# Iridium-Catalyzed Enantioselective Hydrogenation of Imines in Supercritical Carbon Dioxide

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Abstract: Supercritical carbon dioxide (scCO<sub>2</sub>) was shown to be a reaction medium with unique properties for highly efficient iridium-catalyzed enantioselective hydrogenation of prochiral imines. Cationic iridium(I) complexes with chiral phosphinodihydrooxazoles, modified with perfluoroalkyl groups in the ligand or in the anion, were synthesized and tested in the hydrogenation of N-(1-phenylethylidene)aniline. Both the side chains and the lipophilic anions increased the solubility, but the choice of the anion also had a dramatic effect on the enantioselectivity with tetrakis-3,5-bis(trifluoromethyl)phenylborate (BARF) leading to the highest asymmetric induction. (R)-N-phenyl-1-phenylethylamine was formed quantitativley within 1 h in scCO<sub>2</sub>  $[d(CO_2) = 0.75]$ g mL<sup>-1</sup>] at 40 °C and a H<sub>2</sub> pressure of 30 bar with enantiomeric excesses of up to 81% using 0.078 mol % catalyst. The use of scCO<sub>2</sub> instead of conventional solvents such as CH<sub>2</sub>Cl<sub>2</sub> allowed the catalyst loading to be lowered significantly owing to a change in the rate profile of the reaction. The homogeneous nature of the catalytically active species under the reaction conditions was demonstrated and was found to depend strongly on the composition of the reaction mixture and especially on the presence of the substrate. Utilizing the selective extractive properties of scCO<sub>2</sub>, the product could be readily separated from the catalyst, which could be recycled several times without significant loss of activity and enantioselectivity. High-pressure FT-IR and NMR investigations revealed that the reactivity of the products to form the corresponding carbamic acids plays an important role for the application of this new methodology.

#### Introduction

Supercritical carbon dioxide (scCO<sub>2</sub>;  $T_c = 31$  °C,  $p_c = 73.75$ bar,  $d_{\rm c} = 0.468$  g mL<sup>-1</sup>) is receiving considerable and ever increasing interest as an environmentally benign reaction medium with unique properties for chemical synthesis<sup>1</sup> and especially for homogeneously catalyzed reactions.<sup>2</sup> The miscibility of scCO<sub>2</sub> with many gases and the absence of a liquid/ gas-phase boundary in the supercritical state results in the maximum availability of gaseous reactants, avoiding potential problems of mass-transfer limitations.<sup>3</sup> Beneficial effects can also arise from the high compressibility of scCO<sub>2</sub>, allowing for selectivity changes by variation of the density with comparably small changes in the reaction conditions.<sup>4</sup> The chemical interaction of CO<sub>2</sub> with functional groups of the substrate can lead to

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better compatibility with the employed catalysts (temporary protecting group).<sup>4</sup> In favorable cases, the extractive properties of scCO<sub>2</sub><sup>5</sup> may allow remarkable efficient and simple separation of catalysts and products.4,6

The use of scCO<sub>2</sub> as a solvent for reactions involving hydrogen as one of the substrates is particularly attractive. Recent research has demonstrated enhanced reaction rates in the ruthenium-catalyzed hydrogenation of CO<sub>2</sub> to formic acid and its derivatives<sup>3,7</sup> or the rhodium-catalyzed hydroformylation of olefins.<sup>6</sup> Higher regioselectivity at comparable rates has also been observed with certain catalytic systems for hydroformylation,<sup>8</sup> and preliminary results on asymmetric hydroformylation have been reported.<sup>9</sup> The highly enantioselective hydrogenation of C=C double bonds has been demonstrated with prochiral  $\alpha,\beta$ -unsaturated carboxylic acids as substrates.<sup>10,11</sup> The phase behavior of the reaction mixture and the solubility of the catalyst were found to be of paramount importance for the successful

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Scheme 1



application of  $scCO_2$  to asymmetric catalysis in these studies. To increase the solubility of transition metal catalysts in  $scCO_2$ , it has been suggested to incorporate perfluorinated side chains either directly in the metal-attached phosphine ligands<sup>12,13</sup> or in the anions in the case of cationic complexes.<sup>11</sup>

The enantioselective reduction of the C=N double bond is an important synthetic strategy for the preparation of optical active amines (Scheme 1) and has received much attention over the past few years, in both academic and industrial research.<sup>14</sup> A variety of chiral Rh,<sup>15</sup> Ir,<sup>16</sup> Ru,<sup>17</sup> and Ti<sup>18</sup> complexes have been studied as catalysts for the hydrogenation of imines, whereby the late transition metal systems contained mainly chiral diphosphine ligands.<sup>19</sup> The first industrial application of enantioselective imine hydrogenation was developed by a research group at Ciba-Geigy.<sup>20</sup> The catalyst, a chiral ferrocenyldiphosphine—iridium complex, shows extremely high activity and unprecedented productivity (up to 10<sup>6</sup> turnovers) with certain arylimines. The hydrogenation process is used to synthesize a precursor of (*S*)-metolachlor, an important herbicide, with 80% ee on a technical scale.

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Recently, enantiopure phosphinodihydrooxazoles<sup>21-23</sup> were successfully used in the Ir-catalyzed enantioselective hydrogenation of imines in CH<sub>2</sub>Cl<sub>2</sub>.<sup>24</sup> We now report that it is possible to replace the organic solvent with toxicologically and environmentally benign scCO<sub>2</sub> without loss of enantioselectivity, if the phosphinodihydrooxazole-bearing Ir catalysts are suitably adjusted to the specific properties of the reaction medium. Moreover, we provide the first evidence that the use of  $scCO_2$ can result in considerably higher catalyst efficiency owing to a different rate profile rather than by simply increasing the overall rate. Furthermore, scCO<sub>2</sub> was utilized in an integrated process as the medium for reaction and separation, which allowed easy isolation of the pure product and efficient recovery of the catalyst. Detailed investigations including high-pressure NMR and in situ reflectance FT-IR spectroscopy provided insight into the phase behavior, the solubility, and possible interactions of the various reaction components with compressed CO<sub>2</sub>.

## **Results and Discussion**

**Preparation of Ir Catalysts for Use in scCO<sub>2</sub>.** Recent research on catalysis in scCO<sub>2</sub> and the known solubility data for metal complexes in pure scCO<sub>2</sub><sup>25</sup> suggested a very low solubility in this medium for the cationic iridium phosphinodihydrooxazole complexes used as catalysts for imine hydrogenation in conventional organic solvents. Therefore, we synthesized a series of complexes **5**–**7** with perfluorinated groups in the ligand and/or the anion. In the ligands, perfluoroalkyl groups were attached in the periphery of the chiral skeleton to minimize interference with the chirality transfer at the active center. As a "CO<sub>2</sub>-philic" counterion, the tetrakis-3,5-bis(trifluoromethyl)-phenylborate anion (BARF) was chosen.

The unsubstituted 2-(phosphinoaryl)oxazoline ligand **3a** was obtained via orthometalation of the 2-aryloxazoline **1** and subsequent treatment with chlorodiphenylphosphine **2a** as described earlier.<sup>26</sup> Use of the perfluoroalkyl-substituted chlorodiphenylphosphine **2b** gave the new ligand **3b** (Scheme 2). The intermediate **2b** was prepared in 67% yield as a colorless solid by lithiation of 1-bromo-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tride-cafluorooctyl)benzene<sup>27</sup> with *n*-BuLi in diethyl ether, followed by addition of the resulting solution to Cl<sub>2</sub>PNEt<sub>2</sub> in THF, and subsequent treatment with dry gaseous HCl.<sup>28,29</sup>

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Scheme 3



Treatment of the dimeric iridium complex [{ $Ir(cod)(\mu-Cl)_2$ ] (4) (cod = 1,5-cyclooctadiene) with ligand **3a** or **3b** in CH<sub>2</sub>Cl<sub>2</sub> at 50 °C for several hours gave the complexes [Ir(cod)(3)]Cl. The chloro complexes can be isolated, but in general, the solutions were submitted directly to anion exchange by treatment with aqueous solutions of [NH<sub>4</sub>][PF<sub>6</sub>], Na[BPh<sub>4</sub>], or NaBARF at room temperature. Subsequent purification by flash chromatography afforded the iridium complexes **5**–**7** in ca. 90% yield (Scheme 3). Purification was also possible by crystallization, albeit in substantially lower yield than by chromatography (see the experimental procedure for **5b**).

Complexes 5–7 were obtained as bright red solids containing various amounts of CH<sub>2</sub>Cl<sub>2</sub> (0.1-0.7 equiv) even after prolonged drying under vacuum according to elemental and NMR analysis. For simplicity, all concentration values in this paper are based on solvent-free complexes, because of the large molecular weight of the compounds relative to CH<sub>2</sub>Cl<sub>2</sub>. The spectroscopic data for the pairs of compounds **a/b** are very similar. The introduction of the perfluoroalkyl chain leads to a slight decrease of the <sup>31</sup>P resonance from approximately 16.5 to 15.5 ppm for the two sets of borate complexes 6a/b and 7a/b. For comparison, the substitution of the  $[BAr_4]^-$  with the  $[PF_6]^-$  anion leads to a variation of  $\Delta \delta = 3$  to lower field. The chemical shifts of the olefinic proton and carbon nuclei of the cod ligand, which might experience an electronic or steric change at the metal center most directly, are identical within experimental error for the whole series of complexes. This indirect evidence is fully in line with our earlier <sup>103</sup>Rh NMR-based finding that substitution with ethylene-spaced perfluoroalkyl groups in the para position of the PPh<sub>2</sub> moiety keeps structural and electronic changes at the metal center to a minimum.<sup>12</sup>

The lipophilicity of a compound is one of several factors determining its solubility in scCO<sub>2</sub>, with higher lipophilicity resulting generally in higher solubility. Although no quantitative measurements have been performed, the  $R_f$  values obtained from TLC using silica plates under identical conditions give some indication of the lipophilicity of the cationic iridium complexes. The  $R_f$  values increase in the order [Ir(cod)(**3a**)]Cl  $\leq$  [Ir(cod)-(**3b**)]Cl  $\ll$  **6a** < **6b**  $\ll$  **7a** < **7b**, indicating that the anion has a larger influence on the lipophilicity of these ionic complexes than the ligand substitution pattern.

Iridium-Catalyzed Enantioselective Hydrogenation of Imines in Supercritical CO<sub>2</sub> and in CH<sub>2</sub>Cl<sub>2</sub>. The enantioselective hydrogenation of *N*-(1-phenylethylidene)aniline (8a) to give *N*-phenyl-1-phenylethylamine (9a) was used as a test reaction (Scheme 4). Catalytic runs were performed in a window-equipped stainless steel reactor (V = 100 mL) fitted with a dip tube (stainless steel capillary of 0.8 mm inner diameter) and a HPLC valve to allow sampling for offline GC analysis. Control experiments in CH<sub>2</sub>Cl<sub>2</sub> were carried out with identical amounts of substrate and catalysts per solvent volume Scheme 4



 Table 1. Asymmetric Hydrogenation of Imines 8 in CH<sub>2</sub>Cl<sub>2</sub><sup>a</sup>

entry	substrate (mmol)	catalyst (mol %)	conversion (%)	ee ( <i>R</i> ) (%)
1	8a (4.15)	<b>5a</b> (0.15)	99.7	83
2	8a (5.05)	<b>5b</b> (0.11)	100.0	80
$3^b$	<b>8a</b> (5.00)	<b>5b</b> (0.06)	10.0	$nd^c$
4	8a (4.17)	<b>6b</b> (0.13)	99.9	86
$5^d$	8a (4.18)	7a (0.15)	100.0	87
6	<b>8b</b> (4.00)	<b>5a</b> (0.3)	99.3	72
7	<b>8b</b> (3.83)	<b>7a</b> (0.15)	80.3	71

 ${}^{a}p(H_{2}) = 100$  bar, T = 40 °C, reaction time 20 h.  ${}^{b}$  In hexane.  ${}^{c}$  Not determined.  ${}^{d}$  Reaction time 5 h.

**Table 2.** Asymmetric Hydrogenation of Imines **8** in  $scCO_2^a$ 

entry	substrate (mmol)	catalyst (mol %)	conversion (%)	ee ( <i>R</i> ) (%)
1	<b>8a</b> (0.15)	<b>5a</b> (0.15)	99.9	37
2	8a (4.15)	<b>5b</b> (0.14)	100	26
$3^b$	8a (4.13)	<b>5b</b> (0.13)	99.5	26
4	8a (4.17)	<b>6a</b> (0.22)	11.0 (83.1 <sup>d</sup> )	$nd^{c}(60^{d})$
5	8a (4.16)	<b>6b</b> (0.14)	99.8	68
6	8a (4.22)	<b>7a</b> (0.14)	100	81
$7^e$	8a (4.19)	<b>7a</b> (0.15)	100	79
8	8a (4.53)	<b>7b</b> (0.09)	100	80
9	<b>8b</b> (3.85)	<b>5a</b> (0.3)	28.9	$nd^c$
10	<b>8b</b> (3.87)	<b>7a</b> (0.15)	15.5 (28.4 <sup>f</sup> )	$nd^c$
11	<b>8b</b> (2.4)	<b>7a</b> (0.25)	23	$nd^c$

<sup>*a*</sup>  $d(CO_2) = 0.75$  g mL<sup>-1</sup>,  $p(H_2) = 30$  bar, T = 40 °C, reaction time 20 h. <sup>*b*</sup> With addition of 0.5 mL of CH<sub>2</sub>Cl<sub>2</sub>. <sup>*c*</sup> Not determined. <sup>*d*</sup> Reaction time 40 h. <sup>*e*</sup>  $p(H_2) = 10$  bar. <sup>*f*</sup> Reaction time 70 h.

and with maximum stirring (magnetic stirring bar) for best comparison. Reactions were conducted for a standard reaction time of 20 h for screening purposes and monitored by GC for quantitative comparison.

Complex **5a** has been reported to catalyze the hydrogenation of **8a** to (*R*)-**9a** with ca. 84% ee in CH<sub>2</sub>Cl<sub>2</sub> under 100 bar of H<sub>2</sub> at room temperature using a catalyst loading of 0.1 mol %.<sup>24</sup> We found that all new catalysts **5**–**7** lead to quantitative hydrogenation of the imine **8a** in the same solvent, giving rise to formation of (*R*)-**9a** with 80–87% ee under similar conditions (Table 1). As anticipated, the introduction of the perfluoralkyl chain in the para position had little influence on the performance of the catalyst, and almost identical enantioselectivities were observed for complexes **5a** and **5b**. The anion had a marked influence on the reaction rate (Table 3), but only minor effects on the asymmetric induction in the organic medium, whereby the borate complexes **6** and **7** gave marginally higher ee's than their [PF<sub>6</sub>]<sup>-</sup> congeners **5**.<sup>30</sup>

The situation changed dramatically when the reaction was carried out in  $scCO_2$  as a solvent (Table 2). Hydrogenation of **8a** with complex **5a** in  $scCO_2$  gave complete conversion to the corresponding amine **9a** after 20 h, but a disappointingly low enantiomeric excess of 37% (*R*) was observed. Quantitative conversion and similar poor enantioselectivity was obtained with **5b** containing perfluoralkyl chains in the PPh<sub>2</sub> group. The unsubstituted borate complex **6a** showed very low activity in

<sup>(29)</sup> A chiral C<sub>2</sub>-symmetric phosphinite with perfluoralkyl substituents has been previously synthesized from **2b**: Kainz, S.; Koch, D.; Leitner, W. In *Selective Reactions of Metal-Activated Molecules*; Werner, H., Schreier, W., Eds.; Vieweg: Wiesbaden, 1998; p 151.

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scCO<sub>2</sub> (11% conversion after 20 h), whereas **6b** gave again complete conversion after identical reaction time. Both complexes **6a** and **6b** gave similar enantioselectivities between 60% and 70% (*R*), i.e., considerably higher than the corresponding complexes containing the  $[PF_6]^-$  counterion. Finally, the complexes **7** containing the BARF anion led to quantitative conversion within the standard reaction time, and (*R*)-**9a** was now obtained with 81% and 80% ee using **7a** (0.14 mol %) and **7b** (0.09 mol %), respectively. With **7a**, the reaction occurred still smoothly at a hydrogen pressure of only 10 bar, giving 79% ee.

Thus, it can be concluded that the enantioselective hydrogenation of N-(1-phenylethylidene)aniline (8a) can be carried out in scCO<sub>2</sub> with very high activity and with similar levels of enantiocontrol as in CH<sub>2</sub>Cl<sub>2</sub>.<sup>24</sup> However, scCO<sub>2</sub> cannot be regarded simply as a "nonpolar substitute solvent" for organic liquids. For example, catalyst 5b proved insoluble and almost completely inactive in hexane, a solvent with comparable density and polarity as scCO<sub>2</sub>. Moreover, the substrate N-(1-phenylethylidene)benzylamine (8b), which is structurally closely related to 8a, proved to be very difficult to hydrogenate in scCO<sub>2</sub> (Table 2). Independently of the catalyst precursor, conversion of 8b did not exceed 30% in scCO<sub>2</sub> even at prolonged reaction times or higher catalyst loadings. In contrast, the formation of **9b** proceeded smoothly with 71-72% ee in CH<sub>2</sub>Cl<sub>2</sub> (Table 1). To gain more insight into the course of the reaction in  $scCO_2$ and to obtain a more detailed comparison to the conventional solvent system, additional experiments were conducted using catalyst 7a.

Phase Behavior and Solubility of the Metal Species. The phase behavior of the reaction mixure and the nature of the active species (homogeneous vs heterogeneous) are of major concern for the design and the understanding of catalytic systems operating in scCO<sub>2</sub>. In the present case, visual inspection showed that up to 800 mg of the imine 8a were completely soluble in 100 mL of scCO<sub>2</sub> of densities  $d(CO_2) \ge 0.65$  g mL<sup>-1</sup> at or just above the critical temperature of pure CO<sub>2</sub>. No separation of a liquid phase was observed when 8a was converted quantitatively to 9a during the whole course of reaction. Under the reaction conditions, no undissolved solid could be observed, but very small amounts would have been difficult to detect owing to the reactor design. In fact, the difference in activity between 6a and **6b** may well be due to a solubility increase by introduction of the perfluoroalkyl chains in the PPh<sub>2</sub> group, and we cannot fully exclude that parts of the initially charged precursor complexes remain insoluble during catalytic runs also in other cases. The homogeneous nature of the active intermediate generated from catalyst precursor 7a, however, is indicated by a pale yellow color of the reaction medium throughout the reaction and could be verified in the following experiments.

In the first run, catalyst **7a** (0.08 mol %) was placed in the reactor inside a small glass beaker containing a small stirring bar. The opening on the top of the beaker reached just slightly below the lid of the reactor. Substrate **8a** was introduced as a solid into the reactor space around this compartment. The desired amount of CO<sub>2</sub> was then introduced very carefully at T = 34 °C through a valve at the bottom of the reactor to allow the presumably supercritical mixture of **8a** and CO<sub>2</sub> to come into contact with **7a**. To start the reaction, H<sub>2</sub> was introduced and the autoclave was further heated to the reaction temperature of 40 °C. After 20 h, the reactor was cooled and the product (98% (*R*)-**9a**, 81% ee) isolated by CO<sub>2</sub> extraction (vide infra). The beaker was removed, and the reactor was charged again with **8a**, CO<sub>2</sub>, and H<sub>2</sub>. Then, the second run was performed *without* 

*further addition of catalyst*. Quantitative conversion to give (R)-**9a** was again obtained with 78% ee, proving that the catalyst had been dissolved from the compartment and homogeneously dispersed throughout the reaction medium during the first run.

Similar experiments using glass inserts to separate the catalyst from the other reaction components revealed that the solubility of the metal species was strongly dependent on the composition of the reaction mixture. Before introduction of  $H_2$ , the bright red complex 7a remained insoluble and unchanged in the presence of imine 8a and CO<sub>2</sub> even at temperatures and pressures well above the point where complete dissolution of the imine was observed. Introduction of H<sub>2</sub> led to a rapid color change from red to yellow and apparent complete dissolution of the material, resulting in a pale yellow coloration of the supercritical phase. After venting, 50-75% of the total amount of iridium was found consistently in the reactor after removal of the beaker. In the absence of substrate 8a, catalyst 7a also turned yellow, but remained mostly insoluble in the compressed CO<sub>2</sub>/H<sub>2</sub> mixture (92% recovery of Ir in the beaker). Most remarkably, the amine 9a also had no apparent effect on the solubility of the metal species, and >90% iridium was recovered in the glass beaker.<sup>31</sup>

**Combination of Catalysis and Extraction (CESS Process)** and Catalyst Recycling. The solubility behavior of the catalytically active species suggested the possibility to separate 9a selectively from the reaction mixture by supercritical fluid extraction (SFE), leaving the catalyst in the reactor in active form. Most recently, we have described the first examples<sup>4,6</sup> for combinations of homogeneous catalysis and SFE using scCO<sub>2</sub>, and we refer to such integrated processes as "catalysis and extraction using supercritical solutions" (CESS). In the present case, it was possible to extract the amine 9a selectively without changing the conditions between the reaction and extraction stages. Simply purging the reactor after complete conversion with compressed CO<sub>2</sub> at 40 °C and 110 bar allowed 9a to be collected in the form of colorless crystals in a cold trap. Practically quantitative recovery of the amine was achieved after 1 h of extraction using an amount of CO<sub>2</sub> corresponding to 100 L of gaseous CO<sub>2</sub> at ambient conditions. The iridium content of the product was determined by atomic absorption spectroscopy (AAS) to be below 5 ppm.

Recharging the reactor with new substrate **8a** without any addition of catalyst or ligand led to quantitative hydrogenation of **8a** within the standard reaction time with almost identical levels of enantioselectivity in four subsequent experiments (Figure 1). Longer reaction times were required for quantitative conversion in subsequent runs, but the ee of the product remained above 70%. The overall yield from the repeated experiments shown in Figure 1 corresponds to a total turnover number (TON, moles of **9a** per mole of **7a**) of 10 000, and the isolated (R)-**9a** had an average ee of 76%.

**Comparison of the Enantioselective Hydrogenation of 8a** with Catalyst 7a in scCO<sub>2</sub> and in CH<sub>2</sub>Cl<sub>2</sub>. Figure 2 and Table 3 summarize the course of formation of **9a** during hydrogenation of **8a** with different loadings of catalyst **7a** in scCO<sub>2</sub> and CH<sub>2</sub>Cl<sub>2</sub> under otherwise identical conditions. Following the course of reaction by sampling and offline GC analysis under standard conditions in scCO<sub>2</sub> revealed that the reaction was too fast to be monitored with reasonable accuracy at catalyst loadings > 0.1 mol % (Table 3). Stepwise reduction of the catalyst loading showed that quantitative conversion was achieved within less

<sup>(31)</sup> The observations made by visual control and the pronounced influence of the composition of the mixture make other possible explanations for the activity in the second run such as accidental mechanical extrusion extremely unlikely.



Figure 1. Catalyst recycling in the enantioselective hydrogenation of **8a** to give (R)-**9a** using **7a** as catalyst and scCO<sub>2</sub> as medium for reaction and separation (CESS process). The dark gray bars indicate the enantiomeric excess, and the light gray bars show the time required for quantitative conversion.



Figure 2. Conversion/time profile for the enantioselective hydrogenation of imine 8a using catalyst 7a in scCO<sub>2</sub> and CH<sub>2</sub>Cl<sub>2</sub>, respectively.

**Table 3.** Influence of Reaction Conditions on the Asymmetric Hydrogenation of Imine **8a** in  $scCO_2$  and  $CH_2Cl_2^a$ 

entry	catalyst (mol %)	solvent	density (g mL <sup>-1</sup> )	<i>t</i> (h) <sup><i>b</i></sup>	TON <sup>c</sup>	$\begin{array}{c} { m TOF}^d \ ({ m h}^{-1}) \end{array}$	ee (R) (%)
1	<b>7a</b> (0.014)	scCO <sub>2</sub>	0.75	8.8	6830	2140	74
2	<b>7a</b> (0.078)	scCO <sub>2</sub>	0.75	1.2	1280	2820	78
3	<b>7a</b> (0.078)	scCO <sub>2</sub>	0.65	1.5	1275	1280	73
4	<b>7a</b> (0.071)	$CH_2Cl_2$		24	1400	1200	86
5	<b>7a</b> (0.16)	$CH_2Cl_2$		1.5	625	1400	86
6	<b>5a</b> (0.079)	$CH_2Cl_2$		30	1260	600	84
7	<b>5a</b> (0.15)	$CH_2Cl_2$		3	645	600	83

<sup>*a*</sup>  $p(H_2) = 30$  bar, 4.2 mmol of **8a**, T = 40 °C. <sup>*b*</sup> Time required for >98% conversion. <sup>*c*</sup> Turnover number = moles of **9a** per mole of Ir at time *t*. <sup>*d*</sup> Graphically determined initial turnover frequency for the formation of **9a**, given as moles of **9a** per mole of Ir per hour.

than 9 h at 0.014 mol % **7a**. Thus, in a single run, a TON = 6830 could be achieved with an initial turnover frequency (TOF, moles of **9a** formed per mole of **7a** and hour) of 2140 h<sup>-1</sup>. The initial TOF was found to vary somewhat with catalyst loading, and a TOF of 2820 h<sup>-1</sup> was obtained at 0.078 mol %. The ee decreased slightly with decreasing amounts of **7a** from 81% (0.14 mol %) to 78% (0.078 mol %) and finally 74% (0.014 mol %). The initial reaction rate decreased by a factor of 2.2 when the density of CO<sub>2</sub> was lowered from 0.75 g mL<sup>-1</sup> to 0.65 g mL<sup>-1</sup>. At the same time, the ee decreased slightly from 78% to 73%. The latter observations could result from reduced solubility of the active species at lower density, but a direct effect of the density on rate and selectivity cannot be ruled out.

In  $scCO_2$ , no significant variation of the ee was observed upon varying the partial pressures of hydrogen between 10 and Scheme 5

$$[(3a)|rL_n]^{+"} + 8a \xrightarrow{k_1} [(3a)|r(8a)L_n]^{+"} \xrightarrow{k_2} [(3a)|rL_n]^{+"}$$
10 11 10

40 bar (four experiments, ee = 79.3 - 81.7%; see Table 2, entries 6 and 7, for representative results). It is important to note that the ee's were also independent of H<sub>2</sub> pressure in CH<sub>2</sub>Cl<sub>2</sub> between 30 and 100 bar (compare entry 5 in Table 3 with entry 5 in Table 1). Typically, the ee's were higher by 5-8% in CH<sub>2</sub>Cl<sub>2</sub> than in scCO<sub>2</sub> under comparable conditions. The initial TOF was, however, approximately 2 times larger in the high-density supercritical reaction medium. Most intriguingly, the overall shape of the conversion versus time profile was remarkably different in both solvent systems. Two distinct rate regimes were observed in the organic solvent at 0.071 mol % 7a (Figure 2C), an initial phase with a high rate followed by a significant rate decrease after 30-40% conversion. The initial rate in CH<sub>2</sub>Cl<sub>2</sub> was found to be proportional to the amount of catalyst in the investigated concentration range (constant TOF; see Table 3), showing that this rate profile is not governed by mass-transfer limitations under these conditions. In sharp contrast, no rate decrease was observed at the same iridium concentration in  $scCO_2$  up to >90% conversion (Figure 2A). In  $scCO_2$ , the rate remained stable at even lower concentrations, corresponding to Ir loadings as low as 0.014 mol %. Thus, >90% conversion of the imine corresponding to >6800 turnovers could be achieved within less than 6 h in scCO<sub>2</sub> (Figure 2B), whereas more than 22 h was required to achieve similar conversion in CH<sub>2</sub>Cl<sub>2</sub> using a 5 times larger amount of 7a (TON = 1400).

The iridium-catalyzed enantioselective hydrogenation of imines proceeds through a multistep catalytic cycle which is not known in detail. A highly simplified sequence including only the most basic steps is depicted in Scheme 5. In this scheme, the yellow species formed from the reaction of 7a with  $H_2$  corresponds to the catalytically active complex 10. This species reacts with 8a in a reversible reaction to give the intermediate 11, whose reaction with H<sub>2</sub> liberates the amine 9a and regenerates 10. The rate profile in  $scCO_2$  indicates that the reaction is zero order (or at least close to) in substrate and also largely independent of the reaction time (see also the recycling experiments!). This kinetic behavior is consistent with the sequence shown in Scheme 5 if the equilibrium between 10 and 8a lies far to the side of 11 and is established much faster than the subsequent product formation. This would also explain why the catalytically active species **11**, which is the only metal species that is reasonably soluble in scCO<sub>2</sub>, remains in solution until the imine 8a is consumed completely. In principle, the same scheme may apply for the reaction in CH<sub>2</sub>Cl<sub>2</sub>, and indeed the same color changes are observed in this medium. However, the reaction profile in CH<sub>2</sub>Cl<sub>2</sub> is highly nonlinear, demonstrating a strong dependence of the rate on the reaction time and/or the concentration of substrate. This may reflect a rate law with a broken order in substrate or some deactivation process of the catalyst.<sup>32</sup> A precise mechanistic explanation for the greatly enhanced catalytic efficiency observed in scCO<sub>2</sub> has to await further studies including detailed kinetic investigations in scCO<sub>2</sub> and comparison to the yet unknown rate law in CH<sub>2</sub>Cl<sub>2</sub>. It is, however, already clear from the current data that the enhancement of the catalyst efficiency cannot be reduced to a mere enhancement of "H2 availability".

<sup>(32)</sup> These results are also consistent with findings of an ongoing detailed investigation of the reaction kinetics using **5a** in  $CH_2Cl_2$ . Blackmond, D.; Pfaltz, A. Unpublished results.



Figure 3. In situ FT-IR monitoring of the hydrogenation of imine 8a to give the secondary amine 9a with catalyst 7a in scCO<sub>2</sub> using a highpressure reflectance probe. The marked and underlined bands can be identified at identical positions in control spectra of toluene solutions of 9aand 8a, respectively.

Investigations Using High-Pressure Spectroscopy. Due to the rapidly growing number of homogeneously catalyzed reactions which can be carried out efficiently in scCO<sub>2</sub>, there is an increasing demand for in situ techniques to monitor the course of chemical syntheses in this reaction medium. In the present case, the hydrogenation of 8a could be monitored readily by in situ FT-IR spectroscopy utilizing a high-pressure reflectance probe which was mounted directly to a standard windowequipped stainless steel reactor (200 mL). This technique avoids some of the problems frequently encountered with conventional high-pressure IR cells such as difficulties in pumping the reaction medium and inefficient mass transport owing to the small path lengths. The high-pressure reflectance IR probe is based on a silicon waver allowing for a spectral window from 4000 to 600  $cm^{-1}$  and is fed through the lid of the reactor with a home-built screw fitting. This probe design makes the whole setup more flexible than reactors with integrated ATR sensors. The probe is connected to a ASI/Mettler-Toledo ReactIR-1000 FT-IR system, allowing continuous sampling and subsequent deconvolution and analysis of the acquired spectra.

Figure 3 shows the changes of the IR spectra during hydrogenation of **8a** using catalyst **7a** under typical reaction conditions. There were several well-resolved absorption bands growing in due to the formation of the product, and other bands disappeared concomitantly. No bands indicating the formation of an intermediate or side product(s) were detected. The positions of the nonoverlapping dissappearing signals at 1216 and 1643 cm<sup>-1</sup> and the growing band at 1262 cm<sup>-1</sup> are almost identical to those of toluene solutions or of the neat compounds **8a** and **9a**, respectively (see the Supporting Information). Most notably, the spectra provided no indication for the formation of the carbamic acid or the ammonium carbamate from **9a** and CO<sub>2</sub>.

Further information on the solubility and the chemical behavior of the substrates and products in  $scCO_2$  was provided by high-pressure NMR spectroscopy using sapphire tubes with a titanium pressure head.<sup>33</sup> Both substrates **8a** and **8b** were readily soluble in  $scCO_2$  (40 °C,  $d(CO_2) = 0.75$  g mL<sup>-1</sup>) at concentrations of 10 mg mL<sup>-1</sup>. The spectra were identical to

those observed in conventional solvents (see the Supporting Information). The arylamine 9a also gave a clear solution in liquid or supercritical CO<sub>2</sub>. The spectra of **9a** in CDCl<sub>3</sub> and in scCO<sub>2</sub> were almost identical, the N-H resonance appearing as a slightly broadened signal at 4.0 and 3.7 ppm, respectively. In contrast, a white insoluble solid was formed when liquid CO<sub>2</sub> was introduced into the NMR tube containing the secondary amine 9b at room temperature. The solid remained mostly insoluble upon raising the temperatures above  $T_c$  of pure CO<sub>2</sub>, preventing the recording of conclusive NMR spectra. These observations are in accord with the established higher tendency of secondary alkylamines compared to arylamines to form insoluble carbamates by interaction with liquified or supercritical CO2.2b,34 Although no apparent phase separation or precipitate was observed during hydrogenation of 8b under catalytic conditions (<30% conversion), the carbamic acid or carbamate from 9b can also be expected to form under these conditions. The formation of a strongly coordinating carboxylate function provides a plausible explanation for the inefficient hydrogenation of **8b** compared to **8a** in  $scCO_2$ ,<sup>24</sup> but other deactivation processes may equally apply.

## Conclusion

Taken together, the results of this study demonstrate that  $scCO_2$  is an attractive alternative reaction medium for the enantioselective hydrogenation of prochiral imines. From a practical point of view,  $scCO_2$  provides a number of advantages over the organic solvents generally used in imine hydrogenation. In addition to the low toxicity and the environmentally benign character of the supercritical reaction medium, its utilization allows lower catalyst loading as well as efficient product isolation and catalyst recycling (CESS process).

However, it is also evident that scCO<sub>2</sub> cannot be regarded a simple "substitute solvent", and successful "transfer" of reactions

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<sup>(34) (</sup>a) Francis, A. W. J. Phys. Chem. **1954**, 58, 1099. (b) Ashraf-Khorassani, M.; Taylor, L. T.; Zimmermann, P. Anal. Chem. **1990**, 62, 1177.

from conventional solvents to this medium requires detailed knowledge about the physicochemical properties of the reaction mixture and about possible chemical interactions of reaction components with the supercritical fluid. In the present case, it was found that the substrate is of key importance for solubilizing the catalytically active species. Furthermore, high levels of asymmetric induction were observed only with catalysts containing the BARF anion, although other complexes also showed sufficient solubility for catalysis. Additional research is clearly needed to elucidate the peculiar properties of this anion in transition metal catalysis in more detail.

In situ high-pressure NMR and reflectance FT-IR spectrosocpy provided useful information about possible interactions of substrates and products with scCO<sub>2</sub> and allowed a rationalization of the different reactivities of structurally similar substrates. A very remarkable observation of the present study is the fact that catalyst 7a shows a considerably higher efficiency in scCO<sub>2</sub> compared to conventional organic solvent resulting from a different rate profile rather than a simple increase in the overall rate of the process. We can only speculate on the reasons for this beneficial effect at present. Among various possibilities, different chemical interactions and coordination abilities of the different solvent systems with catalytic active species<sup>35</sup> might be of particular importance. The techniques and methodologies described here should prove useful for further elucidation of this system and also for other applications of  $scCO_2$  as a reaction medium in homogeneous catalysis.

## **Experimental Section**

Safety warning: Conducting catalytic reactions and spectroscopic investigations in  $scCO_2$  requires handling of highly compressed gases and must be carried out only using suitable equipment and under appropriate safety conditions.

All manipulations of air-sensitive materials and all catalytic experiments were carried out under argon atmosphere. Solvents were dried, purified, and degassed according to standard methods<sup>36</sup> and stored under argon. The gases (H<sub>2</sub> (99.9%), argon (99.999%), and CO<sub>2</sub> (99.995%)) (Messer Griesheim) were used without further purification. [{Ir(cod)- $(\mu$ -Cl)}<sub>2</sub>] (**4**) (99%, Strem), *n*-BuLi (1.7 M in *n*-hexane, Aldrich), and *sec*-BuLi (1.3 M in cyclohexane, Aldrich) were commercial products and used as received. *N*,*N*,*N*'. Tetramethylethylendiamine (TMEDA; Fluka) was dried and distilled over LiAlH<sub>4</sub> prior to use. Cl<sub>2</sub>PNEt<sub>2</sub><sup>37</sup> and NaBARF<sup>38</sup> were synthesized according to known procedures. The syntheses of **1**, **8a**, **8b**, **3a**,<sup>26</sup> **5a**,<sup>24</sup> and 1-bromo-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)benzene<sup>27</sup> are described elsewhere.

Analytical Methods. Specific rotations were recorded on a JASCO DIP-360 polarimeter (5.0 cm, 20 °C, concentration in grams per 100 mL of solution, estimated error  $\pm$ 5%). NMR spectra were recorded on a Bruker AC 200 or a Bruker AMX 300 spectrometer. Chemical shifts  $\delta$  are recorded in parts per million relative to external CFCl<sub>3</sub> for <sup>19</sup>F, H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P, and TMS for <sup>1</sup>H and <sup>13</sup>C, using the solvent resonance as secondary standard if possible. Elemental analysis and AAS measurements were carried out in the microanalytical laboratory Kolbe, Mülheim/Ruhr.

Synthesis of Bis[4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)phenyl]chlorophosphine (2b). A solution of *n*-BuLi (1.7 M in *n*-hexane, 10 mL, 17 mmol) was added slowly to 1-bromo-4-(3,3,4,4,5,5,6,6,7,7, 8,8,8-tridecafluorooctyl)benzene<sup>27</sup> (8.77 g, 17.4 mmol) in 50 mL of Et<sub>2</sub>O at -50 °C. The yellow cloudy solution was added slowly to a solution of Cl<sub>2</sub>PNEt<sub>2</sub> (1.51 g, 8.6 mmol) in 20 mL of THF at 0 °C and

(37) Butters, T.; Winter, W. Chem. Ber. 1984, 117, 990.

stirred at 0 °C overnight. Dry gaseous HCl was bubbled through the clear solution over a period of 30 min at room temperature. After degassing, filtration, and concentration, the product precipitated at -20 °C as colorless crystals. The product was isolated by filtration and washed twice with Et<sub>2</sub>O to yield **2b** (3.38 g, 3.70 mmol, 67%): <sup>1</sup>H NMR (200.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  2.40 (m, 4H; CH<sub>2</sub>CH<sub>2</sub>CF<sub>2</sub>), 2.90 (m, 4H; CH<sub>2</sub>CF<sub>2</sub>), 7.25 (m, 4H; CH(3)), 7.52 (m, 4H; CH(2)); <sup>13</sup>C{<sup>1</sup>H} NMR (50.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  26.7 (t, *J*<sub>FC</sub> = 4 Hz; CH<sub>2</sub>CH<sub>2</sub>CF<sub>2</sub>), 33.0 (t, *J*<sub>FC</sub> = 22 Hz; CH<sub>2</sub>CF<sub>2</sub>), 129.1 (d, *J*<sub>PC</sub> = 7 Hz; CH(3)), 132.3 (d, *J*<sub>PC</sub> = 25 Hz; CH(2)), 137.5 (d, *J*<sub>PC</sub> = 33 Hz; C(1)), 141.7 (s; C(4)), 105–125 (m; CF<sub>x</sub>); <sup>19</sup>F NMR (282.4 MHz, CDCl<sub>3</sub>)  $\delta$  -81.2 (t, 6F, *J* = 11.4 Hz), -114.8 (m, 4F), -122.1 (m, 4F), -123.1 (m, 4F), -123.7 (m, 4F), -126.4 (m, 4F); <sup>31</sup>P{<sup>1</sup>H} NMR (80.2 MHz, CDCl<sub>3</sub>)  $\delta$  81.3 (s); MS (70 eV, DEI) *m/z* (%) 912 (100) [M<sup>++</sup>].

Synthesis of (-)-(4S)-2-(2-{Bis[4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)phenylphosphanyl}phenyl]-4-isopropyl-4,5-dihydrooxazole (3b). A solution of sec-BuLi (1.3 M in cyclohexane, 4.25 mL, 5.53 mmol) was added dropwise to a cooled (-65 °C) mixture of 3 (1.01 g, 5.03 mmol) and TMEDA (0.83 mL, 5.53 mmol) in hexane (90 mL). After stirring for 1.5 h at -65 °C the yellow solution was allowed to warm to 0 °C, whereby the color changed to orange. A solution of 2b (4.68 g, 5.03 mmol) in THF (30 mL) was added at 0 °C, and the resulting mixture was stirred overnight. After hydrolysis with saturated aqueous NH<sub>4</sub>Cl (10 mL) at room temperature, the product was extracted with  $Et_2O$  (2 × 10 mL), and the combined organic layers were dried over Na2SO4, filtered, and evaporated to dryness. Recrystallization from MeOH/Cl2FCCF2Cl (2:1) afforded the desired product **3b** as a colorless solid (1.21 g, 1.14 mmol, 21%): <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>)  $\delta$  0.73 (d, 3H, J = 6.7 Hz; CH(CH<sub>3</sub>)<sub>2</sub>), 0.83 (d, 3H, J =6.7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.51 (m, 1H; CH(CH<sub>3</sub>)<sub>2</sub>), 2.40 (m, 4H; CH<sub>2</sub>CF<sub>2</sub>), 2.94 (m, 4H; CH<sub>2</sub>CH<sub>2</sub>CF<sub>2</sub>), 3.85-3.94 (m, 2H; CH<sub>2</sub>(5), CH(4)), 4.20 (m, 1H, CH<sub>2</sub>(5)), 6.90 (m, 1H; CH(4')), 7.16-7.42 (m, 10H; arom CH), 7.94 (m, 1H; CH(6'));  ${}^{13}$ C NMR (75.5 MHz, CDCl<sub>3</sub>)  $\delta$  18.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 18.8 (CH(CH<sub>3</sub>)<sub>2</sub>, 26.2 (br, CH<sub>2</sub>CH<sub>2</sub>CF<sub>2</sub>), 32.7 (t,  $J_{FC} = 22$  Hz; (CH<sub>2</sub>CH<sub>2</sub>-CF<sub>2</sub>)), 32.8 (t,  $J_{FC} = 22$  Hz CH<sub>2</sub>CH<sub>2</sub>CF<sub>2</sub>), 32.8 (CH(CH<sub>3</sub>)<sub>2</sub>, 70.1 (CH<sub>2</sub>-(5)), 73.2 (CH(4)), 124.4, 128.1, 128.2, 128.3, 129.9 (d,  $J_{PC} = 3$  Hz), 105-125 (m, *CF<sub>x</sub>*), 130.3, 133.7, 134.1 (d, *J*<sub>PC</sub> = 21 Hz), 134.7 (d, *J*<sub>PC</sub> = 21 Hz) (arom CH), 132.0 (d,  $J_{PC}$  = 19 Hz), 136.6 (d,  $J_{PC}$  = 10 Hz), 138.8 (d,  $J_{PC} = 24$  Hz), 139.5 (d,  $J_{PC} = 14$  Hz) (arom C), 162.7 (d,  $J_{PC}$ = 3 Hz, C(2)). <sup>19</sup>F NMR (282.4 MHz, CDCl<sub>3</sub>)  $\delta$  -81.5 (t, 6F, J = 11.4 Hz), -115.1 (m, 2F), -115.2 (m, 2F), -122.5 (m, 4F), -123.5 (m, 4F), -124.2 (m, 4F), -126.8 (m, 4F); <sup>31</sup>P{<sup>1</sup>H} NMR (121.5 MHz, CDCl<sub>3</sub>)  $\delta$  –6.9 (s); MS (70 eV, DEI) m/z (%) 1065 (15) [M<sup>•+</sup>]. Anal. Calcd for C<sub>40</sub>H<sub>30</sub>F<sub>26</sub>N<sub>1</sub>O<sub>1</sub>P<sub>1</sub> (1065.7): C, 45.08; H, 2.84; F, 46.35; N, 1.31; P, 2.91. Found: C, 45.19; H, 2.88; F, 46.60; N, 1.39; P, 2.96.

(-)-(4*S*)-2-(2-{Bis[4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)phenyl]phosphanyl}phenyl)-4-isopropyl-4,5-dihydrooxazole-( $\eta^4$ -1,5cyclooctadienyl)iridium(I) Hexafluorophosphate (5b). A solution of 3b (456 mg, 0.428 mmol) and 4 (143 mg, 0.213 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was stirred at 50 °C for 3 h in a sealed tube under Ar. After cooling to room temperature, the red solution was treated with an aqueous solution of  $NH_4PF_6$  (0.4 M, 2 × 10 mL), washed with water (10 mL), and dried over Na2SO4. Crystallization from CH2Cl2/CH3OH and drying at  $10^{-4}$  mbar afforded **5b** as a bright red powder (336.4 mg, 0.22 mmol, 52%): <sup>1</sup>H NMR (300.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -0.04 (d, 3H, J = 6.7 Hz;  $CH_3$ ), 0.91 (d, 3H, J = 7.1 Hz;  $CH_3$ ), 1.40–1.61 (m, 1H;  $CH_2$  of cod), 1.63-1.86 (m, 1H; CH<sub>2</sub> of cod), 1.96-2.24 (m, 1H; CH<sub>2</sub> of cod; 1H; CH(CH<sub>3</sub>)<sub>2</sub>), 2.24-2.10 (m, 1H; CH<sub>2</sub> of cod), 2.30-2.73 (m, 4H; CH<sub>2</sub> of cod; 4H; CH2CF2), 2.90-3.13 (m, 1H; CH of cod; 4H; CH2CH2-CF<sub>2</sub>), 3.24–3.36 (m, 1H; CH of cod), 4.29–4.16 (m, 1H; CH(4)), 4.52 (d, 2H; J = 6.5 Hz;  $CH_2(5)$ ), 4.94–5.07 (m, 1H; CH of cod), 5.16– 5.24 (m, 1H; CH of cod), 7.03-7.13 (m, 2H; arom CH), 7.30-7.81 (m, 9H; arom CH), 8.22-8.27 (m, 1H, arom CH); <sup>13</sup>C NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 12.9$  (CH(CH<sub>3</sub>)<sub>2</sub>), 18.9 (CH(CH<sub>3</sub>)<sub>2</sub>, 26.6 (CH<sub>2</sub>-CH<sub>2</sub>CF<sub>2</sub>), 26.8 (CH<sub>2</sub>CH<sub>2</sub>CF<sub>2</sub>), 26.9 (CH<sub>2</sub> of cod), 28.9 (CH<sub>2</sub> of cod), 32.6 (t,  $J_{FC} = 22$  Hz;  $CH_2CF_2$ ), 32.7 ( $CH_2$  of cod), 33.4 ( $CH(CH_3)_2$ ), 36.5 (d,  $J_{PC} = 5$  Hz;  $CH_2$  of cod), 63.3 (CH of cod), 64.0 (CH of cod), 69.1 ( $CH_2(5)$ ), 70.9 (CH(4)), 94.4 (d,  $J_{PC} = 13$  Hz; CH of cod), 98.4 (d,  $J_{PC} = 11$  Hz; CH of cod), 105–125 (m; CF<sub>x</sub>), 129.2 (d,  $J_{PC} = 10$ Hz), 130.2 (d,  $J_{PC} = 11$  Hz), 132.8 (d,  $J_{PC} = 2$  Hz), 134.1 (d,  $J_{PC} = 11$ Hz), 134.3 (d,  $J_{PC} = 8$  Hz), 134.4 (d,  $J_{PC} = 7$  Hz), 134.5 (d,  $J_{PC} = 2$ 

<sup>(35)</sup> For the coordination chemistry of CO<sub>2</sub> and its relevance for catalysis, see: Leitner, W. *Coord. Chem. Rev.* **1996**, *153*, 257.

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Hz), 135.8 (d,  $J_{PC} = 12$  Hz) (arom CH), 121.2 (d, J = 59 Hz), 128.3, 128.7, 129.0, 129.4, 144.9 (d,  $J_{PC} = 2$  Hz), 144.0 (d,  $J_{PC} = 2$  Hz) (arom C), 164.3 (d,  $J_{PC} = 7$  Hz, C(2)); <sup>19</sup>F NMR (282.4 MHz, CD<sub>2</sub>-Cl<sub>2</sub>)  $\delta$  -73.6 (d, 6F,  $J_{PF} = 713$  Hz), -81.3 (t, 6F, J = 8.5 Hz), -114.6 (m, 2F), -114.8 (m, 2F), -122.2 (m, 4F), -123.2 (m, 4F), -123.8 (m, 4F), -126.5 (m, 4F); <sup>31</sup>P{<sup>1</sup>H} NMR (81.0 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  18.0 (s), -141.3 (sep,  $J_{PF} = 710.6$  Hz); <sup>11</sup>B{<sup>1</sup>H} NMR (64.2 MHz, CD<sub>2</sub>-Cl<sub>2</sub>)  $\delta$  -6.5 (s); [ $\alpha$ ]<sub>589</sub> = -134 (CHCl<sub>3</sub>, c = 0.3, 20 °C); MS (ESI/pos (MeOH)) m/z (%) 1366 (100) [M<sup>+</sup>, <sup>193</sup>Ir], isotope cluster 1364–1368; calcd (obsd) 54 (51), 30 (33), 100 (100), 52 (54), 14 (12). Anal. Calcd for C<sub>48</sub>H<sub>42</sub>F<sub>32</sub>Ir<sub>1</sub>N<sub>1</sub>O<sub>1</sub>P<sub>2</sub> (1511.1): C, 38.15; H, 2.80; F, 40.23; Ir, 12.58; N, 0.96; P, 3.98.

(-)-(4S)-2-(2-Diphenylphosphanylphenyl)-4-isopropyl-4,5-dihydrooxazole-( $\eta^4$ -1,5-cyclooctadienyl)iridium(I) Tetrakisphenylborate (6a). A solution of 3a (60.7 mg, 0.16 mmol) and 4 (54.6 mg, 0.08 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was stirred at 50 °C for 4.5 h in a sealed tube under Ar. After cooling to room temperature, a suspension of Na-[BPh<sub>4</sub>] (111.3 mg, 0.33 mmol) in H<sub>2</sub>O (25 mL) was added and the mixture stirred for several hours. Anion exchange was monitored by TLC (silica gel, CH<sub>2</sub>Cl<sub>2</sub>; [Ir(cod)(**3a**)]Cl,  $R_f = 0$ ; [Ir(cod)(**3a**)]BPh<sub>4</sub>,  $R_f$ = 0.40). The aqueous layer was separated, extracted with  $CH_2Cl_2$  (4  $\times$  5 mL), and dried over Na<sub>2</sub>SO<sub>4</sub>. Flash colomn chromatography on silica gel (eluent CH<sub>2</sub>Cl<sub>2</sub>) and evaporation of the solvent afforded 6a as a bright red powder (143.8 mg, 0.14 mmol, 89%): <sup>1</sup>H NMR (300.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = -0.06$  (d, 3H, J = 6.7 Hz; CH<sub>3</sub>), 0.87 (d, 3H, J = 7.1 Hz, CH<sub>3</sub>), 1.42-1.57 (m, 1H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.65-1.79 (m, 1H;  $CH_2$  of cod), 1.95–2.08 (m, 2H;  $CH_2$  of cod), 2.08–2.20 (m, 1H;  $CH_2$ of cod), 2.45-2.69 (m, 4H; CH<sub>2</sub> of cod), 3.03-3.16 (m, 1H; CH of cod), 3.31-3.36 (m, 1H; CH of cod), 4.10 (dt, 1H, J = 9.5 Hz, 2.9Hz; CH(4)), 4.22 (t, 1H, J = 9.5 Hz; CH<sub>2</sub>(5)), 4.39 (dd, 1H, J = 9.5Hz, 3.4 Hz; CH<sub>2</sub>(5)), 4.91-5.01 (m, 1H; CH of cod), 5.01-5.11 (m, 1H; CH of cod), 6.87 (m, 4H; arom CH), 7.03 (m, 8H; arom CH), 7.09-7.16 (m, 2H; arom CH), 7.29-7.37 (m, 8H; arom CH), 7.37-7.73 (m, 11H; arom CH), 8.15-8.20 (m, 1H; arom CH); <sup>13</sup>C NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 12.7 (CH(CH<sub>3</sub>)<sub>2</sub>); 18.9 (CH(CH<sub>3</sub>)<sub>2</sub>; 26.9 (CH<sub>2</sub> of cod), 28.9 (CH2 of cod), 32.7 (CH2 of cod), 33.3 (CH(CH3)2); 36.5  $(d, J_{PC} = 5 \text{ Hz}; CH_2 \text{ of cod}), 63.5 (CH \text{ of cod}), 64.1 (CH \text{ of cod}), 68.9$  $(CH_2(5))$ , 70.9 (CH(4)), 93.9  $(d, J_{PC} = 13 \text{ Hz}; CH \text{ of cod})$ , 97.7  $(d, J_{PC})$ = 11 Hz; CH of cod), 129.2 (d,  $J_{PC}$  = 12 Hz), 130.1 (d,  $J_{PC}$  = 11 Hz), 132.3 (d,  $J_{PC} = 3$  Hz); 132.8 (d,  $J_{PC} = 2$  Hz), 133.0 (d,  $J_{PC} = 3$  Hz), 133.7 (d,  $J_{PC} = 10$  Hz), 134.3 (d,  $J_{PC} = 10$  Hz), 134.4 (d,  $J_{PC} = 8$  Hz), 134.6 (d,  $J_{PC} = 2$  Hz), 135.3 (d,  $J_{PC} = 12$  Hz) (aromm CH), 122.9 (d, J = 58 Hz), 128.7, 129.0, 129.2, 129.9, 130.6 (arom C), 164.1 (d,  $J_{PC}$ = 2 Hz, C(2)), 122.1 (s, 4C; arom CH), 125.9-126.0 (m, 8C; arom *C*H), 136.3 (m, 8C; arom *C*H), 164.5 (q,  $J_{CB} = 49.5 \text{ Hz}$ ); <sup>31</sup>P{<sup>1</sup>H) NMR  $(121.5 \text{ MHz}, \text{CD}_2\text{Cl}_2) \delta 16.5 \text{ (s)}; {}^{11}\text{B}{}^{1}\text{H} \text{NMR} (64.2 \text{ MHz}, \text{CD}_2\text{Cl}_2)$  $\delta$  -7.0 (s); MS (ESI/pos (CH<sub>2</sub>Cl<sub>2</sub>)) *m*/*z* (%) 674 (100) [M<sup>+</sup>, <sup>193</sup>Ir], isotope cluster 672-676; calcd (obsd) 57 (65), 21 (23), 100 (100), 36 (39), 7 (7); (ESI/neg (CH<sub>2</sub>Cl<sub>2</sub>)) m/z (%) 319 (100) [M<sup>-</sup>, <sup>11</sup>B], isotope cluster 318-321; calcd (obsd) 23 (36), 100 (100), 26 (37), 3 (5) (deviation according to unfavorable signal/noice ratio). Anal. Calcd for  $C_{56}H_{56}B_1Ir_1N_1O_1P_1$  (×0.6 mol of  $CH_2Cl_2$ ) (1044.0): C, 65.12; H, 5.52; N, 1.34; P, 2.97. Found: C, 64.96; H, 5.97; N, 1.16; P, 3.08.

(-)-(4S)-2-(2-{Bis[4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)phenyl]phosphanyl}phenyl)-4-isopropyl-4,5-dihydrooxazole-( $\eta^{4}$ -1,5cyclooctadienyl)iridium(I) Tetrakisphenylborate (6b). A solution of 3b (141.8 mg, 0.15 mmol) and 4 (50.4 mg, 0.08 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was stirred at room temperature overnight and then at 50 °C for 2 h in a sealed tube under Ar. After cooling to room temperature, a suspension of Na[BPh4](100 mg, 0.29 mmol) in H2O (25 mL) was added and stirred for several hours. Anion exchange was monitored by TLC (silica gel, CH<sub>2</sub>Cl<sub>2</sub>; [Ir(cod)(**3b**)]Cl,  $R_f = 0$ ; [Ir(cod)(**3b**)]BPh<sub>4</sub>,  $R_f = 0.50$ ). The organic layer was separated, and the aqueous layer extracted with  $CH_2Cl_2$  (4  $\times$  5 mL). The combined organic fractions were washed with H2O and dried over Na2SO4. Flash colomn chromatography on silica gel (eluent CH2Cl2) and evaporation of the solvent afforded 6b as a bright red powder (244.9 mg, 0.15 mmol, 97%): <sup>1</sup>H NMR (300.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -0.05 (d, 3H, J = 6.7 Hz;  $CH_3$ ), 0.78 (d, 3H, J = 7.1 Hz;  $CH_3$ ), 1.18–1.47 (m, 1H;  $CH(CH_3)_2$ ), 1.56-1.71 (m, 1H; CH<sub>2</sub> of cod), 1.86-1.98 (m, 2H; CH<sub>2</sub> of cod), 1.992.13 (m, 1H; CH<sub>2</sub> of cod), 2.20-2.57 (m, 4H; CH<sub>2</sub> of cod, 4H, CH<sub>2</sub>-CF<sub>2</sub>), 2.88-3.00 (m, 1H; CH of cod; 4H, CH<sub>2</sub>CH<sub>2</sub>CF<sub>2</sub>), 3.17-3.26 (m, 1H; CH of cod), 4.00 (dt, 1H, J = 9.0 Hz, 2.7 Hz; CH(4)), 4.13 (t, 1H, J = 9.7 Hz;  $CH_2(5)$ ), 4.29 (dd, 1H, J = 9.6 Hz, 3.3 Hz;  $CH_2(5)$ ), 4.82-4.92 (m, 1H; CH of cod), 4.93-5.02 (m, 1H; CH of cod), 6.77 (m, 4H; arom CH), 6.90–7.00 (m, 2H; arom CH; 8H; arom CH), 7.19– 7.32 (m, 8H; arom CH; 5H; arom CH), 7.45-7.63 (m, 4H; arom CH), 8.05-8.10 (m, 1H; arom CH); <sup>13</sup>C NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 12.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 18.9 (CH(CH<sub>3</sub>)<sub>2</sub>, 26.6 (m; CH<sub>2</sub>CH<sub>2</sub>CF<sub>2</sub>), 26.8 (m; CH<sub>2</sub>-CH<sub>2</sub>CF<sub>2</sub>), 27.0 (CH<sub>2</sub> of cod), 28.9 (CH<sub>2</sub> of cod), 32.6 (t,  $J_{FC} = 22$  Hz;  $CH_2CF_2$ ), 32.7 ( $CH_2$  of cod), 33.4 ( $CH(CH_3)_2$ ), 36.5 (d,  $J_{PC} = 5$  Hz; CH2 of cod), 63.5 (CH of cod), 64.2 (CH of cod), 69.0 (CH2(5)), 70.9 (CH(4)), 94.1 (d,  $J_{PC} = 13$  Hz; CH of cod), 98.0 (d,  $J_{PC} = 10$  Hz; CH of cod), 105–125 (m; CF<sub>x</sub>), 129.3 (d,  $J_{PC} = 11$  Hz), 130.2 (d,  $J_{PC} =$ 11 Hz), 132.9 (d,  $J_{PC} = 3$  Hz), 134.1 (d,  $J_{PC} = 10$  Hz), 134.3, 134.4, 134.5, 135.7 (d,  $J_{PC} = 12$  Hz) (arom CH), 121.1 (d, J = 59 Hz), 128.2, 128.7, 128.9, 129.0, 129.1, 144.1 (d,  $J_{PC} = 3$  Hz), 144.9 (d,  $J_{PC} = 3$ Hz) (arom C), 164.2 (d,  $J_{PC} = 7$  Hz, C(2)), 122.1 (s, 4C; arom CH), 126.0 (m, 8C, arom CH), 136.3 (m, 8C; arom CH,), 164.5 (q,  $J_{CB} =$ 49.8 Hz); <sup>19</sup>F NMR (282.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -81.3 (t, 6F, J = 11.4 Hz), -114.5 (t, 2F, J = 11.4 Hz), -114.7 (t, 2F, J = 11.4 Hz), -122.2 (br; 4F), -123.2 (br; 4F), -123.8 (br; 4F), -126.4 (br; 4F);  ${}^{31}P{}^{1}H{}$ NMR (121.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 15.4 (s); <sup>11</sup>B{<sup>1</sup>H} NMR (64.2 MHz,  $CD_2Cl_2$ )  $\delta$  -6.5 (s); [ $\alpha$ ]<sub>589</sub> = -184 (CHCl\_3, c = 0.25, 20 °C); MS (ESI/pos (CH<sub>2</sub>Cl<sub>2</sub>)) m/z (%) 1366 (100) [M<sup>+</sup>, <sup>193</sup>Ir], isotope cluster 1364-1368; calcd (obsd) 55 (57), 30 (30), 100 (100), 52 (48), 14 (13); (ESI/neg (CH<sub>2</sub>Cl<sub>2</sub>)) m/z (%) 319 (100) [M<sup>-</sup>, <sup>11</sup>B], isotope cluster 318-321; calcd (obsd) 23 (21), 100 (100), 26 (25), 3 (3). Anal. Calcd for C<sub>72</sub>H<sub>62</sub>B<sub>1</sub>F<sub>26</sub>Ir<sub>1</sub>N<sub>1</sub>O<sub>1</sub>P<sub>1</sub> (1685.3): C, 51.31; H, 3.71; F, 29.31; N, 0.83; P, 1.84. Found: C, 51.17; H, 3.89; F, 29.88; N, 0.88; P, 1.41.

(-)-(4S)-2-(2-{Diphenylphosphanylphenyl)-4-isopropyl-4,5-dihydrooxazole-( $\eta^4$ -1,5-cyclooctadienyl)iridium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (7a). A solution of 3a (219.9 mg, 0.59 mmol) and 4 (199.6 mg, 0.29 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was stirred at 50 °C for 1.5 h in a sealed tube under Ar. After cooling to room temperature, a suspension of NaBARF (1.08 g, 1.22 mmol) in H<sub>2</sub>O (40 mL) was added, and the resulting mixture was stirred at room temperature. Anion exchange was monitored by TLC (silica gel, CH2-Cl<sub>2</sub>; [Ir(cod)(**3a**)]Cl,  $R_f = 0$ ; NaBARF,  $R_f = 0$ ; [Ir(cod)(**3a**)]BARF,  $R_f$ = 0.75). The layers were separated, the aqueous layer was extracted with  $CH_2Cl_2$  (4 × 5 mL), and the combined organic phases were dried over MgSO<sub>4</sub>. Flash column chromatography on silica gel (eluent CH<sub>2</sub>-Cl<sub>2</sub>) and evaporation of the solvent afforded 7a as a bright red powder (822.4 mg, 0.54 mmol, 91%): <sup>1</sup>H NMR (300.1 MHz,  $CD_2Cl_2$ )  $\delta$  -0.06 (d, 3H, J = 6.7 Hz; CH<sub>3</sub>), 0.88 (d, 3H, J = 7.1 Hz; CH<sub>3</sub>), 1.44–1.57 (m, 1H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.65-1.78 (m, 1H; CH<sub>2</sub> of cod), 1.98-2.07 (m, 2H; CH<sub>2</sub> of cod), 2.08–2.19 (m, 1H; CH<sub>2</sub> of cod), 2.24–2.69 (m, 4H;  $CH_2$  of cod), 3.04–3.12 (m, 1H; CH of cod), 3.32–3.38 (m, 1H; CH of cod), 4.18 (dt, 1H, J = 9.2 Hz, 2.5 Hz; CH(4)), 4.40 (t, 1H, J = 9.5 Hz;  $CH_2(5)$ ), 4.50 (dd, 1H, J = 9.5 Hz, 3.7 Hz;  $CH_2(5)$ ), 4.92–5.02 (m, 1H; CH of cod), 5.03-5.11 (m, 1H; CH of cod), 7.09-7.16 (m, 2H; arom CH), 7.41-7.74 (m, 23H; arom CH), 8.17-8.22 (m, 1H; arom CH);13C NMR (75.5 MHz, CD2Cl2) & 12.6 (CH(CH3)2), 18.9 (CH-(CH<sub>3</sub>)<sub>2</sub>, 26.9 (CH<sub>2</sub> of cod), 28.9 (CH<sub>2</sub> of cod), 32.7 (CH<sub>2</sub> of cod), 33.4  $(CH(CH_3)_2)$ , 37.0 (d,  $J_{PC} = 5$  Hz;  $CH_2$  of cod), 63.8 (CH of cod), 64.3 (CH of cod), 68.9 (CH<sub>2</sub>(5)), 71.0 (CH(4)), 93.9 (d,  $J_{PC} = 13$  Hz; CH of cod), 97.5 (d,  $J_{\rm PC}$  = 11 Hz; CH of cod), 129.2 (d,  $J_{\rm PC}$  = 10 Hz), 130.2 (d,  $J_{PC} = 10$  Hz), 132.4 (d,  $J_{PC} = 3$  Hz), 132.7 (d,  $J_{PC} = 2$  Hz), 133.1 (d,  $J_{PC} = 3$  Hz), 133.7 (d,  $J_{PC} = 10$  Hz), 134.2 (d,  $J_{PC} = 8$  Hz), 134.4 (d,  $J_{PC} = 7$  Hz), 134.7 (d,  $J_{PC} = 2$  Hz), 135.4 (arom CH), 125.0  $(q, J_{FC} = 272 \text{ Hz}), 122.5, 128.9, 129.3 (q, J_{FC} = 31 \text{ Hz}), 129.5, 129.8,$ 130.6 (arom C), 164.3 (d,  $J_{PC} = 7$  Hz, C(2)), 117.9 (m, 4C; arom CH), 135.3 (br, 8C; arom CH), 162.2 (q,  $J_{CB} = 49.9$  Hz); <sup>19</sup>F NMR (282.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -63.3 (s); <sup>31</sup>P{<sup>1</sup>H} NMR (121.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ 16.5 (s); <sup>11</sup>B{<sup>1</sup>H} NMR (64.2 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -6.7 (s);  $[\alpha]_{589} = -186$ (CHCl<sub>3</sub>, c = 0.25, 20 °C); MS (ESI/pos (CH<sub>2</sub>Cl<sub>2</sub>)) m/z (%) 674 (100) [M<sup>+</sup>, <sup>193</sup>Ir], isotope cluster 672–676 calcd (obsd) 57 (75), 21 (25), 100 (100), 36 (41), 7 (6); (ESI/neg (CH<sub>2</sub>Cl<sub>2</sub>)) m/z (%) 863 (100) [M<sup>-</sup>, <sup>11</sup>B], isotope cluster 862-865; calcd (obsd) 23 (24), 100 (100), 35 (36), 6 (6). Anal. Calcd for  $C_{64}H_{48}B_1F_{24}N_1O_1Ir_1P_1$  (1536.8): C, 50.02; H, 3.15; B, 0.70; F, 29.67; Ir, 12.51; N, 0.91; P, 2.02. Found: C, 50.32; H, 3.20; B, 0.61; F, 29.84; Ir, 12.29; N, 0.87; P, 2.03.

(-)-(4S)-2-(2-{Bis[4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)phenyl]phosphanyl}phenyl)-4-isopropyl-4,5-dihydrooxazole-( $\eta^{4}$ -1,5cyclooctadienyl)iridium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (7b). Treating 5b (30 mg, 0.02 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) with a suspension of NaBARF (1.0 g, 1.13 mmol) in H<sub>2</sub>O (20 mL) at room temperature for 0.5 h followed by workup as described for 7a gave [Ir(cod)(3b)]BARF (7b;  $R_f = 0.85$ ) as a bright red powder (38.1 mg, 0.54 mmol, 86%): <sup>1</sup>H NMR (300.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ -0.04 (d, 3H, J = 6.7 Hz; CH<sub>3</sub>), 0.89 (d, 3H, J = 7.1 Hz; CH<sub>3</sub>), 1.45–1.62 (m, 1H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.65-1.83 (m, 1H; CH<sub>2</sub> of cod), 1.98-2.08 (m, 2H; CH<sub>2</sub> of cod), 2.07-2.21 (m, 1H; CH<sub>2</sub> of cod), 2.32-2.67 (m, 4H; CH<sub>2</sub> of cod; 4H; CH<sub>2</sub>CF<sub>2</sub>), 2.98-3.08 (m, 1H; CH of cod; 4H; CH<sub>2</sub>CH<sub>2</sub>CF<sub>2</sub>), 3.29-3.35 (m, 1H; CH of cod), 4.18 (dt, 1H, J = 8.8 Hz, 3.1 Hz; CH(4)), 4.42 (t, 1H, J = 9.5 Hz;  $CH_2(5)$ ), 4.51 (dd, 1H, J = 9.5 Hz, 3.8 Hz; CH<sub>2</sub>(5)), 4.91–5.03 (m, 1H; CH of cod), 5.04–5.13 (m, 1H; CH of cod), 7.03-7.09 (m, 2H; arom CH), 7.31-7.44 (m, 7H; arom CH), 7.54–7.75 (m, 16H; arom CH);<sup>13</sup>C NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ 12.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 18.8 (CH(CH<sub>3</sub>)<sub>2</sub>, 26.6 (m; CH<sub>2</sub>CH<sub>2</sub>CF<sub>2</sub>), 26.8 (m;  $CH_2CH_2CF_2$ ), 26.9 ( $CH_2$  of cod), 28.9 ( $CH_2$  of cod), 32.6 (t,  $J_{FC} =$ 22.4 Hz; CH<sub>2</sub>CF<sub>2</sub>), 32.7 (CH<sub>2</sub> of cod), 33.4 (CH(CH<sub>3</sub>)<sub>2</sub>); 36.5 (d, J<sub>PC</sub> = 5 Hz; CH<sub>2</sub> of cod), 63.7 (CH of cod), 64.3 (CH of cod), 69.0 (CH<sub>2</sub>-(5)), 71.0 (CH(4)), 94.1 (d,  $J_{PC} = 13$  Hz; CH of cod), 97.8 (d,  $J_{PC} =$ 10 Hz; CH of cod), 105–125 (m;  $CF_x$ ), 128.9 (d,  $J_{PC} = 2$  Hz), 129.0 (d,  $J_{PC} = 2$  Hz), 129.3 (d,  $J_{PC} = 11$  Hz), 130.3 (d,  $J_{PC} = 11$  Hz), 132.8  $(d, J_{PC} = 2 Hz)$ , 134.1  $(d, J_{PC} = 10 Hz)$ , 134.3, 134.4  $(d, J_{PC} = 7 Hz)$ , 134.6 (d,  $J_{PC} = 2$  Hz), 135.7 (d,  $J_{PC} = 13$  Hz) (arom CH), 121.1 (d, J = 59 Hz), 125.0 (q,  $J_{PC}$  = 272 Hz), 126.3, 128.1, 129.2, 129.3 (qq,  $J_{FC}$ = 31 Hz, 3 Hz), 129.5, 144.2 (d,  $J_{PC}$  = 2 Hz), 145.0 (d,  $J_{PC}$  = 2 Hz) (arom C), 117.9 (m, 4C; arom CH), 135.2 (br, 8C, arom CH), 162.2 (q,  $J_{\rm CB}$  = 49.9 Hz), 164.3 (d,  $J_{\rm PC}$  = 6 Hz, C(2)); <sup>19</sup>F NMR (282.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -62.9 (s, 18F), -81.1 (t, 6F, J = 9.0 Hz;), -114.4 (t, 2F, J = 11.4 Hz;), -114.6 (t, 2F, J = 11.4 Hz;), -122.0 (br; 4F), -123.0 (br; 4F), -123.7 (br; 4F), -126.3 (br; 4F); <sup>31</sup>P{<sup>1</sup>H} NMR (121.5.0 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  15.5 (s); <sup>11</sup>B{<sup>1</sup>H} NMR (64.2 MHz, CD<sub>2</sub>-Cl<sub>2</sub>)  $\delta$  -6.6 (s); MS (ESI/pos (CH<sub>2</sub>Cl<sub>2</sub>)) *m*/*z* (%) 1366 (100) [M<sup>+</sup>, <sup>193</sup>Ir], isotope cluster 1364-1368; calcd (obsd) 55 (69), 30 (32), 100 (100), 52 (58), 14 (15); (ESI/neg (CH<sub>2</sub>Cl<sub>2</sub>)) m/z (%) 863 (100) [M<sup>-</sup>, <sup>11</sup>B], isotope cluster 862-865; calcd (obsd) 23 (31), 100 (100), 35 (42), 6 (6). Anal. Calcd for C<sub>80</sub>H<sub>54</sub>B<sub>1</sub>F<sub>50</sub>Ir<sub>1</sub>N<sub>1</sub>O<sub>1</sub>P<sub>1</sub> (2229.4): C, 43.10; H, 2.44; F, 42.61; N, 0.63; P, 1.39. Found: C, 42.75; H, 2.49; F, 43.68; N, 0.89; P, 1.86.

**Hydrogenation of** *N***-(1-Phenylethylidene)aniline (8a).** In a typical experiment, a window-equipped stainless steel reactor (V = 100 mL) with a Teflon-coated magnetic stirring bar was charged with the substrate (820 mg, 4.2 mmol) and the catalyst (9.5 mg,  $6.0 \times 10^{-3}$  mmol, s/c = 700, 0.14 mol % catalyst) under argon atmosphere. A weighted amount of CO<sub>2</sub> was introduced using a compressor to adjust to the desired density of  $d(\text{CO}_2) = 0.75 \text{ g mL}^{-1}$ . The reactor was heated to 33 °C, and hydrogen was introduced to adjust to a partial pressure of 30 bar at this temperature as determined from a calibration curve. The final reaction temperature of 40 °C was reached by further heating within less than 5 min, and the mixture was kept at that temperature for a standard reaction time of 20 h. Modifications of this procedure are indicated in the figure captions and footnotes of the tables.

For standard workup, the reactor was cooled to room temperature and vented carefully through a cold trap. The contents of the trap and the reactor were collected by washing with CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed in vacuo, and the product was isolated by Kugelrohr distillation (typically >99% recovery). The enantiomeric excess was determined by HPLC (Daicel Chiralcel OD-H column, 254 nm, 0.5 mL min<sup>-1</sup>, *n*-heptane/2-propanol, 90:10;  $t_{\rm R} = 12.2$  (*S*), 15.9 (*R*) min). In all experiments the (*R*)-enantiomer was formed predominantly.

Experiments in CH<sub>2</sub>Cl<sub>2</sub> were carried out in a similar reactor (V = 50 mL) with a solvent volume of 20 mL, either under the conditions described in the literature<sup>24</sup> or following the above standard procedure for comparison. The amount of catalyst and substrate was corrected for the change in reaction volume (100 mL vs 20 mL) for the supercritical and the liquid reaction medium, respectively. Stirring was effected using a Teflon-coated magnetic stirring bar at the maximum stirring rate.

In Situ High-Pressure FT-IR Spectroscopy Experiment. A window-equipped stainless steel reactor (V = 200 mL) was charged with the catalyst **7a** (10.5 mg,  $6.8 \times 10^{-3}$  mmol) under argon atmosphere. The reactor was closed with the lid being connected to the high-pressure reflectance probe of a ASI/Mettler-Toledo ReactIR-1000 FT-IR system. CO<sub>2</sub> was introduced using a compressor to adjust to the desired density of the reaction medium of  $d(CO_2) = 0.75 \text{ g mL}^{-1}$ . Hydrogen was introduced to adjust to a partial pressure of 30 bar, the reactor was heated to 40 °C, and the background spectrum was recorded after temperature equilibration. To start the reaction, imine **8a** (1.54 g, 7.81 mmol) was injected with positive CO<sub>2</sub> pressure from a sample compartment connected to the reactor via a ball valve. The reaction was monitored by collecting spectra in 2 min intervals over a period of 4 h.

**High-Pressure NMR Investigations.** A 5 mm high-pressure sapphire NMR tube<sup>33</sup> (V = 0.9 mL) was charged with a solution of compound **8** or **9** (approximately 0.05 mmol in 0.6 mmol of C<sub>6</sub>D<sub>6</sub>) under argon atmosphere. The NMR tube was pressurized with CO<sub>2</sub> (0.65 g) using a compressor to adjust to the desired density of CO<sub>2</sub> (0.75 g mL<sup>-1</sup>). Measurements were conducted at a temperature setting of 40 °C on the NMR spectrometer, allowing at least 30 min for temperature equilibration.

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**Supporting Information Available:** <sup>1</sup>H NMR spectra of compounds **8a,b** and **9a** in CDCl<sub>3</sub> and scCO<sub>2</sub> and reflectance FT-IR spectra of **8a** and **9a** as neat compounds, in toluene, and in scCO<sub>2</sub> (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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