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Tetrahedron: *Asymmetry* 16 (2005) 3400–3405

Palladium/chiral phosphine–olefin complexes: X-ray crystallographic analysis and the use in catalytic asymmetric allylic alkylation

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Received 24 August 2005; accepted 30 August 2005
Available online 21 October 2005

Abstract—X-ray crystallographic studies on π-allylpalladium complexes coordinated with a chiral phosphine–olefin ligand (−)-**1b** demonstrate that the phosphine ligand shows a larger trans-influence than the π-bound olefin. The palladium/chiral phosphine–olefin complex efficiently catalyzed asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate with 96% enantioselectivity.

1. Introduction

The development of new chiral ligands for transition metals is of high importance in the advancement of asymmetric catalysis. Historically, for the late transition metals, the use of phosphorus- and/or nitrogen-based chiral ligands has been most extensively investigated.[1] Many of the effective ligands in this class are bidentate, as in the case of binap[2] and bisoxazolines.[3] In addition to bisphosphine or dinitrogen ligands, P,N-bidentate chiral ligands have also been well-described (e.g., phosphinooxazolines).[4] As conceptually novel chiral ligands, a series of chiral dienes were recently introduced,[5,6] and they showed their high effectiveness in various rhodium-catalyzed asymmetric processes, exhibiting superiority to conventional chiral bisphosphine ligands in some cases.

Although these dienes demonstrate that a good chiral environment can be created by the use of a framework based on substituted olefins, phosphine–olefin hybrid chiral ligands have been rarely studied to date. In fact, until recently, only one report by Grützmacher had addressed this issue, achieving 86% ee in the iridium-catalyzed asymmetric hydrogenation of an imine.[7] Unfortunately, however, these ligands possess another chirality derived from menthol and it is this that is primarily responsible for the stereochemical outcome of the catalytic reaction.

More recently, we have developed new chiral phosphine–olefins **1** and demonstrated that these ligands are highly effective for the rhodium-catalyzed asymmetric 1,4-addition of arylboronic acids to maleimides.[8] Herein we report that these ligands can also be used in the context of palladium-catalyzed asymmetric processes. Structural features of the palladium complexes by X-ray crystallographic analysis are also described.

2. Results and discussion

As shown in Scheme 1, the synthesis of **1** begins with known compound (±)-**2**.[9] Thus, Swern oxidation of alcohol (±)-**2**, followed by ketalization and phosphine oxide introduction, gives (±)-**3**, which can be resolved by chiral HPLC on a Chiralcel OD-H column to give each enantiomer of **3**. The removal of the ketal protection, followed by triflation, affords enantiopure enol triflate (−)-**4**. Grignard cross-coupling of (−)-**4**, and then reduction with silane, completes the synthesis of (−)-(1*S*,4*R*,7*S*)-**1a** (R = Bn) and (−)-(1*S*,4*R*,7*S*)-**1b** (R = Ph).[8]

Treatment of ligand (−)-**1b** with $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (1.0 equiv Pd) in chloroform in the presence of NH_4PF_6 at room temperature generated $[Pd(\eta^3\text{-}C_3H_5)$((−)-**1b**)$]PF_6$ **5** (Scheme 2). Recrystallization of this complex

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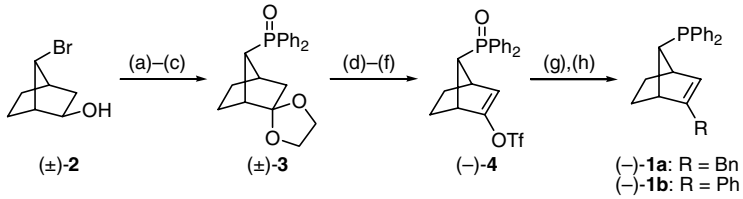
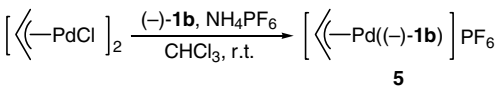
doi:10.1016/j.tetasy.2005.08.050



Scheme 1. Reagents and conditions: (a) oxalyl chloride, DMSO, Et_3N, CH_2Cl_2, 96%; (b) cat. TsOH, ethylene glycol, C_6H_6, 94%; (c) (i) *t*-BuLi, THF; then $ClPPh_2$; (ii) H_2O_2 aq, acetone, 63% (over two steps); (d) chiral HPLC resolution (OD-H column); (e) 1 M HCl aq, THF, 99%; (f) LDA, THF; then $PyNTf_2$, 89%; (g) cat. $NiCl_2$(dppp), BnMgBr, Et_2O, 86% (for R = Bn); or cat. $PdCl_2$(dppf), PhMgBr, Et_2O, 86% (for R = Ph); (h) $HSiCl_3$, Et_3N, C_6H_6, 90% for (−)-**1a** and 84% for (−)-**1b**.



Scheme 2.

from dichloromethane/hexane afforded single crystals suitable for X-ray analysis. The crystal structure of complex **5** is illustrated in Figure 1 and its data summarized in Tables 1 and 2.

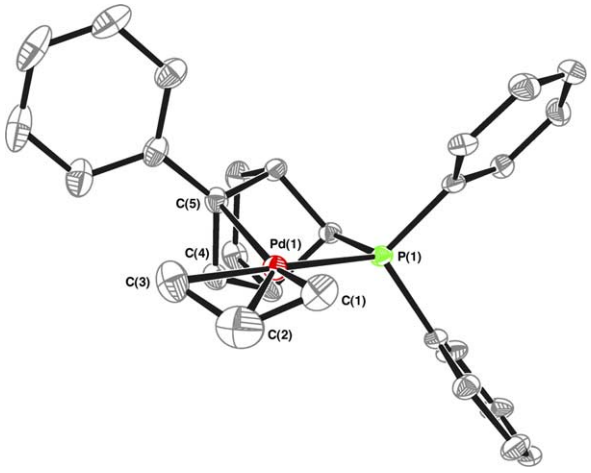
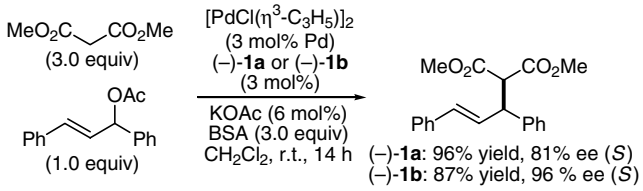


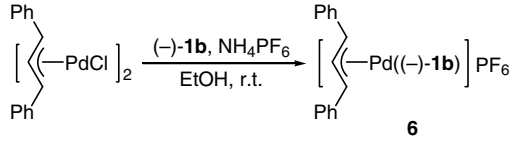
Figure 1. ORTEP illustration of [Pd(η^3-C_3H_5)((−)-**1b**)]PF_6 **5** with thermal ellipsoids drawn at the 50% probability level (hydrogens and PF_6 are omitted for clarity).

Knowing that a mixture of (−)-**1b** and [PdCl(η^3-C_3H_5)]$_2$ gives a Pd/(−)-**1b** complex, we carried out the asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate under Pd/**1** catalysis (Scheme 3). We have determined that the use of benzyl-substituted ligand (−)-**1a** gives the alkylation product in 96% yield with 81% ee (*S*), whereas the use of phenyl-substituted ligand (−)-**1b** affords it in 87% yield with 96% ee (*S*).



Scheme 3.

To analyze this reaction in more detail, we synthesized a Pd/(−)-**1b** complex bearing an η^3-1,3-diphenyl-2-propenyl moiety as shown in Scheme 4. This complex turned out to be a mixture of two diastereomers in solution (ratio = 56:44 in chloroform), but upon recrystallization from dichloromethane/hexane, crystals of one diastereomer were obtained and analyzed by X-ray crystallography (Fig. 2, Tables 1 and 2). It is worth noting that the Pd(1)–C(3) bond length is longer than the Pd(1)–C(1) bond length [2.291(4) Å vs 2.122(6) Å], indicating that the phosphine ligand [*trans* to C(3)] shows larger



Scheme 4.

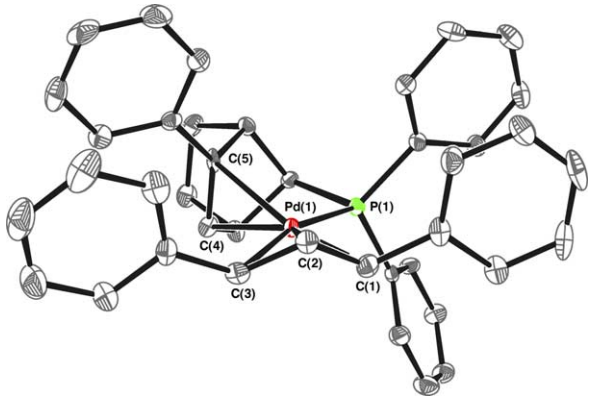


Figure 2. ORTEP illustration of [Pd(η^3-PhCHCHCHPh)((−)-**1b**)]PF_6 **6** with thermal ellipsoids drawn at the 50% probability level (hydrogens and PF_6 are omitted for clarity).

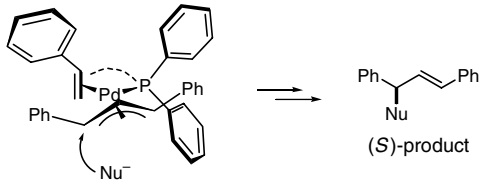


Figure 3. Proposed stereochemical pathway for the asymmetric allylic alkylation catalyzed by Pd/(−)-**1b**.

Table 1. Crystallographic data for complexes **5** and **6**

	Complex **5**	Complex **6**
Formula	$C_{28}H_{28}F_6P_2Pd$	$C_{40}H_{36}F_6P_2Pd$
fw	646.87	799.06
Color, habit	Pale yellow, block	Yellow, needle
Cryst size (mm)	$0.20 \times 0.20 \times 0.20$	$0.60 \times 0.20 \times 0.20$
Cryst syst	Monoclinic	Hexagonal
Space group	$P2_1$	$P6_1$
a (Å)	8.7620(5)	11.2456(4)
b (Å)	17.8940(9)	
c (Å)	9.2613(5)	47.138(3)
α (deg)		
β (deg)	113.0580(10)	
γ (deg)		
V (Å^3)	1336.05(12)	5162.5(5)
Z	2	6
D_{calcd} (g cm^{-3})	1.608	1.542
μ (cm^{-1})	8.73	6.94
F_{000}	652.00	2436.00
$2\theta_{max}$ (deg)	56.4	56.4
Total no. of data (R_{int})	8063 (0.012)	14,005 (0.025)
No. of unique data	8054	13,973
No. of obsd data	5374 (all reflections)	4078 (all reflections)
No. of variables	335	443
$R1$	0.020 ($I > 2.00\sigma(I)$)	0.032 ($I > 2.00\sigma(I)$)
$wR2$	0.055 (all reflections)	0.077 (all reflections)
Goodness-of-fit	1.040	1.035
Flack parameter	0.03(1)	0.01(2)
Residual ρ (e Å^{-3})	+1.07, −0.36	+0.42, −0.35

Table 2. Selected bond distances (Å) and angles (deg) for complexes **5** and **6**

	Complex **5**	Complex **6**
Bond distances		
Pd(1)–C(1)	2.149(3)	2.122(6)
Pd(1)–C(2)	2.176(4)	2.201(4)
Pd(1)–C(3)	2.200(3)	2.291(4)
Pd(1)–C(4)	2.266(2)	2.234(6)
Pd(1)–C(5)	2.344(3)	2.323(6)
Pd(1)–P(1)	2.2793(6)	2.274(1)
C(1)–C(2)	1.373(4)	1.428(8)
C(2)–C(3)	1.378(6)	1.412(8)
C(4)–C(5)	1.382(3)	1.374(5)
Bond angles		
C(1)–Pd(1)–P(1)	106.18(7)	102.2(1)
C(4)–Pd(1)–P(1)	84.01(6)	84.4(1)
C(5)–Pd(1)–P(1)	84.23(6)	84.4(1)
C(3)–Pd(1)–C(4)	102.37(9)	103.4(2)
C(3)–Pd(1)–C(5)	101.6(1)	108.2(2)
C(4)–Pd(1)–C(5)	34.83(8)	35.0(1)

trans-influence than the π-bound olefin ligand [*trans* to C(1)].[10] This trend was also observed in complex **5** [2.200(3) Å vs 2.149(3) Å], which should have smaller impact of the steric factor to take into account. By analogy with the analysis in the literature,[11] a nucleophile would preferentially attack C(3) from outside, leading to an (*S*)-product (Fig. 3), which is consistent with the experimental outcome in Scheme 3. Assuming that this is what happened in the catalytic reaction, the diastereomer shown in Figure 2 would be the more reactive one out of the two diastereomeric Pd(η^3-PhCHCHCHPh) (−)-**1b** intermediates existing in solution, thus affording the alkylation product with high enantiomeric excess in (*S*)-configuration.

3. Conclusions

We have demonstrated that palladium/chiral phosphine–olefin complexes can effectively catalyze asymmetric allylic alkylation reactions. Through X-ray crystallographic analysis of Pd(η^3-allyl) (−)-**1b** complexes, we have also confirmed the difference between phosphines and π-bound olefins in transition-metal complexes; specifically, phosphines show larger trans-influence than π-bound olefins.

4. Experimental

4.1. General

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under argon. THF and Et_2O were purified by passing through a neutral alumina column under nitrogen. Benzene was distilled over benzophenone ketyl under nitrogen. Dichloromethane was distilled over CaH_2 under nitrogen. EtOH was distilled over magnesium turnings under nitrogen. DMSO was distilled over CaH_2 under vacuum. Et_3N was distilled over KOH under vacuum. (±)-**2**,[8] *N*-(2-pyridyl)triflimide,[12] $NiCl_2$(dppp),[13] $PdCl_2$(dppf),[14] [PdCl(η^3-C_3H_5)]$_2$,[15] and [PdCl(η^3-PhCHCHCHPh)]$_2$[16] were synthesized following the literature procedures.

4.2. Synthesis of phosphine–olefin ligands 1

4.2.1. (±)-Spiro[7-diphenylphosphinylbicyclo[2.2.1]heptane-2,2′-[1,3]dioxolane] (±)-3. DMSO (3.98 mL, 56.1 mmol) was slowly added to a solution of oxalyl chloride (2.45 mL, 28.1 mmol) in dichloromethane (60 mL) at −78 °C, and the resulting mixture stirred for 30 min at −78 °C. A solution of (±)-**2** (4.77 g, 25.0 mmol) in dichloromethane (45 mL) was added to this mixture slowly over 3 h, and Et_3N (15.6 mL, 112 mmol) then added dropwise. The reaction mixture was stirred for 1 h at room temperature, and then quenched with water (60 mL). After extraction with dichloromethane, the organic layer was washed successively with HCl (60 mL; 1.0 M aqueous), Na_2CO_3 (60 mL; saturated aqueous), and then NaCl (saturated aqueous). The organic phase thus obtained was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/Et_2O = 2/1 to afford a colorless oil (4.54 g, 24.0 mmol; 96% yield).

A mixture of this oil (4.54 g, 24.0 mmol), *p*-toluenesulfonic acid (457 mg, 2.40 mmol; monohydrate), and ethylene glycol (13.4 mL, 0.24 mol) in benzene (50 mL) was refluxed for 17 h with a Dean–Stark trap. After cooling to room temperature, the mixture was poured into water and extracted with EtOAc. The organic layer was washed with NaCl (saturated aqueous), dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/Et_2O = 5/1 to afford a colorless oil (5.25 g, 22.5 mmol; 94% yield).

t-BuLi (27.0 mL, 40.0 mmol; 1.48 M solution in pentane) was added to a solution of this oil (3.73 g, 16.0 mmol) in THF (320 mL) at −60 °C slowly over 40 min, and the resulting mixture stirred for 30 min at −60 °C. Chlorodiphenylphosphine (3.45 mL, 19.2 mmol) was then added dropwise. After stirring for 15 min at −60 °C, the reaction was quenched with water (0.96 mL), and the solvent removed under vacuum at room temperature. The residue was dissolved in acetone (80 mL), and H_2O_2 (4.5 mL; 30 wt% aqueous) then added to it. The reaction mixture was stirred for 15 min at room temperature, and MnO_2 (260 mg, 2.99 mmol) then added. After stirring for 16 h at room temperature, the precipitate was removed by filtration, and the remaining solution concentrated under vacuum. The residue was extracted with EtOAc, dried over $MgSO_4$, filtered, and concentrated under vacuum. This was chromatographed on silica gel with EtOAc/MeOH = 20/1 to afford (±)-**3** as a white solid (3.60 g, 10.2 mmol; 63% yield). ^{1}H NMR ($CDCl_3$): δ 7.82–7.72 (m, 4H), 7.50–7.40 (m, 6H), 3.86 (dt, J_{HH} = 7.3 and 5.1 Hz 1H), 3.78 (q, J_{HH} = 7.3 Hz, 1H), 3.63 (dt, J_{HH} = 7.3 and 5.1 Hz, 1H), 3.20 (q, J_{HH} = 7.3 Hz, 1H), 2.83–2.80 (m, 2H), 2.43 (s, 1H), 2.30 (s, 1H), 1.88–1.78 (m, 1H), 1.76–1.66 (m, 1H), 1.54–1.42 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 135.9 (d, $^1J_{CP}$ = 98.7 Hz), 134.1 (d, $^1J_{CP}$ = 98.7 Hz), 131.1 (d, $^2J_{CP}$ = 9.3 Hz), 131.0 (d, $^4J_{CP}$ = 2.6 Hz), 130.9 (d, $^4J_{CP}$ = 2.5 Hz), 130.7 (d, $^2J_{CP}$ = 8.8 Hz), 128.3 (d, $^3J_{CP}$ = 10.9 Hz), 128.0 (d, $^3J_{CP}$ = 11.4 Hz), 115.0, 63.8, 63.6, 50.6 (d, $^1J_{CP}$ = 73.4 Hz), 46.0 (d, $^2J_{CP}$ = 1.5 Hz), 41.5, 39.1, 29.7 (d, $^3J_{CP}$ = 14.5 Hz), 23.2 (d, $^3J_{CP}$ = 14.4 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 28.0 (s). Anal. Calcd for $C_{21}H_{23}O_3P$: C, 71.17; H, 6.54. Found: C, 71.36; H, 6.36.

Compound (±)-**3** can be resolved into each enantiomer by a preparative HPLC using a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 13.9 min [(+)-enantiomer], 21.2 min [(−)-enantiomer]. $[\alpha]_D^{20}$ = −21.5 (*c* 1.00, $CHCl_3$).

4.2.2. (−)-(1*S*,4*R*,7*S*)-7-Diphenylphosphinyl-2-trifluoromethanesulfonylbicyclo[2.2.1]hept-2-ene (−)-4. HCl (5.0 mL; 1.0 M aqueous) was added to a solution of (+)-**3** (1.77 g, 5.00 mmol) in THF (25 mL), and the mixture stirred for 18 h at room temperature. After neutralization with NaOH (5.0 mL; 1.0 M aqueous), the solvent was removed under reduced pressure. The residue was extracted with EtOAc, dried over $MgSO_4$, filtered, and concentrated under vacuum. This was chromatographed on silica gel with EtOAc/MeOH = 20/1 to afford a white solid (1.54 g, 4.96 mmol; 99% yield).

n-BuLi (1.92 mL, 3.00 mmol; 1.56 M solution in hexane) was added to a solution of diisopropylamine (0.42 mL, 3.0 mmol) in THF (8.0 mL) at −78 °C. After stirring for 30 min, a solution of the solid obtained above (630 mg, 2.00 mmol) in THF (50 mL) was added dropwise to it, and the resulting solution stirred for 2.5 h at −78 °C. A solution of *N*-(2-pyridyl)triflimide (1.07 g, 3.00 mmol) in THF (5.0 mL) was then added to this mixture, and stirred for 18 h at room temperature. The reaction was quenched with water, concentrated under vacuum, and extracted with EtOAc. The organic layer was washed with NaCl (saturated aqueous), dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/MeOH = 20/1 to give a yellow solid, which was further purified through alumina with hexane/EtOAc = 1/2 to afford (−)-**4** as a white solid (789 mg, 1.78 mmol; 89% yield). ^{1}H NMR ($CDCl_3$): δ 7.73–7.67 (m, 4H), 7.54–7.45 (m, 6H), 5.51 (d, $^3J_{HH}$ = 3.5 Hz, 1H), 3.39 (s, 1H), 3.23 (s, 1H), 2.52 (s, 1H), 2.01–1.92 (m, 2H), 1.64–1.57 (m, 1H), 1.41–1.35 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 151.0, 133.1 (d, $^1J_{CP}$ = 98.7 Hz), 132.7 (d, $^1J_{CP}$ = 98.7 Hz), 131.4 (d, $^4J_{CP}$ = 2.6 Hz), 131.3 (d, $^4J_{CP}$ = 2.5 Hz), 130.6 (d, $^2J_{CP}$ = 9.3 Hz), 130.4 (d, $^2J_{CP}$ = 9.3 Hz), 128.31 (d, $^3J_{CP}$ = 11.9 Hz), 128.26 (d, $^3J_{CP}$ = 11.3 Hz), 118.0 (q, $^1J_{CF}$ = 320.9 Hz), 116.4, 59.4 (d, $^1J_{CP}$ = 75.5 Hz), 45.8, 43.5 (d, $^2J_{CP}$ = 1.0 Hz), 26.8 (d, $^3J_{CP}$ = 12.4 Hz), 25.3 (d, $^3J_{CP}$ = 12.4 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 27.7 (s). $[\alpha]_D^{20}$ = −32.8 (*c* 1.00, $CHCl_3$). Anal. Calcd for $C_{20}H_{18}F_3O_4PS$: C, 54.30; H, 4.10. Found: C, 54.24; H, 4.10.

4.2.3. (−)-(1*S*,4*R*,7*S*)-2-Benzyl-7-diphenylphosphinobicyclo[2.2.1]hept-2-ene (−)-1a. Benzylmagnesium bromide (3.50 mL, 1.5 mmol; 0.43 M solution in Et_2O) was added to a mixture of (−)-**4** (133 mg, 0.30 mmol) and $NiCl_2$(dppp) (8.1 mg, 15 μmol) in Et_2O (1.0 mL) at room temperature, and the resulting mixture refluxed for 24 h. The reaction was quenched with HCl

(1.5 mL; 1.0 M aqueous) and extracted with EtOAc. The organic layer was washed with NaCl (saturated aqueous), dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on alumina with hexane/EtOAc = 1/2 to afford a white solid (99 mg, 0.26 mmol; 86% yield).

Trichlorosilane (0.27 mL, 2.7 mmol) was added to a mixture of this solid (204 mg, 0.53 mmol) and Et_3N (0.55 mL, 4.0 mmol) in benzene (15 mL) at 0 °C, and the resulting mixture stirred for 3 h at 60 °C. After cooling to room temperature, the solvent was removed under vacuum. The residue was dissolved in Et_2O (8.0 mL), and Na_2CO_3 (0.20 mL; saturated aqueous) then added to it. The mixture was passed through a pad of celite, and the resulting solution dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on alumina with hexane/Et_2O = 5/1 to afford (−)-**1a** as a colorless viscous oil (176 mg, 0.48 mmol; 90% yield). ^{1}H NMR ($CDCl_3$): δ 7.38–7.34 (m, 2H), 7.32–7.17 (m, 11H), 7.12–7.09 (m, 2H), 5.59 (s, 1H), 3.44 (d, $^2J_{HH}$ = 15.3 Hz, 1H), 3.40 (d, $^2J_{HH}$ = 15.4 Hz, 1H), 2.79 (s, 1H), 2.52 (s, 1H), 2.28 (d, $^3J_{HH}$ = 7.2 Hz, 1H), 1.82–1.74 (m, 1H), 1.65–1.58 (m, 1H), 1.25–1.16 (m, 1H), 1.05–0.95 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 147.0 (d, $^3J_{CP}$ = 3.1 Hz), 139.9 (d, $^1J_{CP}$ = 43.9 Hz), 139.7 (d, $^1J_{CP}$ = 43.4 Hz), 139.2, 133.0 (d, $^2J_{CP}$ = 19.1 Hz), 132.7 (d, $^2J_{CP}$ = 19.2 Hz), 129.37, 129.36, 128.24 (d, $^3J_{CP}$ = 6.1 Hz), 128.23, 128.13 (d, $^3J_{CP}$ = 4.1 Hz), 128.09, 127.9 ($^3J_{CP}$ = 4.1 Hz), 125.9, 62.2 (d, $^1J_{CP}$ = 5.1 Hz), 48.5 (d, $^2J_{CP}$ = 12.4 Hz), 46.3 (d, $^2J_{CP}$ = 12.9 Hz), 36.9, 27.9 (d, $^3J_{CP}$ = 3.6 Hz), 25.6 (d, $^3J_{CP}$ = 4.1 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −17.5 (s). $[\alpha]_D^{20}$ −56.5 (*c* 0.56, CH_2Cl_2). Anal. Calcd for $C_{26}H_{25}P$: C, 84.75; H, 6.84. Found: C, 84.96; H, 7.10.

4.2.4. (−)-(1*S*,4*R*,7*S*)-7-Diphenylphosphino-2-phenylbicyclo[2.2.1]hept-2-ene (−)-1b. Phenylmagnesium bromide (1.43 mL, 1.70 mmol; 1.19 M solution in Et_2O) was added to a mixture of (−)-**4** (305 mg, 0.69 mmol) and $PdCl_2$(dppf) (5.0 mg, 6.9 μmol) in Et_2O (8.0 mL) at room temperature, and the resulting mixture refluxed for 10 h. The reaction was quenched with HCl (2.0 mL; 1.0 M aqueous) and extracted with EtOAc. The organic layer was washed with NaCl (saturated aqueous), dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc to afford a white solid (220 mg, 0.59 mmol; 86% yield).

Trichlorosilane (0.21 mL, 2.2 mmol) was added to a mixture of this solid (160 mg, 0.43 mmol) and Et_3N (0.45 mL, 3.2 mmol) in benzene (13 mL) at 0 °C, and the resulting mixture stirred for 3 h at 60 °C. After cooling to room temperature, the solvent was removed under vacuum. The residue was dissolved in Et_2O (8 mL), and Na_2CO_3 (0.20 mL; saturated aqueous) was then added to it. The mixture was passed through a pad of celite, and the resulting solution dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on alumina with hexane/Et_2O = 5/1 to afford (−)-**1b** as a white solid (126 mg, 0.36 mmol; 84% yield). ^{1}H NMR ($CDCl_3$): δ 7.45–7.35 (m, 5H), 7.35–7.22 (m, 9H), 7.19 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 6.31 (d, $^3J_{HH}$ = 2.8 Hz, 1H), 3.18 (s, 1H), 2.97 (s, 1H), 2.49 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 1.95–1.80 (m, 2H), 1.33–1.20 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 146.4 (d, $^3J_{CP}$ = 4.1 Hz), 139.7 (d, $^1J_{CP}$ = 48.7 Hz), 139.6 (d, $^1J_{CP}$ = 48.5 Hz), 135.4, 133.0 (d, $^2J_{CP}$ = 19.1 Hz), 132.9 (d, $^2J_{CP}$ = 19.2 Hz), 128.40, 128.35, 123.29 (d, $^3J_{CP}$ = 2.5 Hz), 128.28 (d, $^3J_{CP}$ = 3.1 Hz), 128.2, 128.1 ($^3J_{CP}$ = 3.6 Hz), 127.0, 125.3, 61.8 (d, $^1J_{CP}$ = 5.1 Hz), 47.2 (d, $^2J_{CP}$ = 6.6 Hz), 47.1 (d, $^2J_{CP}$ = 6.6 Hz), 27.8 (d, $^3J_{CP}$ = 3.6 Hz), 25.9 (d, $^3J_{CP}$ = 4.1 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −17.1 (s). $[\alpha]_D^{20}$ = −287 (*c* 0.40, CH_2Cl_2). Anal. Calcd for $C_{25}H_{23}P$: C, 84.72; H, 6.54. Found: C, 84.77; H, 6.79.

4.3. Palladium-catalyzed asymmetric allylic alkylation

A mixture of [PdCl(η^3-C_3H_5)]$_2$ (1.1 mg, 6.0 μmol Pd), ligand (−)-**1** (6.0 μmol), and KOAc (1.2 mg, 12 μmol) in dichloromethane (0.5 mL) was stirred for 25 min at room temperature. 1,3-Diphenyl-2-propenyl acetate (50 mg, 0.20 mmol), dimethyl malonate (69 μL, 0.60 mmol), and *N*,*O*-bis(trimethylsilyl)acetamide (148 μL, 0.60 mmol) were added with additional dichloromethane (1.5 mL). The resulting mixture was stirred for 14 h at room temperature, and passed through a pad of silica gel with EtOAc, and the solvent removed under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/4 to afford the product as a colorless oil.

The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 17.4 min [(*R*)-enantiomer], 24.9 min [(*S*)-enantiomer].

Compound (−)-**1a** as a ligand: 96% yield, 81% ee (*S*).

Compound (−)-**1b** as a ligand: 87% yield, 96% ee (*S*). $[\alpha]_D^{20}$ = −19.6 (*c* 0.55, $CHCl_3$).

4.4. Preparation of [Pd(η^3-C_3H_5)((−)-1b)]PF_6 5

A mixture of [PdCl(η^3-C_3H_5)]$_2$ (7.3 mg, 40 μmol Pd) and (−)-**1b** (14 mg, 40 μmol) in chloroform (1.0 mL) was stirred for 1 h at room temperature. NH_4PF_6 (6.5 mg, 40 μmol) was then added to it and the mixture was stirred for 1 h at room temperature. The resulting mixture was diluted with dichloromethane (3.0 mL) and the precipitate removed by filtration. After removal of the solvent under vacuum, the residue was dissolved in dichloromethane, and pentane added. The precipitate that formed was collected, and then washed with pentane and dried under vacuum to afford a pale yellow solid (18 mg, 28 μmol; 70% yield).

^{31}P{^{1}H} NMR ($CDCl_3$): δ 46.4 (br s), −143.5 (sept, $^1J_{PF}$ = 711 Hz). Anal. Calcd for $C_{28}H_{28}F_6P_2Pd$: C, 51.99; H, 4.36. Found: C, 51.90; H, 4.31.

Crystals suitable for X-ray analysis were obtained by recrystallization from dichloromethane/hexane at room temperature.

CCDC-281684 contains the supplementary crystallographic data for this complex. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.5. Preparation of [Pd(η^3-PhCHCHCHPh)((−)-1b)]PF_6 6

A mixture of [PdCl(η^3-PhCHCHCHPh)]$_2$ (13 mg, 40 μmol Pd) and (−)-**1b** (15 mg, 42 μmol) in EtOH (2.0 mL) was stirred for 1.5 h at room temperature. NH_4PF_6 (10 mg, 61 μmol) was then added to it and the mixture stirred for 20 min at room temperature. The resulting mixture was filtered through a pad of celite with dichloromethane and the solution concentrated under vacuum until the volume became ca. 1 mL. The precipitate that formed was collected, and then washed with pentane and dried under vacuum to afford a yellow solid (29 mg, 36 μmol; 91% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 44.0 (s, major), 38.1 (s, minor), −143.3 (sept, $^1J_{PF} = 712$ Hz). Anal. Calcd for $C_{40}H_{36}F_6P_2Pd$: C, 60.12; H, 4.54. Found: C, 60.15; H, 4.52.

Crystals suitable for X-ray analysis were obtained by recrystallization from dichloromethane/hexane at room temperature.

CCDC-281685 contains the supplementary crystallographic data for this complex. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

Support has been provided in part by a Grant-in-Aid for Scientific Research, the Ministry of Education, Culture, Sports, Science, and Technology, Japan (21 COE on Kyoto University Alliance for Chemistry).

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