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Synthesis of a new type of P,N-ligand with a spiro skeleton for Ir-catalyzed asymmetric hydrogenations

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Dedicated to Professor Henri Kagan on the occasion of his 80th birthday

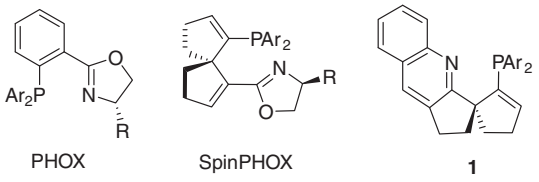
ABSTRACT

A new type of chiral phosphine–quinoline ligand bearing a spiro[4,4]-1,6-nonadiene scaffold was designed and synthesized. Its cationic iridium complex has been characterized by X-ray diffraction analysis and evaluated in the catalytic asymmetric hydrogenation of alkene and imine derivatives, giving the corresponding hydrogenation products with high activity albeit moderate enantioselecitivity.

1. Introduction

The iridium complexes with hybrid P,N-bidentate chiral ligands have been recognized as powerful catalysts in the asymmetric hydrogenation of unfunctionalized alkenes[1] and imines[2] since the pioneering work of Pfaltz et al.[3] on the use of chiral PHOX ligands to mimic Crabtree's catalyst.[4] In this context, a number of chiral P,N-ligands have been developed in recent years by several research groups using a combined phosphine, phosphinite, phosphite, or carbene units with oxazoline or some nitrogen-containing hetero aromatics as the effective chelating moieties.[1] The iridium complexes of these ligands were found to be highly efficient promoting the hydrogenation of a board range of alkenes and imines with high reactivity and excellent enantioselectivity.[1,2,5]

Recently, some chiral ligands based on rigid spiro backbones were found to be highly efficient and enantioselective in transition metal-catalyzed asymmetric reactions.[6,7] In our previous work, a new class of chiral phosphine–oxazoline ligands based on spiro-[4,4]-1,6-nonadiene backbones (SpinPHOX) has been reported to demonstrate excellent asymmetric induction in Ir(I)-catalyzed asymmetric hydrogenation of imines and α,β-unsaturated carboxylic acid derivatives.[8] As an effort toward further exploration of the application of spiro ligands in asymmetric catalysis, herein we report the synthesis of a new type of spiro chiral P,N-ligands **1** and preliminary results on its application in iridium-catalyzed asymmetric hydrogenation of an trisubstituted unfunctionalized alkene and a ketimine.



PHOX SpinPHOX **1**

2. Results and discussion

Spiro[4,4]-1,6-nonadiene-based P,N-ligand **1** was synthesized via a six-step reaction sequence. As shown in Scheme 1, the synthesis of phosphine–quinoline ligand **1** started from (±)-**2**, a racemic *mono*-protected spiro[4,4]-1,6-diketone derivative easily prepared by following a literature procedure.[9] Friedländer condensation of **2** with 2-aminobenzaldehyde in alkaline solution afforded the quinoline derivative **3** in 70% yield. Subsequent deprotection of the ketal moiety of **3** in aqueous CF_3CO_2H solution gave the racemic spiro ketone **4** in 91% yield. Treatment of **4** with LiHMDS followed by quenching with $PhNTf_2$ afforded enol triflate **5** in excellent yield (96%). Pd-catalyzed cross coupling of **5** with $Ph_2P(O)H$ gave a 85% yield of racemic phosphine oxide **6**, which was readily resolved by chiral semi-preparative HPLC (160 mg of (±)-**6** resolved in one shot) to afford both enantiomers in enantiomerically pure forms. One of the enantiomers [(*S*)-**6**] was reduced with $HSiCl_3$ in the presence of a large excess of pyridine, affording the desired chiral ligand (*S*)-**1** in 42% yield.

With the chiral ligand in hand, its cationic iridium(I) complex was easily prepared by following the literature procedure (Scheme 2).[3b] Reaction of the corresponding ligands with $[Ir(cod)Cl]_2$ in CH_2Cl_2 followed by counteranion exchange with $NaBAr_F$ resulted in the formation of complexes (+)-**7** in 87%. Single crystals of the complex (+)-**7** were obtained from slow evaporation of its

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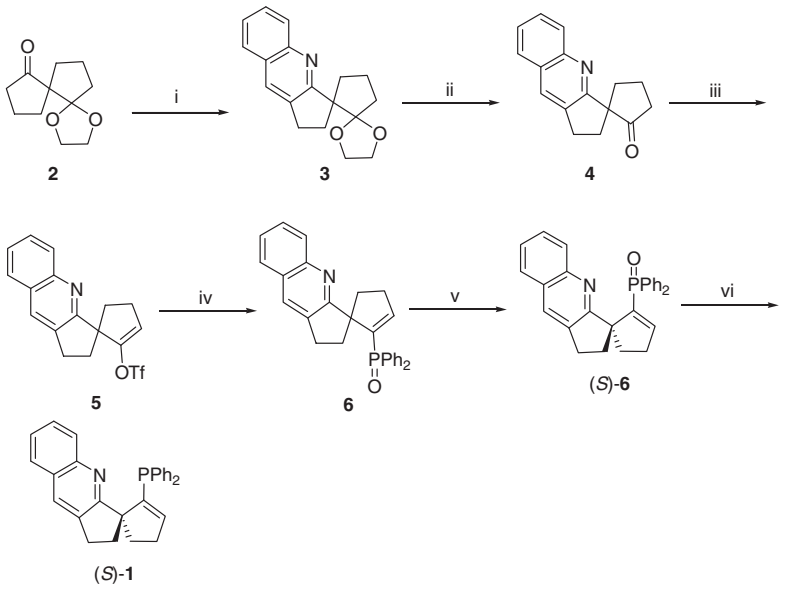
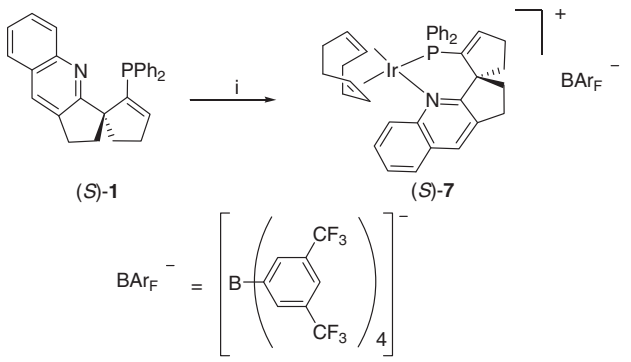


Scheme 1. Synthesis of ligand **1**. Reagents and conditions: (i) 2-aminobenzaldehyde, KOH, EtOH, reflux, 8 h, 70%; (ii) 85% CF_3CO_2H aq, rt, 1 h, 91%; (iii) 1.2 equiv LiHMDS, −78 °C, 1 h; 1.2 equiv $PhNTf_2$, −78 °C to rt, 10 h, 96%; (iv) $Pd(OAc)_2$, dppb, $Ph_2P(O)H$, $(i\text{-Pr})_2NEt$, toluene, 80 °C, 24 h, 85%; (v) resolution on chiral HPLC with a AD-H column (2.0 cm × 25 cm), hexane/*i*PrOH (90:10), 12 mL/min, λ = 254 nm; (vi) $HSiCl_3$, pyridine, benzene, 80 °C, 24 h, 42%.



Scheme 2. Synthesis of iridium complex (*S*)-**7**. Reagents and conditions: (i) $[Ir(cod)Cl]_2$, CH_2Cl_2, reflux, 2 h; $NaBAr_F$, H_2O, rt, 1 h, 86%.

hexane–CH_2Cl_2 solution. As shown in Figure 1, the X-ray diffraction analysis of (+)-**7** disclosed that the absolute configuration of the ligand in the complex is *S* based on the Bijvoet's anomalous dispersion method, thus as its synthetic precursor the absolute configuration of (+)-**6** (Scheme 1) is deduced to be also *S*. The iridium atom was chelated into a six-membered ring with a bite angle (P–Ir–N) of 84.02°, comparable to that observed for Pfaltz's Ir/PHOX complex (85.88°).[10] The bond lengths of Ir–P (2.307 Å) and Ir–N (2.120 Å) in complex (*S*)-**7** are also similar to those found in Ir/PHOX complex (2.305 and 2.097 Å, respectively).[10] Moreover, the two *P*-phenyl groups in (*S*)-**7** adopt the normal axial-equaorial orientations, also observed in Ir/PHOX complex.[10] These structural parameters indicate an overall similar coordination environment of complex (+)-**7** and that of Ir/PHOX complex suggest that similar properties could be expected for both complexes.

Although considerable achievements have been made in the area of asymmetric hydrogenation, the hydrogenation of unfunctionalized olefins and simple imines still remained as great challenges.[1,2] Accordingly, iridium complex (*S*)-**7** was tested in the hydrogenation of 1,2-diphenylpropene **8** and *N*-benzylideneaniline **10** with 1 mol % catalyst loading under 50 atm of H_2 at room tem-

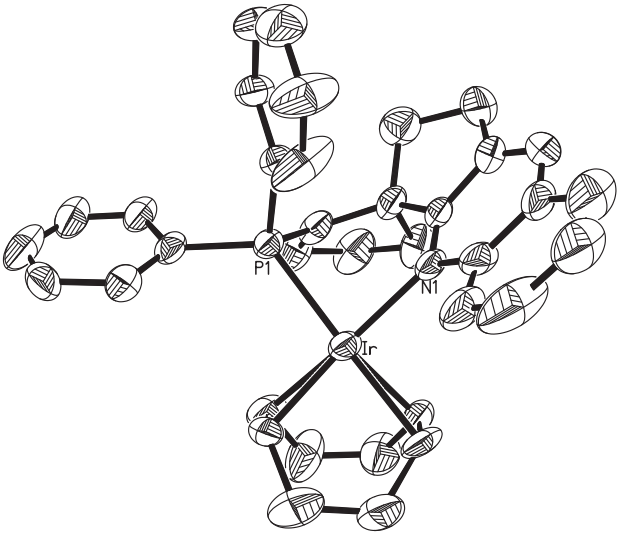
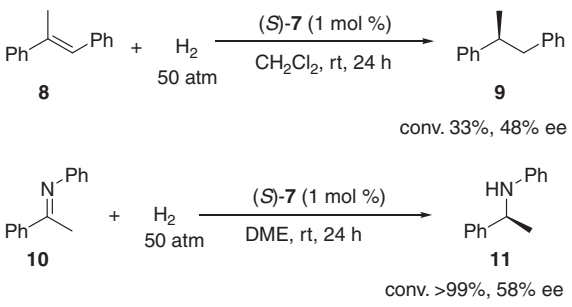


Figure 1. Crystal structure of (*S*)-**7**. The BAr_F^- anion and the hydrogen atoms have been omitted for clarity.



Scheme 3. Asymmetric hydrogenation of olefin **8** and imine **10** catalyzed by chiral iridium complex (*S*)-**7**.

perature, and the results are shown in Scheme 3. Despite the remarkable similarity of (*S*)-**7** with Ir/PHOX complex, however, catalytic activity of (*S*)-**7** is surprisingly low in the hydrogenation of **8**, affording **9** in unsatisfactory conversions and moderate ee values. On the other hand, the hydrogenation reaction for the imine **10** proceeded smoothly with catalyst (*S*)-**7**, affording the amine **11** with full conversion under the experimental conditions. Although the enantioselectivity turns out to be 58% ee in this reaction, the present catalyst with P,N-ligands bearing a spiro skeleton and a quinoline-chelating moiety is obviously promising in the catalysis for further optimization by modifying the quinoline and/or diarylphosphine moieties.

3. Conclusion

In conclusion, a new type of chiral phosphine–quinoline ligand bearing a spiro[4,4]-1,6-nonadiene scaffold has been synthesized, and its cationic iridium complex has been characterized by X-ray diffraction analysis and evaluated in the catalytic asymmetric hydrogenation of alkene and imine derivatives. The complex demonstrated good catalytic activity in the imine hydrogenation, albeit the enantioselecitivity is moderate. The X-ray structure analysis of the complex (*S*)-**7** revealed a similar coordination pattern as that of Ir/PHOX, suggesting that the complex might be promising for further optimization and also effective for other types of asymmetric catalytic reactions.

4. Experimental section

4.1. General

All reactions and manipulations were performed using standard Schlenk techniques with freshly distilled solvents. Melting points were measured on a RY-I apparatus and are uncorrected. ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectra were recorded on Varian Mercury 300 MHz and 400 MHz spectrometers. Chemical shifts (δ values) were reported in parts per million (ppm) downfield from internal TMS (^{1}H NMR) or $CDCl_3$ (^{13}C NMR), external 85% H_3PO_4 (^{31}P NMR) and external CF_3CO_2H (^{19}F NMR), respectively. Optical rotations were determined using a Perkin–Elmer 341 MC polarimeter. The IR spectra were measured on a Bio-Rad FTS-185 FT-IR spectrometer. HRMS(ESI) and HRMS(MALDI) were determined on Waters GCT CA 176 and IonSpect 4.7 TESLA FTMS spectrometers, respectively. Elemental analyses were performed on an Elementar VARIO EL III instrument. HPLC analyses were performed on a JASCO 1580 or JASCO 2089 liquid chromatograph.

4.2. Dispiro[1,3-dioxolane-2,1′-cyclopentane-2′,3″-[3*H*]cyclopenta[*b*]quin oline], 2″,3″-dihydro 3

To a mixture of 1.5 g (7.66 mmol) compound **2** and 1.02 g (8.4 mmol) 2-aminobenzaldehyde in 40 mL ethanol under Ar was added saturated ethanolic KOH (4 mL) dropwise, and the mixture was refluxed for 8 h. After cooling, water was added and the mixture was extracted with EtOAc. The combined organic layers were washed with water and dried over $NaSO_4$. Removal of the solvent gave a crude product, which was purified by chromatography on silica gel with petroleum ether and EtOAc (10:1) as the eluent to afford **3** (1.49 g) as yellow liquid in 70% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.14 (d, *J* = 8.1 Hz, 1H), 7.84 (s, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 3.85–3.75 (m, 2H), 3.63–3.59 (m, 1H), 3.42–3.40 (m, 1H), 3.19–3.11 (m, 1H), 2.95–2.88 (m, 1H), 2.63–2.60 (m, 2H), 2.31–2.26 (m, 1H), 2.07–1.84 (m, 5H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 168.4, 147.9, 136.8, 129.7, 129.6, 127.8, 127.6, 127.2, 125.5, 120.2, 65.2, 64.8, 59.4, 35.8, 34.5, 34.3, 28.4, 19.0 ppm; IR (film) *v* 3054, 2941, 2877, 1622, 1568, 1499, 1434, 1404, 1321, 1140, 1047, 948, 900, 755 cm^{-1}; HRMS (MALDI) *m*/*z*: calcd for $C_{18}H_{20}NO_2$: 282.1489, Found: 282.1492 [M+H$^+$].

4.3. Spiro[cyclopentane-2,3′-[3*H*]cyclopenta[b]quinoline], 2′,3′-dihydro, 1-oxo 4

A mixture of 497 mg (1.77 mmol) compound **3** and 100 mL 85% CF_3CO_2H aqueous solution was heated at 50 °C for 1 h. After cooling to room temperature, the solution was neutralized to pH >7 with solid sodium bicarbonate. Water was added and the mixture was extracted with EtOAc three times. The combined organic layers were washed with brine and dried over $NaSO_4$. Removal of the solvent gave a crude material which was purified by chromatography on silica gel with petroleum ether and EtOAc (10:1) as the eluent to afford **4** (386 mg) as white solid in 91% yield. Mp = 97–99 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 8.4 Hz, 1H), 7.91 (s, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 3.37–3.21 (m, 1H), 3.16–3.01 (m, 1H), 2.71–2.44 (m, 5H), 2.20–2.01 (m, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 220.0, 168.0, 147.8, 135.7, 130.7, 129.1, 128.3, 127.7, 127.4, 125.8, 61.8, 38.1, 36.4, 35.2, 28.2, 19.9 ppm; IR (KBr pellet) *v* 3059, 2970, 2864, 1734, 1622, 1498, 1455, 1440, 1401, 1319, 1163, 1020, 927, 765 cm^{-1}; HRMS (MALDI) *m*/*z*: calcd for $C_{16}H_{16}NO$: 238.1226, found: 238.1238 [M+H$^+$]. Anal. Calcd for ($C_{16}H_{15}NO$ + 0.1(CH_2Cl_2)): C, 78.67; H, 6.23; N, 5.70. Found: C, 78.62; H, 6.54; N, 5.72.

4.4. Trifluoromethanesulfonic acid spiro[2-cyclopentene-1,3′-[3*H*]cyclop enta[*b*]quinoline]-2-yl ester, 2′,3′-dihydro 5

To a solution of 3.49 mL (16.9 mmol) $HN(SiMe_3)_2$ in 60 mL THF under Ar at −78 °C was added 1.6 M *n*-BuLi (6.4 mL, 10.2 mmol) in hexane and the mixture was stirred for 0.5 h at this temperature. To the resulting solution was added slowly a solution of ketone **4** (2.0 g, 8.4 mmol) and $PhNTf_2$ (3.62 g, 10.1 mmol) in 20 mL THF at −78 °C during 20 min. After being stirred for further 1 h at this temperature, the reaction mixture was allowed to warm to room temperature and stand thereafter overnight. The reaction was quenched with saturated sodium bicarbonate solution and the resulting mixture was extracted with EtOAc. The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. The solvent was removed in vacuo, and the residue was purified by chromatography on silica gel column with petroleum ether and EtOAc (50:1–30:1) as the eluent to afford **5** (3.11 g) as a white solid in 96% yield. Mp = 79–80 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.09 (d, *J* = 8.4 Hz, 1H), 7.93 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.64 (dt, *J* = 6.9 Hz, 1.5 Hz, 1H), 7.52–7.46 (m, 1H), 5.91 (t, *J* = 2.4 Hz, 1H), 3.17–3.06 (m, 2H), 2.77–2.71 (m, 1H), 2.63–2.47 (m, 3H), 2.29–2.20 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.1, 151.6, 148.3, 134.5, 131.0, 129.2, 128.4, 127.8, 127.4, 126.0, 116.2, 59.1, 35.9, 35.2, 27.7, 26.4 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ = −74.20 (s) ppm; IR (Film) *v* 3059, 2944, 2858, 2383, 2348, 1653, 1619, 1499, 1420, 1248, 1213, 1140, 1052, 943, 915, 860, 842, 756, 607 cm^{-1}; HRMS (MALDI) *m*/*z*: calcd for $C_{17}H_{15}NO_3F_3S$: 370.0719, found: 370.0729 [M+H$^+$]. Anal. Calcd for $C_{17}H_{14}F_3NO_3S$: C, 55.28; H, 3.82; N, 3.79. Found: C, 55.33; H, 3.89; N, 3.58.

4.5. 2-Diphenylphosphinylspiro[2-cyclopentene-1,3′-[3*H*]cyclopenta[*b*]quinoline], 2′,3′-dihydro 6

To a mixture of 152 mg (0.68 mmol) $Pd(OAc)_2$, 347 mg (0.81 mmol) dppb, 2.5 g (6.93 mmol) enol triflate **5,** and 1.85 g (9.15 mmol) $Ph_2P(O)H$ under Ar was added 25 mL toluene, fol-

lowed by 6 mL DIPEA. The reaction mixture was degassed thrice through freeze-pump-thaw cycles, and was stirred at 80 °C for 24 h. After cooling to room temperature, the mixture was evaporated to dryness, and the residue was subjected to column chromatography with petroleum ether/EtOAc/Et_3N (10:1:0.3–2:1:0.03) as the eluent to afford compound **6** (2.31 g) as a foamy solid in 85% yield. Mp = 76–78 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.89–7.85 (m, 1H), 7.78–7.71 (m, 2H), 7.59–7.53 (m, 2H), 7.49–7.28 (m, 7H), 7.00–6.94 (m, 1H), 6.80–6.74 (m, 2H), 6.33 (dt, J = 10.8 Hz, 2.4 Hz, 1H), 3.26–3.14 (m, 1H), 3.04–2.82 (m, 3H), 2.72–2.55 (m, 2H), 2.31–2.16 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.8, 150.4 (d, J = 13.0 Hz), 147.7, 142.5 (d, J = 98.9 Hz), 135.0, 133.2 (d, J = 103.8 Hz), 131.5, 131.4, 131.3, 131.2, 131.2, 131.1, 130.3, 130.3, 130.0, 128.7, 128.1, 127.9, 127.7, 127.6, 127.1, 127.0, 127.0, 125.2, 64.0 (d, J = 10.4 Hz), 40.7 (d, J = 7.8 Hz), 36.8, 32.9 (d, J = 16.4 Hz), 28.0 ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ = 25.16 (s) ppm; IR (KBr pellet) ν 3053, 2963, 2925, 1592, 1499, 1437, 1426, 1406, 1188, 1119, 1107, 1030, 788, 753, 725, 696, 597, 568, 545, 527, 418 cm^{-1}; HRMS (MALDI) m/z: calcd for $C_{28}H_{25}F_3NOP$: 422.1668, found: 422.1665 [M+H$^+$]. Anal. Calcd for $C_{28}H_{24}F_3NOP$: C, 79.79; H, 5.74; N, 3.32. Found: C, 79.62; H, 5.45; N, 3.06. The resolution of *rac*-**6** was performed with semi-preparative liquid chromatography on a ChiralPak AD-H (2 cm × 25 cm) column. Conditions: hexane/^{i}PrOH = 90:10, flow rate: 12 mL/min, wavelength 254 nm; 40 mg/mL **6** in ethanol, injection volume: 4 mL. t_R = 21.3 min ((*S*)-**6**), t_R = 36.3 min ((*R*)-**6**). (*S*)-**6** $[\alpha]_D^{20}$ = +32.4 (c = 0.53, $CHCl_3$); (*R*)-**6** $[\alpha]_D^{20}$ = −36.1 (c = 0.66, $CHCl_3$).

4.6. (*S*)-2-Diphenylphosphinospiro[2-cyclopentene-1,3′-[3*H*]cyclopenta[*b*] quinoline], 2′,3′-dihydro 1

A mixture of 200 mg (0.48 mmol) (*S*)-**6**, 10 mL benzene, and 0.59 mL (7.1 mmol) pyridine was degassed thrice through freeze-pump-thaw cycles. The mixture was then cooled to 0 °C and 0.24 mL (2.4 mmol) $HSiCl_3$ was added. The reaction mixture was stirred for 0.5 h at 0 °C, and then refluxed for 24 h. After cooling the mixture to room temperature, degassed saturated sodium bicarbonate solution was added to quench the reaction. The resulting mixture was extracted with degassed diethyl ether, and the organic layers were combined and filtered through Celite. The filtrate was evaporated in vacuo, and the residue was purified on silica gel column chromatography eluting with petroleum ether and EtOAc (100:1–50:1), to afford **1** (81 mg) as a colorless oil in 42% yield. $[\alpha]_D^{20}$ = −88.9 (c 0.65, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.94 (d, J = 8.4 Hz, 1H), 7.66–7.54 (m, 3H), 7.42–7.27 (m, 6H), 7.17 (td, J = 8.1 Hz, 2.1 Hz, 2H), 7.02–6.95 (m, 3H), 5.78–5.75 (m, 1H), 3.16–3.08 (m, 1H), 3.00–2.80 (m, 2H), 2.67–2.43 (m, 3H), 2.25–2.07 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.9, 148.1, 146.8, 146.6, 141.8, 136.8, 136.7, 135.64, 135.56, 135.0, 133.9, 133.8, 133.7, 133.6, 130.0, 129.1, 128.4, 128.14, 128.07, 127.9, 127.65, 127.60, 127.5, 127.4, 127.2, 125.2, 64.8, 64.6, 39.4, 37.4, 32.9, 28.52, 28.47 ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ = −22.77 (s) ppm; HRMS (MALDI) m/z: calcd for $C_{28}H_{25}F_3NOP$: 422.1668, found: 422.1667 [M+O+H$^+$].

4.7. (*S*)-2-Diphenylphosphinylspiro[2-cyclopentene-1,3′-[3*H*]-cyclopenta[*b*]quinoline], 2′,3′-dihydro-(η^4-1,5-cyclooctadiene)-iridium(I)tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (*S*)-7

A mixture of 54 mg (0.08 mmol) $[Ir(cod)Cl]_2$ and 65 mg (0.16 mmol) ligands (*S*)-**1** in 6 mL degassed CH_2Cl_2 was refluxed for 2 h. After cooling to room temperature, 185 mg (0.21 mmol) $NaBAr_F$ was added to the mixture. After stirring for 30 min, 5 mL degassed water was added and the resulting mixture was vigorously stirred for 1 h. The organic phase was separated and washed with water. The solvent was removed by vacuum evaporation, and the residue was purified by column chromatography on silica gel with petroleum ether/CH_2Cl_2 (2:1–1:1) as the eluent to afford the complex (*S*)-**7** (212 mg) as an orange powder in 86% yield. Mp = 193–195 °C; $[\alpha]_D^{20}$ = +1.3 (c 0.50, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.42 (d, J = 8.7 Hz, 1H), 7.99 (t, J = 7.5 Hz, 1H), 7.76–7.63 (m, 13H), 7.51 (s, 7H), 7.19–7.11 (m, 1H), 7.05–6.97 (m, 3H), 6.73–6.68 (m, 2H), 4.98–4.91 (m, 1H), 4.71–4.67 (m, 1H), 4.47–4.39 (m, 1H), 3.26–3.21 (m, 1H), 3.08–2.99 (m, 1H), 2.84–2.31 (m, 10H), 2.08–1.63 (m, 5H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 171.6, 161.2 (q, J = 49.5 Hz), 145.4, 143.6 (d, J = 5.6 Hz), 137.3, 134.8, 134.5, 133.0 (d, J = 13.4 Hz), 132.3 (d, J = 2.4 Hz), 131.8 (d, J = 2.5 Hz), 131.3, 131.2, 131.1, 130.4, 130.0, 129.8, 129.7, 129.1 (m), 128.7 (m), 128.4, 128.3, 128.2, 127.9, 127.3, 127.2, 126.5, 126.3, 125.5, 124.8, 122.7, 119.1, 117.4 (m), 88.8 (d, J = 8.7 Hz), 85.3 (d, J = 15.0 Hz), 66.8, 66.6, 65.6, 64.8, 38.5 (d, J = 4.7 Hz), 35.5 (d, J = 4.5 Hz), 34.6, 34.2, 34.0, 31.9, 29.7, 29.6 (m), 29.2, 27.0 (d, J = 2.6 Hz) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ = 17.50 (s) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ = −62.80 (s) ppm; IR (film) ν 2925, 1684, 1653, 1558, 1521, 1457, 1353, 1278, 1161, 1124, 886, 777, 757, 682 cm^{-1}; HRMS (MALDI) m/z: calcd for $C_{36}H_{36}NP^{191}Ir$: 704.2186, found: 704.2162 [M−BAr$_F$]$^+$. Anal. Calcd for $C_{68}H_{48}BF_{24}$-IrNP: C, 52.05; H, 3.08; N, 0.89. Found: C, 51.67; H, 3.15; N, 1.12.

X-ray crystallographic data for (*S*)-**7**, $C_{68}H_{48}BF_{24}IrNP$, M = 1569.05. Crystal (0.327 × 0.265 × 0.230 mm^3) was measured on a Bruker Smart CCD area detector at 293(2) K using Mo-Kα radiation (λ = 0.71073 Å). The integration of the data yielded a total of 20,058 reflections to a maximum 2θ value of 27.00° of which 14,000 were independent. The structure was solved by direct method and refined with the SHELXTL-97 software package using monoclinic space group C_2, with a = 19.2708(12) Å, b = 19.0997(12) Å, c = 18.4687(11) Å; α = 90, β = 95.7260(10), γ = 90°; V = 6763.8(7) Å^3; ρ_{calcd} = 1.541 g/cm^3, Z = 4, R_{int} = 0.0547. Goodness of Fit indicator = 0.927, Final R_1 = 0.0500, wR_2 = 0.1133 on F^2 for observed data, P_{max}, P_{min} = 1.345, −0.489 e Å^{-3}; Absolute structure parameter = −0.002(5). CCDC 767885 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.8. General procedure for the asymmetric hydrogenation of alkenes and imines

Ir complex (*S*)-**7** (0.0015 mmol) and the alkene or imine (0.15 mmol) were dissolved in the reaction solvent (DCM and DME for alkenes and imines, respectively) under argon. The solution was transferred to a stainless steel autoclave under nitrogen atmosphere, and then sealed. After purging with hydrogen for four times, the H_2 pressure inside the autoclave was adjusted to 50 bar. After stirring at room temperature for 24 h, H_2 was released in hood. The conversion was determined by ^{1}H NMR or GC analysis of an aliquot from the crude reaction mixture. The samples used for chiral HPLC determination of ee values were obtained after filtration of the reaction mixture through a pad of silica gel column.

4.8.1. 1,2-Diphenyl-propane 9

33% conversion, 48% ee. The enantiomeric excess was determined by HPLC on Chiralcel OJ column, hexane: isopropanol = 99:1, flowing rate = 0.5 mL/min, UV detection at λ = 254 nm, t_R = 17.1 min (minor), t_R = 25.2 min (major).

4.8.2. *N*-Phenyl-1-phenylethylamine 11

>99% conversion, 58% ee. The enantiomeric excess was determined by HPLC on Chiralcel OD column (hexane: isopropanol = 90:10, flowing rate = 0.5 mL/min, UV detection at λ = 254 nm), t_R = 12.8 min (major), t_R = 16.3 min (minor).

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