Synthesis and Application of Complexes of a Novel Chiral Diphenylphosphino-Functionalized N-Heterocyclic Carbene

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Abstract: Complexes of the ligand (*S*,*S*)-1-(2-diphenylphosphanyl-naphtalen-1-yl)-3-(2-isopropyl-phenyl)-4,5-diphenyl-imidazolin-2-ylidene, a representative of a new class of chiral ligands, were obtained via a short route starting from (*S*,*S*)-1,2-diphenyl-ethylen-1,2-diamine; a Rh-complex was found to promote catalytic hydrogenation of α,β unsaturated esters with up to 99% ee.

Key words: asymmetric catalysis, chiral N-heterocyclic carbenes, chiral P ligands, rhodium, enantioselective hydrogenation

N-Heterocyclic carbenes (NHCs) and their transition metal complexes have recently attracted much interest in organic and organometallic chemistry.[1] Because of strong carbon-metal σ-bonds, NHCs are particularly suited to act as spectator ligands. An emerging area of application of NHCs is asymmetric catalysis using chiral NHCs. So far, only a few reactions catalyzed by complexes of chiral NHCs gave rise to high enantioselectivity. Examples include Ru-catalyzed metathesis,[2] Ir-catalyzed hydrogenation of arylalkenes and α,β-unsaturated esters,[3] Rh-catalyzed hydrosilylation[4] and conjugate addition of arylboronic acid derivatives to enones[5] as well as organocatalytic benzoin additions.[6] Low degrees of enantioselectivity were reported for a Rh-catalyzed hydrogenation,[7] Cu-catalyzed additions of organozinc reagents to enones,[8] and Pd-catalyzed α-arylations of amides.[9]

In view of the great importance of phosphines as ligands in homogeneous catalysis it is astonishing that only a few mixed donor ligands of general type **A** (Figure 1) have been reported.[4a,7,10] While many chiral complexes of monodentate and bidentate N,C_{carb} NHCs are known,[1,11] only one nonracemic chiral P,C_{carb} ligand (**B**), incorporating an imidazolylidene moiety, has been reported.[7] Our interest in P,C_{carb} ligands was activated by a report on Ir-catalyzed hydrogenations with a combination of a monodentate NHC and a monodentate phosphine.[12] As ligand **B** had only induced an ee of 12% in catalytic hydrogenation we decided to develop a new type of ligand. We are now able to report derivatives of the first chiral P,C_{carb} ligand with a dihydroimidazole moiety, **C**, and a stereogenic axis. Highly enantioselective asymmetric hydrogenations were achieved with a Rh complex of **C**.

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The design of the new ligand **C** was based on the following considerations. Grubbs et al.[2a] have obtained excellent results with Ru-complexes of ligand **D**, the dihydroimidazolium salt of which is readily available via a route using Buchwald–Hartwig N-arylation of commercially available enantiopure 1,2-diphenyl-ethylen-1,2-diamine as key step. An interesting aspect of compound **D** is a relay function of the *i*-Pr groups, which are disposed *anti* to the phenyl groups of the dihydroimidazole moiety. We decided to combine this structural feature with a rigid 2-(diphenylphosphino)-naphthyl group connected to the dihydroimidazole moiety via a stereogenic axis. Realization of this part of the ligand was expected to be possible by nucleophilic aromatic substitution as described by Kondo et al. for a series of P,N-ligands.[13]

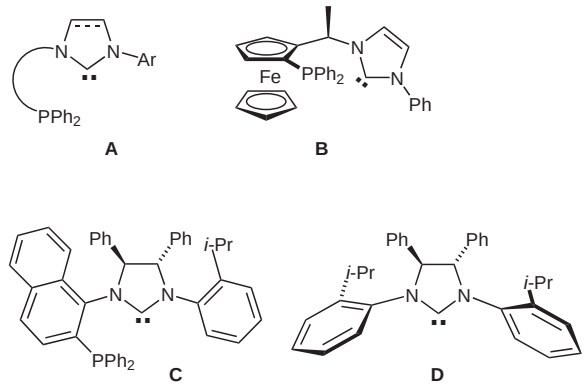
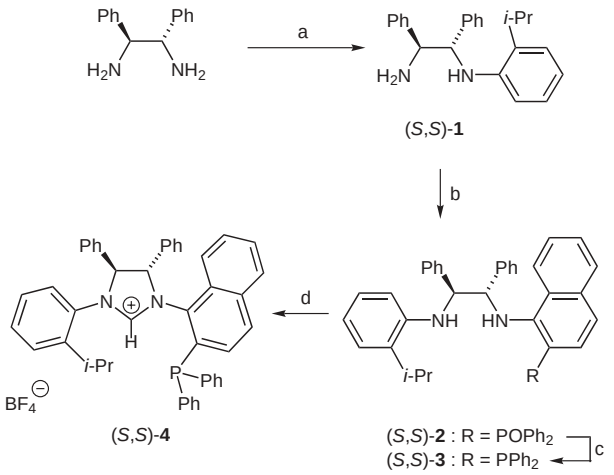


Figure 1 P,C_{carb} ligands

Reaction of (*S*,*S*)-1,2-diphenyl-ethylen-1,2-diamine with 1-bromo-2-(isopropyl)-benzene under standard Buchwald–Hartwig conditions[2a] gave the monoaryl derivative **1** in 84% yield (Scheme 1). Reaction of **1** with 2 equivalents of *n*-BuLi–TMEDA at 0 °C for 2 hours and subsequent addition of 1-methoxy-2-(diphenylphosphinyl)naphthalene[14] yielded diamine **2** in 67% yield. For the success in this substitution reaction it was important to add the phosphine oxide at –20 °C, stir the mixture over night at room temperature and finally heat it at 50 °C for 5 hours.

The phosphine oxide **2** was reduced[13] with $HSiCl_3$ in toluene at 110 °C. Reaction of the resultant crude phosphine **3** with $HC(OEt)_3$ and admixed NH_4BF_4[2a] furnished the dihydroimidazolium tetrafluoroborate **4** in 64% overall yield.[15] This compound displayed ^{31}P NMR resonances at δ = –21.80 ppm and –19.52 ppm with an intensity ratio of

87:13; ^{13}C and ^{1}H NMR spectra also showed two sets of lines with the same intensity ratio. In a ^{1}H NMR experiment {[D_2]1,1,2,2-tetrachloroethane solution} coalescence of NC*H*N signals at δ = 8.08 ppm and 8.05 ppm was found for a temperature of ca. 135 °C. These results are indicative of N-$C_{naphthyl}$ atropisomerism with a fairly high barrier to rotation. Atropisomerism with respect to the *i*-PrC_6H_4-N bond can be excluded because this was not displayed by Grubb's dihydroimidazolium tetrafluoroborate corresponding to **D**.

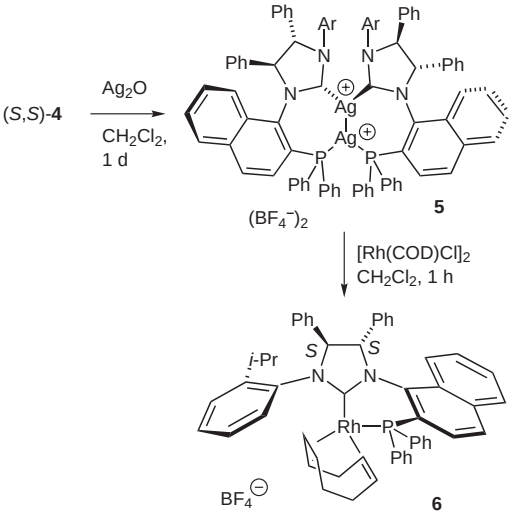


Scheme 1 Synthesis of the dihydroimidazolium salt (*S*,*S*)-**4**: (a) 1-Bromo-2-*i*-propylbenzene, NaO*t*-Bu, $Pd(OAc)_2$ (2.5 mol%), BINAP (5 mol%), toluene, 100 °C, 2 d; (b) 1. *n*-BuLi, TMEDA, r.t., 2 h; 2. 1-methoxy-2-(diphenylphosphinyl)naphthalene, 50 °C, 5 h; (c) $HSiCl_3$, Et_3N, toluene, 110 °C, 7d; (d) NH_4BF_4, $HC(OEt)_3$, 120 °C, 1 d.

Using a procedure of Wang and Lin,[16] reaction of the dihydroimidazolium salt **4** with Ag_2O (1.0 equiv) gave the silver carbene complex **5** (Scheme 2). With one equivalent of Ag_2O full conversion could be achieved. For transmetallation a procedure of Crabtree et al. was employed,[17] involving reaction of crude **5** with $[Rh(COD)Cl]_2$ which gave the rhodium complex **6** as a yellow amorphous solid in 70% overall yield. This compound is stable to air and moisture and could be purified by chromatography on silica gel.

Structures of the new complexes were characterized as follows. Crystallization of the silver complex from ethyl acetate–dichloromethane furnished crystalline **5** in 58% yield. The X-ray crystal structure (Figure 2) of **5** was determined.[18] The crystal contained a Ag-Ag core bound to two ligands in a parallel arrangement. Bond lengths are in the range found for similar silver NHC complexes (Ag-C_{carb} 2.10 Å,[16b] Ag-Ag 2.8 Å,[16a,19] Ag-P 2.38 Å).[20] Conformations around the N-C_{Ar} bonds are as anticipated, i. e. (*M*)-helicities with *anti* arrangements of the *i*-Pr as well as the PPh_2 group with respect to the phenyl groups of the imidazolinylidene moiety.

The ^{31}P NMR ($CDCl_3$) spectrum of **5** displayed a 2:1 mixture of isomers. We assume that these isomers are atropisomers with respect to the *i*-PrC_6H_4-N bond. The barrier



Scheme 2 Preparation of the rhodium-complex **6**

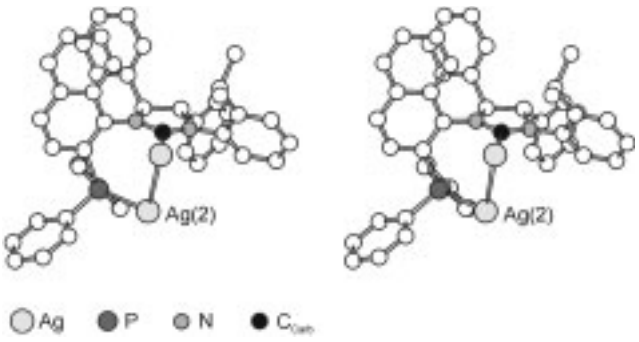


Figure 2 Stereoview of the crystal structure of the silver carbene complex **5**. Hydrogen atoms, the anion and one P,C_{carb} ligand have been omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Ag(1)-C_{carb} 2.104(8), Ag(1)-Ag(2) 2.7630(13), Ag(2)-P 2.413(2), C_{carb}-Ag(1)-Ag(2) 83.8(2), P-Ag(2)-Ag(1) 94.97(6).

to rotation is expected to be higher for **5** then for **4** because of enhanced steric bulk created by coordination to Ag^+.

Transmetallation upon addition of 1.0 equivalent of $[Rh(COD)Cl]_2$ to a solution of the silver complex **5** in dichloromethane cleanly gave the rhodium complex **6** after a reaction time of 1 hour.[21] The ^{31}P NMR ($CDCl_3$) spectrum of **6** also showed two isomers, characterized by doublets [δ = 16.43 (d, J_{RhP} = 167.8 Hz, major isomer), 18.66 (d, J_{RhP} = 162.1 Hz, minor isomer) ppm] with an intensity ratio of 2:1. This indicates that the atropisomers of **5** had been transformed into corresponding atropisomers of **6**. Again, EXSY and ROESY experiments proved that the isomers do not interconvert at room temperature.

The rhodium complex (*S*,*S*)-**6** was tested in several reactions. Interesting results were first obtained in catalytic hydrogenations, using as benchmark substrates dimethyl itaconate and *N*-acetyldehydroamino acid esters (Scheme 3). In the hydrogenation of dimethyl itaconate CH_2Cl_2 was first used as solvent.[22] With a catalyst loading of 0.1 mol% and a pressure of 10 bar conversion was

Table 1 Rhodium-Catalyzed Hydrogenations According to Scheme 3 (Reaction Time 20 h)

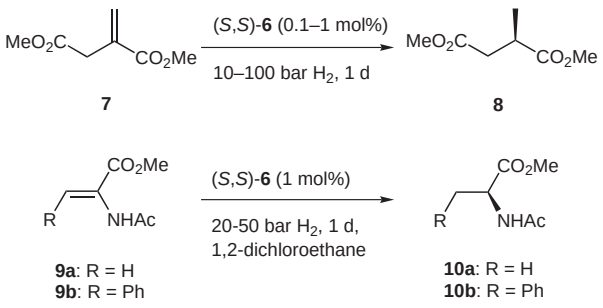
Entry	Mol% of (*S*,*S*)-**6**	Substrate	p (bar)[a]	T (°C)[b]	Solvent	Conv. (%), (yield)[c]	ee (%)[d]
1	0.1	**7**	10	25	CH_2Cl_2	19	89 (*R*)
2	0.1	**7**	20	25	CH_2Cl_2	>99	98 (*R*)
3	0.1	**7**	30	25	CH_2Cl_2	100 (100%)	98 (*R*)
4	0.1	**7**	50	25	CH_2Cl_2	79	97 (*R*)
5	0.1	**7**	100	25	CH_2Cl_2	49	63 (*R*)
6	1	**7**	50	25	CH_2Cl_2	100	97 (*R*)
7	0.1	**7**	20	25	CH_2ClCH_2Cl	9	96 (*R*)
8	0.1	**7**	20	70	CH_2ClCH_2Cl	86	94 (*R*)
9	0.1	**7**	50	25	CH_2ClCH_2Cl	100	98 (*R*)
10	1	**9a**	20	25	CH_2ClCH_2Cl	50	98 (*S*)
11	1	**9a**	20	70	CH_2ClCH_2Cl	100	99 (*S*)
12	1	**9a**	50	25	CH_2ClCH_2Cl	92	97 (*S*)
13	1	**9a**	50	70	CH_2ClCH_2Cl	100 (99%)	99 (*S*)
14	1	**9b**	30	25	CH_2ClCH_2Cl	98	98 (*S*)
15	1	**9b**	30	70	CH_2ClCH_2Cl	97	97 (*S*)
16	1	**9b**	50	25	CH_2ClCH_2Cl	72	99 (*S*)
17	1	**9b**	50	70	CH_2ClCH_2Cl	100 (97%)	97 (*S*)

[a] Pressure of H_2.
[b] Reaction temperature.
[c] Conversion was measured by GC (cf. footnote[d]).
[d] The ee was determined by GC using a Chrompack CP-Chiralsil-L-Val column (25 m × 0.25 mm), flow 100 mL·h^{-1}, 105 °C, t_R[(+)-(*R*)-**10a**] = 4.5 min, t_R[(–)-(*S*)-**10a**] = 4.9 min, t_R(**9a**) = 3.0 min; 150 °C: t_R[(–)-(*R*)-**10b**] = 11.5 min, t_R[(+)-(*S*)-**10b**] = 12.3 min, t_R(**9b**) = 21.6 min; and a Chrompack CP-γ-Cyclodextrin-TA column (30 m × 0.25 mm), flow 60 mL·h^{-1}, 65 °C, t_R[(–)-(*S*)-**8**] = 26.6 min, t_R[(+)-(*R*)-**8**] = 29.1 min, t_R(**7**) = 46.6 min. Absolute configurations see ref.[25]

incomplete and an ee of 89% was obtained (Table 1, entry 1).[23] Optimization of pressure (entries 2–5) revealed an optimum of enantioselectivity at 20 bar. Surprisingly, at higher pressures than 30 bar conversion was incomplete, and at 100 bar the ee was extremely low, indicating formation of a catalytically inactive rhodium hydride species. A further solvent screening showed, that 1,2-dichloroethane was also a suitable solvent (entries 7–9).

The hydrogenation of enamides **9** required 1 mol% of the rhodium complex (*S*,*S*)-**6**. As solvent 1,2-dichloroethane led to the best results. In the case of methyl *N*-acetamidoacrylate (**9a**), full conversion could be only achieved by heating the reaction mixture under a pressure of 50 bar at 70 °C (Table 1, entry 11). Remarkably, use of these conditions gave rise to perfect enantioselectivity (entry 13). In contrast, enantioselectivity of the hydrogenation of methyl (*Z*)-*N*-acetamidocinnamate (**9b**) was practically independent of pressure and temperature (entries 14–17).

In summary, we have prepared a novel chiral P,C_{carb} ligand giving rise to high enantioselectivity in Rh-catalyzed enantioselective hydrogenations with benchmark substrates dimethyl itaconate and *N*-acetyldehydroamino acid derivatives.[24]



Scheme 3 Hydrogenations performed with complex (*S*,*S*)-**6** as catalyst

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References

(1) For recent reviews see: (a) Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry* **2003**, *14*, 951. (b) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162; *Angew. Chem.* **1997**, *109*, 2256. (c) Herrmann, W. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290; *Angew. Chem.* **2002**, *114*, 1342. (d) Arduengo, A. J. III. *Acc. Chem. Res.* **1999**, *32*, 913.

(2) (a) Seiders, T. J.; Ward, D. W.; Grubbs, R. H. *Org. Lett.* **2001**, *3*, 3225. (b) Van Veldhuizen, J. J.; Garber, S. B.; Kingsbury, J. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 4954. (c) Van Veldhuizen, J. J.; Gillingham, D. G.; Garber, S. B.; Kataoka, O.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 12502.

(3) High enantioselectivity: (a) Perry, M. C.; Cui, X.; Powell, M. T.; Hou, D. R.; Reibenspies, J. H.; Burgess, K. *J. Am. Chem. Soc.* **2003**, *125*, 113. (b) Low enantioselectivity: Bolm, C.; Focken, T.; Raabe, G. *Tetrahedron: Asymmetry* **2003**, *14*, 1733.

(4) (a) Herrmann, W. A.; Gooßen, L. J.; Kocher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2805; *Angew. Chem.* **1996**, *108*, 2580. (b) Enders, D.; Gielen, H.; Runsink, J.; Breuer, K.; Brode, S.; Boehn, K. *Eur. J. Inorg. Chem.* **1998**, 913. (c) Enders, D.; Gielen, H. *J. Organomet. Chem.* **2001**, *617*, 70. (d) César, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Angew. Chem. Int. Ed.* **2004**, *43*, 1014; *Angew. Chem.* **2004**, *116*, 1036. (e) Duan, W.-L.; Shi, M.; Rong, G.-B. *Chem. Commun.* **2003**, 2916.

(5) Ma, Y.; Song, C.; Ma, C.; Sun, Z.; Chai, Q.; Andrus, M. B. *Angew. Chem. Int. Ed.* **2003**, *115*, 6051; *Angew. Chem.* **2003**, *115*, 6051.

(6) Enders, D.; Kallfass, U. *Angew. Chem. Int. Ed.* **2002**, *41*, 1743; *Angew. Chem.* **2002**, *114*, 1822.

(7) (a) Seo, H.; Park, H. J.; Kim, B. Y.; Lee, J. H.; Son, S. U.; Chung, Y. K. *Organometallics* **2003**, *22*, 618. (b) A related chiral C,P,C-ligand: Gishig, S.; Togni, A. *Organometallics* **2004**, *23*, 2479.

(8) (a) Guillen, F.; Winn, C. L.; Alexakis, A. *Tetrahedron: Asymmetry* **2001**, *12*, 2083. (b) Pytkowicz, J.; Roland, S.; Mangeney, P. *Tetrahedron: Asymmetry* **2001**, *12*, 2087. (c) Alexakis, A.; Winn, C. L.; Guillen, F.; Pytkowicz, J.; Roland, S.; Mangeney, P. *Adv. Synth. Catal.* **2003**, *3*, 345.

(9) Glorius, F.; Altenhoff, G.; Goddard, R.; Lehmann, C. *Chem. Commun.* **2002**, *22*, 2704.

(10) (a) Lang, H.; Vittal, J. J.; Leung, P.-H. *J. Chem. Soc., Dalton Trans.* **1998**, 2109. (b) Danopoulos, A. A.; Winston, S.; Gelbrich, T.; Hursthouse, M. B.; Tooze, R. P. *Chem. Commun.* **2002**, 482. (c) Tsoureas, N.; Danopoulos, A. A.; Tulloch, A. A. D.; Light, M. E. *Organometallics* **2003**, *22*, 4750. (d) Yang, C. H.; Lee, M.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 1511.

(11) (a) Danopoulos, A. A.; Winston, S.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **2002**, 3090. (b) Poyatos, M.; Mas-Marzá, E.; Mata, J. A.; Sanau, M.; Peris, E. *Eur. J. Inorg. Chem.* **2003**, 1215. (c) Bolm, C.; Kesselgruber, M.; Raabe, G. *Organometallics* **2002**, *21*, 707.

(12) Vázquez-Serrano, L. D.; Owens, B. T.; Buriak, J. M. *Chem. Commun.* **2002**, 2518.

(13) Kondo, K.; Kazuta, K.; Fujita, H.; Sakamoto, Y.; Murakami, Y. *Tetrahedron* **2002**, *58*, 5209.

(14) Hattori, T.; Sakamoto, J.; Hayashizaka, N.; Miyano, S. *Synthesis* **1994**, 199.

(15) Physical data of (*S*,*S*)-**4**: mp 195–197 °C; $[\alpha]_D^{24}$ –297 (*c* 1.13, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) for the major isomer of (*S*,*S*)-**4**: δ = 0.93 (d, *J* = 6.6 Hz, 3 H, CH_3), 1.02 (d, *J* = 6.6 Hz, 3 H, CH_3), 3.45 [sept, *J* = 7.0 Hz, 1 H, $CH(CH_3)_2$], (dd, *J* = 13.6 Hz, J_{PH} = 5.2 Hz, 1 H, CHN), 6.57 (d, *J* = 13.6 Hz, 1 H, CHN), 6.92–7.79 (m, 27 H, CH_{Ar}), 7.82 (d, *J* = 8.5 Hz, 1 H, CH_{Naph}), 7.99 (d, *J* = 7.7 Hz 1 H, CH_{Naph}), 8.11 (br s, 1 H, NCHN), 8.54 (d, *J* = 8.8 Hz, 1 H, CH_{Naph}). ^{13}C NMR (125.8 MHz, $CDCl_3$) for the major isomer of (*S*,*S*)-**4**: δ = 23.60, 24.96, 27.70, 74.97, 79.00 (d, *J* = 14.1 Hz), 124.36, 126.18, 126.88, 127.26, 127.54, 128.54, 128.87, 128.94, 129.11, 129.13, 129.24 (d, *J* = 6.6 Hz), 129.39 (d, *J* = 7.5 Hz), 129.56, 129.72, 129.77, 129.98, 130.08, 130.15, 130.26, 130.66 (d, *J* = 4.7 Hz), 130.96, 131.42, 132.23, 132.38 (d, *J* = 14.1 Hz), 132.68 (d, *J* = 18.8 Hz), 133.30 (d, *J* = 19.8 Hz), 133.76 (d, *J* = 18.8 Hz), 134.05 (d, *J* = 6.6 Hz), 134.30, 134.73 (d, *J* = 5.7 Hz), 136.41 (d, *J* = 25.4 Hz), 144.35, 157.38. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –19.52 (s, minor isomer, 13%), –21.80 (s, major isomer, 87%). HRMS (FAB+, direct insert): *m/z* calcd for $C_{46}H_{40}N_2P$ [M – BF_4]$^+$: 651.2929. Found: 651.2936.

(16) (a) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972. (b) Pytkowicz, J.; Roland, S.; Mangeney, P. *J. Organomet. Chem.* **2001**, *631*, 157.

(17) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663.

(18) X-ray single crystal structure determination of compound **5**: colorless crystal (polyhedron), dimensions $0.12 \times 0.17 \times 0.2$ mm^3, crystal system orthorhombic, space group $P2_12_12$, *Z* = 2, *a* = 16.730 (2) Å, *b* = 22.902 (3) Å, *c* = 11.2472 (15) Å, *V* = 4309.3 (10) $Å^3$, ρ = 1.303 g/cm^3, *T* = 200(2) K, c_{max} = 23.91 deg, radiation MoK_α, λ = 0.71073 Å, 0.3 deg ω-scans with CCD area detector, covering a whole sphere in reciprocal space, 30565 reflections measured, 6649 unique [*R*(int) = 0.0893], 5558 observed [I>2σ(I)], intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS (program SADABS V2.03 for absorption correction; G. M. Sheldrick, Bruker Analytical X-ray-Division, Madison, Wisconsin 2001) based on the Laue symmetry of the reciprocal space, $\mu = 0.56 mm^{-1}$, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL-PLUS (5.10) software package (software package SHELXTL V5.10 for structure solution and refinement, G. M. Sheldrick, Bruker Analytical X-ray-Division, Madison, Wisconsin 1997), 525 parameters refined, hydrogen atoms were treated using appropriate riding models, Flack absolute structure parameter 0.07 (6), goodness of fit 1.21 for observed reflections, final residual values *R*1 (F) = 0.077, *wR*2 (F^2) = 0.167 for observed reflections, residual electron density –1.14 to 1.10 $eÅ^{-3}$. CCDC 236937 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html [or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 (1223)336033; e-mail: deposit@ccdc.cam.ac.uk].

(19) Beck, J.; Reitz, M. *Z. Naturforsch* **1997**, *52b*, 604.

(20) Chojnacki, J.; Becker, B.; Konitz, A.; Potrzebowski, M. J.; Woljnowski, W. *J. Chem. Soc., Dalton Trans.* **1999**, 3063.

(21) Physical data of (*S*,*S*)-**6**: mp 209–211 °C; $[\alpha]_D^{24}$ +10.6 (*c* 0.30, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$, signals of major and minor isomer are distinguished by indices a and i, respectively): δ = 0.52 (d, *J* = 6.4 Hz, 3 H_a, CH_3), 1.15 (d,

J = 6.6 Hz, 3 H_a, CH_3), 1.11–1.23 (m, COD-CH_2), 1.29 (d, J = 6.8 Hz, 3 H_i, CH_3), 1.41 (d, J = 6.6 Hz, 3 H_i, CH_3), 1.34–1.77 (m, COD-CH_2), 2.00–2.34 (m, COD-CH_2), 2.37 (br s, 1 H_i, COD-CH_2), 2.86 [sept, J = 6.7 Hz, 1 H_a, $CH(CH_3)_2$], 3.18 [sept, J = 6.8 Hz, 1 H_i, $CH(CH_3)_2$], 3.62–3.78 (m, 1 H_a + 1 H_i, COD-CH), 3.91–4.05 (m, 1 H_a + 1 H_i, COD-CH), 4.59 (d, J = 10.7 Hz, 1 H_i, CHN), 4.96 (d, J = 5.1 Hz, 1 H_a, CHN), 5.36–5.48 (m, 1 H_a + 1 H_i, COD-CH), 5.50–5.60 (m, 1 H_i, COD-CH), 5.79–5.90 (m, 2 H_a + 1 H_i, 2 CHN, COD-CH), 6.16 (d, J = 7.4 Hz, 1 H_a, CH_{Ar}), 6.23 (d, J = 7.4 Hz, 1 H_i, CH_{Ar}), 6.67 (t, J = 7.8 Hz, 1 H_a, CH_{Ar}), 6.84 (t, J = 7.6 Hz, 1 H_i, CH_{Ar}), 6.89–7.97 (m, 28 H_a + 28 H_i, CH_{Ar}). ^{13}C NMR (125.67 MHz, $CDCl_3$, 253 K, major and minor isomer): δ = 23.58, 23.83, 25.30, 25.32, 25.75, 25.95, 26.04, 28.42, 29.03 (2 C), 34.19, 34.26, 35.77, 36.57, 75.24, 76.70, 78.69, 81.60, 88.31 (dd, J_{CP} = 15.5 Hz, J_{CRh} = 6.2 Hz), 88.57 (dd, J_{CP} = 14.5 Hz, J_{CRh} = 6.4 Hz), 93.03 (m), 94.39 (dd, J_{CP} = 10.3 Hz, J_{CRh} = 4.7 Hz), 100.46 (d, J_{CP} = 6.0 Hz), 101.05 (d, J_{CP} = 6.4 Hz), 102.81 (d, J_{CP} = 5.2 Hz), 104.06 (d, J_{CP} = 6.0 Hz), 121.31 (d, J_{CP} = 49.9 Hz), 122.86 (d, J_{CP} = 49.0 Hz), 122.86, 123.95, 124.64 (m), 125.17, 125.41, 125.77, 126.15, 126.49, 126.54, 126.74 (d, J_{CP} = 4.3 Hz), 127.10 (d, J_{CP} = 6.6 Hz), 127.35, 127.43, 127.69, 127.74, 127.86, 128.33–128.63 (several signals are overlapping in this range), 128.78, 128.88 (d, J_{CP} = 34.9 Hz), 129.11, 129.27, 129.44, 129.66, 130.16, 130.26, 130.56, 130.63, 130.75 (d, J_{CP} = 37.2 Hz), 131.38, 131.53, 132.03, 132.53 (d, J_{CP} = 11.3 Hz), 132.78, 133.52 (d, J_{CP} = 44.26 Hz), 133.75, 133.91, 134.46, 134.95, 135.53, 137.21, 139.14 (d, J_{CP} = 2.1 Hz), 142.32 (d, J_{CP} = 13.2 Hz), 143.70, 144.32 (d, J_{CP} = 12.3 Hz), 144.78, 207.67 (d, J_{RhC} = 44.4 Hz, only visible in $^{13}C\{^{31}P\}$), 209.87 (d, J_{RhC} = 43.5 Hz, only visible in $^{13}C\{^{31}P\}$). ^{31}P NMR (202.47 MHz, $CDCl_3$, 253 K): δ = 17.89 (d, J_{RhP} = 168.1 Hz, major isomer, 66%), 19.90 (d, J_{RhP} = 162.0 Hz, minor isomer, 33%). HRMS (FAB+, direct insert): *m/z* calcd for $C_{54}H_{51}N_2PRh$ [M – BF_4]$^+$: 861.2844. Found: 861.2820.

(22) With $PhCF_3$, *n*-hexane, MeOH, and THF enantioselectivities were lower.

(23) **Representative Procedure for Catalytic Hydrogenation**: Preparation of (*R*)-**8**: An autoclave was charged with dimethyl itaconate (158 mg, 1.00 mmol), (*S*,*S*)-**6** (0.9 mg, 1.0 μmol) and CH_2Cl_2 (15 mL). The autoclave was then sealed and pressurized to 30 bar of H_2. The reaction mixture was stirred for 20 h at r.t. The solution was passed over a short plug of silica gel with CH_2Cl_2 as eluent. After evaporation of the solvent, 2-methyl-succinic acid dimethyl ester was obtained in quantitative yield. The ee value was determined to be 98.2% ee by GC on a chiral phase (analytical data cf. Table 1).

(24) (a) The rhodium complex (*S*,*S*)-**6** was also tested in the catalytic asymmetric addition of phenylboronic acid to enones. Using 3 mol% of the complex (*S*,*S*)-**6** enantioselectivities up to 94% could be achieved (b) J.-M. Becht and E. Bappert, unpublished results.

(25) Ostermeier, M.; Brunner, B.; Korff, C.; Helmchen, G. *Eur. J. Org. Chem.* **2003**, *17*, 3453.