3.64. Found: C, 55.11; H, 3.85.

Preparation of IrBr(cod)[(*S*)-binap] [(*S*)-7b]. A solution of [Ir(μ-Br)(cod)]$_2$ (**1b**) (37.2 mg, 0.049 mol) and (*S*)-BINAP (65.4 mg, 0.105 mol) in toluene (20 mL) was stirred at room temperature for 6 h. Removal of all volatiles under reduced pressure afforded a yellow-orange solid, which was washed with hexane (3 × 5 mL). (*S*)-**7b** was obtained as a yellow-orange solid (61.4 mg, 70%), mp 158 °C (dec). ^{1}H NMR (C_6D_6, 35 °C): δ 5.89−9.37 (m, 32H, *Ph* + *naphthyl*), 3.20−3.69 (m, 5H, =C*H* and −C*H*$_2$−), 2.14−2.31 (m, 4H, −C*H*$_2$−), 1.23−1.40 (m, 3H, −C*H*$_2$−). ^{31}P{^{1}H} NMR (C_6D_6, 35 °C): δ −3.66 (d, $^{2}J_{P-P}$ = 38 Hz), −8.09 (d).

IrI(cod)[(*S*)-binap] [(*S*)-7c]: 91% yield, mp 167 °C (dec). ^{1}H NMR (C_6D_6, 35 °C): δ 5.94−8.75 (m, 32H, *Ph* + *naphthyl*,), 3.78−3.93 (m, 4H, =C*H* and −C*H*$_2$−), 3.19 (m, 1H, −C*H*$_2$−), 2.25−2.80 (m, 3H, −C*H*$_2$−), 1.23−1.89 (m, 4H, −C*H*$_2$−). ^{31}P{^{1}H} NMR (C_6D_6, 35 °C): δ −6.5 (d, $^{2}J_{P-P}$ = 38 Hz), −11.0 (d). Anal. Calcd for $C_{52}H_{44}IIrP_2{\cdot}0.25(CH_2Cl_2)$: C, 58.58; H, 4.19. Found: C, 58.46; H, 3.81.

Preparation of [IrI(O$_2$CCH$_3$)(H){(*S*)-*p*-tolbinap}] [(*S*)-9c]. A mixture of [Ir(μ-I)(cod)]$_2$ (**1c**) (148 mg, 0.174 mol) and (*S*)-*p*-TolBINAP (238 mg, 0.350 mol) in toluene (30 mL) was stirred for 6 h at room temperature. To this mixture was added acetic acid (0.099 mL, 1.7 mol). After the solution was stirred for 15 h, a pale yellow solution was concentrated under reduced pressure to remove all volatiles. The resulting residue was dissolved in dichloromethane, and then addition of hexane induced the precipitation of (*S*)-**9c** as a pale yellow powder (122 mg, 33% yield), mp 121 °C (dec). ^{1}H NMR (C_6D_6, 300 MHz, 35 °C): δ 6.19−8.25 (m, 28H, C$_6$*H*$_4$CH$_3$ + *naphthyl*,), 2.01 (s, 3H, C$_6$H$_4$C*H*$_3$), 2.00 (s, 3H, C$_6$H$_4$C*H*$_3$), 1.72 (s, 3H, O$_2$CC*H*$_3$), 1.69 (s, 3H, C$_6$H$_4$C*H*$_3$), 1.62 (s, 3H, C$_6$H$_4$C*H*$_3$). −24.95 (dd, $^{2}J_{P-H}$ = 22, 17 Hz, 1H, Ir−*H*). ^{31}P {^{1}H} NMR (C_6D_6, 121 MHz, 35 °C): δ −3.0 (d, $^{2}J_{P-P}$ = 17 Hz), −3.8 (d). IR (KBr tablet): 2270 cm^{-1} (Ir−H).

IrCl(O$_2$CCH$_3$)(H)[(*S*)-*p*-tolbinap] [(*S*)-9a]: 39% yield, mp >140 °C (dec). ^{1}H NMR (C_6D_6, 300 MHz, 35 °C): δ 6.18−8.25 (m, 28H, C$_6$*H*$_4$CH$_3$ + *naphthyl*,), 2.01 (s, 3H, C$_6$H$_4$C*H*$_3$), 2.00 (s, 3H, C$_6$H$_4$C*H*$_3$), 1.72 (s, 3H, O$_2$CC*H*$_3$), 1.69 (s, 3H, C$_6$H$_4$C*H*$_3$), 1.67 (s, 3H, C$_6$H$_4$C*H*$_3$), −25.39 (dd, $^{2}J_{H-P}$ = 23, 20 Hz, 1H, Ir−*H*). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz, 35 °C): δ −0.8 (d, $^{2}J_{P-P}$ = 17 Hz), −4.3 (d). IR (KBr tablet): 2270 cm^{-1} (Ir−H).

[IrI(O$_2$CCH$_3$)(H){(*S*)-synphos}] [(*S*)-10c]: 94% yield. ^{1}H NMR (CDCl$_3$, 300 MHz, 35 °C): δ 7.14−7.86 (m, 20H, phenyl *H*), 6.32−6.57 (m, 6H, aromatic *H*), 3.81−4.02 (m, 8H, −C*H*$_2$−), 1.63 (s, 3H, O$_2$CC*H*$_3$), −26.39 (dd, $^{2}J_{H-P}$ = 17, 23 Hz, 1H, Ir−*H*). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz, 35 °C): δ −4.22 (d, $^{2}J_{P-P}$ = 16 Hz), −5.80 (d).

Preparation of [{Ir(H)[(*S*)-binap]}$_2$(μ-Cl)$_3$]$^+$Cl$^-$ [(*S*)-8a]. A mixture of [IrCl(coe)$_2$]$_2$ (**6a**) (120.0 mg, 179.0 μmol) and (*S*)-BINAP (239.0 mg, 384.2 μmol) in toluene (5 mL) was stirred for 3 h at room temperature. Upon addition of 35% hydrochloric acid (79 μL), the color of the solution immediately turned to yellow. After the reaction mixture was stirred overnight, all volatiles were removed under reduced pressure. The residue was dissolved in dichloromethane, and then precipitation by hexane afforded (*S*)-**8a** (290.7 mg, 92% yield) as an air-stable pale yellow powder, mp 162 °C (dec). ^{1}H NMR (CDCl$_3$, 300 MHz, 35 °C): δ 6.3−8.1 (m, aromatic, 64H), −22.70 (dd, $^{2}J_{H-P}$ = 15, 21 Hz, 1H, Ir−H). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz, 35 °C): δ −0.4 (d, $^{2}J_{P-P}$ = 20 Hz), −7.9 (d). IR (film): 2269 cm^{-1} (Ir−H). ESI-MS: *m*/*z* 1738 (M$^+$). Conductivity Λ_0 (CH$_2$Cl$_2$): 301.6 S cm^2 mol^{-1}. Anal. Calcd for $C_{88}H_{66}Cl_4Ir_2P_4{\cdot}0.5(CH_2Cl_2)$: C, 58.53; H, 3.72. Found: C, 58.51; H, 3.73.

Preparation of [{Ir(H)[(*S*)-binap]}$_2$(μ-I)$_3$]$^+$I$^-$ [(*S*)-8c]. A reaction mixture of [IrCl(coe)$_2$]$_2$ (**6a**) (33.5 mg, 39.2 μmol) and (*S*)-BINAP (53.7 mg, 86.2 μmol) in toluene (5 mL) was stirred at room temperature, and then aqueous HI (55%, 29 μL) was added via a syringe. After the reaction mixture was stirred overnight at room temperature, all volatiles were removed under reduced pressure. The residue was dissolved in dichloromethane, and then hexane was added to precipitate (*S*)-**8c** (66.0 mg, 79% yield) as an air-stable pale yellow powder, mp 110 °C (dec). This compound contained some impurities. ^{1}H NMR (CDCl$_3$, 300 MHz, −10 °C): δ 6.6−8.4 (m, aromatic, 64H), −19.0 (dd, $^{2}J_{H-P}$ = 11, 18 Hz, 1H, Ir−H). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz, −10 °C): δ −4.6 (m), −12.8 (m). IR (film): 2228 cm^{-1} (broad, Ir−H). ESI-MS: *m*/*z* 2013 (M$^+$). Conductivity Λ_0 (CH$_2$Cl$_2$): 180.2 S cm^2 mol^{-1}. Anal. Calcd for $C_{88}H_{66}I_4Ir_2P_4{\cdot}0.25(CH_2Cl_2)$: C, 49.06; H, 3.10. Found: C, 48.94; H, 2.90.

[{Ir(H)[(*S*)-binap]}$_2$(μ-Br)$_3$]$^+$Br$^-$ [(*S*)-8b]: 95% yield, mp 162 °C (dec). ^{1}H NMR (CDCl$_3$, 300 MHz, 35 °C): δ 6.2−8.2 (m, aromatic, 64H), −21.52 (dd, $^{2}J_{H-P}$ = 14, 16 Hz, 2H, Ir−H). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz, 35 °C): δ −0.9 (d, $^{2}J_{P-P}$ = 19 Hz), −9.2 (d). IR (film): 2268 cm^{-1} (Ir−H). ESI-MS: *m*/*z* 1872 (M$^+$). Conductivity Λ_0 (CH$_2$Cl$_2$): 139.8 S cm^2 mol^{-1}. Anal. Calcd for $C_{88}H_{66}Br_4Ir_2P_4{\cdot}0.25(CH_2Cl_2)$: C, 53.73; H, 3.40. Found: C, 53.63; H, 3.39.

[{Ir(H)[(*S*)-binap]}$_2$(μ-Cl)$_3$]$^+$PF$_6^-$ [(*S*)-8d]: 89% yield. ^{1}H NMR (CDCl$_3$, 300 MHz, 35 °C): δ 6.24−7.98 (m, aromatic, 64H), −22.68 (dd, $^{2}J_{H-P}$ = 14, 16 Hz, 2H, Ir−H). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz, 35 °C): δ −1.5 (d, $^{2}J_{P-P}$ = 17 Hz), −9.0 (d), −144.7 (sep, J_{P-F} = 704 Hz).

[{Ir(H)[(*S*)-binap]}$_2$(μ-Br)$_3$]$^+$PF$_6^-$ [(*S*)-8e]: 96% yield. ^{1}H NMR (CDCl$_3$, 300 MHz, 35 °C): δ 6.22−8.17 (m, aromatic, 64H), −21.51 (dd, $^{2}J_{H-P}$ = 14, 16 Hz, 2H, Ir−H). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz, 35 °C): δ 2.3, (d, $^{2}J_{P-P}$ = 17 Hz), 10.6 (d), −144.8 (sep, J_{P-F} = 704 Hz).

[{Ir(H)[(*S*)-binap]}$_2$(μ-I)$_3$]$^+$PF$_6^-$ [(*S*)-8f]: 96% yield. This compound contained small amount of unidentified compounds. ^{1}H NMR (CDCl$_3$, 300 MHz, 35 °C): δ 6.63−8.36 (m, aromatic, 64H), −19.0 (br, 1H, Ir−H). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz, 35 °C): δ −6.21 (br), −11.9 (br), −144.8 (sep, J_{P-F} = 704 Hz).

[{Ir(H)[(*S*)-tolbinap]}$_2$(μ-I)$_3$]$^+$I$^-$ [(*S*)-11c]: 58% yield. This compound contained small amount of unidentified compounds. ^{1}H NMR (CDCl$_3$, 300 MHz, 35 °C): δ 6.2−8.4 (m, aromatic, 56H), 2.33 (s, C$_6$H$_4$*Me*, 6H), 2.11 (s, C$_6$H$_4$*Me*, 6H), 2.08 (s, C$_6$H$_4$Me, 6H), 1.91 (s, C$_6$H$_4$*Me*, 6H), −19.11 (dd, *J* = 16, 21 Hz, 2H, Ir−H). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz, 35 °C): δ −6.2 (m), −13.6 (m). IR (film): 2222 cm^{-1} (Ir−H). ESI-MS: *m*/*z* 2125 (M$^+$).

[{Ir(H)[(*S*)-synphos]}$_2$(μ-I)$_3$]$^+$I$^-$ [(*S*)-12c]. This compound was in situ generated and characterized by ^{1}H and ^{31}P NMR spectroscopy and contained a small amount of unidentified compounds. ^{1}H NMR (CDCl$_3$, 300 MHz, 35 °C): δ 6.26−8.27 (m, 52H, aromatic *H*), 3.46−4.34 (m, 16H, −C*H*$_2$−), −19.71 (dd, $^{2}J_{H-P}$ = 14, 16 Hz, 2H, Ir−H). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz, 35 °C): δ −6.3 (br), −13.4 (br).

Structure Determination of (*S*)-4a−c and (*S*)-7c. Single crystals of (*S*)-**4a**, (*S*)-**4b**, and (*S*)-**4c**·CH$_2$Cl$_2$ were obtained by crystallization from a mixture of CH$_2$Cl$_2$ and hexane. Single crystals of (*S*)-**7c**·4(C$_6$H$_6$) were obtained by crystallization from benzene. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite-monochromated Mo Kα radiation. Details of X-ray data collections are listed in Table 5. The structures were solved by direct methods with SIR-97[31] and refined against F^2 with SHELXL-97.[32]

The X-ray crystallographic information files, in CIF format, are available from the Cambridge Crystallographic Data Centre on

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Table 5. Crystal Data and Structure Refinement Details for (*S*)-4a, (*S*)-4b, (*S*)-4c·CH$_2$Cl$_2$, and (*S*)-7c·4C$_6$H$_6$

	4a	**4b**	**4c**·CH$_2$Cl$_2$	**7c**·4C$_6$H$_6$
empirical formula	$C_{52}H_{40}ClIrO_2P_2$	$C_{52}H_{40}BrIrO_2P_2$	$C_{53}H_{42}ICl_2IrO_2P_2$	$C_{52}H_{44}IIrP_2{\cdot}4(C_6H_6)$
fw	986.43	1030.89	1162.81	1362.34
temperature (K)	103(1)	100(1)	100(1)	120(1)
wavelength (Å)	0.71069	0.71075	0.71075	0.71075
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1$	$P2_1$	$P2_1$	$P2_1$
a (Å)	13.8788(2)	14.041(5)	11.134(4)	11.3956(4)
b (Å)	15.29428(19)	15.355(5)	15.215(6)	15.9527(7)
c (Å)	10.75023(17)	13.958(5)	13.984(5)	16.7221(8)
β (deg)	112.2875(5)	134.74(2)	106.04(3)	97.047(2)
volume (Å^3)	2111.43(5)	2137.5(13)	2276.8(15)	3016.9(2)
Z	2	2	2	2
D_{calcd} (Mg/m^3)	1.552	1.602	1.696	1.500
abs coeff (mm^{-1})	3.342	4.174	3.839	2.822
F(000)	984	1020	1140	1368
cryst size (mm)	0.36 × 0.19 × 0.17	0.40 × 0.16 × 0.13	0.24 × 0.18 × 0.18	0.60 × 0.18 × 0.13
θ range for data collection (deg)	2.66 to 32.57	3.02 to 32.57	3.03 to 32.51	3.13 to 32.53
limiting indices	$-21 \leq h \leq 21$	$-21 \leq h \leq 21$	$-16 \leq h \leq 16$	$-17 \leq h \leq 17$
	$-23 \leq k \leq 23$	$-22 \leq k \leq 23$	$-22 \leq k \leq 22$	$-24 \leq k \leq 24$
	$-16 \leq l \leq 16$	$-21 \leq l \leq 21$	$-21 \leq l \leq 21$	$-25 \leq l \leq 25$
no. of reflns collected	88 135	91 111	108 564	154 719
no. of unique reflns	15 241	15 322	16 290	21 637
R(int)	0.0530	0.0427	0.0521	0.0781
θ (deg)	32.57	32.57	32.51	32.53
completeness (%)	99.9	99.4	99.4	99.5
abs corr	numerical	numerical	numerical	numerical
max./min. transmn	0.7914/0.5121	0.7754/0.3199	0.7941/0.5402	0.7102/0.3587
refinement method	full-matrix least-squares on F^2			
no. of data/restraints/params	16 290/0/549	15 322/0/522	16 290/0/549	21 637/0/720
goodness-of-fit on F^2	1.039	1.091	1.016	1.133
R_1/wR_2 [$I > 2\sigma(I)$]	0.0228/0.0486	0.0213/0.0458	0.0229/0.0429	0.0337/0.0770
R_1/wR_2 (all data)	0.0250/0.0493	0.0231/0.0462	0.0268/0.0435	0.0391/0.0798
Flack parameter (x)	-0.009(2)	0.012(3)	-0.0014(18)	0.020(3)
Δ/ρ(max./min.) (e·Å^{-3})	0.893/ −0.959	1.020/−1.161	1.225/−1.372	1.695/−1.823

quoting the deposition numbers CCDC 249402 for (*S*)-**4a**, CCDC 249403 for (*S*)-**4b**, CCDC 249404 for (*S*)-**4c**·CH$_2$Cl$_2$, and CCDC 249405 for (*S*)-**7c**·4(C$_6$H$_6$). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or CCD Home Page: http://www.ccdc.cam.ac.uk).

General Procedure for the Ir-Catalyzed Asymmetric Hydrogenation of Cyclic Imines. A Schlenk flask was charged with an imine and a hydrido(carboxylato)iridium(III) complex under argon. Toluene ([iridium complex] = 0.5 mol/L) was added, and then the resulting yellow solution was transferred to a stainless steel autoclave. The autoclave was charged three times by H$_2$ to displace the argon, and subsequently the pressure was increased to 60 kg/cm^2. The reaction mixture in the autoclave was stirred at ambient temperature. After H$_2$ was released, solvent was removed and then Kügelrohr distillation afforded a colorless oil comprised of the starting imine and the resulting amine. The conversions and the enantiomeric excesses were determined by ^{1}H NMR, GC, or HPLC analysis of the crude product or its derivatives.

2-Phenylpyrrolidine. The conversion was determined by ^{1}H NMR and GC analysis of the crude product, and the enantiomeric excess was determined by GC analysis of the trifluoroacetoamide compound obtained by the reaction of the isolated amine with trifluoroacetic anhydride in CH$_2$Cl$_2$ at room temperature. ^{1}H NMR (CDCl$_3$, 35 °C): δ 7.41−7.36 (m, 3H), 7.35−7.19 (m, 2H), 4.12 (t, J = 8 Hz, 1H), 3.24−3.17 (m, 1H), 3.05−2.97 (m, 1H), 2.24−2.13 (m, 1H), 1.97−1.79 (m, 3H including N−*H*), 1.73−1.61 (m, 1H). GC (J&W Scientific DB-1, temp = 100 °C (2 min), 20 °C up per 1 min, and 250 °C): imine t = 5.8 min, amine t = 5.5 min. Chiral GC (GL Science Chirasil DEX-CB, temp = 115 °C): (*S*) t = 24.6 min, (*R*) t = 25.4 min.

2-Phenylpiperidine. The conversion was determined by ^{1}H NMR and GC analysis of the crude product, and the enantiomeric excess was determined by analysis of the trifluoroacetoamide compound obtained by the reaction of the isolated amine with trifluoroacetic anhydride in CH$_2$Cl$_2$ at room temperature. ^{1}H NMR (CDCl$_3$, 35 °C): δ 7.38−7.19 (m, 5H), 3.61−3.56 (m, 1H), 3.22−3.17 (m, 1H), 2.84−2.76 (m, 1H), 1.90−1.86 (m, 1H), 1.83−1.77 (m, 2H), 1.69−1.45 (m, 4H including N−*H*). GC (J&W Scientific DB-1, temp = 100 °C (2 min), 20 °C up per 1 min, and 250 °C): imine t = 6.8 min, amine t = 6.1 min. Chiral GC (GL Science Chirasil DEX-CB, temp = 115 °C): (*S*) t = 32.3 min, (*R*) t = 35.3 min.

1-Aza-2-phenylcycloheptane. The conversion was determined by ^{1}H NMR and GC analysis of the crude product, and the enantiomeric excess was determined by analysis. ^{1}H NMR (300 MHz,CDCl$_3$, 35 °C): 7.37−7.17 (m, 5H), 3.75 (dd, J = 3.7 Hz, 10 Hz, 1H), 3.14 (dt, J = 5, 14 Hz, 1H), 2.92−2.81 (m, 1H), 2.01−1.92 (m, 1H), 1.88−1.55 (m, 8H). GC (J&W Scientific DB-1, temp = 100 °C (2 min), 20 °C up per 1 min, and 250 °C): imine t = 7.5 min, amine t = 7.4 min. Chiral HPLC (Chiralcel OD-H column, hexane, 1.0 mL/min., 254 nm temp = 30 °C): (*R*) t = 16.8 min, (*S*) t = 19.1 min.

Procedure for the Ir-Catalyzed Asymmetric Hydrogenation of 2-Phenylquinoline. The reaction mixture containing iridium complex (*S*)-**12c** (5.4 mg, 0.0025 mmol) in tetrahydrofuran was transferred by a syringe to a dry 10 mL Schlenk, in which I$_2$ (6.35 mg, 0.05 mmol) and 2-phenylquinoline (103 mg, 0.5 mmol) were placed beforehand. This Schlenk was equipped with a magnetic bar and a stopper and connected to a supply of vacuum/argon. The mixture was degassed with three vaccum/argon cycles. The hydrogenation was performed under H$_2$ (initial pressure was 60 kg/cm^2) at 30 °C. After releasing the hydrogen, the reaction mixture was concentrated. The purification was performed by a short silica gel column eluted with a mixture of cyclohexane and EtOAc (98:2) to give the pure product. The enantiomeric excess of the product was determined by chiral HPLC (Chiralcel OJ, Chiralcel OD-H). ^{1}H NMR (CDCl$_3$, 35 °C): δ 2.02−2.11 (1H, m), 2.13−2.20 (1H, m), 2.74−2.81 (1H, m), 2.90−2,96 (1H, m), 4.08 (1H, br), 4.45−4.49 (1H, m), 6.55−6.58 (1H, m), 6.68−6.69 (1H, m), 7.04−7.05 (2H, m), 7.32−7.44 (5H, m). MS (EI): *m*/*z* 209 (M^+). HPLC (Chiralcel OD-H, hexane and i-PrOH (90:10), detector: 254 nm, flow rate: 1 mL/min) (*S*) $t = 9.5$ min, (*R*) $t = 11.0$ min.

Acknowledgment. This research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan. We thank Professor Emeritus K. Tani for fruitful discussions and suggestions.

Supporting Information Available: X-ray structural information for complexes (*S*)-**4a**, (*S*)-**4b**, (*S*)-**4c**·CH_2Cl_2, and (*S*)-**7c**·4(C_6H_6) together with **1b** and **1c**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM051065J