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Chemoselective asymmetric hydrogenation of α,β-unsaturated carbonyl compounds to allylic alcohols catalysed by [Ir(binap)(cod)]BF_4–aminophosphine *

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Abstract

Asymmetric hydrogenation of (*E*)-4-phenyl-3-buten-2-one by use of [Ir(binap)(cod)]BF_4 and *o*-dimethylaminophenyldiphenylphosphine afforded (*E*)-4-phenyl-3-buten-2-ol in 97% chemoselectivity and in 65% enantiomeric excess. A mixed ligand iridium dihydride complex containing both BINAP and the aminophosphine ligand has been shown to be the catalytically active species.

Introduction

In spite of the prominent role played by optically active allylic alcohols in the synthesis of many biologically active compounds, their synthetic methodology by means of asymmetric catalysis has remained largely unestablished. Usually direct hydrogenation of α,β-unsaturated carbonyl compounds catalysed by Wilkinson-type catalysts give rise to saturated ketones and sometimes saturated alcohols [1]. Recently several examples were reported for chemoselective hydrogen transfer reduction of α,β-unsaturated ketones to allylic alcohols using iridium–phosphine, zirconocene, and hafnocene complexes [2]. To our knowledge, the only practical

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* Dedicated to Professor Akio Yamamoto upon his retirement from Tokyo Institute of Technology and in honour of his contributions to organometallic chemistry.

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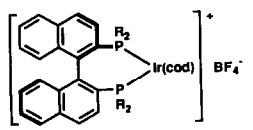
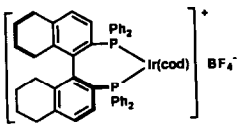
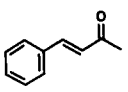


(*R*)-1: R = C_6H_5
(*R*)-2: R = C_6H_{11}



(*S*)-3



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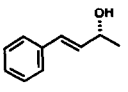
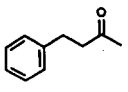


(*R*)-5



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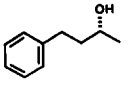
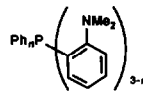
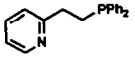


(*R*)-7



8: *n* = 2
9: *n* = 1
10: *n* = 0



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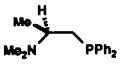


(*S*)-12

13

catalytic method for obtaining optically active allylic alcohols is a kinetic resolution of racemic allylic alcohols by asymmetric hydrogenation using chiral catalysts [3]. We report here a chemoselective asymmetric reduction of the carbonyl function of an α,β-unsaturated ketone, 4-phenyl-3-buten-2-one, catalysed by a new family of Ir–BINAP complexes derived from **1–3** [4*–6] and bidentate, mixed P,N-donor ligands as catalysts [7*].

Results and discussion

We have found that chemoselective asymmetric hydrogenation of (*E*)-4-phenyl-3-buten-2-one (**4**) can be attained in THF by use of [Ir(*R*)-binap)(cod)]BF_4 [(*R*)-**1**] in the presence of 1.5 equiv. of *o*-dimethylaminophenyldiphenylphosphine (**8**) [8] to afford predominantly allylic alcohol (*R*)-**5** (97%) in 65% enantiomeric excess (ee), together with small amounts of the saturated ketone **6** (1.4%), alcohol **7** (1.0%), phenylbuta-1,3-diene (0.4%), and two unidentified byproducts (0.2%) (Table 1, entry 2).

Several cationic Ir- and Rh-complexes have been examined as catalysts for the hydrogenation of **4** (Table 1). The combination of (*R*)-**1** and the hybrid phosphine amine ligand **8** behaved as an effective catalyst for chemoselective asymmetric reduction of the carbonyl function to give allylic alcohol (*R*)-**5** both in aprotic solvents such as toluene (entry 1) and THF (entry 2) and in protic solvents such as

* Reference number with asterisk indicates a note in the list of references.

Table 1

Asymmetric hydrogenation of (*E*)-4-phenyl-3-buten-2-one (**4**) by use of the catalytic systems derived from Ir^+– or Rh^+–BINAP and **8** [a]

Entry	Catalyst	Ligand [b]	s/c [c]	Solvent [d]	Time (h)	Conv. [e] (%)	% of products [e]			ee of **5** [f] (%)
							5	**6**	**7**	
1	(*R*)-**1**	**8**	120	Toluene	42	99	95	0.4	3.6	62 (*R*)
2	(*R*)-**1**	**8**	120	THF	47	72	97	1.4	1.0	65 (*R*)
3	(*R*)-**1**	**8**	110	THF–MeOH	48	76	95	2.9	0.7	62 (*R*)
4	(*R*)-**2**	**8** [g]	120	THF–MeOH	114	100	0.5	61	29	62 (*S*) [h]
5	(*S*)-**3**	**8**	110	THF–MeOH	68	99	92	0	3	49 (*S*)
6	Rh^+ [i]	–	100	THF–MeOH	48	100	0	68	28	–
7	Rh^+ [i]	**8**	90	THF–MeOH	48	87	3	81	12	53 (*R*)

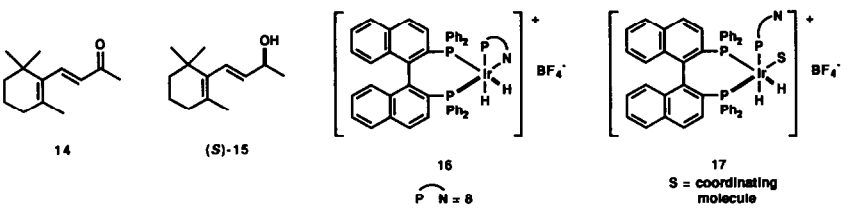
[a] Hydrogenation was carried out in an autoclave (H_2, 50 kg/cm^2) at 60°C. Solvent/substrate ratios (mL/g) were 1–3. [b] Ligand/catalyst ratio (mol/mol) was 1.5. [c] Substrate/catalyst ratio (mol/mol). [d] Ratio of THF and methanol (v/v) was 3:2. [e] As given by GLC analysis. [f] Enantiomeric excess as determined by HPLC analysis with a Chiralcel OD column. The absolute configuration is given in parentheses. [g] A mixture of (*R*)-**2** and **8** in THF and methanol (3:2) was treated with atmospheric pressure of hydrogen before hydrogenation of **4**. [h] Enantiomeric excess of **7** determined by HPLC analysis as for **5**. [i] [Rh((*R*)-binap)(cod)]BF_4.

Table 2

Asymmetric hydrogenation of α,β-unsaturated carbonyl compounds catalysed by various [Ir(binap)]$^+$–auxiliary ligand systems [a]

Entry	Substrate	Catalyst	Ligand [b]	s/c [c]	Time (h)	Conv. [d] (%)	% of products [d]			ee of **5** [e] (%)
							5	**6**	**7**	
1	**4**	(*R*)-**1**	–	130	47	88	1	81	14	–
2	**4**	(*R*)-**1**	(*R*)-BINAP	200	45 [f]	9	1	77	3	–
3	**4**	(*R*)-**1**	**8**	110	48	76	95	3	0.7	62 (*R*)
4	**4**	(*R*)-**1**	**9**	120	48	50	87	8	3	41 (*R*)
5	**4**	(*R*)-**1**	**10**	100	47	32	24	21	4	–
6	**4**	(*R*)-**1**	**11**	200	40 [f]	45	85	11	3	64 (*R*)
7	**4**	(*R*)-**1**	(*S*)-**12**	90	48	11	24	23	3	42 (*R*)
8	**4**	(*S*)-**1**	(*S*)-**12**	100	69	58	11	75	11	12 (*R*)
9	**4**	(*R*)-**1**	**13**	130	42	15	14	43	2	9 (*R*)
10	**4**	(*R*)-**16**	–	170	114 [f]	73	85	4	4	66 (*R*)
11	**14**	(*S*)-**1**	**8**	110	106	100	97 (**15**) [g]			19 (*S*) [h]

[a] Hydrogenation was carried out in an autoclave (H_2, 50 kg/cm^2) in a 3:2 (v/v) mixture of THF–MeOH at 60°C unless otherwise stated. Solvent/substrate ratios (mL/g) were 1–3. [b] Ligand/catalyst ratio (mol/mol) was 1.5 except for entry 2 in which 1 equiv. of (*R*)-BINAP was used. [c] Substrate/catalyst ratio (mol/mol). [d] As given by GLC analysis. [e] Enantiomeric excess as determined by HPLC analysis with a Chiralcel OD column. The absolute configuration is given in parentheses. [f] The reaction was carried out at 30°C. [g] As obtained by ^{1}H NMR analysis. [h] Enantiomeric excess of (*S*)-**15**.



THF–MeOH (entry 3). When [Ir((*S*)-H_8-binap)(cod)]BF_4 [(*S*)-**3**] bearing H_8-BINAP, a more electron-donating BINAP derivative, was used instead of (*R*)-**1**, the chemoselectivity essentially remained high, whereas the enantioselectivity decreased to 49% ee (entry 5). Further increase in basicity of the chiral diphosphine ligand, *i.e.*, use of (*R*)-**2** containing Cy-BINAP [5] in combination with **8**, led to a preferential formation of the saturated ketone **6** and alcohol (*S*)-**7** (62% ee), giving only 0.5% of **5** (entry 4).

Complex [Rh((*R*)-binap)(cod)]BF_4 [9] has also been tested either by itself (entry 6) or in couple with **8** (entry 7) for its efficiency as a catalyst for hydrogenation of **4**. As has been seen for hydrogenation of α,β-unsaturated ketones catalysed by Wilkinson-type catalysts, **6** and **7** were obtained as the major products.

The efficiencies of catalysts for reduction of **4** to **5** are also remarkably dependent on the kinds and structures of auxiliary ligands employed, as shown in Table 2. In the absence of an auxiliary ligand (entry 1) or in the presence of 1 equiv. of (*R*)-BINAP (entry 2), catalysis by (*R*)-**1** favored reduction of **4** to **6** and **7**, forming only 1% of **5**. Moreover, the catalytic activity declined considerably in the latter. When 2-(2′-diphenylphosphinoethyl)pyridine (**11**), a 1,3-P,N-ligand, was employed in pair with (*R*)-**1**, allylic alcohol (*R*)-**5** was produced preferentially (85%) in high enantiomeric excess (64%) (entry 6). Use of bis(*o*-dimethylaminophenyl)phenylphosphine (**9**), a bulkier diamino analogue of **8**, also gave a good chemoselectivity for **5** (87%), but the enantioselectivity was unsatisfactory (41% ee) (entry 4). In the case of tris(*o*-dimethylaminophenyl)phosphine (**10**), an even bulkier triamino analogue of **8**, a remarkable decrease in the chemoselectivity of **5** (**5**:**6**:**7** = 24:21:4) has been observed (entry 5). Since high electron density on Ir(I) can be expected to promote the selective attack of hydrides to the carbonyl group rather than the C=C bond [2a], the decrease in efficiency of the catalysts might be ascribed to the increasing bulkiness of **9** and **10**.

On the other hand, hydrogenation of **4** catalysed by combinations of (*R*)- or (*S*)-**1** and (*S*)-alaphos [(*S*)-**12**], a chiral 1,2-P,N-ligand (entries 7 and 8), or *o*-methoxyphenyldiphenylphosphine (**13**), a P,O-analogue of **8** (entry 9), resulted in low chemo- and enantioselectivities of **5**. A number of other compounds including triphenylphosphine, sparteine, *o*-dimethylaminoanisole, tris(*o*-dimethylaminophenyl)stibine, and tris(*o*-methoxyphenyl)stibine have also been used as the auxiliary ligands to (*R*)-**1** for hydrogenation of **4**. In all cases, however, unsatisfactory results were obtained [**5**:**6**:**7** = (3–12):(52–79):(3–18)].

The above results show that for the asymmetric reduction of **4** to allylic alcohol **5**, combination of a bidentate 1,2- or 1,3-P,N-ligand such as **8** and **11** and a chiral

bis(triarylphosphine)–Ir complex such as (*R*)-**1** is a requisite for obtaining high chemo- as well as enantioselectivities.

As described above, hydrogenation of **4** catalysed by the (*R*)-**2**–**8** system provided saturated alcohol (*S*)-**7** in 62% ee in addition to saturated ketone **6** (Table 1, run 4). Since reduction of **6** with the same catalytic system yielded racemic **7**, allylic alcohol (*S*)-**5** is presumably the primary product in the hydrogenation of **4** which is further reduced to (*S*)-**7**.

β-Ionone (**14**) has also been hydrogenated by use of the catalyst system derived from (*S*)-**1** and **8** to afford (*S*)-**15** in 97% chemoselectivity, but the enantioselectivity is poor (19% ee) (Table 2, run 11).

In order to obtain information about the catalytically active species involved in this hydrogenation reaction, we have separated an iridium dihydride complex from the (*R*)-**1**–**8** system. When a mixture of (*R*)-**1** and **8** was treated with atmospheric pressure of hydrogen in THF, the color of the solution changed from deep red to pale yellow. Addition of hexane to the reaction mixture resulted in precipitation of a pale yellow solid. ^{1}H NMR spectrum of the isolated material in THF-d_8 at room temperature showed two sets of hydride signals centered at δ −8.94 [ddd, J(PH) = 14.0 (*cis*), 25.6 (*cis*), and 130.6 (*trans*) Hz] and −11.41 [ddd, J(PH) = 3.7 (*cis*), 18.9 (*cis*), and 142.8 (*trans*) Hz] [10*], while the ^{31}P{^{1}H} NMR spectrum exhibited three absorptions at δ 12.9 (dd, P_A, J_{AB} = 4.9 and J_{AC} = 15.8 Hz), 10.0 (dd, P_B, J_{BC} = 5.9 Hz), and −0.5 (dd, P_C). Further, the IR spectrum displayed a band at 2304m cm^{-1} which was assigned to ν(Ir–H) [11]. These spectroscopic data, coupled with the preceding results of hydrogenation, indicate that the isolated species might be a P,N-chelate complex of the type **16** possessing a *fac*-geometry defined by three phosphorus atoms. Indeed, tetracoordinated iridium complexes such as [Ir(cod)(*o*-RNHC$_6$H$_4$PPh$_2$)]ClO$_4$ (R = CH$_2$Ph and Et) [12] and hexacoordinated ones such as [IrH$_2$(*o*-(Me)(CH$_2$)NC$_6$H$_4$PPh$_2$)(**8**)] [2a,b], in which the mixed P,N–donor ligands *o*-EtNHC$_6$H$_4$PPh$_2$ and **8** are both chelated to Ir, have recently been reported. In the present case, however, a singlet due to N(CH$_3$)$_2$ appeared at δ 2.58, which is almost the same chemical shift value as that of the free ligand **8** (δ 2.61). The ^{1}H NMR spectrum of the complex measured in CD$_3$OD at −77°C in the presence of excess free **8** also showed one singlet due to N(CH$_3$)$_2$ at δ 2.61. Therefore, coordination of the amine moiety of **8** to Ir in complex **16** still remains uncertain even at low temperature. Moreover, it has also been known that the amine arm of the P,N-chelate in the complex [Ir(cod)(*o*-EtNHC$_6$H$_4$PPh$_2$)]ClO$_4$ can readily be replaced by added coordinating molecules L to give [Ir(cod)(*o*-EtNHC$_6$H$_4$PPh$_2$)L]ClO$_4$ (L = pyridine or acetonitrile) [12]. In addition, THF, methanol, and water can also coordinate to cationic iridium complexes [11c]. These facts led us to propose **17** as an alternative structure for **16** in coordinating solvents [13*]. Interestingly, this isolated dihydride complex also exhibited catalytic activity for asymmetric hydrogenation of **4** to give (*R*)-**5** in 85% chemoselectivity and 66% enantioselectivity (Table 2, run 10), which is in support of the consideration that complex **16** or **17** is the active species involved in the catalytic cycle.

In summary, an appropriate combination of a cationic BINAP–Ir complex and a 1,2- or 1,3-P,N-ligand provides us with a new catalytic system for chemo- and enantioselective hydrogenation of α,β-unsaturated carbonyl compounds such as (*E*)-4-phenyl-3-buten-2-one to the corresponding allylic alcohols.

Experimental

General

Nuclear magnetic resonance [^{1}H (90, 270, and 400 MHz) and ^{31}P (36 and 109 MHz)] spectra were recorded on a JEOL FX90Q, a JEOL JNM-EX270, or a Bruker AM-400 spectrometer with TMS (internal) and 85% phosphoric acid (external) references, respectively. Other spectra were measured on the following instruments: IR, on a Hitachi 295 or a JASCO IR-810; optical rotation, on a JASCO DIP-360. Elemental analyses were performed at the Elemental Analysis Center, Kyoto University. All melting points were determined with a Yanagimoto melting point apparatus and were not corrected.

Gas chromatographic (GLC) analyses were conducted on a Hitachi 263-30 equipped with a flame ionization detector. HPLC analyses were performed with a Shimadzu LC-4A using a SPD-2AS detector.

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out with the standard Schlenk-tube technique under an argon atmosphere purified by passing it through a BASF-Catalyst R3-11 column. THF was distilled from sodium benzophenone ketyl under argon. Hydrocarbon solvents were distilled over calcium hydride. Acetonitrile was distilled from phosphorus pentoxide. Methanol was distilled from magnesium methoxide. Deuterated solvents, THF-d_8, chloroform-d, dichloromethane-d_2, methanol-d_4, and acetone-d_6 were dried over freshly baked molecular sieves (4 Å) and stored in calibrated Schlenk tubes equipped with a J. Young Teflon screwcock. For NMR measurements, these solvents were transferred into the NMR tubes by bulb-to-bulb distillation technique *in vacuo* prior to sealing. (*E*)-4-Phenyl-3-buten-2-one (**4**), β-ionone (**14**), and sparteine sulfate pentahydrate were supplied by Tokyo Kasei Kogyo Co., Inc. and were purified before use. Complex [Ir(cod)$(CH_3CN)_2$]BF_4 was prepared from [Ir(cod)$_2$]BF_4, which in turn was either synthesized by the literature method [14] or purchased from Strem Chemical Co., Inc. and purified by recrystallization from dichloromethane–ether before use. Other compounds, [Rh((*R*)-binap)(cod)]BF_4 [9], *o*-dimethylaminophenyldiphenylphosphine [8], bis(*o*-dimethylaminophenyl)phenylphosphine [8], tris(*o*-dimethylaminophenyl)phosphine [8], 2-(2′-diphenylphosphinoethyl)pyridine [15], (*S*)-alaphos [16], *o*-methoxyphenyldiphenylphosphine [17], dimethylaminoanisole [18], tris(*o*-dimethylaminophenyl)stibine [19] and tris(*o*-methoxyphenyl)stibine [19], were prepared according to the literature methods.

Preparation of [Ir((R)-binap)(cod)]BF_4 [(R)-1]

A solution of [Ir(cod)$(CH_3CN)_2$]BF_4 (245 mg, 0.522 mmol) and (*R*)-BINAP (322 mg, 0.518 mmol) in THF (100 mL) was stirred at room temperature overnight. The olive-green precipitate was removed by filtration through a pad of Celite. The wine-red filtrate was concentrated to about 10 mL, and then to the residue was added ether (20 mL). After 24 h complex (*R*)-**1** (212 mg, 41% yield) was obtained as brown purple crystals; m.p. 209–212°C (dec). ^{1}H NMR (CD_2Cl_2): δ 1.8–2.5 (m, CH_2 of COD and $(CH_2CH_2)_2O$), 3.66–3.77 (m, 0.5 equiv. of $(CH_2CH_2)_2O$), 4.21–4.31 (m, 2H, =CH of COD), 4.46–4.56 (m, 2H, =CH of COD), 6.4–7.8 (m, aromatic protons). ^{31}P NMR ($CDCl_3$): δ 15.1 (s). IR (Nujol): ν_{max} 1055 and 1093

cm^{-1} (BF_4). Anal. Found: C, 60.71; H, 4.59. $C_{52}H_{68}BF_4IrP_2 \cdot (C_4H_8O)_{0.5} \cdot H_2O$ calc.: C, 60.96; H, 4.74%.

Preparation of [Ir((R)-Cy-binap)(cod)]BF_4 [(S)-2]

A mixture of [Ir(cod)$(CH_3CN)_2$]BF_4 (73.8 mg, 0.157 mmol) and (*S*)-(+)-Cy-BINAP (103 mg, 0.159 mmol) in THF (3 mL) was stirred at room temperature for 2 h. The reaction mixture was filtered through a pad of Celite, and the Celite pad was washed with three 1-mL portions of THF. Ether (25 mL) was added to the deep purple combined filtrate after it was concentrated to approx. 2 mL, and the mixture was allowed to stand at ambient temperature for 9 days. The precipitates were collected, washed with ether (4 mL × 3), and dried *in vacuo* at room temperature for 7 h to give (*S*)-**2** (131 mg, 79%) as deep red needles; m.p. 210–216°C (dec). ^1H NMR ($CDCl_3$): δ 0.8–2.4 (m, 52H, aliphatic protons of $4C_6H_{11}$ and COD), 1.23 (t, 0.15 equiv. of $(CH_3CH_2)_2O$, J = 7.02 Hz), 3.48 (q, 0.15 equiv. of $(CH_3CH_2)_2O$), 3.88–4.00 (m, 2H, =CH of COD), 4.77–4.89 (m, 2H, =CH of COD), 7.1–8.3 (m, 12H, aromatic protons). ^{31}P NMR ($CDCl_3$): δ 8.8 (d, J(P1,P2) = 19.7 Hz) and 15.6 (d). IR (Nujol): ν_{max} 1117 and 1071 cm^{-1} (BF_4). Anal. Found: C, 59.52; H, 6.70. $C_{52}H_{68}BF_4IrP_2 \cdot (C_4H_{10}O)_{0.15} \cdot (H_2O)_{0.5}$ calc.: C, 59.93; H, 6.74%.

Preparation of [Ir((R)-H_8-binap)(cod)]BF_4 [(S)-3]

To a yellow suspension of [Ir(cod)$(CH_3CN)_2$]BF_4 (0.64 g, 1.4 mmol) in THF (15 mL) stirred at room temperature a solution of (*S*)-H_8–BINAP (0.86 g, 1.4 mmol) in THF (10 mL) was added dropwise over 10 min. After the mixture was stirred at room temperature for an additional 30 min, it was passed through a pad of Celite. To the deep purple filtrate, ether (300 mL) was added slowly, and the mixture was left to stand at ambient temperature for 60 h. The resulting crystals were separated, washed with ether (30 mL × 3), and dried *in vacuo* at room temperature for 10 h to give (*S*)-**3** (1.30 g, 89%) as deep red plates; m.p. 195–197°C (dec). ^1H NMR ($CDCl_3$): δ 1.19 (t, 0.75 equiv. of $(CH_3CH_2)_2O$, J = 7.02 Hz), 1.16–1.25 (m, H_{7a} and $H_{7'a}$), 1.31 (dt, H_{8a} and $H_{8'a}$, $J_{a,b}$ = 17.15 Hz, $J_{7a,8a} = J_{7b,8a}$ = 5.21 Hz), 1.36–1.46 (m, H_{6a}, $H_{6'a}$, H_{7b}, and $H_{7'b}$), 1.49–1.58 (m, H_{6b} and $H_{6'b}$), 1.77–1.88 (m, H_{8b}, $H_{8'b}$, and 2H of $2CH_2CH_2$ of COD), 1.98–2.12 (m, 4H of $2CH_2CH_2$ of COD), 2.19–2.29 (m, 2H of $2CH_2CH_2$ of COD), 2.36 (ddd, H_{5a} and $H_{5'a}$, $J_{a,b}$ = 17.25 Hz, $J_{5a,6a}$ = 6.03 Hz, $J_{5a,6b}$ = 8.80 Hz), 2.60 (dt, H_{5b} and $H_{5'b}$, $J_{5b,6a} = J_{5b,6b}$ = 5.61 Hz), 3.48 (q, 0.75 equiv. of $(CH_3CH_2)_2O$), 3.94–4.00 (m, 2H, =CH of COD), 4.26–4.33 (m, 2H, =CH of COD), 6.92 (d, H_4 and $H_{4'}$, $J_{3,4}$ = 8.10 Hz), 7.28 (t, 4H, phenyl protons, J = 7.77 Hz), 7.41 (t, 2H, phenyl protons, J = 7.36 Hz), 7.50 (d, H_3 and $H_{3'}$), 7.49–7.58 (m, 14H, phenyl protons). ^{31}P NMR ($CDCl_3$): δ 14.9 (s). IR (Nujol): 1055 and 1093 cm^{-1} (BF_4). Anal. Found: C, 61.25; H, 5.60. $C_{52}H_{52}BF_4IrP_2 \cdot (C_4H_{10}O)_{0.75}$ calc.: C, 61.54; H, 5.59%.

Asymmetric hydrogenation of (E)-4-phenyl-3-buten-2-one (4) catalysed by (R)-1 and 8

This manipulation is illustrative of all Ir^+-catalysed asymmetric hydrogenation of **4**. To a mixture of (*R*)-**1** (10.7 mg, 10.6×10^{-3} mmol), **8** (5.0 mg, 16×10^{-2} mmol), and **4** (175 mg, 1.19 mmol) in an autoclave was added THF/MeOH (3:2, 0.5 mL). Hydrogen gas (50 kg/cm^2) was charged and the mixture was stirred at

60°C for 48 h. Vacuum distillation (100–150°C/ < 0.1 mm) of the reaction mixture gave a colorless oil (150 mg). Composition of the crude products was determined by GLC analysis using a PEG-HT capillary column (0.25 mm i.d. × 25 m; starting from 100°C at a rate of 5°C/min; $t_R = 6.5$ (1-phenylbuta-1,3-diene, 0.4%), 8.7 (unidentified, 0.2%), 10.3 (**6**, 2.2%), 11.2 (unidentified, 0.3%), 12.7 (**7**, 0.5%), 14.9 (**4**, 24.6%), and 16.4 min (**5**, 71.8%)). Conversion of **4** (76%) and product ratios are given in Table 1 (entry 3). The enantiomeric excess (ee) of **5** (62%) was measured by HPLC analysis (column, Daicel Chiralcel OD, 4.6 × 250 mm; hexane/2-propanol, 9:1; flow rate, 0.5 mL/min; $t_R = 23$ [(*R*)-**5**] and 35 min [(*S*)-**5**]). Absolute configuration of **5** was determined by the sign of the optical rotation of **7** obtained upon reduction of **5** [20].

The enantiomeric excess of **7** (62%) was determined on HPLC under the same condition as for **5** ($t_R = 17$ [(*R*)-**7**] and 23 min [(*S*)-**7**]) (Table 1, entry 4).

Asymmetric hydrogenation of 4 catalyzed by [Rh((R)-binap)(cod)]BF_4 and 8

A mixture of [Rh((*R*)-binap)(cod)]BF_4 (13.6 mg, 14.8×10^{-2} mmol), **8** (6.4 mg, 21×10^{-2} mmol), and **4** (198 mg, 1.36 mmol) in THF/MeOH (3:2, 0.5 mL) was stirred in an autoclave under hydrogen (50 kg/cm^2) at 60°C for 48 h. The reaction mixture was distilled *in vacuo* to give a colorless oil (148 mg), which was analyzed in a similar way as described above. The results are given in Table 1 (entry 7).

Hydrogenation catalyzed by [Rh((*R*)-binap)(cod)]BF_4 was performed similarly (Table 1, entry 6).

Asymmetric hydrogenation of β-ionone (14)

Complexes (*R*)-**1** (13.2 mg, 1.31×10^{-2} mmol), **8** (6.0 mg, 2.0×10^{-2} mmol), and **14** (287 mg, 1.49 mmol) were placed in an autoclave and to this was added a 3:2 mixture of THF and methanol (0.75 mL). The mixture was stirred under H_2 (50 kg/cm^2) at 60°C for 106 h. The solvents were evaporated to give an oily residue, whose ^{1}H NMR spectrum showed that the conversion of **14** was 100% and the chemoselectivity of β-ionol (**15**) was 97%. Column chromatography (silica gel, hexane/ethyl acetate 3:1) afforded pure **15** (151 mg, 53%) as a colorless oil. The enantiomeric excess of **15** (19%) was determined by HPLC analysis (Chiralcel OD, 4.6 × 250 mm; hexane/2-propanol, 499:1; flow rate, 0.5 mL/min; $t_R = 68$ [(*S*)-**15**] and 76 min [(*R*)-**15**]). Absolute configuration of (*S*)-**15** was established based on the sign of its optical rotation, $[\alpha]_D^{16}$ −1.52° (*c* 1.22, $CHCl_3$) [21].

Treatment of [Ir((R)-binap)(cod)]BF_4 [(R)-1] with H_2 in the presence of o-dimethylaminophenyldiphenylphosphine (8)

A solution of (*R*)-**1** (209 mg, 0.208 mmol) and **8** (69.0 mg, 0.226 mmol) in THF (10 mL) was treated with H_2 (1.7 kg/cm^2) at room temperature. The color of the mixture changed from red to light yellow within 10 min. Addition of hexane (30 mL) to the reaction mixture caused precipitation of the product, which was separated and dried *in vacuo* to give [IrH_2((*R*)-binap)(**8**)]BF_4 (**16**) (231 mg, 90%) as brown solids; m.p. 207–212°C (dec). ^{1}H NMR (THF-d_8): δ −11.4 (ddd, 1H, $J = 3.7$, 18.9, 142.8 Hz), −8.94 (ddd, 1H, $J = 14.0$, 25.6, 130.6 Hz), 2.58 (s, $N(CH_3)_2$), 6.0–8.0 (m, aromatic protons). ^{31}P NMR (THF-d_8): δ −0.5 (dd, P_C, $J_{AC} = 15.8$ and $J_{BC} = 5.9$ Hz), 10.0 (dd, P_B, $J_{AB} = 4.9$ Hz), 12.9 (dd, P_A). IR (CD_2Cl_2): ν_{max} 2304 cm^{-1} (Ir–H). Anal. Found: C, 61.98; H, 4.62. $C_{64}H_{58}BF_4IrNP_3 \cdot 2H_2O$ calc.: C, 61.53; H, 5.00%.

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