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Enantioselective catalysis of carbonyl-ene and Friedel–Crafts reactions with trifluoropyruvate by 'naked' palladium(II) complexes with SEGPHOS ligands

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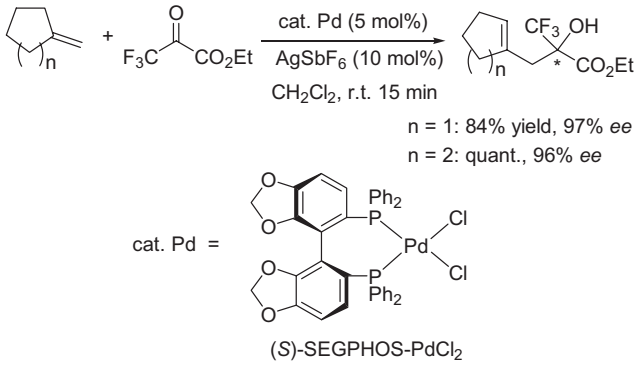
Abstract—Chiral dicationic SEGPHOS–Pd(II) complex gives high chemical yield, (*E*)-olefin selectivity, *anti*-diastereoselectivity, along with high enantioselectivity even with less reactive mono- and 1,2-disubstituted olefins in this much less reactive ketone-ene reactions. The high levels of enantioselectivity not only in carbonyl-ene but also in Friedel–Crafts reactions stem from the effective shielding with diphenyl groups on phosphines caused by the narrow dihedral angle of metal complexes with SEGPHOS.

1. Introduction

The development of enantioselective catalysts for carbon–carbon bond forming reactions (CCF) is of great importance in modern science and technology[1] because enantioselective catalysts construct the enantiomerically enriched carbon skeletons of products in chirally economical and hence environmentally 'green' ways.[2] Standard methods for such enantioselective catalysis are the development of metal complexes bearing chiral and nonracemic organic ligands, normally C_2 symmetric ones, such as BINAP, and generally in enantiopure form.

Carbonyl-ene reactions with ketones are synthetically important carbon–carbon bond forming reactions since they provide rapid access to chiral tertiary alcohols with homo-allylic functionality.[3] However, there has been essentially no successful examples of the asymmetric catalysis of ketone-ene reactions except for the report by Evans,[4] because of low ene reactivities of ketones as compared with aldehydes. Evans reported an excellent example of asymmetric catalysis of glyoxylate-ene reaction with a variety of olefins by chiral bis-oxazoline Cu^{2+} complexes. In relation to the glyoxylate-ene reaction, he also examined pyruvate as a carbonyl enophile to give a low yield of the corresponding ene product, even with a reactive 1,1-disubstituted olefin, methylenecyclohexane (5 equiv), at room temperature under heated conditions (40 °C) for 2 days. The use of a large excess of methylenecyclohexane gave 84% yield using 20 mol% of the Cu^{2+} catalyst under the heated conditions for 2 days. We report herein the success of the asymmetric catalysis of the ketone-ene reaction by a 'naked' dicationic SEGPHOS–Pd(II) complex [SEGPHOS = (4,4′-bi-1,3-benzodioxole)-5,5′-diylbis(diarylphosphine)][5] rather than the nitrile-coordinated dicationic BINAP–Pd(II) complexes[6] to construct the corresponding quaternary carbon centers[7] (Scheme 1) in the synthesis of steroid side chains.[8]



Scheme 1.

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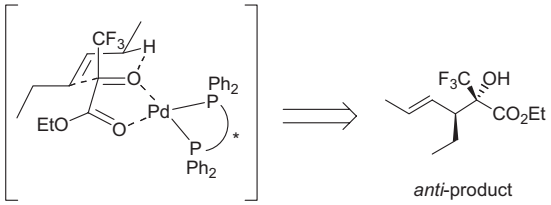
2. Results and discussion

The asymmetric catalysis of ketone-ene reactions was first investigated with 1,1-disubstituted olefins and ethyl trifluoropyruvate by a dicationic Pd(II) complex bearing chiral diphosphine ligands, such as SEGPHOS, in particular. The dicationic SEGPHOS–Pd(II) was prepared in situ from SEGPHOS–$PdCl_2$ and 2 equimolar amount of $AgSbF_6$ in CH_2Cl_2. The ene products were obtained in high yield and enantioselectivity (96–97% ee) in the catalytic reactions at room temperature within 15 min (Scheme 1).

As suggested by the results above, the SEGPHOS–Pd(II) complex is a suitable catalyst for ketone-ene reactions with ethyl trifluoropyruvate. A variety of olefins were then examined under the same conditions (Table 1). A trisubstituted olefin gave the ene product in good yield and enantioselectivity (entry 1). Significantly, the reaction of mono-substituted olefins with low ene reactivity proceeded with high levels of enantioselectivity and (*E*)-selectivity (entries 2 and 3). Less reactive 1,2-disubsituted olefins also exhibited high diastereo- and enantioselectivity, although in decreased yield (entries 4 and 5). An electron-withdrawing trifluoromethyl substituent might be important for accelerating inter-molecular electrophilic attack onto the less ene reactive mono- and 1,2-disubstitued olefins. Indeed nonfluorinated pyruvate provided lower chemical yield under the same reaction conditions (rt). The dicationic SEGPHOS–Pd(II) complex-catalyzed ketone-ene reactions of the less electrophilic ethyl pyruvate can proceed only with 1,1-disubstituted methylenecyclohexane at rt for 1 h (47% yield, 98% ee).

The stereochemical assignment of the diastereomeric products deserves comment. Based on a similarity of the *anti*-diastereoselective reaction catalyzed by $SnCl_4$, the major isomers of the ene products were determined to be *anti* (Scheme 2).[9]



65% yield, 100% (*E*), *anti/syn* = 96/4, 96% *ee*

cf. $SnCl_4$; 34% yield, 100% (*E*), *anti/syn* = 91/9

Scheme 2.

Encouraged by the success in ketone-ene reactions with SEGPHOS–Pd(II) complex, the dihedral angle of metal complexes with various diphosphine ligands was examined. Indeed, the X-ray analysis of SEGPHOS–$PdCl_2$ complex[10] shows that the dihedral angle is significantly narrower (60.1°) than that of BINAP–$PdCl_2$ complex (70.2°)[11] (Fig. 1). Similarly, it is already reported that the dihedral angle of SEGPHOS–Ru is narrower (64.99°) than those of the corresponding BINAP–Ru analogues (73.49°).[5]

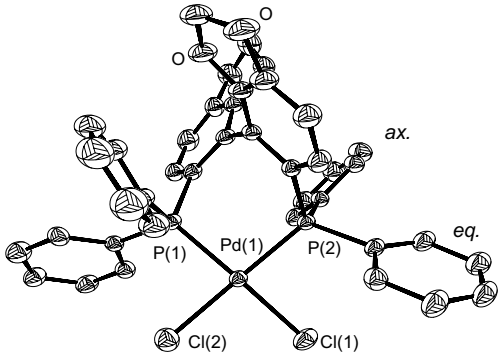
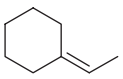
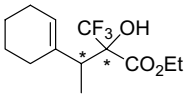
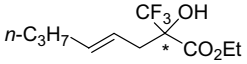
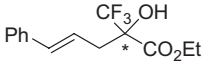
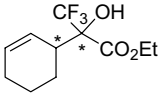
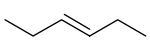
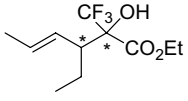


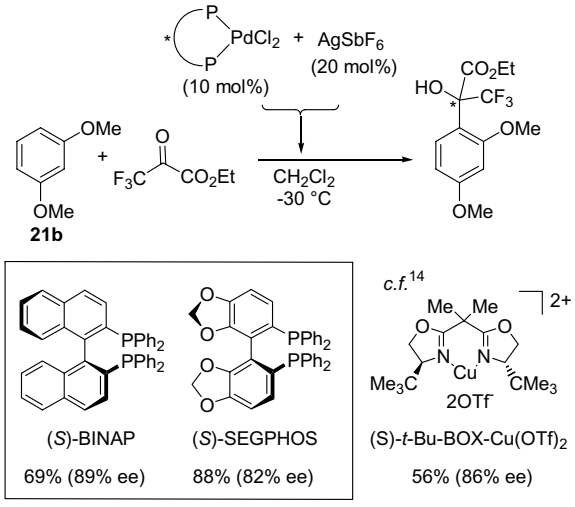
Figure 1. ORTEP drawing of (*S*)-SEGPHOS–$PdCl_2$.

The enantioselectivity with methylenecyclohexane is thus inversely correlated to the dihedral angles of the

Table 1. Asymmetric ene reactions with a variety of olefins

Entry	Olefin	Ene product	Time (h)	Yield (%)	%Ee	Ratio
1			0.5	80	84	*anti/syn* = 98:2
2			0.5	79	97	100% (*E*)
3			0.5	quant.	96	100% (*E*)
4			1	64	92	*anti/syn* = 91:9
5			1	65	96	100% (*E*) *anti/syn* = 96:4

diphosphine ligands from SEGPHOS (96% ee) to BINAP (95% ee), by virtue of the effective shielding with diphenyl groups on phosphines caused by the narrower dihedral angle of metal complexes with SEGPHOS, in particular. The highest enantioselectivity by SEGPHOS is due to the effective shielding by the SEGPHOS diphenylphosphine unit.



Further extension to the Friedel–Crafts (F–C) reaction was examined. The F–C reactions also constitute one of the most useful carbon–carbon bond-formation processes in organic synthesis.[12] However, there has been only very few reports on the asymmetric catalytic F–C reaction.[13] Recently, the asymmetric catalytic F–C reactions of trifluoro-pyruvate leading to the chiral tertiary α-trifluoromethyl-carbinols have been investigated.[14] The asymmetric catalytic F–C reaction of fluoral with silyl enol ethers has also been reported under the Mukaiyama-aldol reaction conditions.[15] The F–C reaction of *tert*-butyldimethylsilyl or triisopropylsilyl enol ether with fluoral was already been examined to afford the F–C product with high % ee rather than the usual aldol product.

We thus examined the asymmetric F–C reaction with trifluoropyruvate catalyzed by Pd(II) complexes not only with SEGPHOS but also with BINAP. This reaction can proceed at lower reaction temperature (−30 °C) to afford the product with high enantioselectivity. The F–C product obtained by the BINAP–Pd(II) catalyst shows higher chemical yield and enantioselectivity than that by the (S)-*t*-Bu-BOX–Cu(OTf)$_2$ catalyst. In sharp contrast to the carbonyl-ene reaction, BINAP ligand provides higher enantioselectivity than SEGPHOS.

In summary, we have demonstrated the ketone-ene reactions even with the less ene reactive mono- and 1,2-disubstitued olefins catalyzed by chiral dicationic SEGPHOS–Pd(II) complex, which provides an important and short access to chiral quaternary carbon with homo-allylic tertiary alcohol and trifluoromethyl functionalities of which the latter is of material and pharmaceutical interest.

3. Experimental

All experiments were carried out under argon atmosphere unless otherwise noted. Dichloromethane and chloroform-d_3 were purchased from Kanto chemical Co., Inc. Column chromatography was performed on Merck Kieselgel 60 and KANTO Silica Gel 60N (spherical, neutral), employing hexane ethyl acetate mixture as eluent unless otherwise noted. GC analysis was conducted on a ShimadzuGC-14B instrument equipped with FID detector by using N_2 (75 kPa) as a carrier gas; peak areas were calculated by a Shimadzu C-R6A as an automatic integrator.

3.1. General procedure for carbonyl-ene reaction

To a solution of (*S*)-SEGPHOS–$PdCl_2$ (15.8 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) was added silver hexafluoroantimonate (15.1 mg, 0.044 mmol) under argon atmosphere. After the mixture was stirred at room temperature for 30 min, ethyl trifluoropyruvate (80 μL, 0.60 mmol) and methylenecyclohexane (48 μL, 0.40 mmol) were added to the mixture. The reaction mixture was stirred at room temperature for 15 min, directly loaded onto a silica gel column and eluted with hexane/ethyl acetate = 5:1 to give the ene product quantitatively as a colourless oil.

3.2. 3-(Cyclohex-1-enyl)-2-hydroxy-2-trifluoromethylbutyric acid ethyl ester

^{1}H NMR ($CDCl_3$) δ 1.20 (dd, 3H, J = 1.2 Hz, J = 7.2 Hz), 1.32 (t, 3H, J = 14.4 Hz), 1.47–1.58 (m, 4H), 1.91–2.00 (m, 4H), 2.78–2.85 (q, 1H, J = 7.0 Hz), 3.74 (s, 1H), 4.21–4.37 (m, 2H), 5.54–5.57 (br s, 1H). ^{13}C NMR ($CDCl_3$) δ 13.2, 13.9, 22.3, 23.0, 25.3, 26.4, 43.2, 63.4, 80.7 (q, J_{C-F} = 27.2 Hz), 123.5 (q, J_{C-F} = 279.2 Hz), 125.7, 137.6, 170.3. ^{19}F NMR ($CDCl_3$) δ 98.7. GC (CP-Cyclodextrin-B-2,3,6-M-19, i.d. 0.25 mm × 25 m, CHROMPACK; carrier gas, nitrogen 75 kPa; column, temp. 105 °C; injection temp. 135 °C), t_R of minor isomer 20.0 min, t_R of major isomer 20.9 min. 84% ee. $[\alpha]_D^{28}$ = −8.3 (*c* 1.1, $CHCl_3$).

3.3. 2-Hydroxy-2-trifluoromethyl-oct-4-enoic acid ethyl ester

^{1}H NMR ($CDCl_3$) δ 0.86 (t, 3H, J = 7.4 Hz), 1.32 (t, 3H, J = 7.2 Hz), 1.28–1.41 (m, 2H), 1.96 (dt, 2H, J = 7.1 Hz, J = 7.1 Hz), 2.54–2.70 (m, 2H), 3.82 (s, 1H), 4.32 (q, 2H, J = 7.1 Hz), 5.31 (ddt, 1H, J = 1.5 Hz, J = 6.6 Hz, J = 15.0 Hz), 5.59 (dt, 1H, J = 7.1, 15.1 Hz). ^{13}C NMR ($CDCl_3$) δ 13.5, 14.0, 22.3, 34.6, 35.2, 63.6, 77.8 (q, J_{C-F} = 28.0 Hz), 120.5, 123.4 (q, J_{C-F} = 277.4 Hz), 137.0, 169.5. ^{19}F NMR ($CDCl_3$) δ 94.2 GC (CP-Cyclodextrin-B-2,3,6-M-19, i.d. 0.25 mm × 25 m, CHROMPACK; carrier gas, nitrogen 75 kPa; column, temp. 100 °C; injection temp. 130 °C), t_R of major isomer 25.7 min, t_R of minor isomer 28.2 min. 97% ee. cf. $[\alpha]_D^{30}$ = −0.35 (*c* 2.1, $CHCl_3$).

3.4. 2-Hydroxy-5-phenyl-2-trifluoromethyl-pent-4-enoic acid ethyl ester

^{1}H NMR ($CDCl_3$) δ 1.52–1.55 (m, 3H), 1.80–1.86 (m, 1H), 1.98–2.02 (m, 2H), 2.93 (br s, 1H), 3.79 (s, 1H), 4.31–4.43 (m, 2H), 5.72 (d, 1H, $J = 10.2$ Hz), 5.91–5.97 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 14.0, 35.6, 63.8, 77.7 (q, $J_{C-F} = 28.5$ Hz), 120.5, 123.3 (q, $J_{C-F} = 277.4$ Hz), 126.3, 127.7, 128.6, 135.5, 136.7, 169.3. ^{19}F NMR ($CDCl_3$) δ 99.5. GC (CP-Chirasil-Dex CB, i.d. 0.25 mm × 25 m, CHROMPACK; carrier gas, nitrogen 75 kPa; column, 140 °C; injection temp. 170 °C), t_R of minor isomer 22.6 min, t_R of major isomer 24.3 min. cf. $[\alpha]_D^{31} = -35.8$ (c 6.8, $CHCl_3$): 96% ee.

3.5. 2-Cyclohex-2-enyl-3,3,3-trifluoro-2-hydroxy-propionic acid ethyl ester

^{1}H NMR ($CDCl_3$) δ 1.52–1.55 (m, 3H), 1.80–1.86 (m, 1H), 1.98–2.02 (m, 2H), 2.93 (br s, 1H), 3.79 (s, 1H), 4.31–4.43 (m, 2H), 5.72 (d, 1H, $J = 10.2$ Hz), 5.91–5.97 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 13.9, 21.4, 23.4, 24.6, 38.7, 63.7, 77.2 (q, $J_{C-F} = 28.1$ Hz), 125.5, 126.4 (q, $J_{C-F} = 277.4$ Hz), 131.8, 169.8. ^{19}F NMR ($CDCl_3$) δ 99.5 GC (CP-Cyclodextrin-B-2,3,6-M-19, i.d. 0.25 mm × 25 m, CHROMPACK; carrier gas, nitrogen 75 kPa; column, 105 °C; injection temp. 135 °C), t_R of major isomer 17.6 min, t_R of minor isomer 20.6 min. cf. $[\alpha]_D^{30} = -2.3$ (c 1.0, $CHCl_3$): 92% ee.

3.6. 3-Ethyl-2-hydroxy-2-trifluoromethyl-hex-4-enoic acid ethyl ester

^{1}H NMR ($CDCl_3$) δ 0.82 (t, 3H, $J = 7.5$ Hz), 0.94 (dq, 1H, $J = 7.5$ Hz, $J = 7.5$ Hz), 1.31 (t, 3H, $J = 14.4$ Hz), 1.28–1.40 (m, 1H), 1.65 (dd, 3H, $J = 1.6$ Hz, $J = 6.5$ Hz), 2.53 (dt, 1H, $J = 6.3$ Hz, $J = 10.5$ Hz), 3.78 (s, 1H), 4.29 (q, 2H, $J = 7.1$ Hz), 5.17 (ddd, 1H, $J = 1.5$ Hz, $J = 9.9$ Hz, $J = 15.3$ Hz), 5.50 (dq, 1H, $J = 6.5$ Hz, $J = 15.3$ Hz). ^{19}F NMR ($CDCl_3$) δ 98.8.

GC (CP-Cyclodextrin-B-2,3,6-M-19, i.d. 0.25 mm × 25 m, CHROMPACK; carrier gas, nitrogen 75 kPa; column, 100 °C; injection temp. 130 °C), t_R of major isomer 16.5 min, t_R of minor isomer 17.4 min. cf. $[\alpha]_D^{25} = +0.21$ (c 1.0, $CHCl_3$): 96% ee.

3.7. 2-(2,4-Dimethoxy-phenyl)-3,3,3-trifluoro-2-hydroxy-propionic acid ethyl ester

^{1}H NMR ($CDCl_3$) δ 1.18 (t, 3H, $J = 7.2$ Hz), 3.69 (s, 3H), 3.73 (s, 3H), 4.20 (dq, 1H, $J = 10.8$ Hz $J = 7.2$ Hz), 4.27 (dq, 1H, $J = 10.8$ Hz, $J = 7.2$ Hz), 4.51 (s, 1H), 6.40 (d, 1H, $J = 2.4$ Hz), 6.44 (dd, 1H, $J = 8.8$ Hz, $J = 2.4$ Hz), 7.36 (dq, 1H, $J = 8.8$ Hz, $J = 1.6$ Hz). ^{13}C NMR ($CDCl_3$) δ 12.8, 54.4, 54.6, 62.3, 76.4 (q, $J_{C-F} = 29.0$ Hz), 98.5, 103.4, 114.7, 122.5 (q, $J_{C-F} = 286.0$ Hz), 128.0, 157.4, 160.6, 168.6. GC (CP-Chirasil-Dex CB, i.d. 0.25 mm × 25 m, CHROMPACK; carrier gas, nitrogen 75 kPa; column, 145 °C); injection temp. 175 °C, t_R of major isomer 36.7 min, t_R of minor isomer 38.2 min. cf. $[\alpha]_D^{25} = +13.1$ (c 3.2, $CHCl_3$): 89% ee.

References

1. (a) Gawley, R. E.; Aube, J. *Principles of Asymmetric Synthesis*; Pergamon: London, 1996; (b) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994; (c) Brunner, H.; Zettlmeier, W. *Handbook of Enantioselective Catalysis*; VCH: Weinheim, 1993; (d) *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 2000; Vol. 2.
2. (a) Anastas, P. T.; Heine, L. G.; Williamson, T. C. *Green Chemical Syntheses and Processes*: *Introduction. In Green Chemical Syntheses and Processes*; (b) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: New York, 1998.
3. (a) Snider, B. B. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: London, 1991; Vols. 2 and 5; (b) Mikami, K.; Shimizu, M. *Chem. Rev.* **1992**, *92*, 1021; (c) Mikami, K.; Terada, M. In *Comprehensive Asymmetric Catalysis*; Springer-Verlag: Berlin, Hedelberg, 1999; Vol. 3, p 1143; (d) Mikami, K.; Nakai, T. *Catalytic Asymmetric Synthesis*; Wiley-VCH: New York, 2000; p 543.
4. Evans, D. A.; Tregay, S. W.; Burgey, C. S.; Paras, N. A.; Vojkovsky, T. *J. Am. Chem. Soc.* **2000**, *122*, 7936.
5. Saito, T.; Yokozawa, T.; Ishizaki, T.; Moroi, T.; Sayo, N.; Miura, T.; Kumobayashi, H. *Adv. Synth. Catal.* **2001**, *343*, 264, EP 850945A **1998**, US 5872273 **1999**.
6. (a) Oi, S.; Kashiwagi, K.; Terada, E.; Ohuchi, K.; Inoue, Y. *Tetrahedron Lett.* **1996**, *37*, 6351; (b) Hori, K.; Kodama, H.; Ohta, T.; Furukawa, I. *J. Org. Chem.* **1999**, *64*, 5017; (c) Oi, S.; Terada, E.; Ohuchi, K.; Kato, T.; Tachibana, Y.; Inoue, Y. *J. Org. Chem.* **1999**, *64*, 8660; (d) Hao, J.; Hatano, M.; Mikami, K. *Org. Lett.* **2000**, *2*, 4059; (e) Becker, J. J.; Van Orden, L. J.; White, P. S.; Gagne, M. R. *Org. Lett.* **2002**, *4*, 727.
7. Reviews: (a) Martin, S. F. *Tetrahedron* **1980**, *36*, 419; (b) Fuji, K. *Chem. Rev.* **1993**, *93*, 2037; (c) Corey, E. J.; Guzman-Perez, A. *Angew. Chem., Ind. Ed.* **1998**, *37*, 388.
8. Feldman, D.; Glorieux, F. H.; Pike, J. W. *Vitamin D*; Academic: San Diego, 1997.
9. Mikami, K.; Loh, T.-P.; Nakai, T. *Tetrahedron Lett.* **1988**, *29*, 6305.
10. X-ray crystallographic was performed with a Rigaku AFC7R diffractometer (graphite monochromator, MoKα radiation, $\lambda = 0.71069$ Å) at 253 K. Crystal data for (*S*)-SEGPHOS–$PdCl_2{\cdot}2C_6H_6$: experimental formula $C_{38}H_{28}Cl_2O_4P_2$ Pd, orthorhombic, space group $P2_12_12_1$ (# 19), $a = 17.5015(19)$ Å, $b = 19.825(3)$ Å, $c = 12.6610(19)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 4393.1(10)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.191$ g cm^{-3} range for date collection $2\theta_{max} = 55.00°$. The structures were solved by direct methods (SHELXL-97). The final cycle of full-matrix least-squares was based on 5567 observed reflections ($I > 2\sigma(I)$) and 521 variable parameters and converged to $R = 0.0464$, $Rw = 0.1804$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-186409. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Selective bond lengths [Å], bond angles [°]: Pd(1)–P(1) 2.255(2), Pd(1)–P(2) 2.261(2), Pd(1)–Cl(1) 2.355(2), Pd(1)–Cl(2) 2.352(3): P(1)–Pd(1)–P(2) 90.95(8), Cl(2)–Pd(1)–P(1) 89.79(9), Cl(1)–Pd(1)–Cl(2) 89.29(1), Cl(1)–Pd(1)–P(2) 91.32(9).^{1}HNMR (300 MHz, $CDCl_3$) δ 5.73 (d, $J = 1.5$ Hz, 2H), 5.89 (d, $J = 1.2$ Hz, 2H), 6.36 (dd, $J = 8.1$, 1.5 Hz, 2H), 6.47 (dd, $J = 12.0$, 8.4 Hz, 2H), 7.28–7.52 (m, 20H), 7.62–7.73 (m,

4H), 7.94 (m, 4H).^{31}PNMR (162 MHz, $CDCl_3$) δ 27.19 (s, 2P).

11. X-ray crystallographic analysis was performed with a Rigaku R-AXIS CS (Imaging Plate) diffractometer (graphite monochromator, MoKα radiation, $\lambda = 0.71069$ Å) at 223 K. Crystal data for (*S*)-BINAP–$PdCl_2$: experimental formula $C_{44}H_{32}Cl_2P_2Pd$, orthorhombic, space group $P2_12_12_1$ (# 19), $a = 15.81470(10)$ Å, $b = 22.2991(2)$ Å, $c = 12.7147(6)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 4483.9(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.155\,g\,cm^{-3}$. The structures were solved by direct methods (SHELXL-97). The final cycle of full-matrix least-squares was based on 4761 observed reflections ($I > 2\sigma(I)$) and 422 variable parameters and converged to $R = 0.1221$, $Rw = 0.3173$. Also see: Ozawa, F.; Kubo, A.; Matsumoto, Y.; Hayashi, T. *Organometallics* **1993**, *12*, 4188.
12. Reviews: (a) Smith, M. B. *Organic Synthesis*; McGraw-Hill: New York, 1994; p 1313; (b) Heaney, H. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 2, p 733; (c) Roberts, R. M.; Khalaf, A. A. *Friedel–Crafts Alkylation Chemistry. A Century of Discovery*; Dekker: New York, 1984; (d) Olah, G. A. *Friedel–Crafts Chemistry*; Wiley-Interscience: New York, 1973.
13. (a) Consult: Bigi, F.; Casiraghi, G.; Casnati, G.; Satori, G.; Gasparri, F. G.; Belicchi, M. F. *J. Org. Chem.* **1985**, *50*, 5018; (b) Erker, G.; Van der Zeijden, A. A. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 512.
14. Zhuang, W.; Gathergood, N.; Hazell, R. G.; Jorgensen, K. A. *J. Org. Chem.* **2001**, *66*, 1009.
15. Ishii, A.; Kojima, J.; Mikami, K. *Org. Lett.* **1999**, *1*, 2013.