Chiral Phosphino- and (Phosphinooxy)-Substituted N-Heterocyclic Carbene Ligands and Their Application in Iridium-Catalyzed Asymmetric Hydrogenation

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Dedicated to Professor *Giambattista Consiglio* on the occasion of his 65th birthday

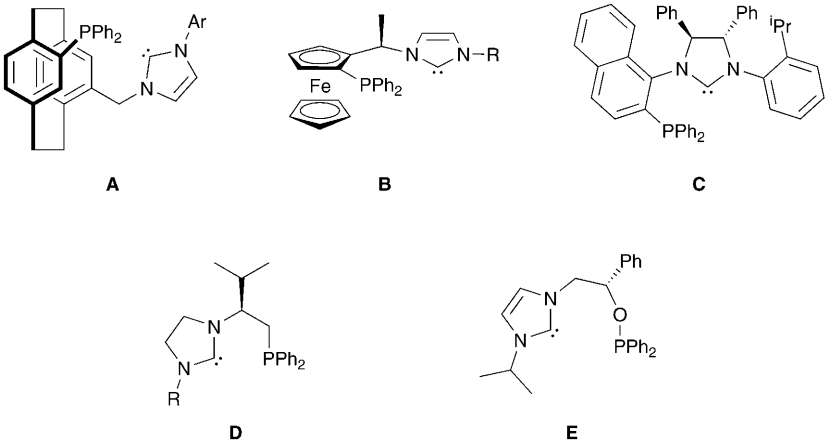
Enantiomerically pure iridium complexes with phosphino- and (phosphinooxy)-substituted N-heterocyclic carbene (NHC) ligands were synthesized. Investigation of their electronic properties showed a similar *trans* influence of the phosphino (or phosphinooxy) and the NHC units. The complexes were tested in iridium-catalyzed hydrogenation. While low conversions were observed with unfunctionalized olefins, the catalysts proved to be suitable for hydrogenation of the α,β-unsaturated ester **20**, allylic alcohol **21**, and imine **22**. The enantioselectivities were, however, moderate.

Introduction. – In recent years, N-heterocyclic carbenes (NHC) have generated growing interest in organometallic chemistry [1]. Their efficiency as ligands in homogeneous catalysis was demonstrated by the development of catalytic systems with unprecedented activities as, for example, in Ru-catalyzed metathesis [2] and Pd-catalyzed coupling reactions [3].

Chiral NHC ligands have also been successfully applied in asymmetric catalysis [4]. Monodentate NHC ligands were investigated first because they were readily accessible from simple chiral building blocks. Subsequently, chiral chelating ligands were introduced, in which the NHC moiety is linked to other coordinating units such as alkoxy [5], phosphine [6], dihydrooxazole [7], or imino [8] groups. Successful applications of these ligands include Ru-catalyzed ring-opening cross-metathesis, Rh-catalyzed hydrosilylation of ketones, Rh- and Ir-catalyzed hydrogenation.

[(Dihydrooxazolyl)NHC] iridium complexes were shown to be efficient catalysts for Ir-catalyzed hydrogenation of unfunctionalized olefins [7b]. In contrast, only very few phosphinoNHC bidentate chiral ligands have been studied. *Bolm* and co-workers reported that iridium complexes of ligand **A** catalyze the hydrogenation of olefins, but require long reaction times and give only moderate enantiomeric excess (ee) [6c]. The chiral phosphinoNHC ligands **B** and **C** were used in rhodium-catalyzed hydrogenation of dimethyl itaconate and α,β-unsaturated esters. While ligand **B** induced only 12% ee [6b], ligand **C** induced almost perfect enantioselectivity [6a]. In view of these results, we decided to evaluate other types of chiral phosphinoNHC bidentate ligands for Ir-catalyzed hydrogenation.

Herein, we report two classes of chiral ligands **D** and **E** and the evaluation of the corresponding Ir complexes as hydrogenation catalysts. Ligands **D** are structurally



related to the efficient pyridylalkyl phosphinite ligands recently developed in our laboratory [9]. Ligands **E**, we thought, would be of interest, because they should be readily accessible from optically active epoxides.

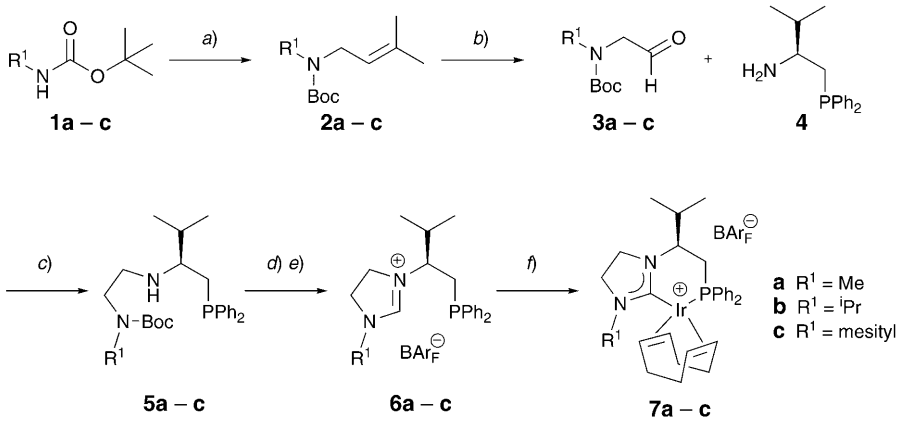
Results and Discussion. – *Synthesis of (PhosphinoNHC)iridium Complexes.* The synthesis of the phosphinoNHC precursors, *i.e.*, of the imidazolium salts **6**, is closely related to a route developed by *Hoveyda* and co-workers to access chiral (hydroxyalkyl)imidazolium salts [5a]. The key step is the reductive amination of aldehyde **3** with chiral phosphinoalkanamine **4**, prepared in four steps from (*S*)-valinol according to a literature procedure (*Scheme 1*) [10].

Boc-protected amines **1** (Boc = (*tert*-butoxy)carbonyl) were deprotonated with KH in DMF and then subjected to nucleophilic substitution with γ,γ-dimethylallyl bromide to give protected unsaturated amines **2**. Since the latter were not stable on silica gel, the crude products were directly converted into aldehydes **3** by ozonolysis. Reductive amination of aldehydes **3** with phosphinoalkanamines **4** in the presence of $NaHB(OAc)_3$ gave compound **5** in good yield. Removal of the Boc group, followed by imidazolium-salt formation with NH_4BF_4 and $HC(OEt)_3$, yielded the desired tetrafluoroborate salts, which were converted to the BAr_F^- (= tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) salts **6** upon treatment with $NaBAr_F$. The weakly coordinating BAr_F^- counterion was used since it is known to improve the performance of iridium complexes as hydrogenation catalysts compared to other weakly coordinating anions such as hexafluorophosphate, tetrafluoroborate, or triflate [11].

The Ir complexes **7a**–**c** were obtained by deprotonation of the corresponding imidazolium salts with freshly sublimed NaO^tBu in the presence of the metal precursor $[Ir_2Cl_2(cod)_2]$ (cod = cycloocta-1,5-diene). Upon addition of NaO^tBu, a fast color change from yellow to dark red was observed.

Synthesis of [(Phosphinooxy)NHC]iridium Complexes. In the synthesis of the phosphinoimidazolium salt **6**, the heterocyclic ring was formed in the last step, because introduction of a phosphino group in general requires strongly basic conditions that are incompatible with an imidazolium group. In the synthesis of (phosphinooxy)imida-

Scheme 1. *Synthesis of Iridium Complexes* **7a–c**



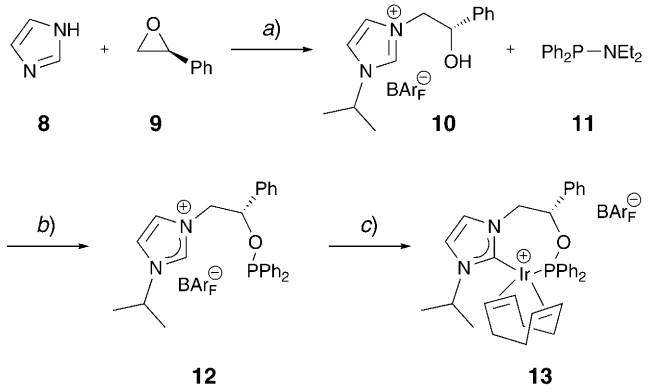
BAr_F^- = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate

a) 1. KH, DMF, 0 → 25°; 2. $Me_2C{=}CHCH_2Br$, DMF, r.t. *b*) 1. O_3/O_2, MeOH/CH_2Cl_2 1:3, −78°; 2. Me_2S, r.t.; 30–48% over two steps. *c*) $NaHB(OAc)_3$, CH_2ClCH_2Cl, r.t.; 74–82%. *d*) CF_3COOH, CH_2Cl_2, r.t.; 82–99%. *e*) 1. $HC(OEt)_3$, NH_4BF_4, 100°; 2. $NaBAr_F$, CH_2Cl_2, r.t.; 48–80%. *f*) $[Ir_2Cl_2(cod)_2]$, NaO^{t}Bu, THF, r.t.; 69–75%.

zolium salt **12**, the phosphinooxy group could be introduced in the last step under only mildly basic conditions. This has the advantage that the structure of the PR_2 unit can be easily varied (*Scheme 2*). Thus, (hydroxyalkyl)imidazolium salt **10** was prepared by condensation of the (*R*)-configurated epoxide **9** with 1*H*-imidazole (**8**), followed by alkylation with isopropyl iodide. The corresponding iodide salt was converted into imidazolium salt **10** by anion exchange with $NaBAr_F$. The BAr_F^- counterion enhanced the solubility of the imidazolium salt **10** in CH_2Cl_2, which was then submitted to phosphorylation with diphenylphosphinic amide **11** in the presence of Et_3N and 4,5-dichloro-1*H*-imidazole as catalyst. Purification of the (phosphinooxy)imidazolium salt **12** proved to be crucial to obtain pure complex **13**. A test experiment with a crude sample of **12** yielded complex **13** with impurities that could not be removed. After extensive experimentation, we established that chromatography with aluminium oxide under inert atmosphere gave pure (phosphinooxy)imidazolium salt **12** without oxidation or hydrolysis of the phosphinooxy moiety. The Ir complex **13** was obtained under the same conditions as those used for the preparation of phosphinoNHC complexes **7a–c**.

Structural Analysis of Iridium Complexes **7** *and* **13**. Iridium complexes **7a–c** were characterized by standard 2D-NMR techniques, which showed two sets of signals at room temperature. Clearly, two species were present in solution. In addition, the ^{1}H-NMR signals of complex **7c** were broad, indicating that the two species could be at the origin of the dynamic behavior. This assumption was confirmed by further analyses of complex **7c** at low temperature. At −27°, the two sets of signals (3:1 ratio) were sharp, and full NMR analyses allowed the assignment of structure **7c** to both species. Particular care was taken to establish the coordination mode of the NHC at the N*C*N position of the ring for both species. A NOESY experiment of complex **7c** at

Scheme 2. *Synthesis of Iridium Complexes* **13**



a) 1. Neat, 50°; 2. ^{i}PrI, MeCN, 80°; 3. NaBAr$_F$, CH_2Cl_2, r.t.; 25%. *b*) 4,5-Dichloro-1*H*-imidazole, Et_3N, CH_2Cl_2, r.t.; 60%. *c*) $[Ir_2Cl_2(cod)_2]$, NaO^{t}Bu, THF, r.t.; 69%.

$-27°$ indicated that the two species interconvert, but no cross-peak was observed for the two *ortho*-methyl groups of the mesityl (=2,4,6-trimethylphenyl) moiety. Rotation of the NHC substituent was, therefore, ruled out.

Further structural information about complex **7c** was obtained from X-ray analysis of complex **7c**′, the analogue of **7c** with BF_4^- instead of BAr_F^- as counterion[1]).

As depicted in *Fig. 1*, the Ir-atom lies in an almost square-planar arrangement, with the cod C=C bonds perpendicular to the coordination plane. A boat-like conformation of the chelate ring is expected with this type of ligand, since the planarity of the NHC moiety forces the C(4), N(1), C(1), and Ir(1) atoms to lie in the same plane (measured torsion angle = 3.9°). With these geometric constraints, complex **7c** can adopt two conformations, in which the isopropyl substituent is either bent over the Ir-atom (conformation observed for **7c**′) or pointing away from the metal (*Fig. 2*).

The assumption that the two conformers of complex **7c** arise from a flip of the chelate ring is consistent with the NOESY plot, which showed an NOE contact between the isopropyl group and the cod for one of the two conformers. Similar observations for the complexes **7a**,**b** led to the same conclusion, although no interconversion between the two conformers was observed on the NMR time scale.

NMR Analyses of complex **13** also indicated the presence of two species in solution. Assignment of the two structures confirmed that they were conformers, but no interconversion was observed in the NOESY experiment. In analogy to the phosphinoNHC complexes **7a**–**c**, the NOESY data suggest that the two conformers arise from a ring flip of the chelate ring.

The electronic properties of complexes **7b** and **7c** are reflected by the ^{13}C-NMR chemical shifts of the cod olefinic C-atoms and the distances from the cod C=C

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[1]) Complexes **7b**′ and **7c**′, analogues of complexes **7b** and **7c** bearing a BF_4^- counter ion, were synthesized from the corresponding tetrafluoroborate imidazolium salts and characterized by X-ray structure analysis.

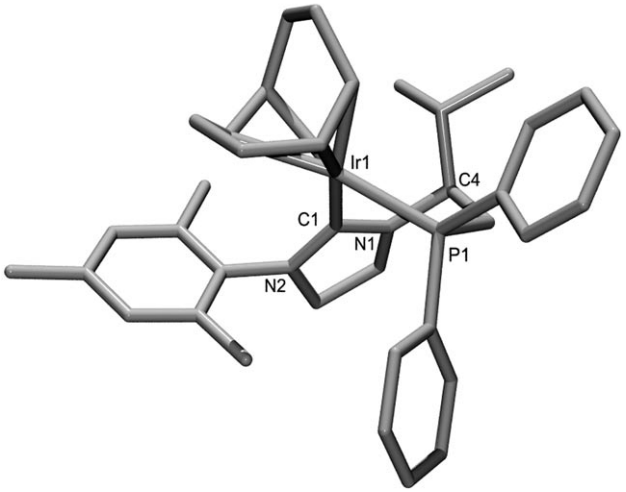
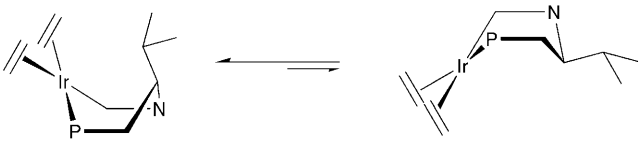


Fig. 1. *Structure of the cation of* **7c**′



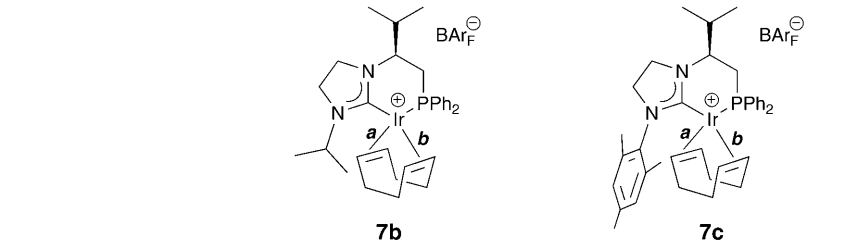
7c'

Fig. 2. *Two Conformations of the cation of* **7c**′

bonds to the Ir-atom, *i.e.*, Ir–(C=C) *trans* to the carbene and *trans* to the phosphino units (*Fig. 3*).

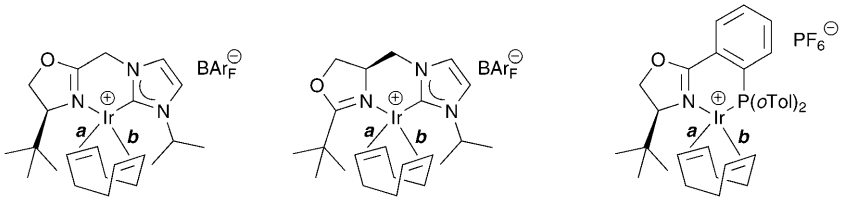
The data of complexes **7b**–**c** were compared with those of the [(dihydrooxazolyl)NHC]iridium complexes **14** and **15** [7g] and (dihydrophosphinooxazole)iridium **16** [12]. The data summarized in *Fig. 3* imply that the phosphino group has the strongest *trans* influence, followed by the NHC and the dihydrooxazole units. This is illustrated by the longest Ir–(C=C)] distance and the largest chemical shift of the cod olefinic C-atoms *trans* to the P-atom in complex **16**. In complexes **7b** and **7c**, the difference between the phosphino and the NHC moiety is less pronounced, as shown by the Ir–(C=C) distances, which all lie in the same range (207–209 pm). Accordingly, in contrast to the [(dihydrooxazolyl)NHC]- and (dihydrophosphinooxazole)iridium complexes **14**–**16**, the (phosphinoNHC)iridium complexes **7b**–**c** have two coordinating units with similar *trans* influence.

Asymmetric Hydrogenation. The (phosphinoNHC)iridium complexes **7a**–**c** and [(phosphinooxy)NHC]iridium complexes **13** were tested in the iridium-catalyzed hydrogenation of three unfunctionalized olefins, **17**–**19**, α,β-unsaturated ester **20**, allylic alcohol **21**, and imine **22**.



7b **7c**

	7b	**7c**
Ir–(C=C) distance [pm]	***a*** = 209[a]) ***b*** = 208[a])	***a*** = 207[a]) ***b*** = 209[a])
δ(C) [ppm] for C=C moieties	C_a 88.8, 81.9[b])	C_a 88.8, 87.2[b])
	C_b 84.0, 81.5[b])	C_b 78.9, 77.8[b])



14 **15** **16**

14	**15**	**16**
a = 207 ***b*** = 200	***a*** = 205[a]) ***b*** = 200[a])	***a*** = 211 ***b*** = 204
C_a 84.6, 82.9	C_a 80.8, 79.9	C_a 95.0, 90.0
C_b 65.7, 60.1	C_b 66.2, 56.0	C_b 67.5, 67.4

[a]) Measured with **7b'** and **7c'**, the analogues of **7b** and **7c** bearing BF_4^- as counter ion.

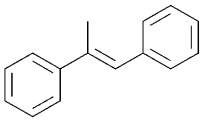
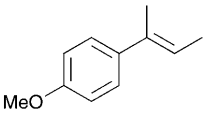
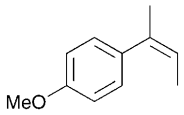
[b]) Data for the major conformer; corresponding data for the minor conformer:
7b: C_a 90.1, 87.2; C_b 79.4, 79.2. **7c**: C_a 86.5, 83.6; C_b 82.5, 81.5.

Fig. 3. *Measured Ir–(C=C) Distances in* **7b′**, **7c′**, *and* **14**–**16**, *and* δ*(C) of the corresponding C=C moieties of* **7b**, **7c**, *and* **14**–**16**

Initial studies were undertaken with unfunctionalized trisubstituted olefins **17**–**19** (*Table 1*). It quickly became apparent that our catalysts were not very active in comparison to [Ir(P,N-ligand)] complexes of type **16**, for which turnover frequency (TOF) values up to 5000 h^{-1} were measured during the hydrogenation of **17** [11b]. Twelve hours at room temperature and 50 bar H_2 were not sufficient to fully hydrogenate substrates **17**–**19**. Complexes **7a**–**c** were also less reactive and less enantioselective than [(dihydrooxazole)NHC]iridium complexes. In the hydrogenation of **17**, the choice of the NHC substituent is crucial for enantioselectivity. An increase from 5% to 63% was observed when the *N*-isopropyl group was replaced by a mesityl group. However, this effect was not observed for the hydrogenation of alkenes **18** and **19**.

In contrast to the results obtained with unfunctionalized olefins **17**–**19**, catalysts **7a**–**c** showed higher activities with functionalized alkenes **20**–**22** (*Table 2*). After 12 h at room temperature and 50 bar H_2, full conversion was obtained with the α,β-unsaturated ester **20**. Furthermore, the reaction time for allylic alcohol **21** and imine **22** was

Table 1. *Asymmetric Hydrogenation of Alkenes* **17**–**19**[a])

Substrate	Catalyst	Time [h]	Yield [%][b])	ee [%][c])
 **17**	**7a**	12	10	*rac*
	7b	12	21	5 (*R*)
	7c	12	38	63 (*R*)
	13	12	12	6 (*R*)
	14	2	>99	87 (*R*)
	15	2	>99	90 (*R*)
 **18**	**7a**	12	68	*rac*
	7b	12	80	*rac*
	7c	12	77	36 (*R*)
	13	12	>99	*rac*
	14	2	>99	69 (*R*)
	15	2	>99	87 (*R*)
 **19**	**7a**	12	52	5 (*S*)
	7b	12	68	*rac*
	7c	12	61	10 (*S*)
	13	12	95	15 (*S*)
	14	2	>99	41 (*S*)
	15	2	>99	66 (*S*)

[a]) 1 mol-% of catalyst and 0.1 mmol of substrate in CH_2Cl_2 (0.5 ml) at r.t. and 50 bar H_2. [b]) Determined by GC. [c]) Determined by HPLC.

reduced to 1 h without loss of conversion (except for catalyst **7c**). The remarkable activity of (phosphinoNHC)iridium complexes **7a**–**c** with imine **22** is emphasized by the comparison with [(dihydrooxazolyl)NHC]iridium complexes **14** and **15**, which did not hydrogenate imine **22** even after 12 h at room temperature and 50 bar H_2.

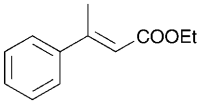
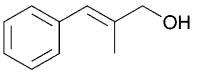
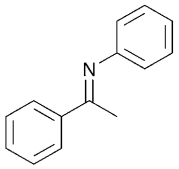
The enantioselectivities of catalysts **7a**–**c** were moderate. For each substrate, the highest enantioselectivity was obtained with catalyst **7b** bearing an isopropyl substituent at the NHC unit, followed by catalyst **7a** and catalyst **7c**. For imine **22**, catalyst **7b** gave 49% ee. By reducing the pressure to 10 bar, an increase of the enantioselectivity to 60% was observed. Further experiments at 100 and 20 bar H_2 confirmed the inverse-pressure dependence of the enantioselectivity in the hydrogenation of imine **22**.

The catalytic activity of [(phosphinooxy)NHC]iridium complex **13** is similar to that of the (phosphinoNHC)iridium complexes **7a**–**c**. However, the enantioselectivities of complex **13** were inferior to those of the best (phosphinoNHC)iridium catalysts.

Conclusions. – Three (phosphinoNHC)iridium complexes, **7a**–**c**, were synthesized starting from the chiral phosphinoalkanamine **4**. In addition, a simple synthesis of the [(phosphinooxy)NHC]iridium complex **13** starting from the chiral epoxide **9** was developed.

In contrast to the [(dihydrooxazolyl)NHC]- and (dihydrophosphinooxazole)iridium complexes **14**–**16**, complexes **7a**–**c** and **13** showed a similar *trans* influence for both coordinating units. They also behaved differently as hydrogenation catalysts. Contrary to the [(dihydrooxazolyl)NHC]iridium complexes, catalysts **7a**–**c** and **13** was not suit-

Table 2. *Asymmetric Hydrogenation of Functionalized Alkenes* **20** *and* **21** *and Imine* **22**[a])

Substrate	Catalyst	Time [h]	Yield [%][b])	ee [%][c])
 **20**	**7a**	12	>99	20 (*S*)
	7b	12	>99	43 (*S*)
	7c	12	>99	6 (*S*)
	13	12	>99	11 (*S*)
 **21**	**7a**	1	>99	35 (−)
	7b	1	>99	42 (−)
	7c	1	>99	26 (−)
	13	1	71	20 (+)
 **22**	**7a**	1	>99	6 (*S*)
	7b	1	>99	49 (*R*)
	7c	1	18	*rac*
	13	1	>99	46 (*S*)
	7b	1[d])	>99	34 (*R*)
	7b	3[e])	>99	57 (*R*)
	7b	3[f])	98	60 (*R*)

[a]) 1 mol-% of catalyst and 0.1 mmol of substrate in CH_2Cl_2 (0.5 ml) at r.t. and 50 bar H_2, unless otherwise stated. [b]) Determined by GC. [c]) Determined by HPLC. [d]) 100 bar H_2 at r.t. [e]) 20 bar H_2 at r.t. [f]) 10 bar H_2 at r.t.

able for hydrogenation of unfunctionalized olefins but showed good catalytic activity with α,β-unsaturated ester **20**, allylic alcohol **21**, and imine **22**.

NMR Analyses of the Ir complexes **7a**–**c** and **13** showed fluxional behavior of the chelate ring. Such lack of rigidity is likely to affect the chirality transfer from the catalyst to the substrate during hydrogenation, thus making the asymmetric induction difficult to control. A possible way to improve these ligands would be to rigidify their structure by introduction of an additional ring.

Financial support by the *Swiss National Science Foundation* is gratefully acknowledged. We thank Dr. *Sylvia Schaffner* and *Markus Neuburger* for the crystal structure analyses and Dr. *Klaus Kulicke* for NMR measurements. We also thank *Novartis* (Basel) and *OMG AG & Co* (Germany) for samples of valuable starting materials.

Experimental Part

General. Reactions with air- or moisture-sensitive compounds were performed under Ar by using standard *Schlenk* techniques or under purified N_2 in a *MBraun* glovebox. Glassware was oven-dried and flame-dried prior to use. All chemicals were purchased from *Fluka Chemie GmbH* (Buchs, Switzerland), with the exception of 3,5-bis(trifluoromethyl)bromobenzene (*Fluorochem Ltd*., Derbyshire, UK). Et_2O, pentane, and THF were dried over sodium/benzophenone, CH_2Cl_2 over CaH_2, and freshly distilled under a stream of N_2 prior to use. Aldehyde **3c** and precursors were already reported in the literature [5a]. CC = Column chromatography. HPLC: *Shimadzu* systems, *SCL-10A* system controller, *CTO-*

10AC column oven, *LC10-AD* pump system, *DGU-14A* degasser, *SPD-M10A* diode-array detector or UV/VIS detector (220 and 254 nm). M.p.: *Büchi-535* melting-point apparatus; not corrected. Optical rotations: sodium lamp, 1-dm cuvette, *c* in g/100 ml. IR Spectra: in cm^{-1}. NMR Spectra: δ in ppm, *J* in Hz. MS: in *m/z* (rel. %).

1,1-Dimethylethyl Methylcarbamate (**1a**). A soln. of $Boc_2(O)$ (24.00 g, 110 mmol) in THF (50 ml) was added to a soln. of 2M $MeNH_2$ (50 ml, 100 mmol) in THF at 0° over 10 min. *N,N*-Dimethylpyridin-4-amine (DMAP; 122 mg, 1 mmol) was added to the mixture, which was then stirred at r.t. for 19 h. The solvent was evaporated and the residue dissolved in Et_2O (150 ml). The org. layer was washed with H_2O and a sat. aq. $NaHCO_3$ soln., dried ($MgSO_4$), and evaporated, and the colorless oil purified by chromatography (silica gel, 7×20-cm column, R_f 0.33, AcOEt/hexane 1:9): **1a** (7.15 g, 55%). Colorless oil. IR (NaCl): 3357*m* (br.), 2976*m*, 2933*m*, 1696*s* (br.), 1531*m*, 1456*w*, 1419*w*, 1391*w*, 1366*m*, 1277*m*, 1250*m*, 1175*s*, 954*w*, 868*w*, 782*w*. ^{1}H-NMR (400.1 MHz, $CDCl_3$, 300 K): 4.41 (br., NH); 2.69 (*s*, MeN); 1.41 (*s*, Me_3C). $^{13}C\{^1H\}$-NMR (100.6 MHz, $CDCl_3$, 300 K): 157.0 (OCON); 79.5 (Me_3C); 28.8 (*Me*$_3$C); 27.6 (MeN). FAB-MS: 132 (10, $M+H]^+$), 76 (63), 57 (100), 41 (44). Anal. calc. for $C_6H_{13}NO_2$ (131.17): C 54.94, H 9.99, N 10.68; found: C 54.92, H 9.79, N 10.51.

1,1-Dimethylethyl (1-Methylethyl)carbamate (**1b**). As described for **1a**, with ^{i}PrNH$_2$ (1.00 g, 16.92 mmol), $Boc_2(O)$ (4.06 g, 18.61 mmol), and DMAP (20 mg, 0.17 mmol): **1b** (2.21 g, 74%). White solid. R_f (AcOEt/hexane 1:9) 0.48. M.p. 69–71°. IR (KBr): 3346*m*, 2978*m*, 2935*m*, 1683*s*, 1539*m*, 1459*m*, 1367*m*, 1256*s*, 1174*s*, 1078*s*, 938*w*, 886*w*, 841*w*, 778*w*, 753*w*, 643*m*, 461*w*, 424*w*. ^{1}H-NMR (400.1 MHz, $CDCl_3$, 300 K): 4.31 (br., NH); 3.71 (*m*, Me_2CH); 1.41 (*s*, Me_3C); 1.11 (*m*, 3 H, *Me*$_2$CH); 1.09 (*m*, 3 H, *Me*$_2$CH). $^{13}C\{^1H\}$-NMR (100.6 MHz, $CDCl_3$, 300 K): 155.6 (N*C*OO); 79.3 (Me_3CO); 43.0 (Me_2C); 28.8 (*Me*$_3$C); 23.5 (*Me*$_2$CH). FAB-MS: 160 (100, $M+H]^+$). Anal. calc. for $C_8H_{17}NO_2$ (159.23): C 60.35, H 10.76, N 8.80, O 20.10; found: C 60.41, H 10.56, N 8.64, O 20.28.

1,1-Dimethylethyl Methyl(2-oxoethyl)carbamate (**3a**). A soln. of **1a** (10.05 g, 76.6 mmol) in DMF (100 ml) at 0° was added to a suspension of KH (3.38 g, 84.3 mmol; free of mineral oil) in DMF at 0° over 0.5 h. The mixture was stirred at r.t. until the gas evolution had ceased (typically 2 h). Then 1-bromo-3-methylbut-2-ene (13.7 g, 91.9 mmol) was added and the resultant mixture stirred at r.t. for an additional hour. The soln. was quenched with sat. aq. $NaHCO_3$ soln. (100 ml) and H_2O (100 ml) and extracted with Et_2O (3×100 ml), and the combined org. layer was dried ($MgSO_4$) and evaporated: **2a** (11.56 g) as a colorless oil, which was not stable on silica gel and used for the next step without purification.

A soln. of crude **2a** in CH_2Cl_2/MeOH 3:1 (500 ml) was cooled to −78°, and ozone was bubbled into the mixture for *ca*. 0.5 h (TLC monitoring). Then the mixture was warmed to r.t. and reduced with Me_2S (7.21 g, 116 mmol). The solvent and excess Me_2S were evaporated. The crude product was purified by CC (silica gel, 7×20 cm column, R_f 0.40, AcOEt/hexane 3:7): **3a** (6.38 g, 48% over two steps). Colorless oil. IR (NaCl): 2976*m*, 2933*m*, 1734*m*, 1695*s*, 1481*m*, 1456*m*, 1392*m*, 1297*w*, 1242*m*, 1158*s*, 1056*w*, 929*w*, 878*w*, 775*w*. ^{1}H-NMR (400.1 MHz, $CDCl_3$, 300 K): 9.56 (*s*, CHO); 3.99–3.87 (*m*, CH_2N); 2.93–2.88 (*m*, MeN); 1.44–1.38 (*m*, 9 H, Me_3C). $^{13}C\{^1H\}$-NMR (100.6 MHz, $CDCl_3$, 300 K): 199.0 (CHO); 156.5 (NCOO); 155.8 (NCOO); 81.1 (Me_3C); 80.9 (Me_3C); 59.6 (CH_2N); 59.1 (CH_2N); 36.2 (MeN); 28.6 (br., Me_3C); two sets of signals due to amide conformers. FAB-MS: 174 (37, $[M+H]^+$), 118 (100), 57 (88). Anal. calc. for $C_8H_{15}NO_3$ (173.21): C 55.47, H 8.73, N 8.09; found: C 54.73, H 8.44, N 8.09.

1,1-Dimethylethyl (1-Methylethyl)(2-oxoethyl)carbamate (**3b**). As described for **3a**, with **1b** (4.83 g, 30.4 mmol), KH (1.34 g, 33.4 mmol), 1-bromo-3-methylbut-2-ene (5.97 g, 40.1 mmol), and Me_2S (2.52 g, 40.6 mmol): **3b** (1.790 g, 30% over two steps). White solid. R_f (AcOEt/hexane 3:7) 0.54. M.p. 36–37°. IR (KBr): 2978*m*, 2805*w*, 2709*w*, 1739*m*, 1696*s*, 1437*m*, 1398*m*, 1366*m*, 1295*m*, 1253*m*, 1219*m*, 1169*s*, 1108*m*, 1019*m*, 900*m*, 857*w*, 823*w*, 773*m*, 680*w*, 456*w*. ^{1}H-NMR (500.1 MHz, $CDCl_3$, 295 K): 9.48 (br., 1 H, CHO), 4.50 (br., 0.64 H, Me_2CH), 4.23 (br., 0.36 H, Me_2CH); 1.60–1.30 (*m*, 9 H, Me_3C); 1.07 (*m*, 6 H, *Me*$_2$CH). $^{13}C\{^1H\}$-NMR (125.7 MHz, $CDCl_3$, 295 K): 200.2 (CHO); 155.8 (NCOO); 154.8 (NCOO); 80.8 (Me_3C); 80.6 (Me_3C); 51.4 (CH_2N); 51.1 (CH_2N); 47.4 (Me_2CH); 46.0 (Me_2CH); 28.4 (br., *Me*$_3$C); 21.1 (*Me*$_2$CH); 20.7 (*Me*$_2$CH); two sets of signals due to amide conformers. FAB-MS: 202 (10, $[M+H]^+$), 172 (39), 146 (21), 116 (34), 72 (60), 57 (100). Anal. calc. for $C_{10}H_{19}NO_3$ (201.26): C 59.68, H 9.51, N 6.96, O 23.85; found: C 59.61, H 9.37, N 7.05, O 23.96.

1,1-Dimethylethyl {2-{[(1S)-1-[(Diphenylphosphino)methyl]-2-methylpropyl]amino}ethyl}methylcarbamate (**5a**). A soln. of **3a** (421 mg, 2.43 mmol) in 1,2-dichloroethane (5 ml) was added to a soln. of

(2*S*)-1-(diphenylphosphino)-3-methylbutan-2-amine (**4**; 600 mg, 2.21 mmol) and $NaHB(OAc)_3$ (933 mg, 4.42 mmol) in 1,2-dichloroethane (3 ml). The mixture was stirred at r.t. for 4 h and quenched with sat. aq. $NaHCO_3$ soln. (10 ml). The aq. layer was extracted with CH_2Cl_2 (3×10 ml), the combined org. phase dried ($MgSO_4$) and evaporated, and the yellow oil purified by CC (silica gel, 3×18-cm column, R_f 0.56, AcOEt/hexane 4:6): **5a** (700 mg, 74%). Colorless oil. $[\alpha]_D^{20} = +52.2$ ($c = 1.00$, $CHCl_3$). IR (NaCl): 3056*w*, 2961*m*, 1694*s*, 1478*m*, 1433*w*, 1392*m*, 1368*w*, 1247*w*, 1155*m*, 879*w*, 741*w,* 696*w*. ^{1}H-NMR (500.1 MHz, $CDCl_3$, 295 K): 7.49–7.43 (*m*, 2 arom. H); 7.43–7.38 (*m*, 2 arom. H); 7.37–7.27 (*m*, 6 arom. H); 3.19 (br., CH_2N); 2.82 (*s*, Me); 2.71–2.58 (br., CH_2N); 2.36 (*m*, PCH_2CH); 2.22 (br., 1 H, CH_2P); 2.25–1.85 (br., 2 H, CH_2P, Me_2CH); 1.44 (br., Me_3C); 0.87 (*d*, $^3J = 6.8$, 3 H, Me_2CH); 0.83 (*d*, $^3J = 7.8$, 3 H, Me_2CH); 1 NH not detected. $^{13}C\{^1H\}$-NMR (125.7 MHz, $CDCl_3$, 295 K): 155.9 (br., NCO); 139.6 (br., arom. C); 138.4 (br., arom. C); 133.4 (arom. CH); 133.2 (arom. CH); 132.7 (br., arom. CH); 132.6 (br., arom. CH); 129.0 (arom. CH); 128.7–128.4 (5 arom. CH); 70.4 (Me_3C); 60.6 (br., PCH_2CH); 49.2 (CH_2N); 45.9 (CH_2N), 35.2 (MeN); 30.8 (br., Me_2CH); 30.6 (br., CH_2P); 28.6 (Me_3C); 18.4 (br., 1 C, Me_2-CH); 17.5 (1 C, Me_2CH). $^{31}P\{^1H\}$-NMR (202.5 MHz, $CDCl_3$, 295 K): −21.2 (*s*). FAB-MS: 429 (100, $[M+H]^+$), 445 (18); oxidation during measurement. Anal. calc. for $C_{25}H_{37}N_2O_2P$ (428.55): C 70.07, H 8.70, N 6.54, O 7.47; found: C 69.83, H 8.52, N 6.60, O 7.55.

*1,1-Dimethylethyl {2-{{(1*S*)-1-[(Diphenylphosphino)methyl]-2-methylpropyl}amino}ethyl}(1-methylethyl)carbamate* (**5b**). As described for **5a**, with **3b** (250 mg, 1.24 mmol), **4** (306 mg, 1.13 mmol), and $NaHB(OAc)_3$ (526 mg, 2.48 mmol): **5b** (413 mg, 80%). Colorless oil that crystallized on standing. R_f (AcOEt/hexane 1:1) 0.69. M.p. 51–52°. $[\alpha]_D^{20} = +60.4$ ($c = 1.00$, $CHCl_3$). IR (KBr): 3068*w*, 2967*m*, 2872*m*, 2815*m*, 1593*s*, 1472*m*, 1412*m*, 1367*m*, 1343*m*, 1299*m*, 1250*w*, 1169*m*, 1122*m*, 1089*w*, 998*w*, 905*w*, 836*w*, 744*m*, 695*m*, 508*w*. ^{1}H-NMR (500.1 MHz, $CDCl_3$, 295 K): 7.46 (*m*, 2 arom. H); 7.40 (*m*, 2 arom. H); 7.36–7.27 (br., 6 arom. H); 4.40–3.80 (br., Me_2CH); 3.30–2.90 (br., CH_2N); 2.65 (br., CH_2N); 2.40 (br., PCH_2CH); 2.27 (br., 1 H, CH_2P); 2.15–1.85 (br., 2 H, CH_2P, Me_2CHC); 1.42 (br., Me_3C); 1.07 (br., Me_2CHN); 0.89 (br., 3 H, Me_2CHC); 0.84 (br., 3 H, Me_2CHC); 1 NH not detected. $^{13}C\{^1H\}$-NMR (125.7 MHz, $CDCl_3$, 295 K): 138.3 (*d*, $^1J(P,C) = 12.6$, arom. C); 133.4 (*d*, $^2J(P,C) = 19.3$, 2 arom. CH); 132.6 (*d*, $^2J(P,C) = 17.5$, 2 arom. CH); 128.8–128.3 (5 arom. CH); 60.5 (br., PCH_2CH); 47.9 (CH_2N); 46.5 (br., Me_2CHC); 42.8 br., (CH_2N); 30.8 (*d*, $^1J(P,C) = 7.0$, CH_2P); 30.5 (br., Me_2CHC); 28.6 (Me_3C); 20.9 (Me_2CHN); 18.6 (1 C, Me_2CHC); 17.5 (1 C, Me_2CHC); 1 arom. C and 1 quat. Me_3C not detected. $^{31}P\{^1H\}$-NMR (202.5 MHz, $CDCl_3$, 295 K): −21.1 (br.). FAB-MS: 457 (100, $[M+H]^+$), 473 (17); oxidation during measurement. Anal. calc. for $C_{27}H_{41}N_2O_2P$ (456.60): C 71.02, H 9.05, N 6.14, O 7.01; found: C 70.91, H 8.97, N 6.22, O 7.03.

*1,1-Dimethylethyl {2-{{(1*S*)-1-[(Diphenylphosphino)methyl]-2-methylpropyl}amino}ethyl}(2,4,6-trimethylphenyl)carbamate* (**5c**). As described for **5a**, with **3c** (675 mg, 2.43 mmol), **4** (600 mg, 2.21 mmol), and $NaHB(OAc)_3$ (937 mg, 4.42 mmol): **5c** (961 mg, 82%). Colorless oil. R_f (AcOEt/hexane 2:8) 0.43. $[\alpha]_D^{20} = +30.5$ ($c = 1.00$, $CHCl_3$). IR (KBr): 3054*m*, 2959*m*, 2927*m*, 2867*m*, 1695*s*, 1479*m*, 1370*m*, 1310*m*, 1254*m*, 1150*m*, 1030*w*, 994*w*, 855*w*, 741*m*, 696*m*. ^{1}H-NMR (500.1 MHz, $CDCl_3$, 295 K): 7.47–7.24 (*m*, 10 arom. H (Ph)); 6.88–6.83 (*m*, 2 arom. H (Mes)); 3.55–3.25 (*m*, CH_2N); 2.76–2.62 (*m*, CH_2N); 2.35 (*m*, PCH_2CH); 2.28–2.24 (*m*, Me (Mes)); 2.24–2.17 (*m*, 1 H, CH_2P); 2.16–2.09 (*m*, 2 Me (Mes)); 2.02–1.87 (*m*, 2 H, CH_2P, Me_2CHC); 1.48 (*s*, 3 H, Me_3C); 1.30 (*s*, 6 H, Me_3C); 0.84 (*m*, Me_2-CHC); 1 NH not detected. $^{13}C\{^1H\}$-NMR (125.7 MHz, $CDCl_3$, 295 K): 139.7 (arom. C); 139.6 (arom. C); 138.3 (arom. C); 138.2 (arom. C); 138.0 (arom. C); 136.8 (arom. C); 136.5 (br., arom. C); 135.9 (arom. C); 135.8 (arom. C); 135.3 (br., arom. C); 133.4 (arom. C); 133.29 (arom. C); 133.28 (arom. C); 133.1 (arom. C); 132.8 (arom. C); 132.7 (arom. C); 132.6 (arom. C); 132.4 (arom. C); 129.4 (arom. C); 129.3 (arom. C); 129.2–128.3 (*m*, arom. C); 60.8 (br., PCH_2CH); 60.5 (*d*, $^2J(P,C) = 12.6$, PCH_2CH); 51.0 (CH_2N); 49.9 (br., CH_2N); 46.6 (br., CH_2N); 30.8 (*d*, $^1J(P,C) = 7.0$, CH_2P); 30.7 (*d*, $^1J(P,C) = 7.3$, CH_2P); 30.6 (br., Me_2CHC); 30.5 (br., Me_2CHC); 28.6 (Me_3C); 28.4 (Me_3C); 21.0 (Me (Mes)); 18.6 (Me); 18.31 (Me); 18.29 (Me); 18.1 (Me); 17.8 (Me); 17.3 (Me); two sets of signals due to amide rotamers; 2 quat. Me_3C not detected. $^{31}P\{^1H\}$-NMR (202.5 MHz, $CDCl_3$, 295 K): −21.2 (br.), −21.3 (*s*). FAB-MS: 533 (100, $[M+H]^+$), 549 (38); oxidation during measurement. Anal. calc. for $C_{33}H_{45}N_2O_2P$ (532.70): C 74.41, H 8.51, N 5.26, O 6.01; found: C 74.43, H 8.49, N 5.29, O 6.12.

*3-{(1*S*)-1-[(Diphenylphosphino)methyl]-2-methylpropyl}-4,5-dihydro-1-methyl-1*H*-imidazolium Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1−)* (**6a**). CF_3COOH (6.00 g, 53.0 mmol) was added to a

soln. of **5a** (450 mg, 1.05 mmol) in CH_2Cl_2 (15 ml) at 0°. The mixture was stirred at r.t. for 20 h and then quenched with H_2O (15 ml) and 5M NaOH until the pH was 10. The aq. layer was extracted with CH_2Cl_2 (2×15 ml). The combined org. extract was dried ($MgSO_4$) and evaporated to yield a yellow oil (327 mg, 95%) of >95% purity (by ^{1}H-NMR). A soln. of this oil (217 mg, 0.661 mmol) and NH_4BF_4 (77 mg, 0.726 mmol) in triethyl orthoformate (4.0 ml, 26.0 mmol) was heated at 110° for 1 h. The precipitate was decanted and dissolved in CH_2Cl_2 (10 ml). Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate(1−) ($NaBAr_F$; 586 mg, 0.661 mmol) was added to the mixture, which was then stirred for 15 min. The soln. was filtered, the filtrate evaporated, and the crude product purified by CC (silica gel, 5×8-cm column, inert atmosphere, CH_2Cl_2 (500 ml)): **6a** (409 mg, 51%). White solid. M.p. 97–98°. $[\alpha]_D^{20} = +26.5$ ($c = 1.00$, $CHCl_3$). IR (KBr): 3076*w*, 2975*w*, 1659*m*, 1612*w*, 1526*w*, 1467*w*, 1435*w*, 1358*s*, 1280*s*, 1123*s*, 930*w*, 889*m*, 838*w*, 748*w*, 711*w*, 674*m*, 501*w*, 450*w*. ^{1}H-NMR (400.1 MHz, $CDCl_3$, 300 K): 7.69 (*m*, 8 H_o (Ar_F)); 7.53 (*m*, 4 H_p (Ar_F)); 7.45–7.25 (*m*, 10 arom. H); 7.05 (*s*, NCHN), 3.65–3.43 (*m*, 3 H, CH_2N); 3.43–3.15 (*m*, 2 H, CH_2N, PCH_2CH); 2.87 (*s*, MeN); 2.57 (*m*, 1 H, CH_2P); 2.27 (*m*, 1 H, CH_2P); 1.78 (*m*, Me_2CH); 0.99 (*d*, $^3J = 6.6$, 3 H, Me_2CH); 0.79 (*d*, $^3J = 6.6$, 3 H, Me_2CH). ^{13}C{^{1}H}-NMR (100.6 MHz, $CDCl_3$, 300 K): 162.0 (*q*, ^1J(B,C) = 49.9, 4 C_{ipso} (ArF)); 156.0 (NCHN); 136.2 (*d*, ^1J(P,C) = 10.2, 1 arom. C); 135.2 (br., 8 C_o (Ar_F)); 134.4 (*d*, ^1J(P,C) = 9.8, 1 arom. C); 133.3 (*d*, J(P,C) = 20.2, 2 arom. CH); 132.8 (*d*, J(P,C) = 19.5, 2 arom. CH); 130.59 (arom. CH); 130.57 (arom. CH); 129.7 (*d*, J(P,C) = 7.4, 2 arom. CH); 129.6 (*d*, J(P,C) = 7.7, 2 arom. CH); 129.3 (*qq*, ^2J(F,C) = 31.1, ^3J(B,C) = 2.9, 8 C_m (Ar_F)); 124.9 (*q*, ^1J(F,C) = 272.5, 8 CF_3); 117.9 (*sept.*, ^3J(F,C) = 3.8, 4 C_p (Ar_F)); 65.8 (*d*, ^2J(P,C) = 14.8, PCH_2CH); 50.0 (CH_2N); 46.0 (*d*, ^4J(P,C) = 3.5, 1 C, CH_2N); 35.2 (MeN); 32.2 (*d*, ^3J(P,C) = 6.7, Me_2CH); 29.3 (*d*, ^1J(P,C) = 15.2, CH_2P); 19.6 (1 C, Me_2CH); 19.4 (1 C, Me_2CH). ^{31}P{^{1}H}-NMR (202.5 MHz, $CDCl_3$, 295 K): −25.4 (*s*). FAB-MS: 339 (100, $[M - BAr_F]^+$), 355 (29); oxidation during measurement. Anal. calc. for $C_{53}H_{40}BF_{24}N_2P$ (1202.64): C 52.93, H 3.35, N 2.33; found: C 53.14, H 3.34, N 2.36.

*3-{(1*S*)-1-[(Diphenylphosphino)methyl]-2-methylpropyl}-4,5-dihydro-1-(1-methylethyl)-1*H*-imidazolium Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1−)* (**6b**). As described for **6a**, with **5b** (167 mg, 0.472 mmol), CF_3COOH (4.47 g, 39.2 mmol), NH_4BF_4 (49 mg, 0.468 mmol): triethyl orthoformate (2.0 ml, 13.0 mmol), and $NaBAr_F$ (414 mg, 0.468 mmol): **6b** (460 mg, 79% over two steps). White solid. M.p. 98–99°. $[\alpha]_D^{20} = +25.1$ ($c = 1.00$, $CHCl_3$). IR (KBr): 3072*w*, 2978*w*, 1643*m*,1470*w*, 1434*w*, 1358*s*, 1279*s*, 1128*s*, 930*w*, 890*w*, 838*w*, 744*w*, 708*m*, 674*m*, 506*w*, 450*w*. ^{1}H-NMR (500.1 MHz, $CDCl_3$, 295 K): 7.70 (*m*, 8 H_o (Ar_F)); 7.53 (*m*, 4 H_p (ArF)); 7.44–7.35 (*m*, 10 arom. H); 7.13 (*s*, NCHN); 3.70–3.55 (*m*, 3 H of NCH_2, Me_2CHN); 3.43 (*m*, 1 H, CH_2N); 3.24 (*m*, PCH_2CH); 2.62 (*m*, 1 H, CH_2P); 2.26 (*m*, 1 H, CH_2P); 1.79 (*m*, Me_2CHC); 1.21 (*m*, Me_2CHN); 0.98 (*d*, ^3J(H,H) = 6.6, 3 H, Me_2CHC); 0.79 (*d*, ^3J(H,H) = 6.4, 3 H, Me_2CHC). ^{13}C{^{1}H}-NMR (125.7 MHz, $CDCl_3$, 295 K): 161.8 (*q*, ^1J(B,C) = 49.9, 4 C_{ipso} (Ar_F)); 153.8 (NCHN); 135.9 (*d*, ^1J(P,C) = 9.8, 1 arom. C); 134.9 (br., 8 C_o (Ar_F)); 135.0 (*d*, ^1J(P,C) = 9.3, 1 arom. C); 132.8 (*d*, J(P,C) = 11.4, 2 arom. CH); 132.7 (*d*, J(P,C) = 11.2, 2 arom. CH); 130.5 (arom. CH); 130.2 (arom. CH); 129.6 (*d*, J(P,C) = 7.4, 2 arom. CH); 129.4 (*d*, J(P,C) = 7.5, 2 arom. CH); 129.0 (*qq*, ^2J(F,C) = 31.1, ^3J(B,C) = 2.9, 8 C_m (Ar_F)); 124.7 (*q*, ^1J(F,C) = 272.5, 8 CF_3); 117.5 (*sept.*, ^3J(F,C) = 3.8, 4 C_p (Ar_F)); 65.3 (*d*, ^2J(P,C) = 11.9, PCH_2CH); 51.4 (Me_2CHN); 45.8 (CH_2N); 44.8 (*d*, ^4J(P,C) = 4.1, 1 C, CH_2N), 31.8 (*d*, ^3J(P,C) = 6.1, Me_2CHN); 28.9 (*d*, ^1J(P,C) = 13.9, CH_2P); 20.57 (Me_2-CHN); 20.47 (Me_2CHN); 19.4 (Me_2CHC); 19.0 (Me_2CHC). ^{31}P{^{1}H}-NMR (202.5 MHz, $CDCl_3$, 295 K): −22.6 (*s*). FAB-MS: 367 (100, $[M - BAr_F]^+$), 383 (37); oxidation during measurement. Anal. calc. for $C_{55}H_{44}BF_{24}N_2P$ (1230.70): C 53.68, H 3.60, N 2.28; found: C 53.49, H 3.64, N 2.36.

*3-{(1*S*)-1-[(Diphenylphosphino)methyl]-2-methylpropyl}-4,5-dihydro-1-(2,4,6-trimethylphenyl)-1*H*-imidazolium Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate(1−)* (**6c**). As described for **6a**, with **5c** (225 mg, 0.423 mmol), CF_3COOH (4.53 g, 39.8 mmol), NH_4BF_4 (36 mg, 0.347 mmol), triethyl orthoformate (4.0 ml, 26.0 mmol), and $NaBAr_F$ (307 mg, 0.347 mmol): **6c** (218 mg, 39% over two steps). Colorless oil. $[\alpha]_D^{20} = +63.2$ ($c = 1.00$, $CHCl_3$). IR (NaCl): 3067*w*, 2970*w*, 2939*w*, 1639*m*, 1357*m*, 1279*s*, 1126*s* (br.), 998*w*, 934*w*, 889*m*, 839*m*, 744*w*, 710*m*, 675*m*, 577*w*, 504*w*. ^{1}H-NMR (500.1 MHz, $CDCl_3$, 295 K): 7.70 (*m*, 8 H_o (Ar_F)); 7.50 (*m*, 4 H_p (Ar_F)); 7.48–7.39 (*m*, 3 arom. H (Ph), 2 arom. H (Mes)); 7.38–7.30 (*m*, NCHN, 5 arom. H (Ph)); 6.98 (br., 2 arom. H (Ph)); 4.25–4.06 (*m*, 3 H, CH_2N); 3.96 (*m*, 1 H, CH_2N); 3.18 (*m*, PCH_2CH); 2.78 (*m*, 1 H, CH_2P); 2.40–2.25 (br., 2 Me); 2.15 (*m*, 4 H, 1 Me, CH_2P); 1.93 (*m*, Me_2-CH); 1.00 (*d*, $^3J = 6.6$, 3 H, Me_2CH); 0.91 (*d*, $^3J = 6.4$, 3 H, Me_2CH). ^{13}C{^{1}H}-NMR (125.7 MHz, $CDCl_3$, 295 K): 161.8 (*q*, ^1J(B,C) = 49.9, 4 C_{ipso} (Ar_F)); 156.9 (NCHN); 142.1 (arom. C (Mes)); 135.7 (*d*, ^1J(P,

C) = 7.9, 1 arom. C (Ph)); 134.9 (br., C_o (ArF)); 133.6 (*d*, ^1J(P,C) = 10.6, 1 arom. C (Ph)); 133.3 (*d*, *J*(P,C) = 10.5, 2 arom. C (Ph)); 131.9 (*d*, *J*(P,C) = 18.7, 2 arom. CH (Ph)); 131.0 (2 arom. CH (Mes)); 130.6 (arom. CH (Ph)); 129.8 (arom. CH (Ph)); 129.8 (*d*, *J*(P,C) = 7.4, 2 arom. CH (Ph)); 129.2 (*d*, *J*(P,C) = 7.2, 2 arom. CH (Ph)); 129.1 (arom. C (Mes)); 129.0 (*qq*, ^2J(F,C) = 31.1, ^3J(B,C) = 2.9, 8 C_m (Ar_F)); 124.7 (*q*, ^1J(F,C) = 272.5, 8 CF_3); 117.5 (*sept.*, ^3J(F,C) = 3.8, 4 C_p (Ar_F)); 64.7 (*d*, ^2J(P,C) = 11.1, PCH_2CH); 50.6 (CH_2N); 45.9 (*d*, ^4J(P,C) = 5.8, 1 C, CH_2N); 31.9 (*d*, ^3J(P,C) = 5.1, Me_2CH); 28.8 (*d*, ^1J(P,C) = 13.9, CH_2P); 21.1 (Me (Mes)); 19.5 (Me_2CH); 18.9 (Me_2CH); 18.5 (br., 2 C, Me (Mes)); 2 arom. C (Mes) not observed. $^{31}P\{^1H\}$-NMR (202.5 MHz, $CDCl_3$, 295 K): −26.0 (*s*). FAB-MS: 443 (100, $[M - BAr_F]^+$), 459 (32); oxidation during measurement. Anal. calc. for $C_{61}H_{48}BF_{24}N_2P$ (1306.80): C 56.07, H 3.70, N 2.14; found: C 55.95, H 3.70, N 2.12.

[(1,2,5,6-η)-Cycloocta-1,5-diene]{1-{(1S)-1-[(diphenylphosphino-κP)methyl]-2-methylpropyl}-4,5-dihydro-3-methyl-2H-imidazol-2-ylidene-κC}iridium(1+) Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate(1−) (**7a**). Freshly sublimed NaO^{t}Bu (18 mg, 0.192 mmol) was added to a soln. of **6a** (231 mg, 0.192 mmol) and $[Ir_2Cl_2(cod)_2]$ (64 mg, 0.096 mmol) in THF (10 ml). The mixture was stirred at r.t. for 2 h and then evaporated. The crude product was purified by CC (silica gel, 15 × 3-cm column, CH_2Cl_2): **7a** (210 mg, 73%). Red solid. $[\alpha]_D^{20} = -17$ (*c* = 0.15, $CHCl_3$). IR (KBr): 3076*w*, 2968*w*, 2887*w*, 2840*w*, 1612*w*, 1526*m*, 1440*m*, 1357*s*, 1279*s*, 1127*s*, 998*w*, 934*w*, 889*m*, 838*w*, 744*w*, 711*m*, 674*m*, 579*w*, 518*w*, 479*w*, 448*w*. ^{1}H-NMR (500.1 MHz, CD_2Cl_2, 295 K): 7.75 (*m*); 7.67 (*m*); 7.42 (*m*); 7.10 (*m*); 5.14 (*m*); 5.08 (*m*); 4.63 (*m*); 4.59 (*m*); 4.46 (*m*); 4.35 (*m*); 3.64–3.48 (*m*); 3.44 (*m*); 3.40–3.32 (*m*); 3.27–3.16 (*m*); 3.15–3.04 (*m*); 3.02–2.67 (*m*); 2.66–2.31 (*m*); 2.25–2.05 (*m*); 1.93–1.74 (*m*); 1.71–1.56 (*m*); 1.54 (*s*); 1.27 (*d*, ^3J(H,H) = 6.1); 1.18 (*d*, ^3J(H,H) = 6.6); 1.12–0.72 (*m*); 1.36 : 1 major/minor ratio. $^{13}C\{^1H\}$-NMR (125.7 MHz, CD_2Cl_2, 295 K): 204.0 (*d*, *J*(P,C) = 12.0, NCN min.); 200.0 (*d*, *J*(P,C) = 13.4, NCN maj.); 161.8 (*q*, ^1J(B,C) = 49.9, 4 C_{ipso} (Ar_F)); 134.9 (br., 8 C_o (Ar_F)); 134.0; 133.6; 133.4; 133.0; 132.2–132.1 (overlapping signals); 131.2; 131.1; 130.9 (br.); 130.7; 130.6; 129.5–128.5 (overlapping signals); 124.7 (*q*, ^1J(F,C) = 272.5, 8 CF_3); 117.6 (*sept.*, ^3J(F,C) = 3.8, 4 C_p (Ar_F)); 89.8 (*d*, *J*(P,C) = 8.6, CH (cod), maj.); 88.7 (*d*, *J*(P,C) = 7.7, CH (cod), min.); 86.8 (*d*, *J*(P,C) = 13.9, CH (cod), min.); 82.4 CH (cod), min.); 81.65 (*d*, *J*(P,C), CH (cod), min.); 81.6 (CH (cod), min.); 79.8 (CH (cod), maj.); 78.4 (CH (cod), maj.); 67.7 (*d*, *J*(P,C) = 6.7); 66.0; 53.2; 51.9; 51.7; 44.3; 39.6; 38.0; 37.5 (*d*, *J*(P,C) = 3.8); 35.6 (br.); 35.3 (*d*, *J*(P,C) = 3.8); 35.0; 30.7; 30.6; 29.8; 28.5; 28.2; 27.3 (br.); 26.8; 26.7; 26.6 (br.); 26.5; 20.9; 20.8; 19.9; 19.6. $^{31}P\{^1H\}$-NMR (202.5 MHz, CD_2Cl_2, 295 K): 17.0 (*s*, 0.75 P, min.); 16.4 (*s*, 1.00 P, maj.). FAB-MS: 639 (100, $[M - BAr_F]^+$). Anal. calc. for $C_{61}H_{51}BF_{24}IrN_2P$ (1502.02): C 48.78, H 3.42, N 1.87; found: C 48.81, H 3.45, N 1.84.

[(1,2,5,6-η)-Cycloocta-1,5-diene]{1-{(1S)-1-[(diphenylphosphino-κP)methyl]-2-methylpropyl}-4,5-dihydro-3-(1-methylethyl)-2H-imidazol-2-ylidene-κC}iridium(1+) Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate(1−) (**7b**). As described for **7a**, with **6b** (291 mg, 0.237 mmol), $[Ir_2Cl_2(cod)_2]$ (79 mg, 0.118 mmol), and NaO^{t}Bu (23 mg, 0.237 mmol): **7b** (250 mg, 69%). Red solid. $[\alpha]_D^{20} = -5$ (*c* = 0.10, $CHCl_3$). IR (KBr): 3065*w*, 2977*w*, 2886*w*, 2839*w*, 1611*w*, 1491*m*, 1453*m*, 1357*s*, 1279*s*, 1127*s*, 999*w*, 933*w*, 889*m*, 839*w*, 743*w*, 711*m*, 675*m*, 585*w*, 535*w*, 524*w*, 447*w*. ^{1}H-NMR (500.1 MHz, CD_2Cl_2, 295 K): 7.72 (*m*); 7.70–7.14 (*m*); 7.03 (*m*); 5.16 (*m*); 5.12 (*m*); 4.67–4.23 (*m*); 4.37 (*m*); 4.23 (*m*); 3.70–3.20 (*m*); 3.19–3.14 (*m*); 3.14–2.96 (*m*); 2.93–2.79 (*m*); 2.76–2.63 (*m*); 2.60–2.48 (*m*); 2.40–2.31 (*m*); 2.28–2.05 (*m*); 1.93–1.76 (*m*); 1.75–1.67 (*m*); 1.63–1.43 (*m*); 1.31–0.40 (*m*); 1.45 : 1 major/minor ratio. $^{13}C\{^1H\}$-NMR (125.7 MHz, CD_2Cl_2, 295 K): 203.5 (*d*, *J*(P,C) = 12.5, NCN, maj.); 198.8 (*d*, *J*(P,C) = 12.5, NCN, min.); 162.3 (*q*, ^1J(B,C) = 49.9, 4 C_{ipso} (Ar_F)); 135.6, 135.4 (br., 8 C_o (Ar_F)); 132.8 (*d*, *J*(P,C) = 2.4); 132.7 (*d*, *J*(P,C) = 2.5); 131.8 (*d*, *J*(P,C) = 9.6); 131.3 (br.); 131.0 (*d*, *J*(P,C) = 9.1); 130.2–128.8 (overlapping signals); 125.1 (*q*, ^1J(F,C) = 272.5, 8 CF_3); 118.1 (*sept.*, ^3J(F,C) = 3.8, 4 C_p (Ar_F)); 90.1 (*d*, *J*(P,C) = 8.6, CH (cod), min.); 88.8 (*d*, *J*(P,C) = 7.7, CH (cod), maj.); 87.2 (*d*, *J*(P,C) = 14.4, CH (cod), min.); 84.0 (CH (cod), maj.); 81.9 (*d*, *J*(P,C) = 16.3, CH (cod), maj.); 81.5 (CH (cod), maj.); 79.4 (CH (cod), min.); 79.2 (CH (cod), min.); 68.7 (*d*, *J*(P,C) = 6.7); 67.0; 53.2 (br.); 52.5; 44.1; 43.5; 43.0; 37.0 (*d*, *J*(P,C) = 4.8); 36.6 (br.); 36.2 (*d*, *J*(P,C) = 4.3); 35.7 (br.); 31.1; 31.0; 27.7; 27.5 (br.); 27.4; 27.3; 27.0; 26.7 (br.); 22.1; 22.0; 21.5; 21.4; 20.9; 20.7; 20.6; 20.3. $^{31}P\{^1H\}$-NMR (202.5 MHz, CD_2Cl_2, 295 K): 15.1 (*s*, 1.00 P, maj.); 14.3 (*s*, 0.72 P, min.). FAB-MS: 667 (100, $[M - BAr_F]^+$). Anal. calc. for $C_{63}H_{55}BF_{24}IrN_2P$ (1530.08): C 49.45, H 3.62, N 1.83; found: C 49.45, H 3.76, N 1.94.

*[(1,2,5,6-η)-Cycloocta-1,5-diene]{1-{(1*S*)-1-[(diphenylphosphino-κ*P*)methyl]-2-methylpropyl}-4,5-dihydro-3-(2,4,6-trimethylphenyl)-2*H*-imidazol-2-ylidene-κ*C*}iridium(1+) Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate(1−)* (**7c**). As described for **7a**, with **6c** (150 mg, 0.115 mmol), $[IrCl_2(cod)_2]$ (39 mg, 0.057 mmol), and NaO^{t}Bu (11 mg, 0.115 mmol): **7c** (138 mg, 75%). Red solid. $[\alpha]_D^{20} = -6$ ($c = 0.1$, $CHCl_3$). IR (KBr): 2971*w*, 2928*w*, 2888*w*, 2840*w*, 1611*w*, 1486*w*, 1435*w*, 1356*s*, 1278*s*, 1127*s*, 1000*w*, 968*w*, 935*w*, 889*w*, 839*w*, 744*w*, 711*w*, 676*m*, 580*w*, 513*w*, 448*w*. ^{1}H-NMR (500.1 MHz, CD_2Cl_2, 246 K): 7.78 (*m*, 8 C_o (Ar_F)); 7.64–7.51 (*m*, arom. CH); 7.47 (*m*, 2 arom. CH, min.); 7.40–7.33 (*m*, arom. CH); 7.18 (*m*, 2 arom. CH, min.); 7.05 (*m*, 2 arom. CH, maj.); 6.88–6.84 (*m*, 4 arom. CH (Mes)); 6.84 (*s*); 5.36 (*m*, 1 CH (cod), min.); 5.11 (*m*, 1 CH (cod), maj.); 4.53 (*m*, 1 CH (cod), min.); 4.33 (*m*, CHN, min.); 4.13 (*m*, 1 CH (cod), maj.); 4.01 (*m*, 1 H, CH_2N); 3.94–3.70 (*m*, 4 H, CH_2N); 3.63–3.47 (*m*, 3 H, CH_2N); 3.44–3.38 (*m*, 1 CH (cod), maj., and 1 CH (cod), min.); 3.37 (*m*, CHN, maj.); 3.27 (*m*, Me_2-C*H*, maj.); 3.18 (*m*, 1 CH (cod), min.); 3.09 (*m*, 1 CH, maj.); 2.91 (*m*, 1 H of CH_2P, maj.); 2.73 (*m*, 1 H of CH_2P, maj.); 2.64 (*m*, 1 H of CH_2P, min.); 2.49 (CH_2 (cod), maj.); 2.49 (*m*, 1 H of CH_2 (cod), maj.); 2.40–0.70 (complex overlapping signals); 3.4 : 1 major/minor ratio. $^{13}C\{^1H\}$-NMR (125.7 MHz, CD_2Cl_2, 246 K): 202.0 (*d*, *J*(P,C) = 9.6, NCN, min.); 194.3 (*d*, *J*(P,C) = 10.5, NCN, maj.); 161.7 (*q*, ^1J(B,C) = 49.9, 4 C_{ipso} (Ar_F)); 138.9; 136.2; 135.9; 135.5; 135.4; 135.0; 134.7 (br., 8 C_o (Ar_F)); 133.9 (*d*, *J*(P,C) = 11.1); 133.4 (*d*, *J*(P,C) = 11.0); 132.0 (*d*, *J*(P,C) = 9.9); 131.8 (br.); 131.6; 131.2 (br.); 131.1; 130.9 (br.); 130.6 (br.); 130.3; 129.0; 129.5–128.4 (overlapping signals); 125.5 (*q*, ^1J(F,C) = 272.5, 8 CF_3); 117.5 (*sept.*, ^3J(F,C) = 3.8, 4 C_p (Ar_F)); 88.8 (*d*, *J*(P,C) = 13.2, CH (cod), maj.); 87.2 (*d*, *J*(P,C) = 8.7, OH (cod), maj.); 86.5 (*d*, *J*(P,C) = 7.5, CH (cod), min.); 83.6 (*d*, *J*(P,C) = 14.4, CH (cod), min.); 82.5 (CH (cod), min.); 81.5 (CH (cod), min.); 78.9 (CH (cod), maj.); 77.8 (CH (cod), maj.); 66.4 (*d*, *J*(P,C) = 7.5 Hz, CHN, min.); 65.5 (br., CHN, maj.); 53.6 (CH_2N, maj.); 52.3 (CH_2N, min.); 52.0 (CH_2N, maj.); 43.2 (CH_2N, min.); 37.1 (*d*, *J*(P,C) = 6.4, Me_2CH, maj.); 36.5 (CH_2 (cod), min.); 35.74 (CH_2 (cod), maj.); 35.71 (CH_2 (cod), min.); 35.5 (br., CH_2 (cod), maj.); 30.2 (*d*, *J*(P,C) = 11.9, Me_2C, min.); 26.9 (CH_2 (cod), maj.); 26.3 (CH_2 (cod), min.); 25.7 (CH_2 (cod), min.); 25.6 (*m*, CH_2P, maj.); 25.5 (CH_2 (cod), maj.); 21.0 (*p*-Me (Mes), min.); 20.9 (1 C, Me_2CH, maj.); 20.8 (*p*-Me (Mes), maj.); 19.6 (br., 2 C, Me_2CH, min, and Me_2-CH, maj.); 19.5 (*o*-Me (Mes), min.); 19.3 (*o*-Me (Mes), maj.); 18.0 (*o*-Me (Mes), min.); 17.9 (*o*-Me (Mes), maj.). $^{31}P\{^1H\}$-NMR (202.5 MHz, CD_2Cl_2, 246 K): 9.9 (*s*, 0.44 P, min.); 6.6 (*s*, 1.00 P, maj.). FAB-MS: 743 (100, $[M - BAr_F]^+$). Anal. calc. for $C_{69}H_{59}BF_{24}IrN_2P$ (1606.18): C 51.60, H 3.70, N 1.74; found: C 51.57, H 3.60, N 1.81.

*3-[(2*R*)-2-Hydroxy-2-phenylethyl]-1-(1-methylethyl)-1*H*-imidazolium Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate(1−)* (**10**). A mixture of 1*H*-imidazole (**8**; 960 mg, 14.1 mmol) and commercially available (2*R*)-2-phenyloxirane (**9**; 1.693 mg, 14.1 mmol) was heated at 50° for 12 h. Degassed MeCN (5 ml) and ^{i}PrI (2.39 g, 14.1 mmol) were added to the mixture at r.t. The soln. was heated at 80° for 3 h. Upon cooling, a solid precipitated from the mixture, which was filtered and carefully washed once with MeCN (5 ml). $NaBAr_F$ (3.75 g, 4.23 mmol) was added to a soln. of the collected imidazolium iodide salt (1.51 g) in CH_2Cl_2 (120 ml). The mixture was filtered, the filtrate evaporated, and the crude product purified by CC (silica gel, 15×7-cm column, 5% MeOH in CH_2Cl_2): **10** (3.84g, 25%). Colorless oil. $[\alpha]_D^{20} = +23.7$ ($c = 1.00$, $CHCl_3$). IR (NaCl): 3645*w*, 3171*w*, 3083*w*, 2992*w*, 1611*w*, 1555*w*, 1461*m*, 1359*s*, 1280*s*, 1120*s*, 927*w*, 889*m*, 834*w*, 762*w*, 738*w*, 710*m*, 673*m*, 579*w*, 528*w*, 446*w*. ^{1}H-NMR (400.1 MHz, $CDCl_3$, 300 K): 7.89 (*m*, 1 arom. CH); 7.72 (*m*, 8 H_o (Ar_F)); 7.54 (*m*, 4 H_p (Ar_F)); 7.32 (*m*, 2 arom. CH); 7.11 (*m*, 2 arom. CH); 7.03 (*m*, CHN); 7.01 (*m*, CHN); 5.05 (*m*, C*H*OH); 4.31 (*m*, 2 H, CH_2N, Me_2CH); 4.15 (*m*, 1 H, CH_2N); 2.32 (br., OH); 1.39 (*m*, Me_2CH); NCHN not observed. $^{13}C\{^1H\}$-NMR (100.6 MHz, $CDCl_3$, 300 K): 162.0 (*q*, ^1J(B,C) = 49.9, 4 C_{ipso} (Ar_F)); 138.1 (arom. C), 135.2 (br., 8 C_o (Ar_F)); 133.1 (NCHN); 130.5 (arom. CH); 130.1 (2 arom. CH); 129.4 (*qq*, ^2J(F,C) = 31.1, ^3J(B,C) = 2.9, 8 C_m (Ar_F)); 125.4 (2 arom. CH); 124.9 (*q*, ^1J(F,C) = 272.5, 8 CF_3); 124.4 (CHN); 120.1 (CHN); 117.9 (*sept.*, ^3J(F,C) = 3.8, 4 C_p (Ar_F)); 72.0 (CHOH); 57.3 (CH_2N); 54.5 (Me_2CH); 22.82 (Me_2CH); 22.78 (Me_2CH). FAB-MS: 231 (100, $[M - BAr_F]^+$. Anal. calc. for $C_{46}H_{31}BF_{24}N_2O$ (1094.52): C 50.48, H 2.85, N 2.56, O 1.46; found: C 50.56, H 2.89, N 2.63, O 1.64.

*[(1,2,5,6-η)-Cycloocta-1,5-diene]{1-{(2*R*)-2-[(diphenylphosphino-κ*P*)oxy]ethyl}-3-(1-methylethyl)-2*H*-imidazol-2-ylidene-κ*C*}iridium(1+) Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate(1−)* (**13**). Phosphinic amide **11** (80 mg, 0.312 mmol) was added to a homogeneous soln. of **10** (228 mg, 0.208 mmol), 4,5-dichloro-1*H*-imidazole (43 mg, 0.312 mmol), and Et_3N (32 mg, 0.312 mmol) in CH_2Cl_2 (3 ml) at 0°.

The mixture was stirred at r.t. for 48 h. The reaction was monitored by $^{31}P\{^1H\}$-NMR (101.2 MHz, CD_2Cl_2, 300 K): δ 115.8 ((phosphinooxy)imidazolinate **12**); 58.2 (phosphinic amide **11**); 17.9 (oxidized phosphinooxy derivative). The soln. was evaporated and the residue purified by CC (aluminum oxide (*Fluka*, adjusted to grade III), inert atmosphere, CH_2Cl_2): **12** (160 mg, 0.124 mmol, 60%). Highly air-sensitive oil. NaO^{t}Bu (12 mg, 0.124 mmol) and $[Ir_2Cl_2(cod)_2]$ (41.6 mg, 0.062 mmol) were added to a soln. of **12** (160 mg, 0.124 mmol) in THF (5 ml). The mixture was stirred at r.t. for 2 h and then evaporated to yield a red solid. The crude product was purified by CC (silica gel, 15×3-cm column, CH_2Cl_2): **13** (135 mg, 69%). Red solid. $[\alpha]_D^{20} = +33$ ($c = 0.10$, $CHCl_3$). IR (KBr): 2955*w*, 2924*w*, 2894*w*, 2848*w*, 1611*w*, 1453*m*, 1358*s*, 1280*s*, 1114*s*, 933*w*, 887*m*, 837*w*, 756*w*, 709*m*, 675*m*, 581*w*, 491*w*, 447*w*. ^{1}H-NMR (500.1 MHz, CD_2Cl_2, 295 K): 7.70–7.35 (*m*); 7.34–7.27 (*m*); 7.21–7.11 (*m*); 6.98 (*m*, CHN, min.); 6.96 (*m*, CHN, min.); 6.81 (*d*, $^3J = 2.0$, CHN, maj.); 6.39 (*d*, $^3J = 2.1$, CHN, maj.); 6.25 (*m*, NCH_2CH, maj.); 5.76 (*dd*, $^2J = 14.0$, $^3J = 6.1$, 1 H, CH_2N, maj.); 5.67 (*dd*, $^2J = 15.2$, $^3J = 7.3$, 1 H, CH_2N, min.); 5.35 (*m*, 1 CH (cod), maj.); 5.23 (*m*, CH (cod), min., and NCH_2CH, min.); 4.96 (*m*, Me_2CH, min.); 4.84 (*sept.*, $^3J = 6.6$, Me_2CH, maj.); 4.65 (*m*, CH (cod), min.); 4.55 (*m*, CH (cod), maj.); 4.45 (*m*, CH (cod), maj.); 4.25 (*m*, 1 H of CH_2N, min.); 4.23 (*dd*, $^2J = 14.0$, $^3J = 4.3$, 1 H of CH_2N, maj.); 4.14 (*m*, 1 CH (cod), min.); 3.54 (*m*, 1 CH (cod), maj.); 3.47 (*m*, 1 CH (cod), min.); 2.53 (*m*, 1 CH_2 (cod), maj.); 2.42 (*m*, 1 CH_2 (cod), maj.); 2.21 (*m*, 1 H of CH_2 (cod), maj.); 2.11 (*m*, 1 CH_2 (cod), maj.); 1.87 (*m*, 1 H of CH_2 (cod), maj.); 1.48 (*d*, $^3J = 6.6$, 3 H of Me_2CH, min.); 1.44 (*d*, $^3J = 6.6$, 3 H of Me_2CH, maj.); 1.25 (*d*, $^3J = 6.6$, 3 H of Me_2CH, min.); 0.81 (*d*, $^3J = 6.6$, 3 H of Me_2CH, min.); 8 H of CH_2 (cod), min., not observed; 5.0:1 major/minor ratio. $^{13}C\{^1H\}$-NMR (125.7 MHz, CD_2Cl_2, 295 K): 171.1 (*d*, $J(P,C) = 13.4$; NCN, maj.); 170.1 (*d*, $J(P,C) = 10.2$, NCN, min.); 162.2 (*q*, $^1J(B,C) = 49.9$, 4 C_{ipso} (Ar_F)); 138.4 (*d*, $J(P,C) = 7.5$); 135.1 (br., 8 C_o (Ar_F)); 134.7; 133.7; 133.3; 133.0 (br.); 132.7 (*d*, $J(P,C) = 2.3$); 132.2 (*d*, $J(P,C) = 2.0$); 132.0; 131.7; 131.6; 131.2 (br.); 130.6; 130.5; 130.1–128.7 (overlapping signals); 128.6; 128.5; 128.1; 126.6; 126.0; 124.9 (*q*, $^1J(F,C) = 272.5$, 8 CF_3); 124.0 (CHN, maj.); 123.1 (CHN, min.); 119.4 (CHN, min); 117.8 (*m*, 5 C, C_p (Ar_F), 1 CHN, maj.); 97.4 (*d*, $J(P,C) = 11.7$, CH (cod), min.); 95.7 (*d*, $J(P,C) = 10.7$, CH (cod), maj.); 89.9 (*d*, $J(P,C) = 11.7$, CH (cod), min.); 89.0 (*d*, $J(P,C) = 14.5$, CH (cod), maj.); 82.1 (NCH_2CH, min.); 81.1 (CH (cod), maj.); 80.7 (CH (cod), min.); 79.5 (CH (cod), maj.); 79.2 (CH (cod), min.); 77.0 (NCH_2CH, maj.); 57.5 (br., CH_2N, min.); 55.8 (br., CH_2N, maj.); 53.8 (Me_2CH, maj.); 53.2 (Me_2CH, min.); 35.3 (br., CH_2 (cod), maj.); 35.1 (br., CH_2 (cod), maj.); 34.9 (br., CH_2 (cod), min.); 34.6 (br., CH_2 (cod), min.); 28.7 (br., CH_2 (cod), min.); 27.7 (br., CH_2 (cod), maj.); 25.2 (Me_2CH, min.); 23.73 (Me_2CH, maj.); 23.71 (Me_2CH, maj.); 23.5 (Me_2CH, min.); one CH_2 (cod), min., not observed. $^{31}P\{^1H\}$-NMR (162.0 MHz, CD_2Cl_2, 295 K): 96.5 (*s*, 1.00 P; maj.); 86.8 (*s*, 0.19 P; min.). FAB-MS: 715 (100, $[M - BAr_F]^+$). Anal. calc. for $C_{61}H_{51}BF_{24}IrN_2PO$ (1578.08): C 50.23, H 3.26, N 1.78; found: C 50.22, H 3.45, N 1.82.

Catalytic Hydrogenation at Elevated Pressure: *General Procedure.* In a glove box, 0.1 mmol of substrate, 1 mol-% of Ir complex, and 0.5 ml of CH_2Cl_2 were subsequently added to a 60-ml autoclave (*Premex AG*, Lengnau, Switzerland) with four glas inserts (1.5 ml) and magnetic stirring bars. The autoclave was pressurized at 50 bar H_2 (99.995%; *Carbagas*, Switzerland) and the mixture was stirred at r.t. for 2 h. After pressure release, the solvent was evaporated, and heptane (3 ml) was added. The resulting suspension was filtered through a short plug of silica gel (0.5×6 cm) eluting with hexane/Et_2O 1:1, and the filtrate was analyzed by GC and chiral HPLC to determine conversion and enantioselectivity [13].

Crystal Structure Analysis[2]). *Crystal Data for* **7b**′. Formula $C_{31}H_{43}BF_4IrN_2P$, M 753.69, $F(000) = 752$; orange block, size 0.20×0.22×0.24 mm; monoclinic, space group $P2_1$, $Z = 2$, $a = 9.6146(1)$ Å, $b = 15.1396(1)$ Å, $c = 11.0797(1)$ Å, $\alpha = 90°$, $\beta = 110.3712(5)°$, $\gamma = 90°$, $V = 1511.91(2)$ Å^3, $D_{calc.} = 1.655$ Mg·m^{-3}. The crystal was measured on a *Nonius-Kappa-CCD* diffractometer at 173 K with graphite-monochromated MoK_α radiation with λ 0.71073 Å, Θ_{max} 32.600°. Minimal/maximal transmission 0.37/0.41, $\mu = 4.517$ mm^{-1}. The COLLECT suite was used for data collection and integration. From a total of 21652 reflections, 10991 were independent (merging $r = 0.026$). From these, 10142 were considered

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[2]) CCDC-293590 (**7b**′) and CCDC-293591 (**7c**′) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* http://www.ccdc.cam.ac.uk/data_request/cif.

as observed ($I > 3.00\sigma(I)$) and were used to refine 362 parameters. The structure was solved by direct methods with the program SIR92. Least-squares refinement against F was carried out on all non-H atoms with the program CRYSTALS. $R = 0.0202$ (observed data), $wR = 0.0238$ (all data), g.o.f. = 1.0632. Minimal/maximal residual electron density = −2.85/2.24 e Å^{-3}. *Chebychev* polynomial weights were used to complete the refinement. Plots were produced with CAMERON.

Crystal data for **7c′**. Formula $C_{37}H_{47}BF_4IrN_2P$, M 829.79, $F(000) = 832$; orange block, size 0.16 × 0.20 × 0.22 mm, monoclinic, space group $P2_1$, $Z = 2$, $a = 10.20430(10)$ Å, $b = 11.02200(10)$ Å, $c = 15.4744(2)$ Å, $\alpha = 90°$, $\beta = 91.4777(4)°$, $\gamma = 90°$, $V = 1739.85(3)$ Å^3, $D_{calc.} = 1.584$ Mg·m^{-3}. The crystal was measured on a *Nonius-Kappa-CCD* diffractometer at 173 K with graphite-monochromated MoK_α radiation with λ 0.71073 Å, Θ_{max} 32.634°. Minimal/maximal transmission 0.46/0.53, $\mu = 3.933$ mm^{-1}. The COLLECT suite was used for data collection and integration. From a total of 24740 reflections, 12640 were independent (merging $r = 0.040$). From these, 11832 were considered as observed ($I > 3.00\sigma(I)$) and were used to refine 417 parameters. The structure was solved by direct methods with the program SIR97. Least-squares refinement against F was carried out on all non-H atoms with the program CRYSTALS. $R = 0.0200$ (observed data), $wR = 0.0238$ (all data), g.o.f. = 1.0669. Minimal/maximal residual electron density = −2.02/2.20 e Å^{-3}. *Chebychev* polynomial weights were used to complete the refinement. Plots were produced with CAMERON.

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Received January 31, 2006