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# Unprecedented Reactivity of Iridium(I) Secondary Phosphine Oxide Complexes: Formation of P-Coordinated Phosphinate Complexes by P−Aryl Bond Cleavage

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Aryl−iridium(III) hydride complexes with a P-coordinated phosphinate were formed from $[Ir(cod)Cl]_2$ and secondary phosphine oxide−oxazoline ligands under basic conditions. The structure of these complexes, whose formation involved C−P cleavage, was assigned by X-ray analysis and NMR spectroscopy.

## Introduction

The activation of C−H or C−heteroatom bonds by transition-metal complexes is a well-known process that forms the basis for numerous important synthetic methods.[1] While insertions of metal centers into C−H and C−halogen bonds have been studied extensively,[2,3] analogous oxidative addition reactions involving other C−heteroatom bonds[4] or C−C bonds[5] are far less documented. The literature on insertions into C−P bonds is especially scarce,[6] although the cleavage of P−aryl bonds has been identified as a deactivation mode of transition-metal catalysts with arylphosphine ligands. Examples are Rh- and Co-catalyzed hydroformylations,[7,8] Pd-catalyzed Heck reactions,[9] Ni- and Pd-catalyzed allylic substitutions,[10] and Ir-catalyzed dehydrogenation reactions of cycloalkanes.[11]

Here we report an unusual P−aryl bond cleavage reaction in iridium complexes with a secondary phosphine oxide ligand, leading to iridium hydride complexes with a P-coordinated phenylphosphinate unit.

## Results and Discussion

In the course of our work on Ir-catalyzed asymmetric hydrogenation,[12] we became interested in P,N ligands containing a secondary phosphine oxide (SPO).[13] The ligands **4** and **5** were easily prepared from the corresponding oxazolines **1** and **2** by lithiation and reaction with phenyl(diethylamino)chlorophosphine[14] (**3**) followed by hydrolysis (Scheme 1).

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After column chromatography the air-stable ligands were obtained in yields of 74% (**4**) and 80% (**5**). The diastereoisomers ($S,S_P$)-**5** and ($S,R_P$)-**5** were separated by semipreparative HPLC. The configuration of these compounds was assigned by X-ray analysis.[15]

Iridium complexes of such ligands ([Ir(cod)(SPO^N]-$BAr_F$; $BAr_F$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) proved to be active catalysts in the asymmetric hydrogenation of imines, comparable to analogous [Ir(cod)(PHOX)]$BAr_F$ complexes.[15]

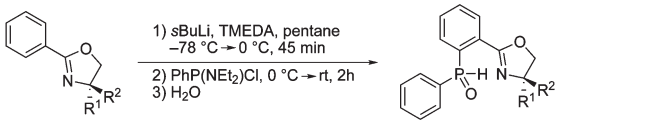
We undertook the preparation of zwitterionic iridium complexes by deprotonation of the corresponding [Ir(cod)-(SPO^N]$^+$ complexes to evaluate their application as hydrogenation catalysts. Although the reaction of the SPO^N ligands and $[Ir(cod)Cl]_2$ in basic methanol gave the desired complexes **6** and **7** (Scheme 2), attempts to isolate these zwitterionic iridium(I) complexes failed. However *rac*-**6**, ($S,R_P$)-**7**, and ($S,S_P$)-**7** could be characterized in solution by $^1H$, $^{13}C$, and $^{31}P$ NMR spectroscopy.

Unfortunately, the zwitterionic complexes were very sensitive and, moreover, their performance in asymmetric hydrogenation was disappointing. However, in our complexation studies we observed the formation of unexpected side products that had undergone drastic changes in the ligand structure. The product composition strongly depended on the conditions and the ligand used for complexation. Whereas ligand **4** was cleanly converted to the corresponding Ir complex **6**, complexation with ligand ($S,S_P$)-**5** or ($S,R_P$)-**5** led to substantial amounts of a side product in addition to the expected complex ($S,R_P$)-**7** or ($S,S_P$)-**7**, respectively.

Reaction of ligand ($S,S_P$)-**5** (1.0 equiv), $[Ir(cod)Cl]_2$ (0.5 equiv), and NaOH (2.5 equiv) in deuterated methanol for 15 min gave two complexes, the expected SPO complex ($S,R_P$)-**7** and an unknown product, as indicated by $^{31}P\{^1H\}$ NMR (Scheme 3). After concentration of the reaction mixture, yellow air-stable crystals were formed in the NMR tube, which according to NMR analysis corresponded to the unknown product. The structure of this complex was elucidated by single-crystal X-ray diffraction (structure **8**, Figure 1).

The iridium atom in this complex is surrounded by a C,N-coordinated phenyloxazoline ligand and a P-coordinated deprotonated phosphinic acid monoester. The remaining three coordination sites in the distorted-octahedral complex are occupied by the P,N-bound SPO ligand ($S,S_P$)-**5** and a deuteride. This unusual structure results from cleavage of the P−aryl bond and formation of a C,N-coordinated Ir(I)-phenyloxazoline complex. The Ir-bound phosphorus moiety is transformed to a phosphinic acid methyl ester by addition of methoxide with concomitant protonation of the Ir(I) atom leading to an Ir(III)−hydride complex (Scheme 4). During this transformation the cod ligand is replaced by a second molecule of the SPO ligand. The deuteride ligand was located in the difference Fourier map. The resonances in the $^2H$ NMR spectrum confirmed the existence of this deuteride (−21.3 ppm) and a phosphinic acid trideuteromethyl ester (2.76 ppm). Furthermore, two doublets consistent with two P ligands in a cis arrangement were observed in the $^{31}P\{^1H\}$ NMR spectrum (53.5 and 49.9 ppm, $^2J_{P,P}$ = 18 Hz) and a

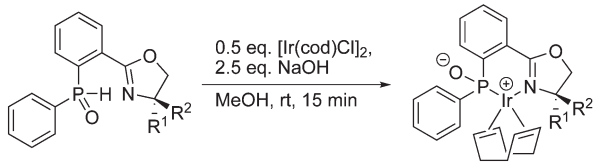
**Scheme 1. Ligand Synthesis**




**1**: $R^1 = R^2$ = Me
**2**: $R^1$ = *t*Bu, $R^2$ = H

**4**: $R^1 = R^2$ = Me (74%)
**5**: $R^1$ = *t*Bu, $R^2$ = H (80%, dr = 1:1)

**Scheme 2. Observed Zwitterionic Iridium(I) Complexes in Solution**




*rac*-**4**: $R^1 = R^2$ = Me
($S,S_P$)-**5**: $R^1$ = *t*Bu, $R^2$ = H
($S,R_P$)-**5**: $R^1$ = *t*Bu, $R^2$ = H

**6**: $R^1 = R^2$ = Me
($S,R_P$)-**7**: $R^1$ = *t*Bu, $R^2$ = H
($S,S_P$)-**7**: $R^1$ = *t*Bu, $R^2$ = H

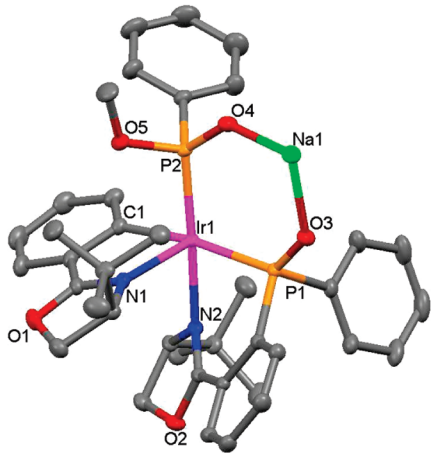
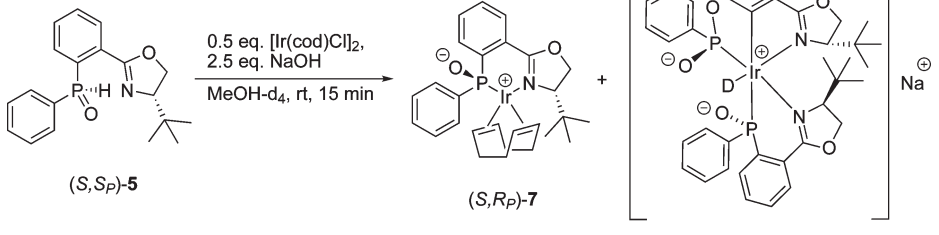



**Figure 1.** Crystal structure of complex (4*S*,4′*S*,1$R_P$,1′$S_P$)-**8** (ellipsoids at the 50% probability level). Solvent molecules and hydrogen atoms are omitted for clarity.

**Scheme 3. Complexation of ($S,S_P$)-5 in MeOH-$d_4$**

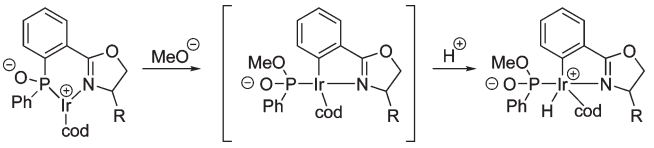



($S,S_P$)-**5**

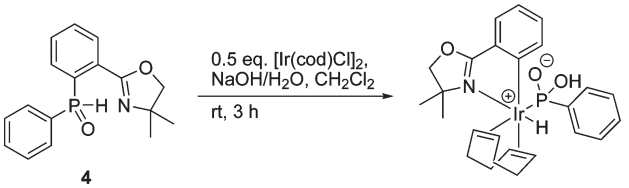
($S,R_P$)-**7**

**8**

**Scheme 4. Proposed Mechanism for the P−Ar Bond Cleavage**



**Scheme 5. Complexation of *rac*-4 under Basic Conditions in $CH_2Cl_2$**




characteristic peak for the Ir−D stretching (2069 $cm^{-1}$) in the IR spectrum. In the solid state, the Ir complex **8** forms a dimeric structure, in which the two sodium ions are connected by two bridging methanol molecules (see the Supporting Information).

An analogous reaction was observed when $[Ir(cod)Cl]_2$ and **4** were reacted in a biphasic mixture of aqueous NaOH and $CH_2Cl_2$ (Scheme 5). The red reaction solution contained several unidentified species, as indicated by $^{31}P$ NMR spectroscopy; thereafter complex **9** was isolated as red highly air-sensitive crystals and analyzed by X-ray diffraction. The solid-state structure of this iridium(III)−hydride complex is shown in Figure 2.

Instead of a deprotonated secondary phosphine oxide and a monomethyl phosphinate anion as in structure **8** (Figure 1), cyclooctadiene and *P*-phenylphosphinate are bound at the metal center of complex **9**. The short O−O distance of 2.53 Å between the two symmetry-related phosphinate groups is an indication of hydrogen bridges in the solid state, resulting in a dimeric structure. Evidence for the prescence of a hydride, which could not be localized by X-ray diffraction, was provided by $^1H$ NMR spectroscopy (−16.43 ppm).

Motivated by these unexpected results, we decided to search for conditions that allowed the synthesis of phosphinate complexes on a preparative scale.

Reaction of 2 equiv of the secondary phosphine oxide ($S$, $S_P$)-**5** or ($S$,$R_P$)-**5**, $[Ir(cod)Cl]_2$, and NaOH in methanol for 2 h at room temperature provided, after column chromatography and recrystallization from $CH_2Cl_2$/hexane, the corresponding iridium hydride complexes in moderate yields of 25% (**10**) and 58% (**11**) (Scheme 6). Characteristic bands for Ir−H streching (2233 $cm^{-1}$ (**10**), 2177 $cm^{-1}$ (**11**)) were observed in the IR spectra. Crystals of complex **11** suitable for X-ray analysis were obtained using a vapor diffusion method (Figure 3). The O−O distance of 2.43 Å is consistent with an intramolecular hydrogen bridge between the phosphinate and the SPO units in the solid state. The prescence of an Ir-bound hydride, which could not be localized by X-ray diffraction, was confirmed by $^1H$ NMR spectroscopy (−21.71 ppm).

The analogous reaction of the racemic ligand **4**, $[Ir(cod)Cl]_2$, and NaOH (Scheme 7) gave after column chromatography the iridium(III) hydride complex **12** in 85% yield as a mixture of four diastereoisomers (49:35:12:4). The four diastereoisomers (each a pair of enantiomers) result from the combination of the stereogenic centers at the two phosphorus atoms and the stereogenic center at the iridium atom. The diastereoisomeric ratio implies a moderately diastereoselective

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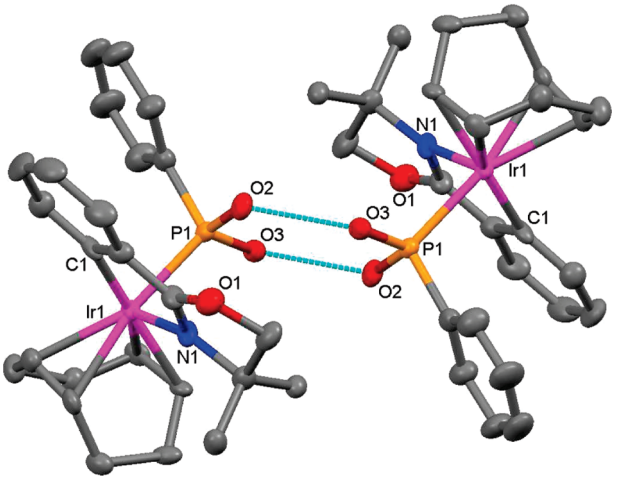



**Figure 2.** Crystal structure of complex **9** (ellipsoids at the 50% probability level). Hydrogen atoms are omitted for clarity.

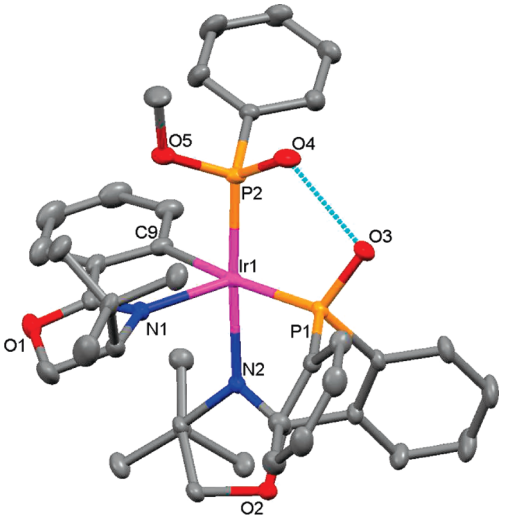
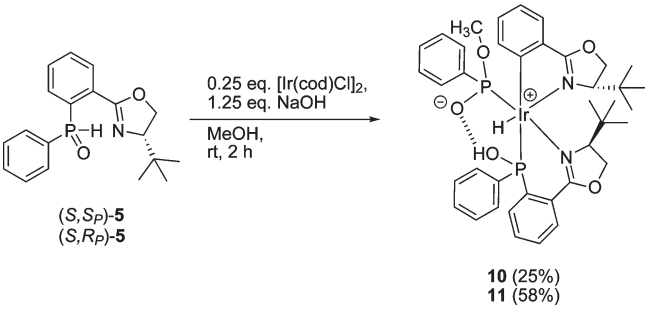



**Figure 3.** Crystal structure of complex (4$S$,4′$S$,1$S_P$,1′$R_P$)-**11** (ellipsoids at the 50% probability level). Hydrogen atoms are omitted for clarity.

**Scheme 6. Optimized Synthesis of Complexes (4$S$,4′$S$,1$R_P$,1′$S_P$)-10 and (4$S$,4′$S$,1$S_P$,1′$R_P$)-11**

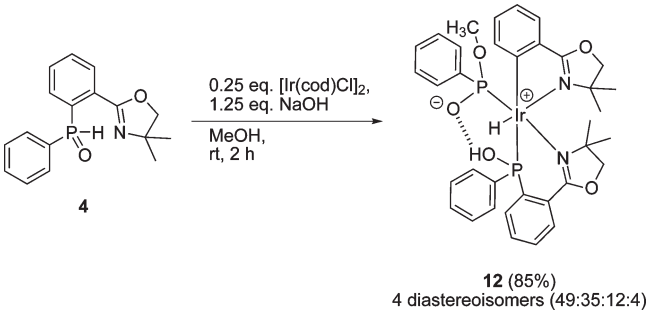


formation of the complexes rather than a statistical combination of the chiral units. By two-dimensional hetereonuclear correlation experiments the $^{1}H$, $^{13}C$, and $^{31}P$ resonances of the phosphorus atoms, the hydrides, and methyl ester groups were assigned to the corresponding diastereoisomer (Table 1). A more detailed interpretation of the complex NMR data was not possible. ESI-MS data (*m*/*z* 823 $[M + H]^{+}$) and elemental analysis were consistent with structure **12**.

## Conclusion

We have shown that zwitterionic iridium(I) complexes with secondary phosphine oxide ligands undergo an unprecedented rearrangement under basic conditions, yielding hydrido−iridium(III) complexes with a P-coordinated phosphinate unit. These complexes are remarkably stable and survive purification by chromatography on silica gel. This unexpected P−aryl bond cleavage reaction, which leads to a hitherto unknown class of Ir−phosphinate complexes, represents a new reactivity pattern of Ir−SPO complexes.

**Scheme 7. Synthesis of Complex 12 (Mixture of Four Diastereoisomers)**




## Experimental Section

**General Comments.** All manipulations were conducted under nitrogen or argon atmosphere, using standard Schlenk or glovebox techniques (MBraun Labmaster 130) except for the synthesis of complex **10**−**12**. Absolute solvents were purchased from Fluka (absolute over molecular sieves), degassed using three freeze−pump−thaw cycles, and stored under argon. Commercial chemicals were used without further purification. Freshly crushed NaOH pellets were weighted in and used immediately for the corresponding reaction. Chloro(diethylamino)phenylphosphine (**3**)[14] and phenyloxazolines **1**[16] and **2**[17] were prepared according to literature procedures.

NMR spectra were recorded on Bruker Avance 400 and 500 MHz NMR spectrometers. NMR spectra are referenced to the residual hydrogen signal of the deuterated solvent ($^{1}H$), to the signals of the deuterated solvent ($^{13}C$), and to the residual deuterium signal of the non-deuterated solvent ($^{2}H$). $^{1}H$ and $^{13}C$ signals were assigned using DEPT135 experiments and two-dimensional correlation experiments (COSY, HMQC, HMBC, NOESY). *pro-S*/*pro-R* are abbreviated by $H_S/H_R$ for stereoheterotopic $CH_2$ groups. IR spectra were measured as KBr pellets on a Perkin-Elmer 1600 FTIR spectrometer or as the pure substance using the ATR technique on a Shimadzu FTIR-8400S instrument. EI-MS spectra were measured on a Finnigan MAT 95Q instrument and ESI-MS on a Varian 1200 L quadrupole MS/MS spectrometer. Microanalytical data were obtained using Leco CHN-900 analyzers. X-ray structural data were collected on a Nonius KappaCCD diffractometer.

**Synthesis of Complex (4*S*,4′*S*,1$R_P$,1′$S_P$)-8.** The secondary phosphine oxide (*S*,$S_P$)-**5** (29.5 mg, 90.1 μmol), 30.3 mg $[Ir(cod)Cl]_2$ (45.1 μmol), and 9.01 mg of NaOH (225 μmol) were dissolved in 2 mL of MeOH-$d_4$, and the mixture was stirred for 15 min at room temperature. The red solution was reduced to 0.4 mL under reduced pressure and analyzed by NMR. Yellow crystals suitable for X-ray analysis formed in the NMR tube after standing for 1 h at room temperature. The red mother liquor was removed, and the residue was dried under high vacuum to give **8** as a yellow solid (4.7 mg, 6%). $^{1}H$ NMR

**Table 1. Assigned NMR Data for the Diastereoisomers of Complex 12 (A−D, 49:35:12:4) in $CD_2Cl_2$ (δ/ppm)[a]**

| | diastereoisomer A | diastereoisomer B |
|---|---|---|
| | $^{1}H$ | |
| IrH | −20.19 (t, $^{2}J_{H,P}$ = 17.8 Hz, $^{2}J_{H,P}$ = 17.8 Hz) | −20.54 (dd, $^{2}J_{H,P}$ = 24.9 Hz, $^{2}J_{H,P}$ = 18.7 Hz) |
| OMe | 3.26 (d, $^{3}J_{H,P}$ = 7.9 Hz) | 3.08 (d, $^{3}J_{H,P}$ = 10.8 Hz) |
| | $^{13}C\{^{1}H\}$ | |
| OMe | 51.0 (d, $^{2}J_{C,P}$ = 7 Hz) | 49.6 (d, $^{2}J_{C,P}$ = 10 Hz) |
| | $^{31}P\{^{1}H\}$ | |
| POMe | 66.0 (dd, $^{2}J_{P,P}$ = 23 Hz, $^{2}J_{H,P}$ = 17 Hz) | 56.1 (t, $^{2}J_{P,P}$ = 23 Hz, $^{2}J_{H,P}$ = 23 Hz) |
| POx | 55.9 (dd, $^{2}J_{P,P}$ = 23 Hz, $^{2}J_{H,P}$ = 18 Hz) | 57.6 (dd, $^{2}J_{P,P}$ = 22 Hz, $^{2}J_{H,P}$ = 18 Hz) |
| | diastereoisomer C | diastereoisomer D |
| | $^{1}H$ | |
| IrH | −20.06 (dd, $^{2}J_{H,P}$ = 18.0 Hz, $^{2}J_{H,P}$ = 14.9 Hz) | −20.46 (dd, $^{2}J_{H,P}$ = 23.6 Hz, $^{2}J_{H,P}$ = 18.8 Hz) |
| OMe | 3.10 (d, $^{3}J_{H,P}$ = 12.1 Hz) | 3.15 (d, $^{3}J_{H,P}$ = 10.6 Hz) |
| | $^{13}C\{^{1}H\}$ | |
| OMe | 50.3 (d, $^{2}J_{C,P}$ = 8 Hz) | 49.5 (d, $^{2}J_{C,P}$ = 10 Hz) |
| | $^{31}P\{^{1}H\}$ | |
| POMe | 62.9 (dd, $^{2}J_{P,P}$ = 19 Hz, $^{2}J_{H,P}$ = 14 Hz) | 55.2 (t, $^{2}J_{P,P}$ = 20 Hz, $^{2}J_{H,P}$ = 20 Hz) |
| POx | 43.6 (t, $^{2}J_{P,P}$ = 18 Hz, $^{2}J_{H,P}$ = 18 Hz) | 44.8 (t, $^{2}J_{P,P}$ = 20 Hz, $^{2}J_{H,P}$ = 20 Hz) |

[a] $^{1}H$ at 500.1 MHz, $^{13}C\{^{1}H\}$ at 125.8 MHz, and $^{31}P\{^{1}H\}$ at 202.4 MHz at 295 K.

(400.1 MHz, $CD_2Cl_2$, 300 K, $\delta$/ppm): 0.15 (s, 9 H, $-C(CH_3)_3$), 0.77 (s, 9 H, $-C(CH_3)_3$), 1.86 (dd, $^3J_{H,H}$ = 9.4 Hz, $^3J_{H,H}$ = 3.1 Hz, 1 H, Ox 4-H), 2.21 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H, Ox 4-H), 3.26 (t, $^2J_{H,H}$ = 8.9 Hz, $^3J_{H,H}$ = 8.9 Hz, 1 H, Ox 5-$H_S$), 3.80 (t, $^2J_{H,H}$ = 9.2 Hz, $^3J_{H,H}$ = 9.2 Hz, 1 H, Ox 5-$H_S$), 3.99 (dd, $^2J_{H,H}$ = 9.1 Hz, $^3J_{H,H}$ = 1.8 Hz, 1 H, Ox 5-$H_R$), 4.38 (dd, $^2J_{H,H}$ = 8.9 Hz, $^3J_{H,H}$ = 3.0 Hz, 1 H, Ox 5-$H_R$), 6.74 ($m_c$, 2 H, Ar H), 6.84 (t, $J_{H,H}$ = 7.8 Hz, 1 H, Ar H), 7.14 ($m_c$, 1 H, Ar H), 7.20 (t, $J_{H,H}$ = 7.1 Hz, 2 H, Ar H), 7.27 (t, $J_{H,H}$ = 6.8 Hz, 2 H, Ar H), 7.33 ($m_c$, 2 H, Ar H), 7.44 ($m_c$, 3 H, Ar H), 7.51 (t, $J_{H,H}$ = 8.1 Hz, 2 H, Ar H), 7.74 (dt, $J_{H,H}$ = 7.5 Hz, $J_{H,H}$ = 0.9 Hz, 1 H, Ar H), 7.92 (dd, $J_{H,H}$ = 7.7 Hz, $J_{H,P}$ = 2.1 Hz, 1 H, Ar H), 8.38 (dt, $J_{H,P}$ = 7.3 Hz, $J_{H,H}$ = 7.3 Hz, $J_{H,H}$ = 0.8 Hz, 1 H, Ar H). $^2$H NMR (76.8 MHz, $CH_2Cl_2$, 295 K, $\delta$/ppm): $-21.3$ (br s, 1 H, IrD), 2.76 (br s, 3 H, $POCD_3$). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CD_2Cl_2$, 300 K, $\delta$/ppm): 53.5 (d, $^2J_{P,P}$ = 19 Hz), 49.9 (d, $^2J_{P,P}$ = 18 Hz). IR (neat, $\tilde{\nu}$/cm$^{-1}$): 3057 w, 2951 w, 2890 w, 2068 w, 1602 s, 1480 m, 1449 m, 1432 m, 1385 w, 1360 m, 1315 w, 1238 m, 1210 w, 1103 m, 1021 s, 955 m, 781 m, 733 s, 690 s.

**Synthesis of Complex *rac*-9.** To a solution of the secondary phosphine oxide *rac*-**4** (74.4 mg, 248 $\mu$mol) and $[Ir(cod)Cl]_2$ (83.5 mg, 124 $\mu$mol) in 3.5 mL $CH_2Cl_2$ was added 3.5 mL of aqueous 1 M NaOH. The biphasic reaction mixture was vigorously stirred for 1 h at room temperature. Then the red organic layer was transferred by a syringe into a 25 mL Schlenk tube. The aqueous phase was extracted once with 5 mL of $CH_2Cl_2$. The combined organic layers were concentrated under reduced pressure and overlaid with pentane. After 3 days at room temperature, the red-green mother liquor was removed through a cannula and the red crystals were washed once with pentane. Crystals suitable for X-ray analysis were embedded into perfluorinated polyether in the glovebox and measured. The residual crystals were dried under high vacuum to afford **9** as a highly air-sensitive, red solid (2 mg, 1%). $^1$H NMR (500.1 MHz, $CD_2Cl_2$, 295 K, $\delta$/ppm): $-16.43$ (d, $^2J_{H,P}$ = 16.2 Hz, 1 H, IrH), 0.08 (s, 6 H, $-C(CH_3)_2$), 2.06 ($m_c$, 1 H, cod C*H*H), 2.26 ($m_c$, 2 H, cod $CH_2$), 2.41 ($m_c$, 4 H, cod $CH_2$), 2.68 ($m_c$, 1 H, cod C*H*H), 3.38 (br s, 1 H, Ox 5-H), 3.95 ($m_c$, 1 H, cod CH), 4.14 (d, $^2J_{H,H}$ = 6.0 Hz, 1 H, Ox 5-H), 4.56 ($m_c$, 1 H, cod CH), 4.77 ($m_c$, 1 H, cod CH), 5.14 ($m_c$, 1 H, cod CH), 6.91 ($m_c$, 2 H, Ar H), 7.00 ($m_c$, 3 H, Ar H), 7.08−7.18 (m, 3 H, Ar H), 7.31 (d, $^3J_{H,H}$ = 7.0 Hz, 1 H, Ar H). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CD_2Cl_2$, 300 K, $\delta$/ppm): 40.5 (s).

**General Procedure for the Preparation of Iridium(III) Hydride Monomethyl Phosphinate Complexes 10−12.** The secondary phosphine oxide (2.0 equiv), $[Ir(cod)Cl]_2$ (0.5 equiv), and NaOH (2.5 equiv) were dissolved in MeOH (0.8 M), and the mixture was stirred at room temperature for 1.5 h under argon and 30 min under air. The solvent was removed under reduced pressure. The residue was purified by column chromatography ($SiO_2$; $CH_2Cl_2 \rightarrow CH_2Cl_2$/MeOH (50:1)) and recrystallized from $CH_2Cl_2$/hexane.

**Complex (4*S*,4′*S*,1*R*$_P$,1′*S*$_P$)-10.** This complex was prepared according to the general procedure from 77.6 mg of the secondary phosphine oxide (*S*,*S*$_P$)-**5** (237 $\mu$mol), 39.8 mg of $[Ir(cod)Cl]_2$ (59.3 $\mu$mol), and 11.9 mg of NaOH (296 $\mu$mol). After chromatography (2 × 10 cm column), **10** was obtained as an air-stable, yellow solid (26.3 mg, 25%). $R_f$ = 0.19 ($SiO_2$, $CH_2Cl_2$). $^1$H NMR (500.1 MHz, $CD_2Cl_2$, 295 K, $\delta$/ppm): $-21.26$ (dd, $^2J_{H,P}$ = 28.9 Hz, $^2J_{H,P}$ = 17.6 Hz, 1 H, IrH), 0.25 (s, 9 H, $-C(CH_3)'_3$), 0.82 (s, 9 H, $-C(CH_3)_3$), 2.08 (dd, $^3J_{H,H}$ = 8.9 Hz, $^3J_{H,H}$ = 1.9 Hz, 1 H, Ox 4-H), 2.45 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, Ox 4′-H), 3.14 (d, $^3J_{H,P}$ = 10.9 Hz, 3 H, $POCH_3$), 3.52 (t, $^2J_{H,H}$ = 8.9 Hz, $^3J_{H,H}$ = 8.9 Hz, 1 H, Ox 5′-H), 3.90 (t, $^2J_{H,H}$ = 9.1 Hz, $^3J_{H,H}$ = 9.1 Hz, 1 H, Ox 5-H), 4.19 (d, $^2J_{H,H}$ = 9.6 Hz, 1 H, Ox 5′-H), 4.49 (dd, $^2J_{H,H}$ = 8.9 Hz, $^3J_{H,H}$ = 2.2 Hz, 1 H, Ox 5-H), 7.01 ($m_c$, 2 H, Ar 4′-H and Ar 5′-H), 7.22 (t, $^3J_{H,H}$ = 6.2 Hz, $^4J_{H,P}$ = 6.2 Hz, 1 H, Ar 3′-H), 7.27 ($m_c$, 3 H, PPh *m*-H and PPh *p*-H), 7.38−7.43 (m, 6 H, Ar 6′-H, PPh *m*-H, PPh *o*-H, and PPh *p*-H), 7.49 ($m_c$, 2 H, PPh *o*-H), 7.58 (t, $^3J_{H,H}$ = 7.7 Hz, 1 H, Ar 5″-H), 7.86 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, Ar 4″-H), 8.08 (dd, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,P}$ = 3.7 Hz, 1 H, Ar 6″-H), 8.28 (t, $^3J_{H,P}$ = $^3J_{H,H}$ = 7.9 Hz, 1 H, Ar 3″-H). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CD_2Cl_2$, 295 K, $\delta$/ppm): 24.7 (s, $-C(CH_3)_3$), 24.8 (s, $-C(CH_3)'_3$), 34.4 (s, $-C(CH_3)_3$), 34.7 (s, $-C(CH_3)'_3$), 49.1 (d, $^2J_{C,P}$ = 9 Hz, $POCH_3$), 70.0 (s, Ox 5′-$CH_2$), 71.1 (s, Ox 5-$CH_2$), 71.5 (s, Ox 4-CH), 74.7 (s, Ox 4′-CH), 121.5 (s, Ar 5′-CH), 126.5 (d, $^3J_{C,P}$ = 4 Hz, Ar 6′-CH), 126.9 (d, $^3J_{C,P}$ = 11 Hz, PPh *m*-CH), 127.0 (d, $^2J_{C,P}$ = 17 Hz, Ar 1″-C), 127.3 (d, $^3J_{C,P}$ = 10 Hz, PPh *m*-CH), 128.5 (s, PPh *p*-CH), 129.1 (s, PPh *p*-CH), 129.8−130.0 (m, 2 C, Ar 4′-CH and Ar 5″-CH), 130.1−130.4 (m, 3 C, Ar 6″-CH, PPh *o*-CH, and PPh *o*-CH), 130.8 (s, Ar 3″-CH), 132.8 (d, $^3J_{C,P}$ = 6 Hz, Ar 4″-CH), 134.3 (s, Ar 1′-C), 140.9 (d, $^2J_{C,P}$ = 37 Hz, Ar 2″-C), 143.1 (s, Ar 3′-CH), 143.8 (d, $^1J_{C,P}$ = 114 Hz, PPh *i*-C), 143.9 (d, $^1J_{C,P}$ = 35 Hz, PPh *i*-C), 165.6 ($m_c$, Ox 2′-C), 170.5−172.6 (m, Ox 2-C), 179.1 (d, $^2J_{C,P_{trans}}$ = 7 Hz, Ar 2′-C). $^{31}P\{^1H\}$ NMR (202.4 MHz, $CD_2Cl_2$, 295 K, $\delta$/ppm): 66.5 (dd, $^2J_{P,P}$ = 22 Hz, $^2J_{P,H}$ = 16 Hz), 62.0 (dd, $^2J_{P,P}$ = 29 Hz, $^2J_{P,H}$ = 20 Hz). IR (KBr, $\tilde{\nu}$/cm$^{-1}$): 3050 w, 2955 s, 2233 w, 1614 s, 1561 w, 1544 w, 1481 m, 1435 m, 1386 m, 1364 m, 1319 w, 1240 m, 1211 w, 1112 s, 1023 s, 957 m, 813 w, 783 w, 737 s, 704 s, 603 w, 492 w. MS (ESI+, $CH_2Cl_2$/MeOH, 10:1): *m*/*z* 879 ($[M+H]^+$). $[\alpha]^D_{20}$ = +350° (*c* = 0.205, $CH_2Cl_2$). Anal. Calcd (found): C, 53.35 (53.67); H, 5.40 (5.35); N, 3.19 (2.91).

**Complex (4*S*,4′*S*,1*S*$_P$,1′*R*$_P$)-11.** This complex was prepared according to the general procedure from 25.8 mg of the secondary phosphine oxide (*S*,*R*$_P$)-**5** (78.8 $\mu$mol), 13.2 mg of $[Ir(cod)Cl]_2$ (19.7 $\mu$mol), and 3.9 mg of NaOH (97.5 $\mu$mol). After chromatography (2 × 10 cm column), **11** was obtained as an air-stable, yellow solid (20.0 mg, 58%). Single crystals suitable for X-ray analysis were grown by slow diffusion of hexane into a saturated solution of complex **11** in $CH_2Cl_2$. $R_f$ = 0.18 ($SiO_2$, $CH_2Cl_2$). $^1$H NMR (500.1 MHz, $CD_2Cl_2$, 295 K, $\delta$/ppm): $-21.71$ (dd, $^2J_{H,P}$ = 25.6 Hz, $^2J_{H,P}$ = 19.1 Hz, 1 H, IrH), 0.24 (s, 9 H, $-C(CH_3)'_3$), 0.59 (s, 9 H, $-C(CH_3)_3$), 3.22 (d, $^3J_{H,H}$ = 6.8 Hz, 1 H, Ox 4′-H), 3.25 (d, $^3J_{H,P}$ = 10.7 Hz, 3 H, $POCH_3$), 3.71 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, Ox 4-H), 4.19 (t, $^2J_{H,H}$ = 8.1 Hz, $^3J_{H,H}$ = 8.1 Hz, 1 H, Ox 5′-H), 4.31 (t, $^2J_{H,H}$ = 8.9 Hz, $^3J_{H,H}$ = 8.9 Hz, 1 H, Ox 5-H), 4.74 (d, $^2J_{H,H}$ = 9.2 Hz, 2 H, Ox 5-H and Ox 5′-H), 6.31 (t, $^3J_{H,H}$ = 6.5 Hz, $^4J_{H,P}$ = 6.5 Hz, 1 H, Ar 3′-H), 6.55 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, Ar 4′-H), 6.91 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, Ar 5′-H), 7.06 (dd, $^3J_{H,P}$ = 10.5 Hz, $^3J_{H,H}$ = 7.9 Hz, 2 H, PPh *o*-H), 7.20 (t, $^3J_{H,H}$ = 6.6 Hz, 2 H, PPh *m*-H), 7.24−7.32 (m, 2 H, 2 PPh *p*-H), 7.35 ($m_c$, 3 H, Ar 5″-H and PPh *m*-H), 7.43 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, Ar 6′-H), 7.57 ($m_c$, 4 H, Ar 4″-H, Ar 6″-H and PPh *o*-H), 8.02 (t, $^3J_{H,P}$ = $^3J_{H,H}$ = 7.9 Hz, 1 H, Ar 3″-H). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CD_2Cl_2$, 295 K, $\delta$/ppm): 24.9 (s, $-C(CH_3)_3$), 26.1 (s, $-C(CH_3)'_3$), 35.7 (s, $-C(CH_3)'_3$), 35.8 (s, $-C(CH_3)_3$), 50.2 (d, $^2J_{C,P}$ = 10 Hz, $POCH_3$), 71.4 (s, Ox 4′-CH), 71.6 (s, Ox 4-CH), 71.8 (s, Ox 5′-$CH_2$), 72.4 (s, Ox 5-$CH_2$), 122.0 (s, Ar 5′-CH), 126.2 (d, $^3J_{C,P}$ = 4 Hz, Ar 6′-CH), 126.8 (s, Ar 3″-CH), 126.9 (d, $^3J_{C,P}$ = 11 Hz, PPh *m*-CH), 128.0 (d, $^2J_{C,P}$ = 19 Hz, Ar 1″-C), 128.3 (d, $^3J_{C,P}$ = 8 Hz, Ar 6″-CH), 128.6 (d, $^3J_{C,P}$ = 9 Hz, PPh *m*-CH), 128.9 (d, $^4J_{C,P}$ = 2 Hz, PPh *p*-CH), 129.1 (d, $^2J_{C,P}$ = 12 Hz, PPh *o*-CH), 129.2 (d, $^4J_{C,P}$ = 1 Hz, Ar 5″-CH), 129.4 (d, $^4J_{C,P}$ = 2 Hz, PPh *p*-CH), 130.5 (d, $^4J_{C,P}$ = 4 Hz, Ar 4′-CH), 131.3 (d, $^2J_{C,P}$ = 10 Hz, PPh *o*-CH), 131.9 (d, $^3J_{C,P}$ = 6 Hz, Ar 4″-CH), 134.1 (s, Ar 1′-C), 143.0 (d, $^1J_{C,P}$ = 97 Hz, PPh *i*-C), 145.1 (d, $^1J_{C,P}$ = 38 Hz, PPh *i*-C), 146.2 (s, Ar 3′-CH), 147.0 (d, $^2J_{C,P}$ = 41 Hz, Ar 2″-C), 167.6−168.5 (m, Ox 2-C), 169.3 ($m_c$, Ox 2′-C), 181.1 (d, $^2J_{C,P_{trans}}$ = 7 Hz, Ar 2′-C). $^{31}P\{^1H\}$ NMR (202.4 MHz, $CD_2Cl_2$, 295 K, $\delta$/ppm): 58.6 (t, $^2J_{P,P}$ = $^2J_{P,H}$ = 22 Hz), 51.5 (t, $^2J_{P,P}$ = $^2J_{P,H}$ = 18 Hz). IR (neat, $\tilde{\nu}$/cm$^{-1}$): 3048 w, 2953 m, 2919 m, 2177 w, 1613 s, 1476 m, 1435 m, 1387 m, 1363 m, 1319 w, 1248 m, 1233 m, 1213 m, 1111s,

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1091 m, 1014 s, 945 s, 731 s, 692 s. MS (ESI+, $CH_2Cl_2$/MeOH (10:1)): $m/z$ 879 ($[M + H]^+$). $[\alpha]^D_{20} = +444°$ ($c$ = 0.209, $CH_2Cl_2$). Anal. Calcd (found): C, 53.35 (53.41); H, 5.40 (5.25); N, 3.19 (2.87).

**Complex 12.** This complex was prepared according to the general procedure from 47.2 mg of the secondary phosphine oxide *rac*-**4** (157 $\mu$mol), 26.5 mg of $[Ir(cod)Cl]_2$ (39.4 $\mu$mol), and 7.88 mg of NaOH (197 $\mu$mol). After chromatography (2 × 16 cm column), **12** was obtained as an air-stable, yellow solid (55.0 mg, 85%). $R_f$ = 0.20 ($SiO_2$, $CH_2Cl_2$). MS (ESI+, $CH_2Cl_2$/MeOH, 10:1): $m/z$ 823 ($[M + H]^+$). Anal. Calcd (found): C, 51.15 (50.86); H, 4.78 (4.80); N, 3.41 (3.15).

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**Supporting Information Available:** Text and figures giving procedures and analytical data for all ligands and complexes and a table, figure, and CIF files giving X-ray crystallographic data for complexes (4*S*,4′*S*,1$R_P$,1′$S_P$)-**8**, *rac*-**9**, and (4*S*,4′*S*,1$S_P$,-1′$R_P$)-**11**. This material is available free of charge via the Internet at http://pubs.acs.org.