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# Synthesis and Catalytic Applications of Chiral Hydridoiridium(III) Complexes with Diamine/Bis(monophosphane) and Diamine/Diphosphane Coordination

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*Dedicated to Professor Gottfried Huttner on the occasion of his 70th birthday*

**Keywords:** Iridium / N ligands / P ligands / Asymmetric catalysis

The $P_2/N_2$-coordinated *cis*-dihydridoiridium(III) chelate complexes (*OC*-6-13)-[$IrH_2(H_2N\cap NH_2)(PR_3)_2$]$BF_4$ [$PR_3$ = $PPh_3$, $H_2N\cap NH_2$ = 1,2-$(H_2N)_2C_6H_4$ (**1a**); (1*R*,2*R*)-$(H_2N)_2C_6H_{10}$ {(*R*,*R*)-dach} (**1b**); (*R*)-2,2′-diamino-1,1′-binaphthyl {(*R*)-dabin} (**1c**); $PR_3$ = P*i*Pr$_3$, $H_2N\cap NH_2$ = (*R*,*R*)-dach (**2a**), (*R*)-dabin (**2b**); $PR_3$ = $PCy_3$, $H_2N\cap NH_2$ = (*R*)-dabin (**3**)] were obtained by treating the respective diamine ligands with labile precursors such as [$IrH_2(OCMe_2)_2(PPh_3)_2$]$BF_4$, [($\eta^4$-1,5-$C_8H_{12}$)Ir($PPh_3$)$_2$]$BF_4$, or [$IrH_5(PR_3)_2$]/$HBF_4$ (R = *i*Pr, Cy). While oxidative addition of HCl to [($\eta^4$-1,5-$C_8H_{12}$)Ir{(*S*,*S*)-bdpcp}]$BF_4$ [(*S*,*S*)-bdpcp = (1*S*,2*S*)-$(Ph_2P)_2C_5H_8$] yields the usual mononuclear adduct [($\eta^4$-1,5-$C_8H_{12}$)Ir(H)(Cl){(*S*,*S*)-bdpcp}]$BF_4$ (**4**), similar treatment of [($\eta^4$-1,5-$C_8H_{12}$)Ir{(*R*)-binap}]$BF_4$ furnishes the triply chlorido-bridged diiridium complex [{(*R*)-binap}$_2$$Ir_2H_2(\mu$-Cl)$_3$]$BF_4$ (**5**). Opening of the μ-Cl bridges of **5** by N,N nucleophiles was used to synthesise the three diamine/(*R*)-binap complexes [Ir(H)(Cl)-($H_2N\cap NH_2$){(*R*)-binap}]$BF_4$ [$H_2N\cap NH_2$ = (1*R*,2*R*)-$H_2NCH(Ph)CH(Ph)NH_2$ {(*R*,*R*)-dpen} (**6a**), (*R*,*R*)-dach (**6b**), and $H_2NCMe_2CMe_2NH_2$ {tmen} (**6c**). Whereas the dihydrides [$IrH_2${(*R*,*R*)-dach}$(PR_3)_2$]$BF_4$ and [$IrH_2${(*R*)-dabin}-$(PR_3)_2$]$BF_4$ (R = *i*Pr, Ph) are only poor (pre)catalysts for the enantioselective hydrogenation of acetophenone, complexes **6a**–**c** catalyze the formation of 1-phenylethanol in good enantiomeric excess [$ee_{max}$ = 82–84 % (*S*)] in the presence of base. The crystal structures of **1a**, **4**, and **5** have been determined. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

## Introduction

We recently[1] described some 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl-coordinated diamine(diphosphane)-rhodium(I) complexes such as [Rh{(*R*,*R*)-$H_2NCH(Ph)CH(Ph)NH_2$}{(*R*)-binap}]$BF_4$ and the like, which were made without difficulty by treating [($\eta^4$-1,5-$C_8H_{12}$)Rh{(*R*)-binap}]$BF_4$ with N,N-chelate ligands under hydrogen. Oxidative addition of HCl led to the rhodium(III) derivative (*OC*-6-43)-[Rh(H)(Cl){(*R*,*R*)-$H_2NCH(Ph)CH(Ph)NH_2$}{(*R*)-binap}]$BF_4$. From a structural point of view, this latter complex can be regarded as an analog of the neutral ruthenium(II) compound (*OC*-6-43)-[Ru(H)(Cl){(*R*,*R*)-$H_2NCH(Ph)CH(Ph)NH_2$}{(*R*)-binap}], which is well known to be an excellent (pre)catalyst for the stereoselective hydrogenation of ketones and imines.[2a]

If activated by a strong base in 2-propanol, the diamine-(diphosphane)rhodium complexes were also found to act as enantioselective catalysts for the reduction of acetophenone, although both their activity and selectivity ($ee_{max.}$ = 71 %)[1] were inferior to those of the established $Ru^{II}$-based systems.[3]

In our search for complexes of the Group 9 transition metals with possibly improved catalytic properties we set out to synthesize and investigate some cationic hydrido compounds of iridium(III) with coordination spheres dominated by (preferentially chiral) diamine and (di)phosphane ligands, namely [$IrH_2(H_2N\cap NH_2)(PR_3)_2$]$BF_4$ (R = Ph, *i*Pr, Cy) and [Ir(H)(X)($H_2N\cap NH_2$)($Ph_2P\cap PPh_2$)]$BF_4$ (X = H or Cl).

## Results and Discussion

### Complexes

Either of the cationic $Ir^I$ or $Ir^{III}$ complexes [($\eta^4$-1,5-$C_8H_{12}$)Ir$(PR_3)_2$]$^+$ and [$IrH_2(OCMe_2)_2(PR_3)_2$]$^+$ (R = Ph),[4] respectively, or the pentahydrides [$IrH_5(PR_3)_2$] (R = *i*Pr, Cy)[5] could be used as starting material for the preparation of the target compounds [$IrH_2(H_2N\cap NH_2)(PR_3)_2$]$^+$. Thus, stoichiometric 1:1 reactions of the solvento complex [Ir-$H_2(OCMe_2)_2(PPh_3)_2$]$BF_4$ with 1,2-phenylenediamine (1,2-phdn) or (1*R*,2*R*)-1,2-diaminocyclohexane [(*R*,*R*)-dach] resulted in smooth replacement of the loosely bound acetone

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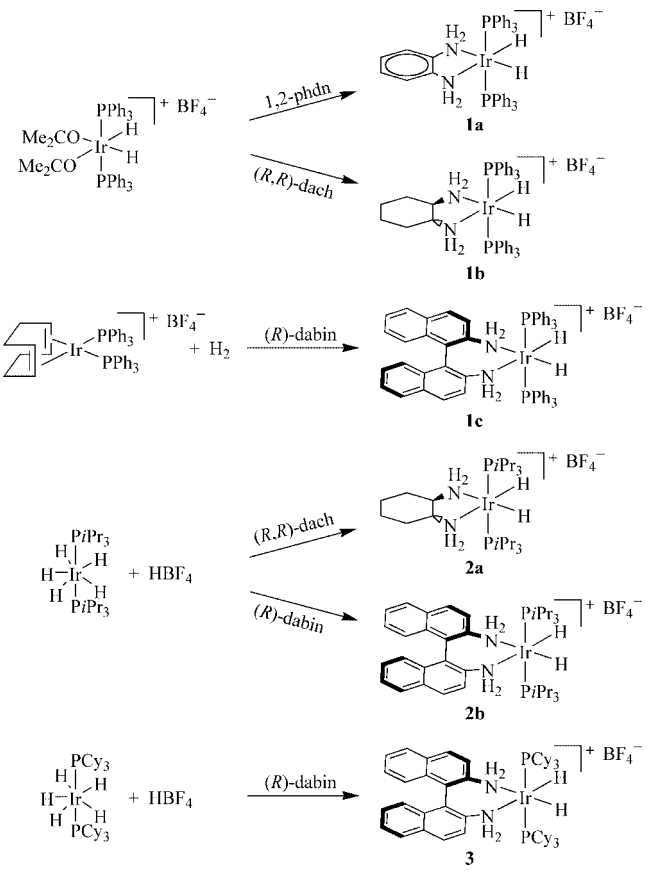
ligands by the two diamines to give $[IrH_2(1,2\text{-phdn})(PPh_3)_2]BF_4$ (**1a**)[6] and $[IrH_2\{(R,R)\text{-dach}\}(PPh_3)_2]BF_4$ (**1b**), as expected (Scheme 1). Since the weakly solvated dihydrides $[IrH_2(solv)_2(PR_3)_2]^+$ are formed in the presence of a coordinating solvent, either by hydrogenation of $[(\eta^4\text{-}1,5\text{-}C_8H_{12})Ir(PR_3)_2]^+$[4] or by protonation of $[IrH_5(PR_3)_2]$ with a strong acid,[4c,5b] both the dieneiridium(I) complexes and the pentahydrides could be employed as precursors as well. For example, treatment of $[(\eta^4\text{-}1,5\text{-}C_8H_{12})Ir(PPh_3)_2]BF_4$ with an equimolar amount of (*R*)-2,2′-diamino-1,1′-binaphthyl [(*R*)-dabin] in $CH_2Cl_2$ under hydrogen gave $[IrH_2\{(R)\text{-dabin}\}(PPh_3)_2]BF_4$ (**1c**) as an additional diamine-containing bis(triphenylphosphane) complex, whereas the triisopropyl- and tricyclohexylphosphane analogues $[IrH_2\{(R,R)\text{-dach}\}(PiPr_3)_2]BF_4$ (**2a**), $[IrH_2\{(R)\text{-dabin}\}(PiPr_3)_2]BF_4$ (**2b**), and $[IrH_2\{(R)\text{-dabin}\}(PCy_3)_2]BF_4$ (**3**) were obtained from $[IrH_5(PiPr_3)_2]$ or $[IrH_5(PCy_3)_2]$ by acidolysis with $HBF_4$ (54% in $Et_2O$) and subsequent reaction with the required diamine in a 1:1 molar ratio (Scheme 1).




Scheme 1. Synthesis of complexes **1**–**3**.

The *OC*-6-13 stereochemistry of compounds **1**–**3** (Scheme 1) follows from the observation of their IrH resonances between $\delta$ = –21 and –27 ppm, which is typical for hydridoiridium(III) complexes with hard donor ligands *trans* to H.[4b] Further confirmation of the coordination geometry depicted in Scheme 1 came from the *cis*-$^2J_{P,H}$ coupling constants of 16–18 Hz found in all cases.

Crystals of $[IrH_2(1,2\text{-phdn})(PPh_3)_2]BF_4$ (**1a**) suitable for an X-ray diffraction study were grown from dichloromethane. As anticipated, the structure determination revealed the presence of N–H···F hydrogen-bonded ion-pairs with the iridium atom in the close to octahedral coordination environment inferred from the NMR spectroscopic data above (Figure 1). The hydride ligands could not be located from the final density maps in any of the structures reported in this paper but were placed, with *d*(Ir–H) restrained to 1.6 Å, at the positions calculated by Orpen's HYDEX energy-minimizing procedure.[7,8] The metal-to-phosphane distances of 2.292(1) and 2.302(1) Å are slightly shorter than, but still comparable to, the Ir–P bond lengths previously reported by Crabtree for the structurally related acetone complex $[IrH_2(OCMe_2)_2(PPh_3)_2]BF_4$ [*d*(Ir–P) = 2.313 and 2.321 Å].[4c] A feature of interest is the coordination of the *ortho*-phenylenediamine ligand, with the two Ir–$NH_2$ distances amounting to 2.163(4) and 2.202(5) Å. The Ir–$NH_2$ linkages of **1a** tend to be longer than the iridium–amine bond lengths of, for example, (*OC*-6-12)-$[IrCl_2\{Me_2P(CH_2)_2NH_2\}_2]PF_6$ [*d*(Ir–$NH_2$) *trans* to Ir–N: 2.090 Å),[9a] (*OC*-6-43)-[Ir(H)(Cl)$\{Ph_2P(CH_2)_2NH_2\}_2$]Cl [*d*(Ir–N) *trans* to Ir–P: 2.136 and 2.137 Å),[10a] and (*OC*-6-13)-$[IrCl_2\{Ph_2P(CH_2)_2NH_2\}_2]BF_4$ [*d*(Ir–N) *trans* to Ir–P: 2.142 and 2.152 Å),[9b] which reflects the high *trans*-bond-weakening influence of the two hydrides opposite to the amine donors.

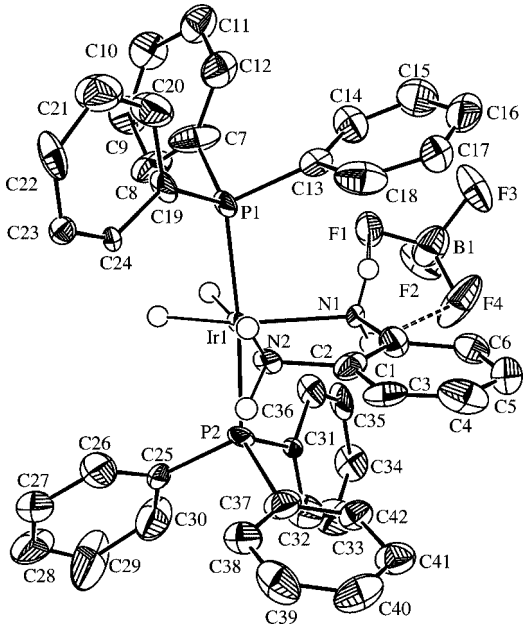


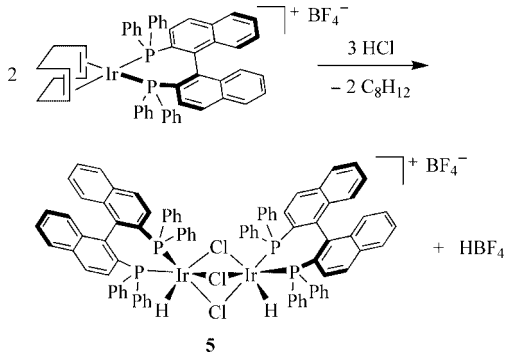

Figure 1. Structure of the ion-pair $[IrH_2(1,2\text{-phdn})(PPh_3)_2]BF_4$ (**1a**); phenyl H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir1–P1 2.302(1), Ir–P2 2.292(1), Ir–N1 2.163(4), Ir–N2 2.202(5); P1–Ir–P2 174.37(6), P1–Ir–N1 93.5(1), P1–Ir–N2 90.8(1); hydrogen-bonding interactions (D–H, H···A, D···A [Å], D–H···A [°]): N1–H···F1 0.92, 2.27, 2.854(5), 121.1; N1–H···F4 0.92, 2.42, 2.997(6), 120.5; N2–H···F2_#1 0.92, 2.17, 2.863(7), 131.2; N2–H···F3_#1 0.92, 2.37, 3.001(6), 125.3. Symmetry transformation used to generate equivalent atoms: #1 = $x$ + 1/2, $y$ + 1/2, $z$.

In exploratory studies aimed at synthesizing the $P_2/N_2$-coordinated hydride complexes $[Ir(H)(X)(H_2N\cap NH_2)(Ph_2P\cap PPh_2)]BF_4$ (X = H, Cl), which have one chiral bidentate rather than two achiral monodentate phosphorus ligands, two diene(diphosphane) complexes $[(\eta^4\text{-}1,5\text{-}C_8H_{12})Ir(Ph_2P\cap PPh_2)]BF_4$ {$Ph_2P\cap PPh_2$ = (*R*)-binap[11] and (1*S*,2*S*)-1,2-bis(diphenylphosphanyl)cyclopentane [(*S*,*S*)-bdpcp]} were selected as potential starting materials. As mentioned by way of introduction, related rhodium chemistry has shown that the bis(chelates) $[Rh(H_2N\cap NH_2)\{(R)\text{-binap}\}]BF_4$ {$H_2N\cap NH_2$ = $H_2NCMe_2CMe_2NH_2$ (tmen), (1*R*,2*R*)-$H_2NCH(Ph)CH(Ph)NH_2$ [(*R*,*R*)-dpen], or (1*R*,2*R*)-1,2-$(H_2N)_2C_6H_{10}$ [(*R*,*R*)-dach]} are smoothly formed when $[(\eta^4\text{-}1,5\text{-}C_8H_{12})Rh\{(R)\text{-binap}\}]BF_4$ is hydrogenated in the presence of the required diamine ligand.[1] In view of the greater stability of the Ir–H bond than the Rh–H bond, we expected that similar treatment of the diene(diphosphane) iridium precursors $[(\eta^4\text{-}1,5\text{-}C_8H_{12})Ir(Ph_2P\cap PPh_2)]BF_4$ would result in the formation of mixed-ligand complexes $[IrH_2(H_2N\cap NH_2)(Ph_2P\cap PPh_2)]BF_4$ by oxidative addition of dihydrogen to initially formed $[Ir(H_2N\cap NH_2)(Ph_2P\cap PPh_2)]BF_4$ intermediates. However, only mixtures of various hydride-containing complexes were produced, from which none of the hoped-for compounds could be isolated.

Expecting that it might be easier to substitute the hard nitrogen donors for the σ,π-bonded diolefin ligand at the $Ir^{III}$ rather than the $Ir^{I}$ oxidation stage, we prepared the complex $[(\eta^4\text{-}1,5\text{-}C_8H_{12})Ir(H)(Cl)\{(S,S)\text{-bdpcp}\}]BF_4$ (**4**) by oxidative addition of hydrogen chloride to its $[(\eta^4\text{-}1,5\text{-}C_8H_{12})Ir\{(S,S)\text{-bdpcp}\}]BF_4$ precursor. Compound **4** was shown by NMR spectroscopy, together with an X-ray structure analysis, to bear *trans*-bonded chlorido and hydrido ligands. The structure consists of discrete $[(\eta^4\text{-}1,5\text{-}C_8H_{12})Ir(H)(Cl)\{(S,S)\text{-bdpcp}\}]^+$ cations (Figure 2) and $BF_4^-$ anions. The Ir–Cl bond *trans* to the hydride is long at 2.490(4) Å,[12] which is entirely consistent with the strong *trans* influence of hydrido ligands.

In contrast to the "normal" oxidative addition of HCl to $[(\eta^4\text{-}1,5\text{-}C_8H_{12})Ir\{(S,S)\text{-bdpcp}\}]BF_4$, the reaction of hydrogen chloride with $[(\eta^4\text{-}1,5\text{-}C_8H_{12})Ir\{(R)\text{-binap}\}]BF_4$ did not lead to a mononuclear $Ir^{III}$ complex but instead gave the triply chlorido-bridged binuclear product $[\{(R)\text{-binap}\}_2Ir_2H_2(\mu\text{-}Cl)_3]BF_4$ (**5**) (Scheme 2). It is well known that $Ir^{III}$ has a pronounced tendency to form cationic[13] confacial-bioctahedral structures held together by three connecting mononegative donors such as halide, hydride, alkoxide, amide, and the like. Reported examples include the (*R*)-binap-coordinated complexes $[\{(R)\text{-binap}\}_2Ir_2H_2(\mu\text{-}OR)_2(\mu\text{-}Cl)]Cl$ (R = H, $CH_3$), which were obtained by oxidative addition of the O–H bonds of water and methanol




Scheme 2. Formation of diiridium complex **5**.

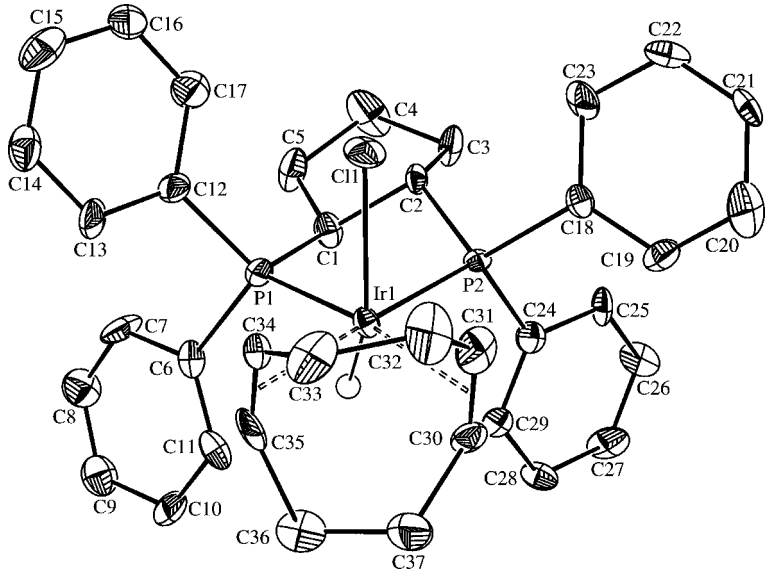



Figure 2. Structure of the cation of $[(\eta^4\text{-}1,5\text{-}C_8H_{12})Ir(H)(Cl)\{(S,S)\text{-bdpcp}\}]BF_4$ (**4**); carbon-bonded H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir–Cl1 2.490(4), Ir–P1 2.332(4), Ir–P2 2.319(4); Cl1–Ir–P1 88.8(1), Cl1–Ir–P2 84.0(1), P1–Ir–P2 85.5(1).

to [{(*R*)-binap}$_2$Ir$_2$(μ-Cl)$_2$],[13h] as well as the recently described halide salts [{(*S*)-binap}$_2$Ir$_2$H$_2$(μ-X)$_3$]X (X = Cl, Br, I), which were formed by sequential treatment of [(η$^2$-C$_8$H$_{14}$)$_4$Ir$_2$(μ-Cl)$_2$] first with the chelate phosphane and then with aqueous HX.[13p]

We propose that [(η$^4$-1,5-C$_8$H$_{12}$)Ir{(*R*)-binap}]BF$_4$ reacts with hydrogen chloride to initially give an HCl adduct similar to **4**, where the greater bulkiness of the two "Ph$_2$Pnaphthyl" binap building blocks than that of the two "Ph$_2$Palkyl" halves of the chelate ring in the mononuclear complex

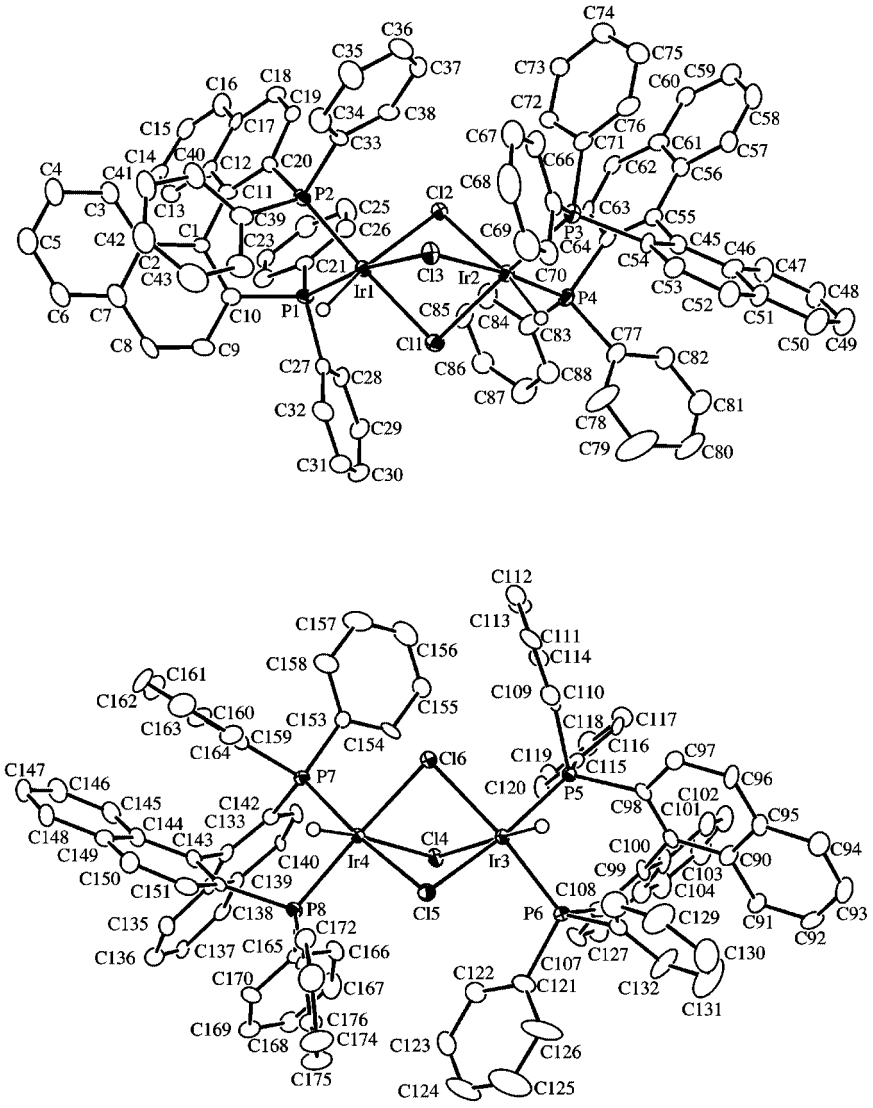


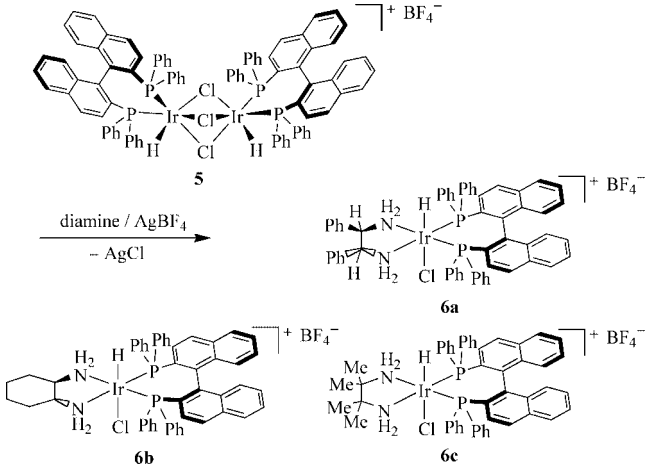

Figure 3. Structures of the two crystallographically independent cations of [{(*R*)-binap}$_2$Ir$_2$H$_2$(μ-Cl)$_3$]BF$_4$ (**5**); aryl H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] for cation I: Ir1–Cl1 2.470(1), Ir1–Cl2 2.534(1), Ir1–Cl3 2.428(1), Ir1–P1 2.251(1), Ir1–P2 2.257(1), Ir2–Cl1 2.436(1), Ir2–Cl2 2.532(1), Ir2–Cl3 2.458(1), Ir2–P3 2.252(1), Ir2–P4 2.245(1); Cl1–Ir1–Cl2 78.99(4), Cl1–Ir1–Cl3 79.37(5), Cl1–Ir1–P1 94.37(5), Cl1–Ir1–P2 173.17(5), Cl2–Ir1–Cl3 79.27(4), Cl2–Ir1–P1 106.40(5), Cl2–Ir1–P2 100.72(5), Cl3–Ir1–P1 170.74(5), Cl3–Ir1–P2 93.85(5), P1–Ir1–P2 92.26(5), Cl1–Ir2–Cl2 79.65(4), Cl1–Ir2–Cl3 79.45(5), Cl1–Ir2–P3 170.01(5), Cl1–Ir2–P4 94.66(5), Cl2–Ir2–Cl3 78.77(4), Cl2–Ir2–P3 106.54(5), Cl2–Ir2–P4 100.37(5), Cl3–Ir2–P3 93.89(5), Cl3–Ir2–P4 174.11(5), P3–Ir2–P4 91.94(5), Ir1–Cl1–Ir2 86.10(1), Ir1–Cl2–Ir2 82.76(1), Ir1–Cl3–Ir2 86.52(1). Selected dihedral angles, given as (plane)/(plane) [°]: (Ir1,Cl1,Cl2)/(Ir2,Cl1,Cl2) 58.43(4), (Ir1,Cl1,Cl3)/(Ir2,Cl1,Cl3) 54.49(5), (Ir1,Cl2,Cl3)/(Ir2,Cl2,Cl3) 58.44(4), (Ir1,Cl1,Ir2)/(Ir1,Cl2,Ir2) 61.00(1), (Ir1,Cl1,Ir2)/(Ir1,Cl3,Ir2) 57.72(1), (Ir1,Cl2,Ir2)/(Ir1,Cl3,Ir2) 61.28(1), (naphthyl C1–C10)/(naphthyl C11–C20), 76.1(1); (naphthyl C45–C54)/(naphthyl C55–C64), 67.7(1). Corresponding parameters for cation II: Ir3–Cl4 2.530(1), Ir3–Cl5 2.426(1), Ir3–Cl6 2.463(1), Ir3–P5 2.259(1), Ir3–P6 2.250(1), Ir4–Cl4 2.542(1), Ir4–Cl5 2.452(1), Ir4–Cl6 2.440(1), Ir4–P7 2.260(1), Ir4–P8 2.257(1); Cl4–Ir3–Cl5 79.80(4), Cl4–Ir3–Cl6 79.03(4), Cl4–Ir3–P5 107.61(5), Cl4–Ir3–P6 98.80(5), Cl5–Ir3–Cl6 79.83(4), Cl5–Ir3–P5 168.85(5), Cl5–Ir3–P6 93.89(5), Cl6–Ir3–P5 93.21(5), Cl6–Ir3–P6 173.61(5), P5–Ir3–P6 93.18(5), Cl4–Ir4–Cl5 79.10(4), Cl4–Ir4–Cl6 79.23(4), Cl4–Ir4–P7 100.53(5), Cl4–Ir4–P8 105.97(5), Cl5–Ir4–Cl6 79.78(5), Cl5–Ir4–P8 92.68(5), Cl5–Ir4–P7 174.44(5), Cl6–Ir4–P7 94.69(5), Cl6–Ir4–P8 170.00(5), P7–Ir4–P8 92.74(5), Ir3–Cl4–Ir4 82.33(1), Ir3–Cl5–Ir4 86.38(1), Ir3–Cl6–Ir4 85.83(1); (Ir3,Cl4,Cl5)/(Ir4,Cl4,Cl5) 58.37(5), (Ir3,Cl4,Cl6)/(Ir4,Cl4,Cl6) 59.38(5), (Ir3,Cl5,Cl6)/(Ir4,Cl5,Cl6) 54.29(3), (Ir3,Cl4,Ir4)/(Ir3,Cl5,Ir4) 60.85(1), (Ir3,Cl4,Ir4)/(Ir3,Cl6,Ir4) 61.92(1), (Ir3,Cl5,Ir4)/(Ir3,Cl6,Ir4) 57.23(1), (naphthyl C89–C98)/(naphthyl C99–C108), 73.0(1); (naphthyl C133–C142)/(naphthyl C143–C152), 72.0(1).

facilitates the decoordination of the cyclooctadiene ligand through "steric pressure".[14a,14b] Bridge-closing combination of the remaining "[{(*R*)-binap}Ir(H)(Cl)]$^+$ fragments would then form [{(*R*)-binap}$_2$Ir$_2$H$_2$(μ-Cl)$_2$]$^{2+}$, which stabilizes to **5** by the addition of an extra chloride ion provided by the excess of HCl.[14c]

The bimetallic structure of **5** was confirmed by X-ray analysis. Single crystals grown from an acetone/diethyl ether solvent mixture were found to have the idealized composition [{(*R*)-binap}$_2$Ir$_2$H$_2$(μ-Cl)$_3$]BF$_4$·Me$_2$CO·1/2 H$_2$O·1/4 Et$_2$O and to contain, in addition to the different solvent molecules, two crystallographically independent ion pairs in the asymmetric unit. Perspective views of the molecular models that resulted for the cationic parts are presented in Figure 3. The structures of the two cations are very close to $C_2$-symmetric, with the twofold rotation axes passing through the midpoints of the Ir···Ir vectors and the chlorido ligands Cl2 and Cl4 *trans* to the Ir–H bonds. In solution, this molecular $C_2$ symmetry is mirrored by a deceptively simple AA′BB′ $^{31}$P{$^1$H} NMR pattern arising from the two chiral diphosphane ligands (pairs of "doublets", where only $|^2J_{P,P} + {}^4J_{P,P}|$ = 20.0 Hz is resolved). The pair-wise shared coordination planes spanned by one metal center and two bridging chlorido ligands are inclined to each other at angles between 120.62° and 125.71°, with the interplanar angles of the Ir(μCl)Ir bridges varying from 118.08(1)° to 122.77(1)° (ranges of the supplementary dihedral angles given in the legend to Figure 3: 59.38(5)–54.29(3)° and 61.92(1)–57.23(1)°, respectively). The angles between the normals to the four pairs of naphthyl least squares planes amount to 67.7(1)° and 76.1(1)° in cation I and 72.0(1)° and 73.0(1)° in cation II. Though much less than the dihedral angle of 81.4° displayed by the pairs of naphthalene rings in the related [{(*R*)-binap}$_2$Ir$_2$H$_2$(μ-OCH$_3$)$_2$(μ-Cl)]$^+$ cation,[13h] these values clearly fall within the limits of about 65–77° that have previously been reported for several mono- and binuclear binap compounds of Ru$^{II}$, Rh$^{I}$, Ir$^{I}$, and Ir$^{III}$.[13p,15] As anticipated, the Ir–Cl bonds *trans* to Ir–H [2.530(1)–2.534(1) Å] are significantly longer than those opposite to the Ir–P bonds [2.426(1)–2.470(1) Å] and are amongst the longest Ir$^{III}$–μ–Cl distances reported to date.[16] The Ir–P bond lengths of **7** vary between 2.246(1) and 2.260(1) Å and thus compare favorably with the metal-to-phosphorus distances of 2.248 and 2.262 Å measured for the aforementioned chlorido/methoxido-bridged diiridium(III) complex.[13h] The obtuse P–Ir–P angles of 91.94(5)–93.18(5)° likewise closely resemble those of other structurally characterized iridium complexes bearing (*R*)- or (*S*)-binap ligands.[13h,13p,15g,15h]

Completely unexpectedly, the reaction of [(η$^4$-1,5-C$_8$H$_{12}$)-Ir(H)(Cl){(*S*,*S*)-bdpcp}]BF$_4$ (**4**) with different H$_2$N∩NH$_2$ chelate ligands did not result in diene/diamine exchange. Depending on the reaction conditions, the less basic aromatic or aliphatic amines 2,2′-diamino-1,1′-binaphthyl and 1,2-diphenylethylenediamine either left the compound unchanged or furnished mixtures with the dehydrochlorinated iridium(I) precursor [(η$^4$-1,5-C$_8$H$_{12}$)Ir{(*S*,*S*)-bdpcp}]BF$_4$. Complete removal of hydrogen chloride from the Ir$^{III}$ center was observed in the reaction of the HCl adduct with the stronger basic aliphatic diamine 1,2-(H$_2$N)$_2$C$_6$H$_{10}$. Brønsted base-assisted dehydrohalogenations, as observed between **4** and diamines, are the infrequently encountered reverse reaction of HX oxidative addition; they are comparatively common with Ir$^{III}$.[17] In fact, similar amine-induced eliminations of HCl have recently been reported for some triply chlorido-bridged binuclear hydrides of iridium(III) bearing trimethylene-linked N-heterocyclic carbenes (NHCs) as terminal ligands.[13o] Whereas those [{(NHC)(CH$_2$)$_3$(NHC)}$_2$Ir$_2$H$_2$(μ-Cl)$_3$]PF$_6$ dimers underwent complete degradation in the presence of nitrogen bases, binap-chelated diiridium complex **5** reacts with several diamines to smoothly produce the diamine(diphosphane) target compounds [Ir(H)(Cl)(H$_2$N∩NH$_2$){(*R*)-binap}]BF$_4$ [H$_2$N∩NH$_2$ = (*R*,*R*)-dpen (**6a**), (*R*,*R*)-dach (**6b**), and tmen (**6c**)] by nucleophilic opening of the chlorido bridges. In order to favor the formation of these three cationic species (Scheme 3), the liberated chloride was removed by precipitation with AgBF$_4$, although the addition of Ag$^+$ is not imperative with the completely aliphatic and, hence, more electron-rich diamines tmen and dach. Diiridium complex **5** does not undergo the bridge-opening reaction upon combination with (*R*)-2,2′-diamino-1,1′-binaphthyl, either because of too much steric pressure in the resulting [Ir(H)(Cl){(*R*)-dabin)}{(*R*)-binap}]$^+$ cation or because of a too low nucleophilicity of the aromatic (*R*)-dabin ligand.




Scheme 3. Synthesis of mixed-ligand complexes **6a**–**c**.

Complexes **6a**–**c** proved difficult to crystallize and therefore could only be characterized spectroscopically. Their $^1$H NMR spectra were found to display hydride signals at around $\delta$ = –20 ppm as doublets of doublets. Two $^2J_{P,H}$ coupling constants amounting to around 16 and 18 Hz place these hydrido ligands in a position *cis* to two chemically inequivalent binap P atoms which, accordingly, give rise to two $^{31}$P{$^1$H} doublets ($\delta$ = –13 to –10 and –1 ppm; *cis*-$^2J_{P,P} \approx$ 22 Hz). These data indicate that the stereochemistry of **6a**–**c** is either *OC*-6-43 with the hydride trans to Cl, as proposed for [Rh(H)(Cl){(*R*,*R*)-dpen}{(*R*)-binap}]-BF$_4$,[1] or *OC*-6-23, where the Ir–H bond is opposite to one

of the $NH_2$ functionalities. Although we could not corroborate the actual structure by X-ray analysis, the geometry with the hydride *trans* to chloride shown in Scheme 3 is favored over the *trans*-H–Ir–N alternative by comparison with the IrH NMR spectroscopic data of some [Ir(H)(Cl)(aminophosphane)$_2$]X chelate complexes having crystallographically established *OC*-6-43 stereochemistry, for example [Ir(H)(Cl)($H_2N(CH_2)_2PPh_2)_2$]Cl[10a] and [Ir(H)(Cl){*o*-HN(R)$C_6H_4PPh_2$}$_2$]X (R = Et, $CH_2Ph$; $X^-$ = $Cl^-$, $OH^-$, $MeCO_2^-$).[18] Similar to **6a**–**c**, all of these compounds display $\delta$(IrH) in the range –22 to –20 ppm with *cis*-$^2J$(P,H) ≈ 18 Hz.[19]

## Catalytic Hydrogenation of Acetophenone

Both the chiral chlorido-hydrido complexes [Ir(H)(Cl)($H_2N\cap NH_2$){(*R*)-binap}]$BF_4$ [$H_2N\cap NH_2$ = (*R*,*R*)-dpen (**6a**), (*R*,*R*)-dach (**6b**), or tmen (**6c**)] and the dihydrides [$IrH_2${$H_2N\cap NH_2$}$(PR_3)_2$]$BF_4$ [$H_2N\cap NH_2/PR_3$ = (*R*,*R*)-dach/$PPh_3$ (**1b**), (*R*)-dabin/$PPh_3$ (**1c**), (*R*,*R*)-dach/P*i*$Pr_3$ (**2a**), or (*R*)-dabin/P*i*$Pr_3$ (**2b**)] were investigated for their ability to form stereoselective >C=O hydrogenation catalysts. In fact, all of them catalyzed the asymmetric hydrogenation of acetophenone to (*S*)-1-phenylethanol at substrate-to-catalyst (*s*:*c*) ratios ranging from 200:1 to 5000:1 in the presence of a strong base (typically 50 equiv. of KOH) in alcoholic solution under $H_2$ (20 bar) at 40–60 °C (Table 1). The success of these hydrogenation reactions depends critically on the presence of extra base in the catalytic system and the use of a protic reaction medium. Thus, virtually no catalytic >C=O reduction occurred in alcohols in the absence of base or in an aprotic solvent such as benzene containing a basic additive. Methanol proved to be the solvent of choice, as reactions in ethanol and 2-propanol proceeded slower and resulted in reduced enantioselectivity (Table 1, entries 2–4).

The likelihood of the ketone reduction proceeding by direct metal-assisted transfer of $H^{\delta-}/H^{\delta+}$ equivalents from the $H_2$ molecule to the carbonyl dipole was substantiated by ruling out the alternative pathway involving $H^{\delta-}/H^{\delta+}$ transfer from the solvent. Thus, when a solution of acetophenone in $CH_3OH$ was hydrogenated with $D_2$ (10 bar) employing the combined **6b**/KOH catalyst, α-deuterated $PhCD(OH)CH_3$ was formed as the main alcohol product, which was demonstrated by NMR spectroscopy as described previously.[10b] The observation of minor amounts of $PhCH(OH)CH_3$ as a by-product of the deuteration reaction cannot be attributed to the methanol molecule serving as a hydrogen source because no formation of $PhCH(OH)CH_3$ or $PhCD(OH)CH_3$ was observed when the reaction was carried out in the absence of hydrogen gas in $CH_3OH$ or $CD_3OH$. The formation of the non-deuterated isotopomer rather points to "$D_2 + CH_3OH = CH_3OD + HD$" and "$HD + CH_3OH = CH_3OD + H_2$" exchange processes accompanying the catalysis. We have shown in previous work[10b] that the exchange of isotopes between a protic solvent and the hydrogen atmosphere, which is typical of heterolytic activation of the hydrogen molecule during reaction,[20] is a characteristic feature of iridium-based >C=O hydrogenation catalysts bearing ligands that, like the diamines used in the present study, have acidic primary or secondary amine ends.

Table 1. Enantioselective hydrogenation of acetophenone in the presence of base-modified iridium(III) precatalysts; $p(H_2)$ = 20 bar.

| No. | Precatalyst | *t* [h] | PhCH(OH)Me [%] | *ee* [%] (config.) |
|---|---|---|---|---|
| 1 | **6a**[a] | 1.5 | 100 | 82 (*S*) |
| 2 | **6b**[a] | 1.5 | 100 | 75 (*S*) |
| 3 | **6b**[b] | 2 | 61 | 59 (*S*) |
| 4 | **6b**[c] | 4 | 42 | 38 (*S*) |
| 5 | **6c**[a] | 1.5 | 100 | 73 (*S*) |
| 6 | **1b**[a] | 2 | 51 | 24(*S*) |
| 7 | **1c**[a] | 1 | 37 | <2 (*S*) |
| 8 | **2a**[a] | 2 | 69 | <2 (*S*) |
| 9 | **2b**[a] | 2 | 37 | 9 (*S*) |
| 10 | **6a**[d] | 3 | 11 | 80 (*S*) |
| 11 | **6b**[d] | 3 | 62 | 66 (*S*) |
| 12 | **5**/(*R*,*R*)-dpen[e] | 2 | 100 | 84 (*S*) |
| 13 | **5**/(*R*,*R*)-dach[e] | 2 | 100 | 71 (*S*) |

[a] Acetophenone (5.0 mmol), 0.01 mmol of $Ir^{III}$ complex, KOH (50 equiv.), methanol (3 mL); *T* = 50 °C. [b] In ethanol at *s*:*c* = 500:1; *T* = 40 °C. [c] In 2-propanol at *s*:*c* = 200:1; *T* = 60 °C. [d] 33.0 mmol of acetophenone, $6.6\times10^{-3}$ mmol of $Ir^{III}$ complex, and 0.33 mmol of KOH in methanol (4 mL); *T* = 50 °C. [e] In situ catalysts activated with 25 equiv. of KOH in methanol; *s*:*c* = 250:1, *T* = 50 °C.

As compared to complexes **1b**/**1c** and **2a**/**2b**, where only the diamine ligands can contribute to the (poor) stereoselective outcome of the catalytic runs (Table 1, entries 6–9), compounds **6a**–**c**, which possess an additional (*R*)-binap ligand, form much more enantioselective systems, as expected. Best results of 82–84% *ee* were obtained with the preformed complex [Ir(H)(Cl){(*R*,*R*)-dpen}{(*R*)-binap}]$BF_4$ (**6a**) and its in situ generated equivalent [{(*R*)-binap}$_2Ir_2H_2(\mu\text{-}Cl)_3$]$BF_4$/(*R*,*R*)-dpen [**5**/(*R*,*R*)-dpen; Table 1, entries 1 and 12).[21] With (*R*,*R*)-dach as the diamine co-ligand, the *ee* achieved with both the preformed and the in situ catalysts **6b** and **5**/(*R*,*R*)-dach was seen to drop to 71–75% (Table 1, entries 2 and 13). Further replacement of the (*R*,*R*)-dach chelate by the achiral diamine $H_2NCMe_2CMe_2NH_2$ in precatalyst **6c** left the optical yield of the (*S*) isomer (73%; Table 1, no. 5) essentially unchanged, thus suggesting that it is preferentially the diphosphane which determines the asymmetric induction. Comparison of these results with those obtained with isoelectronic $Ru^{II}$-based catalysts reveals some interesting trends.

At first glance, the combined system [Ir(H)(Cl)(tmen){(*R*)-binap}]$BF_4$/KOH/MeOH appears to be superior in selectivity [73% for (*S*)-PhCH(OH)Me] to the [Ru(H)(Cl)(tmen){(*R*)-binap}]-derived dihydride [Ru(H)$_2$(tmen){(*R*)-binap}], which produced the (*S*) isomer of 1-phenylethanol in only 6–14% yield when used in 2-propanol without added base.[2b,2c] However, the seemingly poor performance of this ruthenium complex results from catalyst deactivation by formation of diastereomeric alkoxides such as [Ru(H){(*S*)-OCH(Me)Ph}(tmen){(*R*)-binap}] and [Ru(H)-

{(*R*)-OCH(Me)Ph}(tmen){(*R*)-binap}] during the build up of the acidic product alcohol. This unwanted side reaction can be prevented by the addition of base or by lowering the polarity of the solvent. Running the Ru-catalyzed reaction in 2-propanol in the presence of base or in benzene (where Ir complex **6c** remains completely inactive) thus established an inherent enantioselectivity of 51–68% (*R*) for the ruthenium-based (*R*)-binap/tmen system,[2b,2c] which is therefore comparable to **6c** with respect to the *ee* values that can be attained but yields the opposite enantiomer. In the presence of base, the $Ru^{II}$ complex [Ru(H)(Cl){(*R*,*R*)-dach}{(*R*)-binap}] catalyzes the hydrogenation of acetophenone (neat or dissolved in benzene) to afford (*S*)-PhCH(OH)Me in 88% *ee*,[2a,2c] which makes it a somewhat more selective catalyst than [Ir(H)(Cl){(*R*,*R*)-dach}{(*R*)-binap}]$BF_4$ (**6b**), which gives the (*S*) form of the alcohol in only around 75% *ee*. With base-modified [Ru(H)(Cl){(*R*,*R*)-dpen}{(*R*)-binap}], the Morris group has achieved 73% *ee* for the formation of (*S*)-PhCH(OH)Me,[2a] while the catalytic species generated in basic media from the dichlorido precursor [$RuCl_2$\{(*S*,*S*)-dpen\}{(*S*)-tolbinap}] (tolbinap is the di-*p*-tolyl analogue of binap) afforded the (*R*) enantiomer in 78–83% yield, as reported independently by Noyori and coworkers[22] and Rautenstrauch and Morris et al.[2d] Hence, the selectivity of the corresponding iridium-based system [Ir(H)(Cl){(*R*,*R*)-dpen}{(*R*)-binap}]$BF_4$/KOH/MeOH [82% *ee* for the (*S*) isomeric alcohol] compares favorably with that observed for the two established ruthenium catalysts possessing the same ligands. However, the $Ru^{II}$ complexes, which work very fast at substrate-to-catalyst ratios as high as $10^5$–$10^6$, form much more active systems: the most active $Ir^{III}$ catalyst studied in this work is formed from the only moderately selective complex **6b** in the presence of 50 equiv. of KOH. This system furnished 62% of 1-phenylethanol within 3 h at *s*:*c* = 5000, albeit with a reduced selectivity of 66% *ee* for the (*S*) isomer (Table 1, entry 11). Under identical conditions, the most selective precatalyst **6a** maintains an optical yield of 80% *ee* (*S*) but shows poor activity, transforming only 11% of the ketone to the product alcohol (Table 1, entry 10).

## Conclusions

This work has shown that cationic dihydridoiridium(III) complexes with two monodentate phosphanes and one chelating diamine can easily be made by treating different $H_2N\cap NH_2$ ligands with a number of readily accessible substitutionally labile precursors. The preparation of the mixed-ligand bis(chelates) [Ir(H)(Cl)($H_2N\cap NH_2$){(*R*)-binap}]$BF_4$ [$H_2N\cap NH_2$ = (*R*,*R*)-dpen (**6a**), (*R*,*R*)-dach (**6b**), or tmen (**6c**)] is more involved and requires dinuclear [{(*R*)-binap}$_2$$Ir_2H_2(\mu\text{-}Cl)_3$]$BF_4$ as a synthetic intermediate. While *cis*-dihydrides such as [$IrH_2$\{(*R*,*R*)-dach\}$(PR_3)_2$]$BF_4$ and [$IrH_2$\{(*R*)-dabin\}$(PR_3)_2$]$BF_4$ (R = *i*Pr, Ph) are only poor (pre)catalysts for the enantioselective hydrogenation of acetophenone to 1-phenylethanol, the combined systems (**6a**–**c**)/KOH/MeOH catalyze the formation of the product alcohol with a degree of enantioselectivity which, in the most favorable cases, closely matches that of established isoelectronic $Ru^{II}$-based catalysts containing identical phosphorus and nitrogen donor ligands.

## Experimental Section

**General:** All manipulations were performed under nitrogen or argon, unless stated otherwise. Solvents were distilled from the appropriate drying agents prior to use. NMR: Bruker DPX 300 (300.1 MHz for $^1H$, 75.5 MHz for $^{13}C$, and 121.5 MHz for $^{31}P$) with $SiMe_4$ as internal or $H_3PO_4$ as external standard (downfield positive) at ambient temperature ("m" = deceptively simple multiplet). GC: Shimadzu GC-17A (FID). Silver tetrafluoroborate, $HBF_4$ (54% in $Et_2O$), and the diphosphane and diamine ligands (*R*)-2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl [(*R*)-binap], 1,2-phenylenediamine (1,2-phdn), (*R*)-2,2′-diamino-1,1′-binaphthyl [(*R*)-dabin], (1*R*,2*R*)- and (1*S*,2*S*)-1,2-diphenylethylenediamine [(*R*,*R*)-, (*S*,*S*)-dpen], and (1*R*,2*R*)-1,2-diaminocyclohexane [(*R*,*R*)-dach] were used as purchased. 1,1′,2,2′-Tetramethylethylenediamine (tmen),[23] (1*S*,2*S*)-1,2-bis(diphenylphosphanyl)cyclopentane [(*S*,*S*)-bdpcp],[24] [$(\eta^4\text{-}1,5\text{-}C_8H_{12})_2Ir_2(\mu\text{-}Cl)_2$],[25] [$(\eta^4\text{-}1,5\text{-}C_8H_{12})$-$Ir(PPh_3)_2$]$BF_4$,[4d,4e] [$IrH_2(OCMe_2)_2(PPh_3)_2$]$BF_4$,[4d,4e] [$IrH_5$(P-*i*$Pr_3)_2$],[5d] and [$IrH_5(PCy_3)_2$][5e] were prepared according to published procedures or slight modifications thereof. The complex [$(\eta^4$-1,5-$C_8H_{12})$Ir\{(*R*)-binap\}]$BF_4$ was previously made from [$(\eta^4$-1,5-$C_8H_{12})$$Ir(NCMe)_2$]$BF_4$ which, in turn, was synthesized from [$(\eta^4$-1,5-$C_8H_{12})_2Ir_2(\mu\text{-}Cl)_2$] via [$(\eta^4$-1,5-$C_8H_{12})_2Ir$]$BF_4$ as a further intermediate.[11] A more direct route is given here: A 1:2:2 molar mixture of [$(\eta^4$-1,5-$C_8H_{12})_2Ir_2(\mu\text{-}Cl)_2$] (425 mg, 0.63 mmol), (*R*)-binap (785 mg, 1.26 mmol), and $AgBF_4$ (245 mg, 1.26 mmol) in 30 mL of methanol was stirred for 24 h at ambient conditions with the exclusion of light. Precipitated silver chloride was then removed by filtration through diatomaceous earth (Celite® 521), which was washed with small portions of $CH_2Cl_2$ until the residue on the filter was colorless. Evaporation of the filtrate to a final volume of about 2 mL followed by dilution with 30 mL of diethyl ether gave the product as a raspberry-colored solid, which was filtered off, washed with diethyl ether (3 × 5 mL), and dried under vacuum; yield: 950 mg (75%). $^1H$ NMR ($CD_2Cl_2$): $\delta$ = 1.84–2.30 (m, 8 H, $CH_2$), 4.15, 4.40 (both m, 2 H each, both CH), 6.39–7.78 (m, 32 H, aryl H) ppm. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ = 16.05 (s) ppm [ref.[11] $\delta$ = 15.1 ppm in $CDCl_3$]. $C_{52}H_{44}BF_4IrP_2$ (1008.9): calcd. C 61.85, H 4.39; found C 62.08, H 4.54.

[$(\eta^4$-1,5-$C_8H_{12})$Ir\{(*S*,*S*)-bdpcp\}]$BF_4$ was isolated in 60% yield from a similar 1:2:2 reaction of [$(\eta^4$-1,5-$C_8H_{12})_2Ir_2(\mu\text{-}Cl)_2$] with $AgBF_4$ and the diphosphane in methanol: $^1H$ NMR ($CD_2Cl_2$): $\delta$ = 1.16, 1.70–2.36 (both m, 2 + 12 H, both $CH_2$), 2.74 (m, 2 H, PCH), 4.00, 4.73 (both m, 2 H each, both diene CH), 7.31–7.89 (m, 20 H, aryl H) ppm. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ = 20.70 (s) ppm. $C_{37}H_{40}BF_4IrP_2$ (825.70): calcd. C 53.82, H 4.88; found C 53.61, H 4.71.

**[$IrH_2$(1,2-phdn)($PPh_3)_2$]$BF_4$ (1a):** A solution of [$IrH_2(OCMe_2)_2$-$(PPh_3)_2$]$BF_4$ (440 mg, 0.49 mmol) in 15 mL of thf was stirred with 1,2-phenylenediamine (55 mg, 0.50 mmol) at room temperature. After a short while the product separated from the reaction mixture as a colorless solid, which was filtered off, washed with diethyl ether (2 × 3 mL), and dried under vacuum. Yield: 198 mg (44%). $^1H$ NMR ($CD_2Cl_2$): $\delta$ = –20.84 (t, $^2J_{P,H}$ = 16.7 Hz, 2 H, $IrH_2$), 4.04 (br., 4 H, $NH_2$), 6.77, 7.03 (AA′BB′-type m, 4 H, phenylene H), 7.30–7.51 (m, 30 H, phenyl H) ppm. $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ = 128.58, 129.66 (both s, phenylene C-3,6 and C-4,5), 129.88 (t, $^3J_{P,C}$

= 20.2 Hz, phenyl C-3,5), 131.70 (s, phenyl C-4), 132.26 (t, $^1J_{P,C}$ = 103.9 Hz, phenyl C-1), 133.99 (t, $^2J_{P,C}$ = 24.5 Hz, phenyl C-2,6), 139.81 (phenylene C-1,2) ppm. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ = 24.49 (s) ppm. $C_{42}H_{40}BF_4IrN_2P_2$ (913.71): calcd. C 55.21, H 4.41, N 3.07; found C 54.71, H 4.25, N 2.72.

**$[IrH_2\{(R,R)$-dach$\}(PPh_3)_2]BF_4$ (1b):** This complex was prepared as described for **1a** from $[IrH_2(OCMe_2)_2(PPh_3)_2]BF_4$ (200 mg, 0.22 mmol) and the diamine ligand (25 mg, 0.22 mmol) in 10 mL of thf. Yield: 121 mg (60%) of a colorless solid. $^1H$ NMR ($CD_2Cl_2$): $\delta$ = –21.07 (t, $^2J_{P,H}$ = 17.6 Hz, 2 H, $IrH_2$), 0.33, 0.71, 1.20–1.33, 1.39, 1.75 (all m, 2 + 2 + 4 + 2 + 2 H, $CH_2$ and $NH_2$), 2.79 (m, 2 H, CH), 7.4–7.7 (m, 30 H, $C_6H_5$) ppm. $^{13}C\{^1H\}$ NMR: $\delta$ = 25.13 (s, $C_6H_{10}$ C-4,5), 36.28 (s, $C_6H_{10}$ C-3,6), 60.96 (s, $C_6H_{10}$ C-1,2), 129.96 (t, $^3J_{P,C}$ = 20.2 Hz, phenyl C-3,5), 131.62 (s, phenyl C-4), 133.66 (t, $^1J_{P,C}$ = 104.0 Hz, phenyl C-1), 134.10 (t, $^2J_{P,C}$ = 24.6 Hz, phenyl C-2,6) ppm. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ = 21.92 (s) ppm. $C_{42}H_{46}BF_4IrN_2P_2$ (919.81): calcd. C 54.84, H 5.04, N 3.05; found C 54.45, H 5.49, N 2.91.

**$[IrH_2\{(R)$-dabin$\}(PPh_3)_2]BF_4$ (1c):** A solution of $[(\eta^4$-1,5-$C_8H_{12})$-$Ir(PPh_3)_2]BF_4$ (106 mg, 0.12 mmol) and an equimolar quantity of (*R*)-dabin (34 mg) in 10 mL of $CH_2Cl_2$ was stirred for 20 min under an atmosphere of hydrogen, which caused the mixture to change color from red to pale yellow. The off-white product was isolated by adding diethyl ether (80 mL), then washed with $Et_2O$ and dried under vacuum. Yield: 109 mg (83%). $^1H$ NMR ([D$_6$]acetone): $\delta$ = –23.48 (t, $^2J_{P,H}$ = 18.1 Hz, 2 H, $IrH_2$), 3.62 (br., 4 H, $NH_2$), 5.90, 6.05, 6.44 (all d, $^3J_{H,H}$ = 8.8, 10.4, and 8.2 Hz, 2 H each, all aryl H), 7.17, 7.28, 7.37, 7.91 (all m, 44 H, aryl H) ppm. $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): $\delta$ = 24.33 (s) ppm. Complex **1c** as well as its analogues **2a**, **2b**, and **3** were found to retain varying amounts of residual $CH_2Cl_2$ solvent so that no satisfactory elemental analyses could be obtained: $C_{56}H_{48}BF_4IrN_2P_2$ (1090.0): calcd. C 61.71, H 4.44, N 2.57; found C 59.45, H 4.38, N 2.31; calcd. for $C_{56}H_{48}BF_4IrN_2P_2{\cdot}CH_2Cl_2$ (1162.9): calcd. C 57.84, H 4.33, N 2.41.

**$[IrH_2\{(R,R)$-dach$\}(P\mathit{i}Pr_3)_2]BF_4$ (2a):** Tetrafluoroboric acid (54% in $Et_2O$) was added dropwise to a solution of $[IrH_5(P\mathit{i}Pr_3)_2]$ (525 mg, 1.02 mmol) in 15 mL of benzene until no further evolution of hydrogen was observed. The diamine ligand (116 mg, 1.02 mmol) was then added and the resulting mixture stirred for 1 h at room temperature. The residue remaining after evaporation to dryness was redissolved in 5 mL of $CH_2Cl_2$ and the product was isolated as an off-white solid by adding 50 mL of diethyl ether. Yield: 418 mg (57%). $^1H$ NMR ($C_6D_6$): $\delta$ = –23.28 (t, $^2J_{P,H}$ = 18.0 Hz, 2 H, $IrH_2$), 0.58 (m, 4 H, $CH_2$), 1.19 (dd, $^3J_{H,H}$ = 7.1, $^3J_{P,H}$ = 15.4 Hz, 36 H, $CH_3$), 1.37 (m, 4 H, $CH_2$), 2.17 (m, 6 H, PCH), 2.46, 2.60 (both br., 2 H each, both $NH_2$), 3.88 (m, 2 H, NCH) ppm. $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ = 44.02 (s) ppm. $C_{24}H_{58}BF_4IrN_2P_2$ (715.71): calcd. C 40.28, H 8.17, N 3.91; found C 39.13, H 7.90, N 3.78; calcd. for $C_{24}H_{58}BF_4IrN_2P_2{\cdot}CH_2Cl_2$ (800.64): calcd. C 37.50, H 7.55, N 3.50. Compounds **2b** and **3** were obtained analogously:

**$[IrH_2\{(R)$-dabin$\}(P\mathit{i}Pr_3)_2]BF_4$ (2b):** Synthesized from $[IrH_5(P\mathit{i}Pr_3)_2]$ (228 mg, 0.44 mmol), treated with $HBF_4$ as described above, and (*R*)-dabin (125 mg, 0.44 mmol) in 15 mL of benzene in 82% yield (320 mg). $^1H$ NMR ($CD_2Cl_2$): $\delta$ = –26.56 (t, $^2J_{P,H}$ = 18.3 Hz, 2 H, $IrH_2$), 0.86 (dd, $^3J_{H,H}$ = 6.6, $^3J_{P,H}$ = 14.8 Hz, 36 H, $CH_3$), 2.06 (m, 6 H, PCH), 4.98, 5.10 (both br., 2 H each, both $NH_2$), 6.69 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, aryl 3-H), 7.15 ("t", $\Sigma^3J_{H,H}$ = 15.0 Hz, 2 H, aryl 6-H), 7.35 (m, 4 H, aryl 7,8-H), 7.82 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, aryl 5-H), 7.98 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, aryl 4-H) ppm. $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ = 44.35 (s) ppm. $C_{38}H_{60}BF_4IrN_2P_2$ (885.87): calcd. C 51.52, H 6.83, N 3.16; found C 49.73, H 6.60, N 3.08; calcd. for $C_{38}H_{60}BF_4IrN_2P_2{\cdot}CH_2Cl_2$ (970.81): calcd. C 48.25, H 6.44, N 2.89.

**$[IrH_2\{(R)$-dabin$\}(PCy_3)_2]BF_4$ (3):** Synthesized from $[IrH_5(PCy_3)_2]$ (115 mg, 0.15 mmol), treated with $HBF_4$ as outlined for **2a**, and the diamine (43 mg, 0.15 mmol) in 10 mL of benzene in 80% yield (135 mg). $^1H$ NMR ($CD_2Cl_2$): $\delta$ = –26.57 (t, $^2J_{P,H}$ = 18.1 Hz, 2 H, $IrH_2$), 1.15–1.87 (m, 66 H, cyclohexyl H), 2.06 (m, 6 H, PCH), 4.99, 5.21 (both br., 2 H each, both $NH_2$), 6.82 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, aryl 3-H), 7.15 ("t", $\Sigma^3J_{H,H}$ = 15.0 Hz, 2 H, aryl 6-H), 7.42 (m, 4 H, aryl 7,8-H), 7.98 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, aryl 5-H), 8.10 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, aryl 4-H) ppm. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ = 20.92 (s) ppm. $C_{56}H_{84}BF_4IrN_2P_2$ (1126.27): calcd. C 59.72, H 7.52, N 2.49; found C 58.66, H 7.14, N 2.32; calcd. for $C_{56}H_{84}BF_4IrN_2P_2{\cdot}CH_2Cl_2$ (1211.2): calcd. C 56.52, H 7.16, N 2.31.

**$[(\eta^4$-1,5-$C_8H_{12})Ir(H)(Cl)\{(S,S)$-bdpcp$\}]BF_4$ (4):** Dropwise addition of a saturated solution of hydrogen chloride in diethyl ether to a suspension of $[(\eta^4$-1,5-$C_8H_{12})Ir\{(S,S)$-bdpcp$\}]BF_4$ (204 mg, 0.25 mmol) in 20 mL of thf gave a clear yellow solution, from which the product separated within 1 h as pale-yellow microcrystals. Yield (after washing three times with 2 mL of $Et_2O$ and drying): 190 mg (89%). $^1H$ NMR ($CD_2Cl_2$): $\delta$ = –14.05 (dd, *cis*-$^2J_{P,H}$ = 7.1 and 11.5 Hz, 1 H, IrH), 0.96, 1.47 (both m, 1 H each, both $CH_2$), 1.85–2.86 (m, 14 H, $CH_2$ and phosphane CH), 3.89, 4.27, 5.32 (all m, 1 + 2 + 1 H, diene CH), 7.21–7.82 (m, 20 H, aryl H) ppm. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ = 6.03, 15.30 (both d, $J_{P,P}$ = 15.6 Hz) ppm. $C_{37}H_{41}BClF_4IrP_2$ (862.16): calcd. C 51.55, H 4.79; found C 50.98, H 4.66.

**$[\{(R)$-binap$\}_2Ir_2H_2(\mu$-Cl$)_3]BF_4$ (5):** A solution of dry HCl gas in diethyl ether was added dropwise to a stirring solution of $[(\eta^4$-1,5-$C_8H_{12})Ir\{(R)$-binap$\}]BF_4$ (205 mg, 0.20 mmol) in 10 mL of thf under ambient conditions. The red mixture gradually became yellow and the addition of $HCl{\cdot}Et_2O$ was stopped when no further color change was discernible. The product was precipitated after stirring for an additional 10 min and concentration of the solution to about 1 mL by adding 20 mL of diethyl ether. It was then washed twice with 2 mL of $Et_2O$ and dried under vacuum. Yield: 172 mg (94%). $^1H$ NMR ($CD_2Cl_2$): $\delta$ = –22.73 (dd, $^2J_{P,H}$ = 15.6 and 21.5 Hz, 2 H, IrH), 6.30–8.03 (m, 64 H, aryl H) ppm. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ = –6.54, 1.59 (both AA′BB′-type "d", $|^2J_{P,P} + {}^4J_{P,P}|$ = 20.0 Hz) ppm. $C_{88}H_{66}BCl_3F_4Ir_2P_4$ (1825.0): calcd. C 57.89, H 3.65; found C 57.83, H 3.50.

**$[Ir(H)(Cl)\{(R,R)$-dpen$\}\{(R)$-binap$\}]BF_4$ (6a):** A mixture of (*R*,*R*)-dpen (44 mg, 0.21 mmol) and $AgBF_4$ (20 mg, 0.10 mmol) in 5 mL of thf was added to a solution of **5** (185 mg, 0.10 mmol) in 5 mL of thf. After stirring for 30 min under ambient conditions, the precipitate of AgCl was filtered off and the filtrate was concentrated to about 1 mL. Precipitation with 20 mL of diethyl ether, followed by filtration and washing with $Et_2O$ (2 × 3 mL) gave 108 mg (47%) of the product as a yellowish white solid. $^1H$ NMR ($CD_2Cl_2$): $\delta$ = –19.81 (dd, $^2J_{P,H}$ = 15.9 and 18.0 Hz, 1 H, IrH), 2.91, 3.00, 3.29, 3.89 (all br., 1 H each, $NH_2$), 4.39 (m, 2 H, CH), 6.18–8.12 (m, 42 H, aryl H) ppm. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ = –9.99, –0.64 (both d, $J_{P,P}$ = 22.3 Hz) ppm. $C_{58}H_{49}BClF_4IrN_2P_2$ (1150.5): calcd. C 60.55, H 4.29, N 2.43; found C 61.15, H 4.53, N 2.38. Similar procedures were used for the preparation of complexes **6b** and **6c**.

**$[Ir(H)(Cl)\{(R,R)$-dach$\}\{(R)$-binap$\}]BF_4$ (6b):** Synthesized from **5** (100 mg, 0.05 mmol) and the diamine (13 mg, 0.11 mmol) in 10 mL of thf. Yield: 84 mg (73%). $^1H$ NMR ($CD_2Cl_2$): $\delta$ = –20.35 (dd, $^2J_{P,H}$ = 15.5 and 18.2 Hz, 1 H, IrH), 1.19–2.09 (m, 8 H, $CH_2$), 2.85 (br., 4 H, $NH_2$), 3.01, 4.81 (both m, 1 H each, both CH), 6.28–8.15 (m, 32 H, aryl H) ppm. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ = –10.69, –1.10 (both d, $J_{P,P}$ = 22.3 Hz) ppm. $C_{50}H_{47}BClF_4IrN_2P_2$ (1052.4): calcd. C 57.07, H 4.50, N 2.66; found C 56.96, H 4.32, N 2.43.

**[Ir(H)(Cl)(tmen){(*R*)-binap}]$BF_4$ (6c):** Synthesized from **5** (120 mg, 0.07 mmol) and the diamine ligand (16 mg, 0.14 mmol) in thf (10 mL). Yield: 64 mg (48%). $^1$H NMR ($CD_2Cl_2$): $\delta$ = –20.00 (dd, $^2J_{P,H}$ = 15.6 and 17.4 Hz, 1 H, IrH), 1.02, 1.08, 1.12, 1.20 (all s, 3 H each, all $CH_3$), 2.06, 2.37, 3.96, 4.85 (all br., 1 H each, all $NH_2$), 6.23–8.12 (m, 32 H, aryl H) ppm. $^{31}$P{$^1$H} NMR ($CD_2Cl_2$): $\delta$ = –12.92, –1.10 (both d, $J_{P,P}$ = 22.4 Hz) ppm. $C_{50}H_{49}BClF_4IrN_2P_2$ (1054.4): calcd. C 56.96, H 4.68, N 2.66; found C 56.83, H 4.58, N 2.34.

**General Procedure for Catalytic >C=O Hydrogenation:** A 10-mL Schlenk tube equipped with a small magnetic stirring bar was charged with an alcoholic solution of the catalyst complex (typically 0.01 mmol in 3.0 mL of methanol). The required amounts of potassium hydroxide and acetophenone (see Table 1) were then added, the mixture was stirred for 10 min under ambient conditions, and the tube was inserted into an argon-filled stainless steel autoclave. The autoclave was sealed and vented several times with $H_2$ (Messer–Griesheim; 99.999%), subsequently pressurized to 20 bar, and the contents stirred at 40–60 °C. At the end of the reaction, the pressure was vented, the solvent removed under vacuum, and the residue was diluted with diethyl ether to precipitate the catalyst as a brownish black solid. The solution was decanted and chromatographed on a silica gel column using diethyl ether as the eluent. Volatile material was distilled off and the mixture of products was analyzed by $^1$H NMR spectroscopy. Conversions and product compositions were determined on the basis of the integrations of the PhC(O)C$H_3$ and PhCH(OH)C$H_3$ signals. Enantiomeric excesses were measured by GC using a Chrompack Chirasil-Dex CB column.

**X-ray Structure Determinations:** The crystal used for the structure analysis of **1a** was grown from dichloromethane. Recrystallization of **4** and **5** from acetone/diethyl ether mixtures afforded single crystals of solvent-containing addition compounds identified as [($\eta^4$-1,5-$C_8H_{12}$)Ir(H)(Cl){(*S*,*S*)-bdpcp}]$BF_4$·$Me_2CO$ and [{(*R*)-binap}$_2$-$Ir_2H_2(\mu$-Cl)$_3$]$BF_4$·$Me_2CO$·1/2 $H_2O$·1/4 $Et_2O$ ("**4·Me$_2$CO**" and "**5·solv**" hereafter). Diffraction measurements were made at –173(2) °C with a Bruker-Nonius Kappa CCD instrument for compounds **1a** and **5·solv** and at –160(2) °C with an Enraf–Nonius CAD4 MACH3 diffractometer for **4·Me$_2$CO**, both of which used Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å); diffraction data were corrected for absorption by appropriate numerical[26] (**1a**: $T_{min}$ = 0.277, $T_{max}$ = 0.801), refined[27] (**4·Me$_2$CO**: $T_{min}$ = 0.227, $T_{max}$ = 0.621), or empirical[28] (**5·solv**: $T_{min}$ = 0.738, $T_{max}$ = 1.000) methods. The structures were solved by direct methods and subsequently refined by full-matrix (**1a**, **4·Me$_2$CO**) or, in view of the large dimensions of **5·solv**, by block-matrix least-squares procedures on $F^2$ with allowance for anisotropic thermal motion of all non-hydrogen atoms employing both the SHELXTL NT 6.12[29] and the WinGX[30a] package with some of the relevant programs (SIR-97,[31] SHELXL-97,[32] XHYDEX,[7] ORTEP-3[30b]) implemented therein. The crystal of **1a** under study proved to be a pseudomerohedral twin. The twin law used during the refinement was –1 0 0 0 –1 0 0 0 –1 and resulted in a twin component ratio of approximately 5:1 (BASF 0.2122).

**1a:** 0.40 × 0.40 × 0.06 mm$^3$, $C_{42}H_{40}IrN_2P_2$·$BF_4$ (913.71); monoclinic, $C_2$, $a$ = 9.1624(9), $b$ = 17.197(2), $c$ = 24.204(2) Å, $\beta$ = 99.947(7)°, $V$ = 3756.3(9) Å$^3$, $Z$ = 4, $d_{calcd.}$ = 1.616 g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 3.693 mm$^{-1}$; 3.33° ≤ $\Theta$ ≤ 28.01°, 30833 reflections collected (–11 ≤ $h$ ≤ +12, –21 ≤ $k$ ≤ +22, –31 ≤ $l$ ≤ +31), 8279 unique ($R_{int}$ = 0.0643); $wR_2$ = 0.1270 for all data and 475 parameters, $R_1$ = 0.0572 for 6804 intensities $I > 2\sigma(I)$; absolute structure parameter $x$ = –0.02(2).[33]

**4·Me$_2$CO:** 0.38 × 0.30 × 0.13 mm$^3$, $C_{37}H_{41}ClIrP_2$·$BF_4$·$C_3H_6O$ (920.18); orthorhombic, $P2_12_12_1$, $a$ = 10.431(1), $b$ = 19.128(3), $c$ = 19.438(7) Å, $V$ = 3878(2) Å$^3$, $Z$ = 4, $d_{calcd.}$ = 1.576 g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 3.644 mm$^{-1}$; 2.10° ≤ $\Theta$ ≤ 25.17°, 4928 reflections collected (–3 ≤ $h$ ≤ +12, –3 ≤ $k$ ≤ +22, –3 ≤ $l$ ≤ +23), 4652 unique ($R_{int}$ = 0.0471); $wR_2$ = 0.1373 for all data and 454 parameters, $R_1$ = 0.0578 for 3712 intensities $I > 2\sigma(I)$; absolute structure parameter $x$ = –0.010(17).[33]

**5·solv:** 0.26 × 0.18 × 0.16 mm$^3$, $C_{88}H_{66}Cl_3Ir_2P_4$·$BF_4$·$C_3H_6O$·$HO_{0.5}$·$CH_{2.5}O_{0.25}$ (1910.5); orthorhombic, $P2_12_12_1$, $a$ = 21.205(2), $b$ = 24.821(4), $c$ = 32.830(3) Å, $V$ = 17279(4) Å$^3$, $Z$ = 8, $d_{calcd.}$ = 1.469 g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 3.299 mm$^{-1}$; 2.67° ≤ $\Theta$ ≤ 28.00°, 172715 reflections collected (–20 ≤ $h$ ≤ +28, –32 ≤ $k$ ≤ +32, –42 ≤ $l$ ≤ +43), 39510 unique ($R_{int}$ = 0.0462); $wR_2$ = 0.1264 for all data and 1943 parameters, $R_1$ = 0.0427 for 32060 intensities $I > 2\sigma(I)$; absolute structure parameter $x$ = 0.010(4).[33]

CCDC-640544 (for **1a**), -640546 (for **4·Me$_2$CO**), and -640545 (for **5·solv**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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