Iridium-Catalyzed Enantioselective Hydrogenation of Imines in Supercritical Carbon Dioxide

Sabine Kainz, Axel Brinkmann, Walter Leitner,*,† and Andreas Pfaltz*

Contribution from the Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim/Ruhr, Germany

Received December 14, 1998

Abstract: Supercritical carbon dioxide ($scCO_2$) 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 $scCO_2$ [$d(CO_2) = 0.75$ g mL^{-1}] at 40 °C and a H_2 pressure of 30 bar with enantiomeric excesses of up to 81% using 0.078 mol % catalyst. The use of $scCO_2$ instead of conventional solvents such as CH_2Cl_2 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 $scCO_2$, 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 ($scCO_2$; $T_c = 31$ °C, $p_c = 73.75$ bar, $d_c = 0.468$ g mL^{-1}) is receiving considerable and ever increasing interest as an environmentally benign reaction medium with unique properties for chemical synthesis[1] and especially for homogeneously catalyzed reactions.[2] The miscibility of $scCO_2$ 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.[3] Beneficial effects can also arise from the high compressibility of $scCO_2$, allowing for selectivity changes by variation of the density with comparably small changes in the reaction conditions.[4] The chemical interaction of CO_2 with functional groups of the substrate can lead to better compatibility with the employed catalysts (temporary protecting group).[4] In favorable cases, the extractive properties of $scCO_2$[5] may allow remarkable efficient and simple separation of catalysts and products.[4,6]

The use of $scCO_2$ 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_2 to formic acid and its derivatives[3,7] or the rhodium-catalyzed hydroformylation of olefins.[6] Higher regioselectivity at comparable rates has also been observed with certain catalytic systems for hydroformylation,[8] and preliminary results on asymmetric hydroformylation have been reported.[9] The highly enantioselective hydrogenation of C=C double bonds has been demonstrated with prochiral α,β-unsaturated carboxylic acids as substrates.[10,11] The phase behavior of the reaction mixture and the solubility of the catalyst were found to be of paramount importance for the successful

† Fax: +49-208-306-2993. E-mail: leitner@mpi-muelheim.mpg.de.

(1) *Chemical Synthesis in Supercritical Fluids*; Jessop, P. G., Leitner, W., Eds.; Wiley-VCH: New York, 1999.

(2) Selected recent reviews: (a) Jessop, P. G.; Ikariya, T.; Noyori, R. *Science* **1995**, *269*, 1065. (b) Morgenstern, D. A.; LeLacheur, R. M.; Morita, D. K.; Borkowsky, S. L.; Feng, S.; Brown, G. H.; Luan, L.; Gross, M. F.; Burk, M. J.; Tumas, W. In *Green Chemistry*; Anastas, P. T., Williamson, T. C., Eds.; ACS Symposium Series 626; American Chemical Society: Washington, DC, 1996; pp 132. (c) Dinjus, E.; Fornika, R.; Scholz, M. In *Chemistry under Extreme or Non-Classical Conditions*; van Eldik, R., Hubbard, C. D., Eds.; Wiley: New York, 1996; pp 219. (d) Jessop, P. G. In *Fine Chemicals Catalysis II*; Blackmond, D., Leitner, W., Eds.; *Top. Catal.* **1998**, *5*, 95.

(3) (a) Jessop, P. G.; Ikariya, T.; Noyori, R. *Nature* **1994**, *368*, 231. (b) Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 344.

(4) Fürstner, A.; Koch, D.; Langemann, K.; Leitner, W.; Six, C. *Angew. Chem.* **1997**, *109*, 2562; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2466.

(5) (a) Zosel, K.; *Angew. Chem.* **1978**, *90*, 748; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 702. (b) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction*, 2nd ed.; Butterworth: Boston, 1994.

(6) Koch, D.; Leitner, W. *J. Am. Chem. Soc.* **1998**, *120*, 13398.

(7) For general reviews on this area see: (a) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259. (b) Leitner, W. *Angew. Chem.* **1995**, *107*, 2391; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2207.

(8) (a) Rathke, J. W.; Klingler, R. J.; Krause, T. R. *Organometallics* **1991**, *10*, 1350. (b) Guo, Y.; Akgerman, A. *Ind. Eng. Chem. Res.* **1997**, *36*, 4581. (c) Bach, I.; Cole-Hamilton, D. J. *Chem. Commun.* **1998**, 1463.

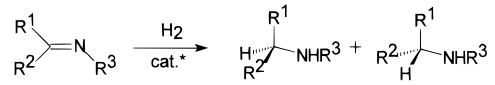
(9) Kainz, S.; Leitner, W. *Catal. Lett.* **199**8, 55, 223.

(10) Xiao, J.; Nefkens, S. C. A.; Jessop, P. G.; Ikariya, T.; Noyori, R. *Tetrahedron Lett.* **1996**, *37*, 2813.

(11) Burk, J.; Feng, S.; Gross, M. F.; Tumas, W. *J. Am. Chem. Soc.* **1995**, *117*, 8277.

10.1021/ja984309i CCC: $18.00
Published on Web 06/26/1999

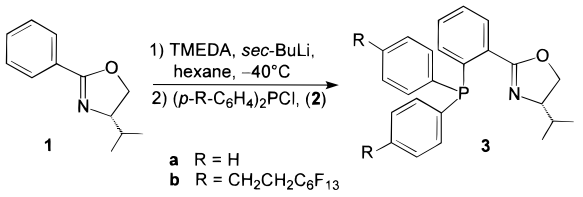
Scheme 1



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[12,13] or in the anions in the case of cationic complexes.[11]

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.[14] A variety of chiral Rh,[15] Ir,[16] Ru,[17] and Ti[18] complexes have been studied as catalysts for the hydrogenation of imines, whereby the late transition metal systems contained mainly chiral diphosphine ligands.[19] The first industrial application of enantioselective imine hydrogenation was developed by a research group at Ciba-Geigy.[20] The catalyst, a chiral ferrocenyldiphosphine−iridium complex, shows extremely high activity and unprecedented productivity (up to 10^6 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.

Scheme 2



Recently, enantiopure phosphinodihydrooxazoles[21−23] were successfully used in the Ir-catalyzed enantioselective hydrogenation of imines in CH_2Cl_2.[24] We now report that it is possible to replace the organic solvent with toxicologically and environmentally benign $scCO_2$ 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, $scCO_2$ 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_2.

Results and Discussion

Preparation of Ir Catalysts for Use in $scCO_2$. Recent research on catalysis in $scCO_2$ and the known solubility data for metal complexes in pure $scCO_2$[25] 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_2-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.[26] 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-tridecafluorooctyl)benzene[27] with *n*-BuLi in diethyl ether, followed by addition of the resulting solution to Cl_2PNEt_2 in THF, and subsequent treatment with dry gaseous HCl.[28,29]

(12) Kainz, S.; Koch, D.; Baumann, W.; Leitner, W. *Angew. Chem.* **1997**, *109*, 1699; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1628.

(13) For recent applications of this concept in catalysis see: (a) Garrol, M. A.; Holmes, A. B. *Chem. Commun.* **1998**, 1395. (b) Morita, D. K.; Pesiri, D. R.; Scott, A. D.; Glaze, W. H.; Tumas, W. *Chem. Commun.* **1998**, 1397. (c) Palo, D. R.; Erkey, C. *Ind. Eng. Chem. Res.* **1998**, *37*, 4203. (d) Reference 6.

(14) (a) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994; pp 82. (b) Johansson, A. *Contemp. Org. Synth.* **1995**, *2*, 393. (c) James, B. R. In *Catalysis of Organic Reactions, Chemical Industries;* Scaros, M. G., Prunier, M. L., Eds.; Dekker: New York, 1995; Vol. 62, p 167.

(15) (a) Vastag, S.; Bakos, J.; Törös, S.; Takach, N. E.; King, R. B.; Heil, B.; Markó, L. *J. Mol. Catal.* **1984**, *22*, 283. (b) Bakos, J.; Tóth, I.; Heil, B.; Markó, L. *J. Organomet. Chem.* **1985**, *279*, 23. (c) Kang, G.-J.; Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kutney, J. P. *J. Chem. Soc., Chem. Commun.* **1988**, 1466. (d) Becalski, A. B.; Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kang, G.-J.; Rettig, S. *J. Inorg. Chem.* **1991**, *30*, 5002. (e) Burk, M. J.; Martinez, J. P.; Feaster, J. E.; Cosford, N. *Tetrahedron* **1994**, *50*, 4399. For hydrogenation of benzylimines of aryl methyl ketones in a two-phase system, see: (f) Bakos, J.; Orosz, A.; Heil, B.; Laghmari, M.; Lhoste, P.; Sinou, D. *J. Chem. Soc., Chem. Commun.* **1991**, 1684. (g) Lensink, C.; deVries, J. G. *Tetrahedron: Asymmetry* **1992**, *3*, 235.

(16) (a) Spindler, F.; Pugin, B.; Blaser, H.-U. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 558. (b) Spindler, F.; Pugin, B. (Ciba-Geigy AG). EP Patent 0256982, 1988. (c) Ng Cheon Chan, Y. P.; Osborn, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 9400. (d) Ng Cheon Chan, Y. P.; Meyer, D.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1990**, 869. (e) Sablong, R.; Osborn, J. A. *Tetrahedron: Asymmetry* **1996**, *7*, 3059. (f) Morimoto, T.; Achiwa, K. *Tetrahedron: Asymmetry* **1995**, *6*, 2661. (g) Tani, K.; Onouchi, J.; Yamagata, T.; Kataoka, Y. *Chem. Lett.* **1995**. 955.

(17) (a) Oppolzer, W.; Wills, M.; Starkemann, C.; Bernardinelli, G. *Tetrahedron Lett.* **1990**, *31*, 4117. (b) Fogg, D. E.; James, B. R. In *Catalysis of Organic Reactions, Chemical Industries;* Scaros, M. G., Prunier, M. L., Eds.; Dekker: New York, 1995; Vol. 62, p 435. For the use of Ru−diamine complexes in the enantioselective transfer−hydrogenation of imines, see: (c) Uematsu, N.; Fujii, A.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 4916.

(18) (a) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 7562. Willoughby, C. A.; Buchwald, S. L. *J. Org. Chem.* **1993**, *58*, 7629. (b) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8952. (c) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11703.

(19) (a) Miao, C. K.; Sorcek, R.; Jones P.-J. *Tetrahedron Lett.* **1993**, *34*, 2259. (b) Sreckumar, R.; Pillai, C. N. *Tetrahedron: Asymmetry* **1993**, *4*, 2095.

(20) (a) Blaser, H.-U.; Spindler, F. In *Fine Chemicals Catalysis I*; Blackmond, D., Leitner, W., Eds.; *Top. Catal.* **1997**, *4*, 275. (b) Togni, A. *Angew. Chem.* **1996**, *108*, 1581; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1475.

(21) Sprinz, J.; Helmchen, G. *Tetrahedron Lett.* **1993**, *34*, 1769.

(22) Dawson, G. J.; Frost, C. G.; Williams, J. M. J., Coote, S. J. *Tetrahedron Lett.* **1993**, *34*, 3149.

(23) (a) von Matt, P.; Pfaltz, A. *Angew. Chem.* **1993**, *105*, 614; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 566. (b) Review: Pfaltz, A. *Acta Chem. Scand.* **1996**, *50*, 189.

(24) (a) Schnider, P.; Koch, G.; Prétôt, R.; Wang, G.; Bohnen, F. M.; Krüger, C.; Pfaltz, A. *Chem. Eur. J.* **1997**, *3*, 887. (b) Schnider, P. Ph.D. Thesis, University of Basel, 1996.

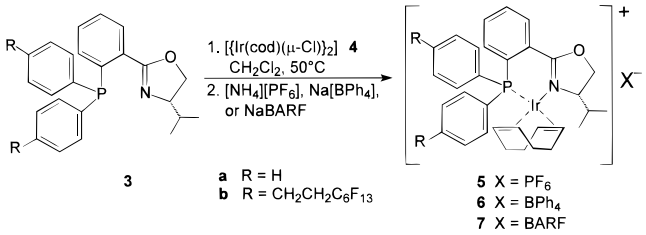
(25) Smart, N. G.; Carleson, T.; Kast, T.; Clifford, A. A.; Burford, M. D.; Wai, C. M. *Talanta* **1997**, *44*, 137.

(26) Koch, G.; Lloyd-Jones, G. C.; Loiseleur, O.; Pfaltz, A.; Prétôt, R.; Schaffner, S.; Schnider, P.; von Matt, R. *Recl. Trav. Chim. Pay-Bas* **1995**, *114*, 206.

(27) Kainz, S.; Luo, Z.; Curran, D. P.; Leitner, W. *Synthesis* **1998**, 1425.

(28) Casalnuovo, A. L.; RajanBabu, T. V.; Ayers, T. A.; Warren, T. H. *J. Am. Chem. Soc.* **1994**, *116*, 9869.

Scheme 3



Treatment of the dimeric iridium complex [{Ir(cod)(μ-Cl)}$_2$] (**4**) (cod = 1,5-cyclooctadiene) with ligand **3a** or **3b** in CH_2Cl_2 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_4][PF_6], Na[BPh_4], 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_2Cl_2 (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_2Cl_2. 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 ^{31}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 ^{103}Rh NMR-based finding that substitution with ethylene-spaced perfluoroalkyl groups in the para position of the PPh_2 moiety keeps structural and electronic changes at the metal center to a minimum.[12]

The lipophilicity of a compound is one of several factors determining its solubility in $scCO_2$, 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 ≤ [Ir(cod)(**3b**)]Cl ≪ **6a** < **6b** ≪ **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_2 and in CH_2Cl_2. 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_2Cl_2 were carried out with identical amounts of substrate and catalysts per solvent volume 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.

Scheme 4

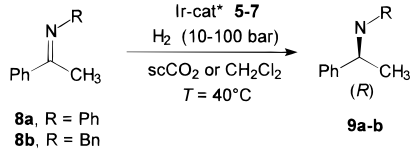


Table 1. Asymmetric Hydrogenation of Imines **8** in CH_2Cl_2[a]

entry	substrate (mmol)	catalyst (mol %)	conversion (%)	ee (*R*) (%)
1	**8a** (4.15)	**5a** (0.15)	99.7	83
2	**8a** (5.05)	**5b** (0.11)	100.0	80
3[b]	**8a** (5.00)	**5b** (0.06)	10.0	nd[c]
4	**8a** (4.17)	**6b** (0.13)	99.9	86
5[d]	**8a** (4.18)	**7a** (0.15)	100.0	87
6	**8b** (4.00)	**5a** (0.3)	99.3	72
7	**8b** (3.83)	**7a** (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 (*R*) (%)
1	**8a** (0.15)	**5a** (0.15)	99.9	37
2	**8a** (4.15)	**5b** (0.14)	100	26
3[b]	**8a** (4.13)	**5b** (0.13)	99.5	26
4	**8a** (4.17)	**6a** (0.22)	11.0 (83.1[d])	nd[c] (60[d])
5	**8a** (4.16)	**6b** (0.14)	99.8	68
6	**8a** (4.22)	**7a** (0.14)	100	81
7[e]	**8a** (4.19)	**7a** (0.15)	100	79
8	**8a** (4.53)	**7b** (0.09)	100	80
9	**8b** (3.85)	**5a** (0.3)	28.9	nd[c]
10	**8b** (3.87)	**7a** (0.15)	15.5 (28.4[f])	nd[c]
11	**8b** (2.4)	**7a** (0.25)	23	nd[c]

[a] $d(CO_2)$ = 0.75 g mL^{-1}, $p(H_2)$ = 30 bar, T = 40 °C, reaction time 20 h. [b] With addition of 0.5 mL of CH_2Cl_2. [c] Not determined. [d] Reaction time 40 h. [e] $p(H_2)$ = 10 bar. [f] Reaction time 70 h.

Complex **5a** has been reported to catalyze the hydrogenation of **8a** to (*R*)-**9a** with ca. 84% ee in CH_2Cl_2 under 100 bar of H_2 at room temperature using a catalyst loading of 0.1 mol %.[24] 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_6]$^-$ congeners **5**.[30]

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_2 group. The unsubstituted borate complex **6a** showed very low activity in

(29) A chiral C_2-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.

(30) The BARF anion was found to yield particularly active and selective catalysts in the enantioselective hydrogenation of nonfunctionalized C=C double bonds using the similar complexes in organic solvents: Lightfoot, A.; Schnider, P.; Pfaltz, A. *Angew. Chem.* **1998**, *110*, 3047; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2897.

$scCO_2$ (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 $scCO_2$ with very high activity and with similar levels of enantiocontrol as in CH_2Cl_2.[24] However, $scCO_2$ 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 $scCO_2$. Moreover, the substrate *N*-(1-phenylethylidene)benzylamine (**8b**), which is structurally closely related to **8a**, proved to be very difficult to hydrogenate in $scCO_2$ (Table 2). Independently of the catalyst precursor, conversion of **8b** did not exceed 30% in $scCO_2$ even at prolonged reaction times or higher catalyst loadings. In contrast, the formation of **9b** proceeded smoothly with 71−72% ee in CH_2Cl_2 (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 $scCO_2$. In the present case, visual inspection showed that up to 800 mg of the imine **8a** were completely soluble in 100 mL of $scCO_2$ of densities $d(CO_2) \geq 0.65$ g mL^{-1} at or just above the critical temperature of pure CO_2. 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_2 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_2 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_2 to come into contact with **7a**. To start the reaction, H_2 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_2 extraction (vide infra). The beaker was removed, and the reactor was charged again with **8a**, CO_2, and H_2. 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_2 even at temperatures and pressures well above the point where complete dissolution of the imine was observed. Introduction of H_2 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_2/H_2 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.[31]

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[4,6] for combinations of homogeneous catalysis and SFE using $scCO_2$, 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_2 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_2 corresponding to 100 L of gaseous CO_2 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 $scCO_2$ and in CH_2Cl_2. Figure 2 and Table 3 summarize the course of formation of **9a** during hydrogenation of **8a** with different loadings of catalyst **7a** in $scCO_2$ and CH_2Cl_2 under otherwise identical conditions. Following the course of reaction by sampling and offline GC analysis under standard conditions in $scCO_2$ 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

(31) 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.

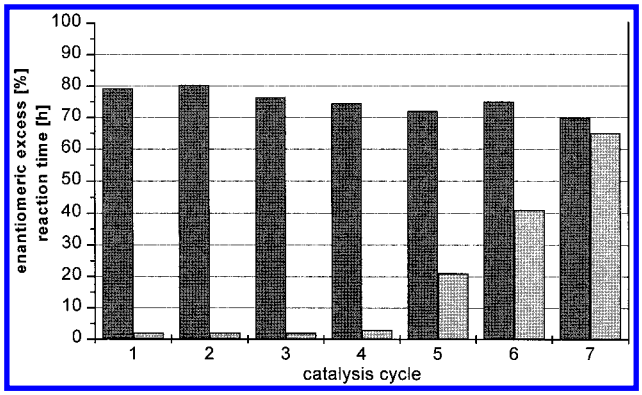


Figure 1. Catalyst recycling in the enantioselective hydrogenation of **8a** to give (*R*)-**9a** using **7a** as catalyst and $scCO_2$ as medium for reaction and separation (CESS process). The dark gray bars indicate the enantiomeric excess, and the light gray bars show the time required for quantitative conversion.

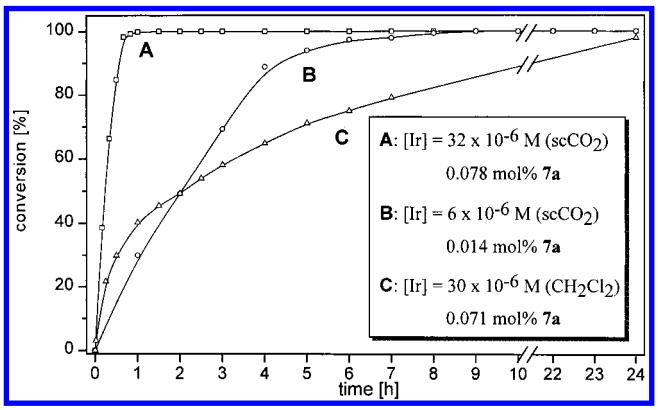


Figure 2. Conversion/time profile for the enantioselective hydrogenation of imine **8a** using catalyst **7a** in $scCO_2$ and CH_2Cl_2, respectively.

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

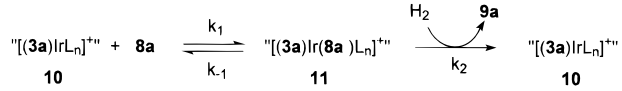
entry	catalyst (mol %)	solvent	density (g mL^{-1})	*t* (h)[b]	TON[c]	TOF[d] (h^{-1})	ee (*R*) (%)
1	**7a** (0.014)	$scCO_2$	0.75	8.8	6830	2140	74
2	**7a** (0.078)	$scCO_2$	0.75	1.2	1280	2820	78
3	**7a** (0.078)	$scCO_2$	0.65	1.5	1275	1280	73
4	**7a** (0.071)	CH_2Cl_2		24	1400	1200	86
5	**7a** (0.16)	CH_2Cl_2		1.5	625	1400	86
6	**5a** (0.079)	CH_2Cl_2		30	1260	600	84
7	**5a** (0.15)	CH_2Cl_2		3	645	600	83

[a] $p(H_2) = 30$ bar, 4.2 mmol of **8a**, $T = 40$ °C. [b] Time required for >98% conversion. [c] Turnover number = moles of **9a** per mole of Ir at time *t*. [d] 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^{-1}. The initial TOF was found to vary somewhat with catalyst loading, and a TOF of 2820 h^{-1} 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_2 was lowered from 0.75 g mL^{-1} to 0.65 g mL^{-1}. 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 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_2 pressure in CH_2Cl_2 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_2Cl_2 than in $scCO_2$ 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_2Cl_2 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 $scCO_2$ (Figure 2B), whereas more than 22 h was required to achieve similar conversion in CH_2Cl_2 using a 5 times larger amount of **7a** (TON = 1400).

Scheme 5



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_2 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 $scCO_2$, remains in solution until the imine **8a** is consumed completely. In principle, the same scheme may apply for the reaction in CH_2Cl_2, and indeed the same color changes are observed in this medium. However, the reaction profile in CH_2Cl_2 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.[32] A precise mechanistic explanation for the greatly enhanced catalytic efficiency observed in $scCO_2$ has to await further studies including detailed kinetic investigations in $scCO_2$ and comparison to the yet unknown rate law in CH_2Cl_2. It is, however, already clear from the current data that the enhancement of the catalyst efficiency cannot be reduced to a mere enhancement of "H_2 availability".

(32) 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.

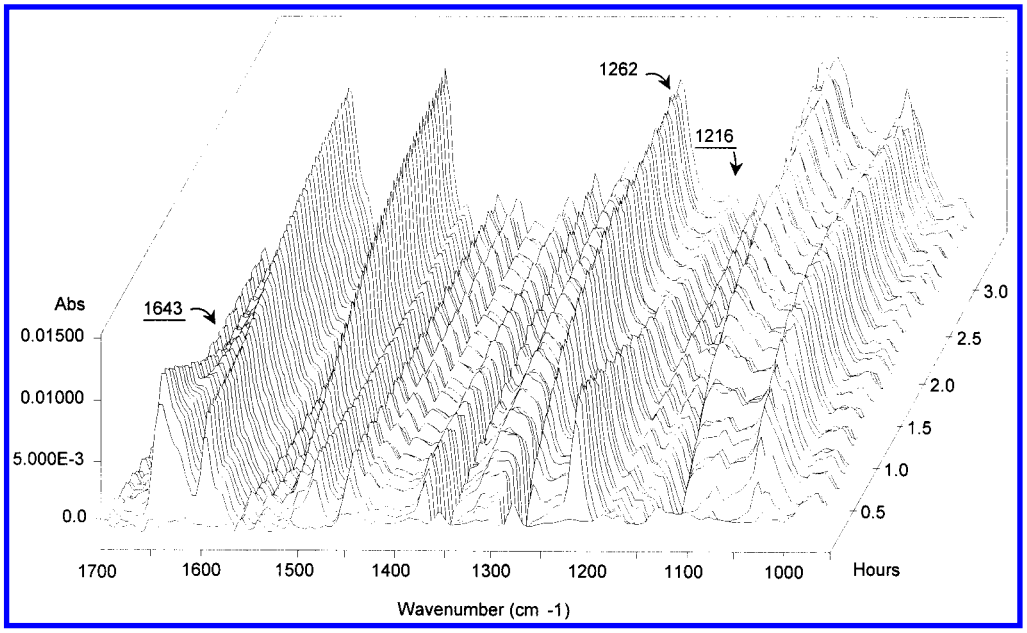


Figure 3. In situ FT-IR monitoring of the hydrogenation of imine **8a** to give the secondary amine **9a** with catalyst **7a** in $scCO_2$ using a high-pressure reflectance probe. The marked and underlined bands can be identified at identical positions in control spectra of toluene solutions of **9a** and **8a**, respectively.

Investigations Using High-Pressure Spectroscopy. Due to the rapidly growing number of homogeneously catalyzed reactions which can be carried out efficiently in $scCO_2$, 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 window-equipped 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^{-1} and the growing band at 1262 cm^{-1} 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_2.

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.[33] Both substrates **8a** and **8b** were readily soluble in $scCO_2$ (40 °C, $d(CO_2) = 0.75$ g mL^{-1}) at concentrations of 10 mg mL^{-1}. 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_2. The spectra of **9a** in $CDCl_3$ and in $scCO_2$ 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_2 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_2, 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 CO_2.[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 $scCO_2$,[24] 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 $scCO_2$ cannot be regarded a simple "substitute solvent", and successful "transfer" of reactions

(33) (a) Roe, D. C. *J. Magn. Reson.* **1985**, *63*, 388. (b) Horváth, I.; Ponce, E. C. *Rev. Sci. Instrum.* **1991**, *62*, 1104. (c) The tube used here was manufactured in the laboratories of C. J. Elsevier, J. van't Hoff Research Institute, University of Amsterdam.

(34) (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 $scCO_2$ 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 $scCO_2$ 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[35] 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[36] and stored under argon. The gases (H_2 (99.9%), argon (99.999%), and CO_2 (99.995%)) (Messer Griesheim) were used without further purification. [{Ir(cod)-(μ-Cl)}$_2$] (**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*′,*N*′-Tetramethylethylendiamine (TMEDA; Fluka) was dried and distilled over $LiAlH_4$ prior to use. Cl_2PNEt_2[37] and NaBARF[38] were synthesized according to known procedures. The syntheses of **1, 8a**, **8b**, **3a**,[26] **5a**,[24] and 1-bromo-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)benzene[27] 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 ±5%). NMR spectra were recorded on a Bruker AC 200 or a Bruker AMX 300 spectrometer. Chemical shifts δ are recorded in parts per million relative to external $CFCl_3$ for ^{19}F, H_3PO_4 for ^{31}P, and TMS for ^{1}H and ^{13}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[27] (8.77 g, 17.4 mmol) in 50 mL of Et_2O at −50 °C. The yellow cloudy solution was added slowly to a solution of Cl_2PNEt_2 (1.51 g, 8.6 mmol) in 20 mL of THF at 0 °C and 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_2O to yield **2b** (3.38 g, 3.70 mmol, 67%): ^{1}H NMR (200.1 MHz, CD_2Cl_2) δ 2.40 (m, 4H; CH_2CH$_2$CF$_2$), 2.90 (m, 4H; CH_2CF$_2$), 7.25 (m, 4H; C*H*(3)), 7.52 (m, 4H; C*H*(2)); ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2) δ 26.7 (t, J_{FC} = 4 Hz; *C*H$_2$CH$_2$CF$_2$), 33.0 (t, J_{FC} = 22 Hz; *C*H$_2$CF$_2$), 129.1 (d, J_{PC} = 7 Hz; *C*H(3)), 132.3 (d, J_{PC} = 25 Hz; *C*H(2)), 137.5 (d, J_{PC} = 33 Hz; *C*(1)), 141.7 (s; *C*(4)), 105−125 (m; *C*F$_x$); ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −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); ^{31}P{^{1}H} NMR (80.2 MHz, $CDCl_3$) δ 81.3 (s); MS (70 eV, DEI) *m*/*z* (%) 912 (100) [M$^{\bullet+}$].

Synthesis of (−)-(4*S*)-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_4Cl (10 mL) at room temperature, the product was extracted with Et_2O (2 × 10 mL), and the combined organic layers were dried over Na_2SO_4, filtered, and evaporated to dryness. Recrystallization from MeOH/Cl_2FCCF_2Cl (2:1) afforded the desired product **3b** as a colorless solid (1.21 g, 1.14 mmol, 21%): ^{1}H NMR (300.1 MHz, $CDCl_3$) δ 0.73 (d, 3H, J = 6.7 Hz; CH(CH_3)$_2$), 0.83 (d, 3H, J = 6.7 Hz, CH(CH_3)$_2$), 1.51 (m, 1H; C*H*(CH$_3$)$_2$), 2.40 (m, 4H; CH_2CF$_2$), 2.94 (m, 4H; CH_2CH$_2$CF$_2$), 3.85−3.94 (m, 2H; CH_2(5), C*H*(4)), 4.20 (m, 1H, CH_2(5)), 6.90 (m, 1H; C*H*(4')), 7.16−7.42 (m, 10H; arom C*H*), 7.94 (m, 1H; C*H*(6')); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 18.3 (CH(*C*H$_3$)$_2$), 18.8 (CH(*C*H$_3$)$_2$, 26.2 (br, CH_2CH$_2$CF$_2$), 32.7 (t, J_{FC} = 22 Hz; (CH$_2$CH_2-CF$_2$)), 32.8 (t, J_{FC} = 22 Hz CH_2CH$_2$CF$_2$), 32.8 (*C*H(CH$_3$)$_2$, 70.1 (*C*H$_2$-(5)), 73.2 (*C*H(4)), 124.4, 128.1, 128.2, 128.3, 129.9 (d, J_{PC} = 3 Hz), 105−125 (m, *C*F$_x$), 130.3, 133.7, 134.1 (d, J_{PC} = 21 Hz), 134.7 (d, J_{PC} = 21 Hz) (arom *C*H), 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)). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −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); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$) δ −6.9 (s); MS (70 eV, DEI) *m*/*z* (%) 1065 (15) [M$^{\bullet+}$]. Anal. Calcd for $C_{40}H_{30}F_{26}N_1O_1P_1$ (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-(η^4-1,5-cyclooctadienyl)iridium(I) Hexafluorophosphate (5b). A solution of **3b** (456 mg, 0.428 mmol) and **4** (143 mg, 0.213 mmol) in CH_2Cl_2 (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 Na_2SO_4. Crystallization from CH_2Cl_2/CH_3OH and drying at 10^{-4} mbar afforded **5b** as a bright red powder (336.4 mg, 0.22 mmol, 52%): ^{1}H NMR (300.1 MHz, CD_2Cl_2) δ −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_2 of cod), 1.96−2.24 (m, 1H; CH_2 of cod; 1H; C*H*(CH$_3$)$_2$), 2.24−2.10 (m, 1H; CH_2 of cod), 2.30−2.73 (m, 4H; CH_2 of cod; 4H; CH_2CF$_2$), 2.90−3.13 (m, 1H; C*H* of cod; 4H; CH_2CH$_2$-CF$_2$), 3.24−3.36 (m, 1H; C*H* of cod), 4.29−4.16 (m, 1H; C*H*(4)), 4.52 (d, 2H; J = 6.5 Hz; CH_2(5)), 4.94−5.07 (m, 1H; C*H* of cod), 5.16−5.24 (m, 1H; C*H* of cod), 7.03−7.13 (m, 2H; arom C*H*), 7.30−7.81 (m, 9H; arom C*H*), 8.22−8.27 (m, 1H, arom C*H*); ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ = 12.9 (CH(*C*H$_3$)$_2$), 18.9 (CH(*C*H$_3$)$_2$, 26.6 (*C*H$_2$-CH$_2$CF$_2$), 26.8 (*C*H$_2$CH$_2$CF$_2$), 26.9 (*C*H$_2$ of cod), 28.9 (*C*H$_2$ of cod), 32.6 (t, J_{FC} = 22 Hz; *C*H$_2$CF$_2$), 32.7 (*C*H$_2$ of cod), 33.4 (*C*H(CH$_3$)$_2$), 36.5 (d, J_{PC} = 5 Hz; *C*H$_2$ of cod), 63.3 (*C*H of cod), 64.0 (*C*H of cod), 69.1 (*C*H$_2$(5)), 70.9 (*C*H(4)), 94.4 (d, J_{PC} = 13 Hz; *C*H of cod), 98.4 (d, J_{PC} = 11 Hz; *C*H of cod), 105−125 (m; CF$_x$), 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

(35) For the coordination chemistry of CO_2 and its relevance for catalysis, see: Leitner, W. *Coord. Chem. Rev.* **1996**, *153*, 257.

(36) Perrin, D. D.; Armagedo, W. L. F. *Purification of Laboatory Chemicals*, 3rd ed.; Pergamon Press: Oxford, 1988.

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

(38) (a) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920. (b) Nishida, H.; Takada, N.; Yoshimura, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600.

Hz), 135.8 (d, J_{PC} = 12 Hz) (arom *C*H), 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)); ^{19}F NMR (282.4 MHz, CD_2Cl_2) δ −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); ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2) δ 18.0 (s), −141.3 (sep, J_{PF} = 710.6 Hz); ^{11}B{^{1}H} NMR (64.2 MHz, CD_2Cl_2) δ −6.5 (s); $[\alpha]_{589}$ = −134 ($CHCl_3$, c = 0.3, 20 °C); MS (ESI/pos (MeOH)) *m*/*z* (%) 1366 (100) [M$^+$, ^{193}Ir], isotope cluster 1364−1368; calcd (obsd) 54 (51), 30 (33), 100 (100), 52 (54), 14 (12). Anal. Calcd for $C_{48}H_{42}F_{32}Ir_1N_1O_1P_2$ (1511.1): C, 38.15; H, 2.80; F, 40.23; Ir, 12.72; N, 0.93; P, 4.10. Found: C, 38.18; H, 2.86; F, 40.33; Ir, 12.58; N, 0.96; P, 3.98.

(−)-(4*S*)-2-(2-Diphenylphosphanylphenyl)-4-isopropyl-4,5-dihydrooxazole-(η^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_2Cl_2 (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_4] (111.3 mg, 0.33 mmol) in H_2O (25 mL) was added and the mixture stirred for several hours. Anion exchange was monitored by TLC (silica gel, CH_2Cl_2; [Ir(cod)(**3a**)]Cl, R_f = 0; [Ir(cod)(**3a**)]BPh_4, R_f = 0.40). The aqueous layer was separated, extracted with CH_2Cl_2 (4 × 5 mL), and dried over Na_2SO_4. Flash colomn chromatography on silica gel (eluent CH_2Cl_2) and evaporation of the solvent afforded **6a** as a bright red powder (143.8 mg, 0.14 mmol, 89%): ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ = −0.06 (d, 3H, J = 6.7 Hz; CH_3), 0.87 (d, 3H, J = 7.1 Hz, CH_3), 1.42−1.57 (m, 1H; CH(CH_3)$_2$), 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_2 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, 2.9 Hz; CH(4)), 4.22 (t, 1H, J = 9.5 Hz; CH_2(5)), 4.39 (dd, 1H, J = 9.5 Hz, 3.4 Hz; CH_2(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); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 12.7 (CH(*C*H_3)$_2$); 18.9 (CH(*C*H_3)$_2$; 26.9 (*C*H_2 of cod), 28.9 (*C*H_2 of cod), 32.7 (*C*H_2 of cod), 33.3 (*C*H(CH_3)$_2$); 36.5 (d, J_{PC} = 5 Hz; *C*H_2 of cod), 63.5 (*C*H of cod), 64.1 (*C*H of cod), 68.9 (*C*H_2(5)), 70.9 (*C*H(4)), 93.9 (d, J_{PC} = 13 Hz; *C*H of cod), 97.7 (d, J_{PC} = 11 Hz; *C*H 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 *C*H), 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 *C*H), 125.9−126.0 (m, 8C; arom *C*H), 136.3 (m, 8C; arom *C*H), 164.5 (q, J_{CB} = 49.5 Hz); ^{31}P{^{1}H) NMR (121.5 MHz, CD_2Cl_2) δ 16.5 (s); ^{11}B{^{1}H} NMR (64.2 MHz, CD_2Cl_2) δ −7.0 (s); MS (ESI/pos (CH_2Cl_2)) *m*/*z* (%) 674 (100) [M$^+$, ^{193}Ir], isotope cluster 672−676; calcd (obsd) 57 (65), 21 (23), 100 (100), 36 (39), 7 (7); (ESI/neg (CH_2Cl_2)) *m*/*z* (%) 319 (100) [M$^-$, ^{11}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.

(−)-(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-(η^4-1,5-cyclooctadienyl)iridium(I) Tetrakisphenylborate (6b). A solution of **3b** (141.8 mg, 0.15 mmol) and **4** (50.4 mg, 0.08 mmol) in CH_2Cl_2 (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[BPh_4](100 mg, 0.29 mmol) in H_2O (25 mL) was added and stirred for several hours. Anion exchange was monitored by TLC (silica gel, CH_2Cl_2; [Ir(cod)(**3b**)]Cl, R_f = 0; [Ir(cod)(**3b**)]BPh_4, R_f = 0.50). The organic layer was separated, and the aqueous layer extracted with CH_2Cl_2 (4 × 5 mL). The combined organic fractions were washed with H_2O and dried over Na_2SO_4. Flash colomn chromatography on silica gel (eluent CH_2Cl_2) and evaporation of the solvent afforded **6b** as a bright red powder (244.9 mg, 0.15 mmol, 97%): ^{1}H NMR (300.1 MHz, CD_2Cl_2) δ −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_2 of cod), 1.86−1.98 (m, 2H; CH_2 of cod), 1.99−2.13 (m, 1H; CH_2 of cod), 2.20−2.57 (m, 4H; CH_2 of cod, 4H, CH_2-CF_2), 2.88−3.00 (m, 1H; CH of cod; 4H, C$H_2CH_2CF_2$), 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); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 12.9 (CH(*C*H_3)$_2$), 18.9 (CH(*C*H_3)$_2$, 26.6 (m; *C*$H_2CH_2CF_2$), 26.8 (m; *C*H_2-CH_2CF_2), 27.0 (*C*H_2 of cod), 28.9 (*C*H_2 of cod), 32.6 (t, J_{FC} = 22 Hz; *C*H_2CF_2),), 32.7 (*C*H_2 of cod), 33.4 (*C*H(CH$_3$)$_2$), 36.5 (d, J_{PC} = 5 Hz; *C*H_2 of cod), 63.5 (*C*H of cod), 64.2 (*C*H of cod), 69.0 (*C*H_2(5)), 70.9 (*C*H(4)), 94.1 (d, J_{PC} = 13 Hz; *C*H of cod), 98.0 (d, J_{PC} = 10 Hz; *C*H of cod), 105−125 (m; CF_x), 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 *C*H), 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 *C*H), 126.0 (m, 8C, arom *C*H), 136.3 (m, 8C; arom *C*H,), 164.5 (q, J_{CB} = 49.8 Hz); ^{19}F NMR (282.4 MHz, CD_2Cl_2) δ −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_2Cl_2) δ 15.4 (s); ^{11}B{^{1}H} NMR (64.2 MHz, CD_2Cl_2) δ −6.5 (s); $[\alpha]_{589}$ = −184 ($CHCl_3$, c = 0.25, 20 °C); MS (ESI/pos (CH_2Cl_2)) *m*/*z* (%) 1366 (100) [M$^+$, ^{193}Ir], isotope cluster 1364−1368; calcd (obsd) 55 (57), 30 (30), 100 (100), 52 (48), 14 (13); (ESI/neg (CH_2Cl_2)) *m*/*z* (%) 319 (100) [M$^-$, ^{11}B], isotope cluster 318−321; calcd (obsd) 23 (21), 100 (100), 26 (25), 3 (3). Anal. Calcd for $C_{72}H_{62}B_1F_{26}Ir_1N_1O_1P_1$ (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.

(−)-(4*S*)-2-(2-{Diphenylphosphanylphenyl)-4-isopropyl-4,5-dihydrooxazole-(η^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_2Cl_2 (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_2O (40 mL) was added, and the resulting mixture was stirred at room temperature. Anion exchange was monitored by TLC (silica gel, CH_2Cl_2; [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 $MgSO_4$. Flash column chromatography on silica gel (eluent CH_2Cl_2) and evaporation of the solvent afforded **7a** as a bright red powder (822.4 mg, 0.54 mmol, 91%): ^{1}H NMR (300.1 MHz, CD_2Cl_2) δ −0.06 (d, 3H, J = 6.7 Hz; CH_3), 0.88 (d, 3H, J = 7.1 Hz; CH_3), 1.44−1.57 (m, 1H; CH(CH_3)$_2$), 1.65−1.78 (m, 1H; CH_2 of cod), 1.98−2.07 (m, 2H; CH_2 of cod), 2.08−2.19 (m, 1H; CH_2 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);^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 12.6 (CH(*C*H_3)$_2$), 18.9 (CH-(*C*H_3)$_2$, 26.9 (*C*H_2 of cod), 28.9 (*C*H_2 of cod), 32.7 (*C*H_2 of cod), 33.4 (*C*H(CH$_3$)$_2$), 37.0 (d, J_{PC} = 5 Hz; *C*H_2 of cod), 63.8 (*C*H of cod), 64.3 (*C*H of cod), 68.9 (*C*H_2(5)), 71.0 (*C*H(4)), 93.9 (d, J_{PC} = 13 Hz; *C*H of cod), 97.5 (d, J_{PC} = 11 Hz; *C*H of cod), 129.2 (d, J_{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 *C*H), 125.0 (q, J_{FC} = 272 Hz), 122.5, 128.9, 129.3 (q, J_{FC} = 31 Hz), 129.5, 129.8, 130.6 (arom *C*), 164.3 (d, J_{PC} = 7 Hz, *C*(2)), 117.9 (m, 4C; arom *C*H), 135.3 (br, 8C; arom *C*H), 162.2 (q, J_{CB} = 49.9 Hz); ^{19}F NMR (282.4 MHz, CD_2Cl_2) δ −63.3 (s); ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2) δ 16.5 (s); ^{11}B{^{1}H} NMR (64.2 MHz, CD_2Cl_2) δ −6.7 (s); $[\alpha]_{589}$ = −186 ($CHCl_3$, c = 0.25, 20 °C); MS (ESI/pos (CH_2Cl_2)) *m*/*z* (%) 674 (100) [M$^+$, ^{193}Ir], isotope cluster 672−676 calcd (obsd) 57 (75), 21 (25), 100 (100), 36 (41), 7 (6); (ESI/neg (CH_2Cl_2)) *m*/*z* (%) 863 (100) [M$^-$, ^{11}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.

(−)-(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-(η^4-1,5-cyclooctadienyl)iridium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)-borate (7b). Treating **5b** (30 mg, 0.02 mmol) in CH_2Cl_2 (10 mL) with a suspension of NaBARF (1.0 g, 1.13 mmol) in H_2O (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%): ^{1}H NMR (300.1 MHz, CD_2Cl_2) δ −0.04 (d, 3H, J = 6.7 Hz; CH_3), 0.89 (d, 3H, J = 7.1 Hz; CH_3), 1.45−1.62 (m, 1H; CH(CH_3)$_2$), 1.65−1.83 (m, 1H; CH_2 of cod), 1.98−2.08 (m, 2H; CH_2 of cod), 2.07−2.21 (m, 1H; CH_2 of cod), 2.32−2.67 (m, 4H; CH_2 of cod; 4H; CH_2CF$_2$), 2.98−3.08 (m, 1H; CH of cod; 4H; CH_2CH$_2$CF$_2$), 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_2(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);^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 12.8 (CH(*C*H$_3$)$_2$), 18.8 (CH(*C*H$_3$)$_2$, 26.6 (m; *C*H$_2$CH$_2$CF$_2$), 26.8 (m; *C*H$_2$CH$_2$CF$_2$), 26.9 (*C*H$_2$ of cod), 28.9 (*C*H$_2$ of cod), 32.6 (t, J_{FC} = 22.4 Hz; *C*H$_2$CF$_2$), 32.7 (*C*H$_2$ of cod), 33.4 (*C*H(CH$_3$)$_2$); 36.5 (d, J_{PC} = 5 Hz; *C*H$_2$ of cod), 63.7 (*C*H of cod), 64.3 (*C*H of cod), 69.0 (*C*H$_2$-(5)), 71.0 (*C*H(4)), 94.1 (d, J_{PC} = 13 Hz; *C*H of cod), 97.8 (d, J_{PC} = 10 Hz; *C*H 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 *C*H), 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 *C*H), 135.2 (br, 8C, arom *C*H), 162.2 (q, J_{CB} = 49.9 Hz), 164.3 (d, J_{PC} = 6 Hz, *C*(2)); ^{19}F NMR (282.4 MHz, CD_2Cl_2) δ −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); ^{31}P{^{1}H} NMR (121.5.0 MHz, CD_2Cl_2) δ 15.5 (s); ^{11}B{^{1}H} NMR (64.2 MHz, CD_2Cl_2) δ −6.6 (s); MS (ESI/pos (CH_2Cl_2)) *m*/*z* (%) 1366 (100) [M$^+$, ^{193}Ir], isotope cluster 1364−1368; calcd (obsd) 55 (69), 30 (32), 100 (100), 52 (58), 14 (15); (ESI/neg (CH_2Cl_2)) *m*/*z* (%) 863 (100) [M$^-$, ^{11}B], isotope cluster 862−865; calcd (obsd) 23 (31), 100 (100), 35 (42), 6 (6). Anal. Calcd for $C_{80}H_{54}B_1F_{50}Ir_1N_1O_1P_1$ (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, 6.0×10^{-3} mmol, s/c = 700, 0.14 mol % catalyst) under argon atmosphere. A weighted amount of CO_2 was introduced using a compressor to adjust to the desired density of $d(CO_2) = 0.75$ 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_2Cl_2. 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^{-1}, *n*-heptane/2-propanol, 90:10; t_R = 12.2 (*S*), 15.9 (*R*) min). In all experiments the (*R*)-enantiomer was formed predominantly.

Experiments in CH_2Cl_2 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[24] 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, 6.8×10^{-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_2 was introduced using a compressor to adjust to the desired density of the reaction medium of $d(CO_2) = 0.75$ 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_2 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[33] (V = 0.9 mL) was charged with a solution of compound **8** or **9** (approximately 0.05 mmol in 0.6 mmol of C_6D_6) under argon atmosphere. The NMR tube was pressurized with CO_2 (0.65 g) using a compressor to adjust to the desired density of CO_2 (0.75 g mL^{-1}). Measurements were conducted at a temperature setting of 40 °C on the NMR spectrometer, allowing at least 30 min for temperature equilibration.

Acknowledgment. This work was supported by the Max-Planck-Gesellschaft, the Deutsche Forschungsgemeinschaft (Gerhard-Hess-Programm), the Fonds der Chemischen Industrie, and the European Community (COST-D10). Generous gifts of chemicals by Clariant GmbH, Werk Gendorf are gratefully acknowledged. We thank Dr. R. Mynott, W. Wisniewski, and K. Wittmann at MPI Mülheim (NMR) and Dr. R. Ferwerda and Dr. H. Behl at Mettler Toledo/Applied Systems (FT-IR) for support during the high-pressure spectroscopy studies and J. Rosentreter (Mülheim) for GC analyses. Special thanks are due to Professors D. G. Blackmond, Mülheim, C. J. Elsevier, Amsterdam, and P. G. Jessop, Davis, for stimulating discussions. This paper is dedicated to Prof. R. Selke on the occasion of his 65th birthday.

Supporting Information Available: ^{1}H NMR spectra of compounds **8a,b** and **9a** in $CDCl_3$ and $scCO_2$ and reflectance FT-IR spectra of **8a** and **9a** as neat compounds, in toluene, and in $scCO_2$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA984309I