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Development of Chiral Phosphine Ligands Bearing a Carboxyl Group and Their Application to Catalytic Asymmetric Reaction

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Abstract: A new chiral phosphine ligand bearing a carboxyl group, 3-(diphenylphosphino)butanoic acid, was developed and used for palladium catalyzed asymmetric allylic alkylation of cyclic *cis*-allylic acetates such as 2-cyclopentenyl, 2-cyclohexenyl, and 2-cycloheptenyl acetate. These acetates reacted with triethyl sodiophosphonoacetate in the presence of the palladium catalyst with the ligand to give the corresponding alkylation products in good enantiomeric excesses.

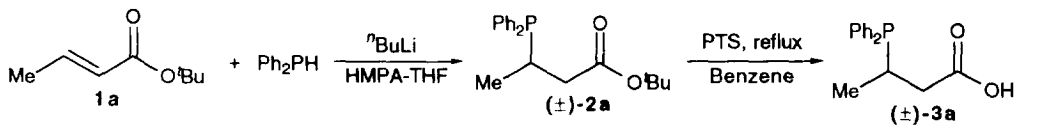
Asymmetric carbon-carbon bond formation utilizing a chiral catalyst is one of the most important and attractive subjects in synthetic organic chemistry.[1] Recently, palladium catalyzed asymmetric allylic alkylation has been fairly extensively investigated and a wide variety of chiral phosphine ligands have been developed.[2-4] While high enantioselectivities (> 80%) were achieved in certain cases, such high asymmetric inductions were mostly observed using *trans*-allylic substrates.[2] In contrast, relatively little work has been done using cyclic *cis*-allylic substrates such as 3-cyclohexenyl acetate,[3,4] and there appears to be only one example of the asymmetric allylic alkylation in excellent enantiomeric excess.[4] Thus, hitherto known palladium catalyzed asymmetric allylic alkylations still have a limitation in terms of allylic substrates. We have recently reported the synthesis of a new type of chiral cycloalkylphosphines bearing a carboxyl group and have shown that the carboxyl group plays an important role in the asymmetric induction.[5] We also found that these chiral phosphine ligands were effective to the asymmetric allylic alkylations using cyclic *cis*-allylic substrates (30–78%ee). On the basis of these results, the development of more effective chiral phosphine ligands was envisaged. We describe here the convenient synthesis of a chiral alkylphosphinocarboxylic acid ligand and its application to asymmetric allylic alkylations.

Results and Discussion

Synthesis of Chiral Phosphinocarboxylic Acids. The synthesis of 3-(diphenylphosphino)butanoic acid is outlined in eq 1. 1,4-Addition of lithium diphenylphosphide to *tert*-butyl crotonate (**1a**) in tetrahydrofuran (THF) containing hexamethylphosphoric triamide (HMPA) at –78 °C for 0.5 h gave *tert*-butyl 3-(diphenylphosphino)-butanoate **2a** in a quantitative yield. The subsequent treatment of **2a** with *p*-toluenesulfonic acid in benzene under reflux for 3 h led to racemic 3-(diphenylphosphino)butanoic acid (±)-**3a** quantitatively. Furthermore, this synthetic method was successively applied to the synthesis of a cycloalkyl homologue. For example, *tert*-butyl 2-(diphenylphosphino)cyclopentanecarboxylate **2b** was prepared from *tert*-butyl 2-cyclopentenecarboxylate **1b** . Treatment of **2b** with acid gave 2-(diphenylphosphino)cyclopentanecarboxylic acid **3b** in a similar manner to that described above (overall yield 95 %). This new synthetic method, which includes 1,4-addition of

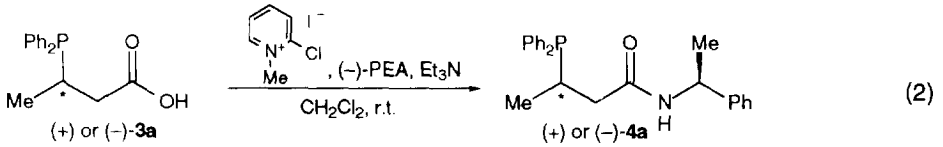
Dedicated to the memory of Professor Hidemasa Takaya, deceased on 5 October 1995

diphenylphosphine to α,β-unsaturated esters, is convenient for the preparation of these phosphinocarboxylic acids compared with the method reported previously.[5]

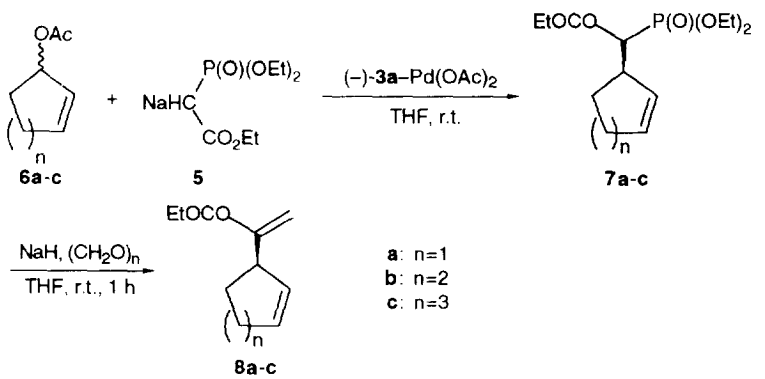


Racemic **3a** was treated with (+)-α-methylbenzylamine (PEA) in acetone to give white diastereomeric ammonium salts. After filtration, recrystallization of these diastereomeric salts from acetone three times gave the pure salt, $[\alpha]_D^{30}$ 33.0 (c 0.87, $CHCl_3$). Treatment of a chloroform solution of this salt with dilute hydrochloric acid gave enantiomerically pure (+)-**3a**, $[\alpha]_D^{34}$ 29.8 (c 0.97, $CHCl_3$), of which absolute configuration is not yet determined. Enantiomerically pure (−)-**3a**, $[\alpha]_D^{34}$ −29.3 (c 0.84, $CHCl_3$), was obtained similarly using (−)-PEA.

(+)- and (−)-**3a** resolved as described above were confirmed to be enantiomerically pure by HPLC analysis of their diastereomeric amides **4a**, derived from each of **3a** and (−)-PEA(eq 2).[6]



Asymmetric Allylic Alkylation. The reaction of triethyl sodiophosphonoacetate **5** with cyclic *cis*-allylic acetates **6a-c** was carried out in the presence of the chiral palladium catalyst prepared from the chiral phosphine (−)-**3a** and palladium acetate in THF at room temperature to give optically active allylic alkylation products **7a-c** (Scheme 1), (Table1). These results indicate that enantiomeric excesses somewhat increased with increasing ring sizes of the substrates. Alkylated products **7a-c** were successively transformed, after the treatment with sodium hydride and paraformaldehide, into the Wittig–Horner reaction products **8a-c**. The specific rotations of **8b** and **8c** are as follows: **8b**, $[\alpha]_D^{29}$ 80.7 (c 0.80, CH_2Cl_2); **8c**, $[\alpha]_D^{28}$ 33.0 (c 0.47, CH_2Cl_2).



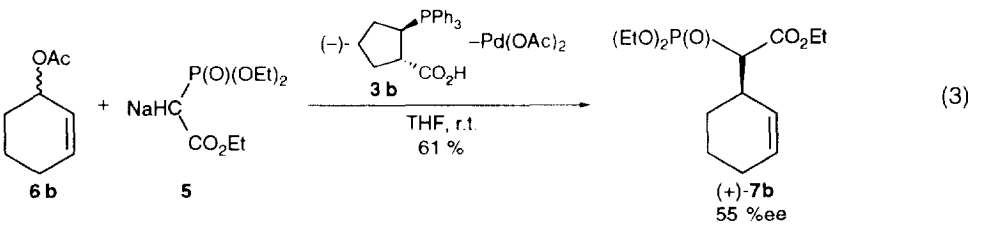
Scheme 1

Table 1. Asymmetric Allylic Alkylation of Cyclic *cis*-Allylic Acetate Catalyzed by (–)-3-(Diphenylphosphino)butanoic acid (–)-**3a**–Palladium Complex[a]

entry	allylic substrate	product	yield(%)[b]	%ee[c]
1	**6a**	(+)-**7a**	71	59
2[d]	**6b**	(+)-**7b**	77	86
3	**6c**	(+)-**7c**	50	88

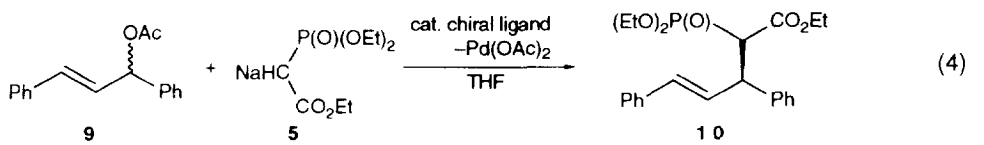
[a]Reactions were run with 0.01–0.02 equiv of $Pd(OAc)_2$ and 0.04–0.08 equiv of (–)-**3a** in THF. [b]Isolated yield based on acetate **6a-c**. [c]Enantiomeric excesses were determined by the method described previously.[5] [d]The reaction was carried out under reflux.

On the other hand, the use of (–)-*trans*-2-(diphenylphosphino)cyclopentanecarboxylic acid (–)-**3b** resulted in a drop of enantiomeric excess (eq 3).[5] This result was unexpected in the view of the fact that **3a** has a high degree of conformational freedom compared to **3b**.



(3)

Furthermore, in order to investigate the influence of the structures of allylic substrates on enantioselectivity, the reaction of 3-acetoxy-1,3-diphenyl-1-propene **9** with **5** was examined in the presence of the phosphine (–)-**3a**–palladium complex. The allyl substituted product (–)-**10** was obtained in 91 % yield with a remarkably decreased enantiomeric excess (33 %ee), while the same reaction using the phosphine (–)-**3b**–palladium complex as a catalyst afforded **10** in 74 % yield (77 %ee).[5]



(4)

Table 2. Asymmetric Allylic Alkylation of 1-Acetoxy-1,3-diphenyl-1-propene **9** Catalyzed by Chiral Phosphinocarboxylic Acid-Palladium Complexes[a]

entry	chiral ligand	reaction conditions		yield(%)[b]	%ee[c]
		temp	time(h)		
1	(–)-**3a**	60 °C	4	91	33
2[d]	(–)-**3b**	reflux	2	74	77

[a]Reactions were run with 0.01–0.02 equiv of $Pd(OAc)_2$ and 0.04–0.08 equiv of (–)-**3a** or **3b** in THF. [b]Isolated yield based on acetate **9**. [c]Enantiomeric excesses were determined by the method described previously.[5] [d]This result was already published.[5]

These findings (eq 3, Table 1, and 2) are consistent with the following interpretation: *Flexible* ligands such as **3a** are effective for asymmetric allylic alkylations of *rigid* substrates. On the other hand, *rigid* ligands such as **3b** are suited for the alkylations of *flexible* substrates. This is consistent with the result that the combination of a

flexible ligand and a *flexible* substrate led lower enantioselectivity (entry 1 in Table 2).

In conclusion, the following points are pertinent: (1) a new chiral alkylphosphine ligand bearing a carboxyl group, 3-(diphenylphosphino)butanoic acid **3a**, has been developed; (2) **3a**–palladium catalyst has proven to be a highly enantioselective catalyst for the allylic alkylation of cyclic *cis*-allylic substrates.

Experimental Section

General Procedures. A melting point was determined with a Büchi 530 melting point apparatus and was not corrected. ^{1}H and ^{13}C NMR, and ^{31}P NMR spectra were obtained on a JEOL JNM-A500 spectrometer in $CDCl_3$ operating at 500 and 125, and 202MHz respectively, with Me_4Si and with H_3PO_4 as internal standard. IR spectra were recorded with a JEOL JIR-5500 spectrometer. High-resolution mass spectra (HRMS) were recorded on a JEOL DX-300 mass spectrometer. Analytical high performance liquid chromatography (HPLC) was carried out with a Shimadzu HPLC system equipped with a stationary phase column, Nomura Chemical Co. Ltd., DEVELOSIL Packed Column (4.6 mm X 250 mm), and hexane/ethyl acetate (3/1) as eluting solvent. Optical rotations were measured with a JASCO DIP-1000 polarimeter. All reactions were carried out using degassed solvents under an argon atmosphere.

Materials. 2-Cyclopentenyl acetate, 2-cyclohexenyl acetate, 2-cycloheptenyl acetate and diphenylphosphine were prepared according to the reported procedures.[7,8] *tert*-Butyl 1-cyclopentenecarboxylate **1b** was prepared in 84 % yield from the reaction of 1-cyclopentenecarboxylic acid with 2-methylpropene in the presence of catalytic amount of conc. H_2SO_4 in dichloromethane.

***tert*-Butyl 3-(diphenylphosphino)butanoate 2a.** To a cooled solution of diphenylphosphine (3.48 g, 18.7 mmol) in dry THF (35 mL) at -78 °C was added dropwise *n*-BuLi (1.64 M in hexane, 10.5 mL, 17.3 mmol). After the mixture was stirred at -78 °C for 0.5 h, a solution of *tert*-butyl crotonate (2.05 g, 14.4 mmol) in THF (10 mL) was added dropwise, followed by addition of HMPA (3 mL), to the mixture, and the reaction mixture was stirred at this temperature for 2 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl (50 mL), and extracted with ether, and the extract was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on silica gel [elution with Et_2O/hexane (1/4)] to give **2a** in quantitative yield (4.73 g, 100 %). The phosphine **2a** is susceptible to air oxidation.

2a: IR (neat) 1726, 1435, 1367, 1146, 742, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.08 (dd, *J*=15.0, 7.0 Hz, 3H, Me), 1.43 (s, 9H, C(C*H*$_3$)$_3$), 2.05 (ddd, *J*=15.3, 11.0, 5.5 Hz, 1H, one of C*H*$_2$), 2.38 (ddd, *J*=15.3, 8.2, 3.1 Hz, 1H, one of C*H*$_2$), 2.79-2.87 (m, 1H, PC*H*), 7.29-7.35 (m, 6H, phenyl *H*), 7.45-7.55 (m, 4H, phenyl *H*); ^{13}C-NMR ($CDCl_3$) δ 16.5 (d, $^2J_{CP}$=16.6 Hz, CH*C*H$_3$), 27.2 (d, $^1J_{CP}$=10.3 Hz, Ph$_2$P*C*H), 28.7 (s, C(*C*H$_3$)$_3$), 39.5 (d, $^2J_{CP}$=18.6 Hz, *C*H$_2$), 80.5 (s, *C*(CH$_3$)$_3$), 128.3 (d, $^3J_{CP}$=7.3 Hz, *meta C*), 128.4 (d, $^3J_{CP}$=7.2 Hz, *meta C*), 128.8 (s, *para C*), 128.9 (s, *para C*), 133.5 (d, $^2J_{CP}$=19.7 Hz, *ortho C*), 136.3 (d, $^1J_{CP}$=14.5 Hz, *ipso C*), 136.4 (d, $^1J_{CP}$=14.5 Hz, *ipso C*), 172.0 (d, $^3J_{CP}$=15.5 Hz, *C*=O); ^{31}P-NMR ($CDCl_3$) δ -0.29; HRMS calcd for $C_{20}H_{25}O_2P$ 328.15940, found 328.16080.

3-(Diphenylphosphino)butanoic acid 3a. A solution of **2a** (4.73 g, 14.4 mmol) in benzene (80 mL) containing *p*-toluenesulfonic acid (6.20 g, 32.6 mmol) was heated at reflux for 3 h. After water (100 mL) was added to the reaction mixture, the mixture was extracted with $CHCl_3$ (3 x 100 mL), dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on silica gel [elution with $CHCl_3$/MeOH(10/1)] to give (±)-**3a** in essentially quantitative yield (3.88 g, 99 %).

(±)-**3a**: IR (neat) 3500-2400, 1703, 1435, 1377, 742, 696 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.11 (dd, *J*=15.0, 7.0

Hz, 3H, Me), 2.20 (ddd, *J*=15.7, 11.0, 5.7 Hz, 1H, one of CH_2), 2.51 (ddd, *J*=15.7, 8.2, 3.2 Hz, 1H, one of CH_2), 2.82-2.91 (m, 1H, PC*H*), 7.32-7.36 (m, 6H, phenyl *H*), 7.45-7.55(m, 4H, phenyl *H*); ^{13}C-NMR ($CDCl_3$) δ 16.7 (d, $^2J_{CP}$=16.6 Hz, $CHCH_3$), 26.8 (d, $^1J_{CP}$=10.3 Hz, Ph_2PCH), 38.1 (d, $^2J_{CP}$=18.6 Hz, CH_2), 128.5 (d, $^3J_{CP}$=7.2 Hz, *meta C*), 128.6 (d, $^3J_{CP}$=7.2 Hz, *meta C*), 129.0 (s, *para C*), 129.1 (s, *para C*), 133.5 (d, $^2J_{CP}$=20.0 Hz, *ortho C*), 133.6 (d, $^2J_{CP}$=18.6 Hz, *ortho C*), 135.9 (d, $^1J_{CP}$=14.5 Hz, *ipso C*), 136.0 (d, $^1J_{CP}$=13.5 Hz, *ipso C*), 178.6 (d, $^3J_{CP}$=15.5 Hz, *C*=O); ^{31}P-NMR ($CDCl_3$) δ -0.61; MS m/e 272 (M^+); HRMS calcd for $C_{12}H_{17}O_2P$ 272.0967, found 272.0989.

Resolution of 3a. A solution of **3a** (2.0 g, 7.4 mmol) and D-(+)-α-methylbenzylamine (PEA)(0.533 g, 4.4 mmol) in acetone (5 mL) was heated under reflux for 0.5 h and was then cooled to -78 °C to induce to crystallize, followed by standing at 0 °C for 3 h. After the precipitating diastereomeric salt (+)-**3a**•(+)-PEA was filtered under a nitrogen atmosphere, washed with cold acetone, and dried, the crude salt was recrystallized three times from acetone to give the pure salt, $[\alpha]_D^{30}$ 33.0 (c 0.87, $CHCl_3$). A chloroform solution of the salt was washed with dil. HCl, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was passed through a short silica gel column with $CHCl_3$-MeOH (10/1) to give optically pure (+)-**3a** (0.62 g), $[\alpha]_D^{34}$ 29.8 (c 0.97, $CHCl_3$). Optically pure (–)-**3a**, $[\alpha]_D^{34}$ -29.3 (c 0.84, $CHCl_3$), was obtained similarly by the use of (–)-PEA.

The enantiomeric purities of (+)- and (–)-**3a** were determined by HPLC analysis of diastereomeric amides (+)- and (–)-**4a**. General procedure for the synthesis of (+)- and (–)-**4a** is as follows: To a suspension of (+)- of (–)-**3a** (0.13 mmol) and 2-chloro-1-methylpyrimidine iodide (48 mg, 0.19 mmol) in dry CH_2Cl_2 (3 mL) was added a solution of triethylamine (40 mg, 0.40 mmol) and (–)-PEA in CH_2Cl_2 (2 mL). The reaction mixture was stirred for 10 h at room temperature, quenched with 2N HCl, washed with water, and dried over Na_2SO_4. After evaporation of the solvent *in vacuo*, crude (+)- or (–)-**4a** was obtained and analyzed by HPLC.

***tert-Butyl trans*-2-(diphenylphosphino)cyclopentanecarboxylate 2b.** This compound was prepared from *tert*-butyl cyclopentenecarboxylate and diphenylphosphine following the same procedure as that given above for the preparation of *tert*-butyl 3-(diphenylphosphino)butanoate **2a**.

2b: mp(^{i}PrOH) 93-96 °C; IR (KBr) 1721, 1371, 1155, 742, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 9H, $C(CH_3)_3$), 1.52-2.07 (m, 6H, CH_2), 2.72-2.80 (m, 1H, COC*H*), 2.92-2.98 (m, 1H, PC*H*), 7.27-7.36 (m, 6H, phenyl *H*), 7.43-7.48 (m, 2H, phenyl *H*), 7.52-7.56 (m, 2H, phenyl *H*); ^{13}C-NMR ($CDCl_3$) δ 26.38 (d, $^3J_{CP}$=5.2 Hz, CH_2), 27.9 (s, $C(CH_3)_3$), 31.3 (d, $^2J_{CP}$=18.6 Hz, CH_2), 32.6 (d, $^3J_{CP}$=4.1 Hz, CH_2), 37.6 (d, $^1J_{CP}$=8.3 Hz, Ph_2PCH), 48.9 (d, $^2J_{CP}$=21.7 Hz, CHCO), 79.9 (s, $C(CH_3)_3$), 128.3 (d, $^3J_{CP}$=3.1 Hz, *meta C*), 128.3 (d, $^3J_{CP}$=2.1 Hz, *meta C*), 128.7 (s, *para C*), 128.8 (s, *para C*), 133.4 (d, $^2J_{CP}$=18.6 Hz, *ortho C*), 133.8 (d, $^2J_{CP}$=19.7 Hz, *ortho C*), 137.7 (d, $^1J_{CP}$=13.5 Hz, *ipso C*), 138.0 (d, $^1J_{CP}$=13.5 Hz, *ipso C*), 175.3 (d, $^3J_{CP}$=6.2 Hz, *C*=O); ^{31}P-NMR ($CDCl_3$) δ -2.6; HRMS calcd for $C_{22}H_{27}O_2P$ 354.1750, found 354.1744.

***trans*-2-(Diphenylphosphino)cyclopentanecarboxylic acid 3b.** This compound was prepared from *tert-Butyl trans*-2-(diphenylphosphino)cyclopentanecarboxylate **2b** following the same procedure as that given above for the preparation of 3-(diphenylphosphino)butanoic acid **3a** by the procedure described above using **1b** (2.55 g, 15.2 mmol) and diphenylphosphine (3.39 g, 18.2 mmol) in 4.30 g (14.4 mmol, 95 %) overall yield. Physical data of this compound are consistent with those of previously prepared 2-(diphenylphosphino)-cyclopentanecarboxylic acid.[5]

Asymmetric Allylic Alkylation of 6a-c or 9 with 5. General Procedure. A chiral ligand (0.04–0.08 mmol) and palladium acetate (2.2–4.5 mg, 0.01–0.02 mmol) were placed in a two-necked flask equipped with magnetic stirring bar, a serum cap and three-way stopcock. The flask was filled with nitrogen

after evacuation and to it was added dry THF (3 mL). The mixture was stirred for 0.5 h at room temperature, and a THF solution (2 mL) of **6a-c** or **9** (1 mmol) was added. The mixture was stirred for 0.5 h at room temperature, and a solution of **5**, generated from triethyl phosphonoacetate (1.6 mmol) and sodium hydride (60% dispersion in mineral oil, 60 mg, 1.5 mmol) in dry THF (5 mL) was added. The reaction mixture was kept stirring at given temperatures for 2–87h. After the reaction mixture was quenched with pH 7 phosphate buffer, the mixture was extracted with ethyl acetate, washed with water and brine, dried (Na_2SO_4), and evaporated. The residue was purified over preparative TLC on silica gel to give the product **7a-c** or **10**. The enantiomeric purities of **7a-c** and **10** were determined by HPLC analysis as described previously.[5]

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