Stereoselective reaction of (±)-7-Phenyldinaphtho[2,1-*b*;1′,2′-*d*]phosphole with an optically active palladium complex. Molecular structure and fluxional behavior of Pd{(*S*)-$C_6H_4CH(CH_3)N(CH_3)_2$}{(*P*)-$PPh(C_{20}H_{12})$}Cl

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Abstract

Reaction of (±)-7-phenyldinaphtho[2,1-*b*;1′,2′-*d*]phosphole (**1**) with one-half equivalent of an optically active palladium complex, {Pd[(*S*)-$C_6H_4CH(CH_3)N(CH_3)_2$](μ-Cl)}$_2$ ((*S*)-**3a**), proceeded stereoselectively to give one of the diastereomers, Pd{(*S*)-$C_6H_4CH(CH_3)N(CH_3)_2$}{(*P*)-$PPh(C_{20}H_{12})$}Cl ((*S*)(*P*)-**4a**), accompanying racemization of **1**. The X-ray crystallographic analysis of (*S*)(*P*)-**4a** determined the absolute configuration of the coordinated phosphole unequivocally to be *P*. The fluxional behavior of **4a** and the related complex is also discussed.

Key words: Palladium; Phosphine; Fluxionality; Isomerism; Stereoselectivity; X-ray diffraction

1. Introduction

In 1992, we briefly reported the synthesis and properties of 7-phenyldinaphtho[2,1-*b*;1′,2′-*d*]phosphole (**1**), which is a new monodentate chiral phosphine having a "helical chirality" [1]. Recently, Australian and Italian chemists have reported similar results independently [2]. We have also reported detailed X-ray structural studies of **1** and showed that spontaneous resolution occurred during the crystallization of **1** [3]. The value of the barrier for racemization, caused by passing through one of the peri hydrogens, H_1 and H_{13} ($\Delta G^{\ddagger}(-20°C) = 59.4$ kJ mol^{-1} estimated from temperature-dependent ^{13}C NMR [1] or $\Delta G^{\ddagger}(-19°C) = 56 \pm 1$ kJ mol^{-1} estimated from temperature-dependent ^{1}H NMR [2]), is too low to achieve optical resolution of **1** at room temperature. The assumption that the value is due to the racemization barrier and not to the pyramidal inversion at the phosphorus atom was confirmed because 7-oxo-7-phenyldinaphtho[2,1-*b*;1′,2′-*d*]phosphole (**2**), in which the pyramidal inversion at the phosphorus atom is impossible, showed a similar value of the racemization barrier, $\Delta G^{\ddagger}(-20°C) = 59.4$ kJ mol^{-1}, obtained from temperature-dependent ^{13}C NMR spectra [1].

In this paper we describe the stereoselective reaction of (±)-**1** with the optically active palladium complex, {Pd[(*S*)-$C_6H_4CH(CH_3)N(CH_3)_2$](μ-Cl)}$_2$ ((*S*)-**3a**), to give Pd{(*S*)-$C_6H_4CH(CH_3)N(CH_3)_2$}{(*P*)-$PPh(C_{20}H_{12})$}Cl ((*S*)(*P*)-**4a**). We also describe the X-ray structural analysis of the palladium complex (*S*)(*P*)-**4a** and its fluxional behavior detected by temperature-dependent ^{1}H NMR spectra, and compare the fluxional behavior with that of Pd{$C_6H_4CH_2N(CH_3)_2$}{$PPh(C_{20}H_{12})$}Cl (**4b**) which was obtained from the reaction of **1** with an analogous, but achiral, palladium complex {Pd[$C_6H_4CH_2N(CH_3)_2$](μ-Cl)}$_2$ (**3b**).

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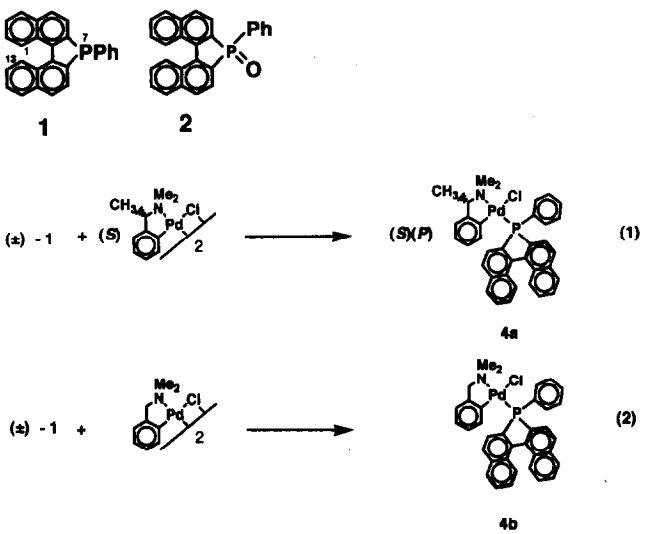
2. Results and discussion

2.1. Reaction of Pd complexes 3 with phosphole 1

We have previously reported the stereoselective reaction of (*S*)-**3a** and the analogous naphthylamine complex with racemic tertiary phosphines, and their use as resolving agents for chiral monodentate phosphines [4]. The same complex **3a** has also been reported to be a useful chiral auxiliary for optical resolution of BINAP (2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) [5] and other chiral biphosphines [6]. Thus the stereochemical interaction of chiral palladium complexes with the new type of chiral phosphine is of interest, and we have carried out the reaction of the optically active complex **3a** with phosphole **1**. Reaction of (±)-**1** with one-half equivalent of (*S*)-**3a** in benzene, and subsequent recrystallization of the reaction product from acetone, gave the 1 : 1 phosphole-coordinated complex (*S*)(*P*)-**4a** as yellow crystals, m.p. 171–173°C (decomp.), in good yield (80%). X-Ray crystallographic analysis of the complex (*S*)(*P*)-**4a** determined the absolute configuration of the coordinated phosphole unequivocally to be *P* (*vide infra*). Although there is a possibility that the phosphole-coordinated palladium complex obtained from the reaction is a diastereomeric mixture, the complex **4a** is considered to be homogeneous and of a single optical isomer for the following reasons: the complex has a fairly sharp decomposition point at 171–173°C; various samples from different parts of the crystal showed identical IR spectra taken as Nujol mulls. Thus stereoselective coordination of the (*P*)-phosphole to the palladium center, accompanying racemization of the (±)-phosphole, has occurred. The palladium complex (*S*)(*P*)-**4a** showed temperature-dependent ^{1}H NMR spectra. The fluxional behavior of the palladium complex was compared with that of an analogous phosphole-coordinated complex **4b**, obtained as yellow crystals in moderate yield from the reaction of phosphole **1** with an achiral palladium complex **3b**.

TABLE 1. Crystal parameters and experimental data for X-ray diffraction of Pd{(*S*)-$C_6H_4CH(CH_3)N(CH_3)_2$}{(*P*)-$PPh(C_{20}H_{12})$}Cl (**4a**)

Crysta data	
$C_{36}H_{31}ClNPPd$	D_m = 1.431(1) mg m^{-3}
M_r = 636.5	Cu Kα radiation (40 kV, 160 mA)
Monoclinic	λ = 1.54178 Å
$P2_1$	Cell parameters from
a = 13.165(3) Å	25 reflections
b = 13.457(2) Å	2θ = 29.07–32.88°
c = 8.519(1) Å	μ = 6.88 mm^{-1}
β = 106.38(1)°	T = 286(1) K
V = 1448.0(4) Å^3	0.16×0.06×0.16 mm^3
Z = 2	Triangle prism
D_x = 1.492 Mg m^{-3}	Orange
	$F(000)$ = 664
Data collection	
Rigaku AFC-5R	3840 observed reflections
$2\theta-\omega$ scans	$[8.0\sigma(F_o) < F_o]$, 0.05 < sin θ/λ
(0.90+0.15 tan θ)°: scan width	$2\theta_{max}$ = 120.0°
4.0 deg min^{-1}: scan rate (ω)	h = −14 → +14
Absorption correction:	k = −15 → +15
empirical [8]	l = 0 → +9
T_{min} = 1.000, T_{max} = 1.242	3 standard reflections
4545 measured reflections	monitored every 200 reflections
4272 independent reflections	Intensity variation:
R_{sym} (on F) = 0.011	no significant
Refinement	
Refinement on F	$(\Delta\rho)_{max}$ = 0.98 e Å^{-3}
Final R = 0.0242	$(\Delta\rho)_{min}$ = −0.92 e Å^{-3}
wR = 0.0312	$(\Delta/\sigma)_{max}$ = 0.0015 (for Pd: x)
S = 0.814	Atomic scattering factors
3840 reflections	from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2b)
484 parameters	
All H atoms refined	
$w = 1/\sigma^2(F)$	



2.2. X-Ray crystal structure of (S)(P)-4a

Compound (*S*)(*P*)-**4a** crystallizes in the enantiomorphous monoclinic space group $P2_1$ (Table 1). The molecular structure, a stereoview of the molecule and a stereoview of the unit cell are illustrated in Figs. 1, 2 and 3 respectively [7]. Table 2 describes the fractional coordinates for non-hydrogen atoms. Table 3 lists selected bond distances and angles in the molecule. The absolute configuration of the coordinated phosphole ligand in the complex **4a** was determined unequivocally to be *P* based on the known absolute configuration of (−)(*S*)-*N*,*N*-dimethyl-α-phenethylamine used for the

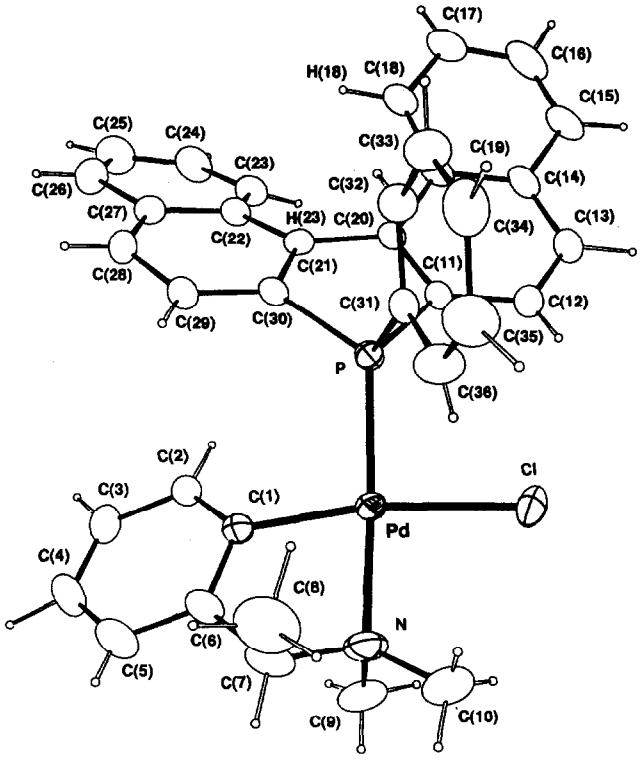


Fig. 1. Molecular structure of (*S*)(*P*)-**4a** showing the atom numbering scheme.

preparation of complex **3a**. The coordination geometry around the Pd atom is a distorted square plane. The phosphole ligand coordinates *trans* to the nitrogen atom, while the chloro ligand is opposite the coordinated carbon atom of the *ortho*-metallated phenethylamine ligand. There is significant deviation of the palladium complex from a planar geometry as shown in Table 4 which gives dihedral angles between selected planes. The geometry of the coordinated phosphole is similar to that of the non-coordinated molecule [3]. Although the five-membered ring of the phosphole and each benzene ring in the binaphthyl moiety are essentially planar, both naphthyl rings are bent away significantly from each other. The fused aromatic rings are bent at the C(11)–C(20), C(14)–C(19), C(21)–C(30) and C(22)–C(27) bonds. These distortions result in dihedral angles of 24.1(2)° between the mean planes of the inner pair of rings (pl 7 and pl 9) and 41.3(3)° between the mean planes of the outer rings (pl 6 and pl 8), which become slightly larger on coordination; the corresponding values in the free ligand are 18.7(2)° and 38.2(2)° respectively (Table 4). The contact distance between the peri hydrogens, H(18) and H(23), is 2.36(8) Å which is only 0.03 Å longer than that found in the non-coordinated phosphole. From the molecular geometry of **4a** itself the reason for the selective formation of only one diastereomer is not clear. However, from closer examination of the crystal packing of the molecule in the unit cell (Fig. 3), it may be seen that the (*S*)(*P*)-isomer is preferred to the (*S*)(*M*)-isomer.

2.3. *Fluxional behavior of the Pd complexes* **4**

The palladium complex **4a** is expected to be present as a pair of diastereomers, (*S*)(*P/M*)-**4a**, in solution. ^{1}H NMR of **4a** in $CDCl_3$ exhibits temperature-dependent spectra. At 30°C, the spectrum shows broad signals for the aliphatic region, but at lower temperature the spectra are resolved. At −50°C, the CMe and benzylic CH protons appear as two sets of signals: two doublets at δ 1.46 and 1.73 for the CMe protons and two broad multiplets at δ 3.41 and 4.01 for the CH proton. The signal ratio in each set is about 2.9:7.1. The NMe protons also appear as two sets of signals: each is composed of two singlets in a ratio of about

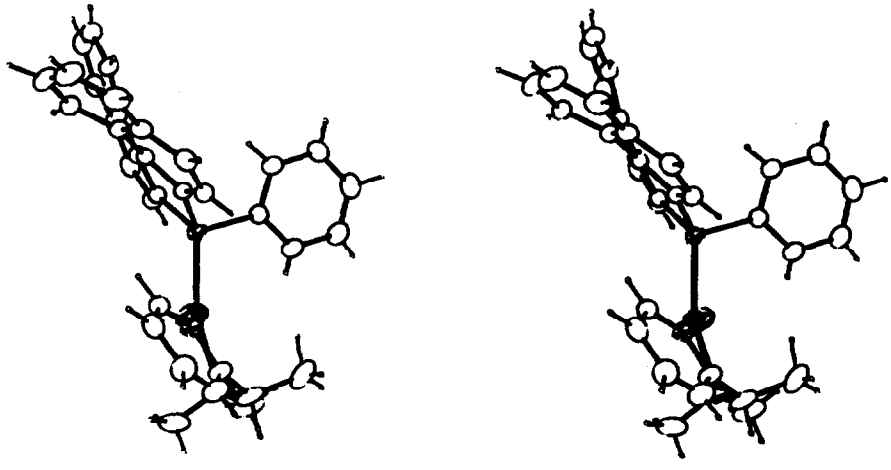


Fig. 2. Stereoscopic drawing of the molecule of (*S*)(*P*)-**4a**.

2.9:7.1 at δ 2.38 and 2.42 and at δ 2.72 and 2.64 respectively. At 35°C these signals coalesce, and at 60°C they change to a doublet at δ 1.64 ($J = 6.4$ Hz) for CMe, two slightly broad signals at δ 2.57 and 2.61 for NMe_2 and a single broad signal at δ 3.68 for CH. The two NMe groups of complex **4a** are non-equivalent even at high temperature and the upper field signal appears as a poorly resolved doublet ($J \approx 2$Hz) due to the coupling with the *trans*-coordinated phosphole. The variable-temperature ^{1}H NMR spectra for CH and NMe_2 of **4a** are given in Fig. 4a. At first glance these signal changes can be considered to be due to equilibration between the two diastereomers, (*S*)(*P*)-**4a** and (*S*)(*M*)-**4a**, via racemization of the coordinated phosphole ligand. An analogous palladium complex **4b**, derived from the achiral palladium complex **3b** and **1**, also showed very similar temperature-dependent ^{1}H NMR spectra (Fig. 4b). At 60°C, the NMe_2 and benzylic CH_2 protons appear as singlets at δ 2.83 and 4.06 respectively. At approximately 23°C these signals coalesce, and at lower temperatures split into two sets of signals despite the absence of diastereomers for **4b**. At −50°C, two singlet signals at δ 2.70 and 2.97 for NMe_2 protons and a doublet of doublets centered at δ 3.73 ($J = 13.6$ Hz and $J_{PH} = 3.4$ Hz) and a doublet at δ 4.47 ($J = 13.6$ Hz) for benzylic CH_2 protons are observed; only one of the methylene protons shows coupling with the *trans* phosphorus atom. In this case, however, the signal ratio is 1:1. These observations suggest that the temperature-dependent spectra are due to an analogous process, namely equilibration between rotational isomers around the Pd–P bond and not to the presence of diastereomers. Although the aromatic region of the ^{1}H NMR spectrum of **4a** at low temperature also indicates the presence of diastereomers, the spectrum could not be analyzed easily due to the complexity. In complex **4a** inequivalent amounts of the rotamers resulted from the presence of the chiral amine ligand. The dissociation of the *N*-coordination of the amine ligand is not plausible, because two different *N*-methyl groups are present even at high temperature for **4a**. Dissociation of the phosphole is also not possible because a small P–H coupling between one of the *N*-methyl groups and the phosphole can be recognized at 60°C. The activation energies of the rotational barrier were estimated to be $\Delta G^{\ddagger}(22.5°C) = 59.8$ kJ mol^{-1} for **4b** and $\Delta G^{\ddagger}_{minor}$ (25°C) = 64.4 kJ mol^{-1} and $\Delta G^{\ddagger}_{major}$ (25°C) = 65.7 kJ mol^{-1} for **4a** from the variable ^{1}H NMR data of the *N*-methyl protons by the temperature coalescence method [9].

3. Experimental details

^{1}H NMR spectra were obtained at 270.05 MHz using a JEOL GSX-270 spectrometer or at 500.0 MHz using a JEOL GX-500 spectrometer. Chemical shifts are reported with respect to the solvent ($CDCl_3$, δ 7.26). ^{13}C NMR spectra were obtained at 67.80 MHz using a JEOL GSX-270 spectrometer or at 125.65 MHz using a JEOL GX-500 spectrometer. The spectra were recorded using $CDCl_3$ as both a lock and solvent unless otherwise specified. Chemical shifts are reported with respect to the solvent ($CDCl_3$, δ 76.9). ^{31}P NMR spectra were obtained at 109.25 MHz using a JEOL GSX-270 spectrometer. Chemical shifts are reported using 85% H_3PO_4 as an external standard. IR spectra were obtained on a Hitachi 295 IR spectrophotometer. UV spectra were recorded on a Shimadzu UV-visible recording spectrophotometer (UV-265FS). Flash chromatography was performed on silica gel (Merck 9385). Thin-layer chromatography was performed on E. Merck precoated silica gel plates (60F-

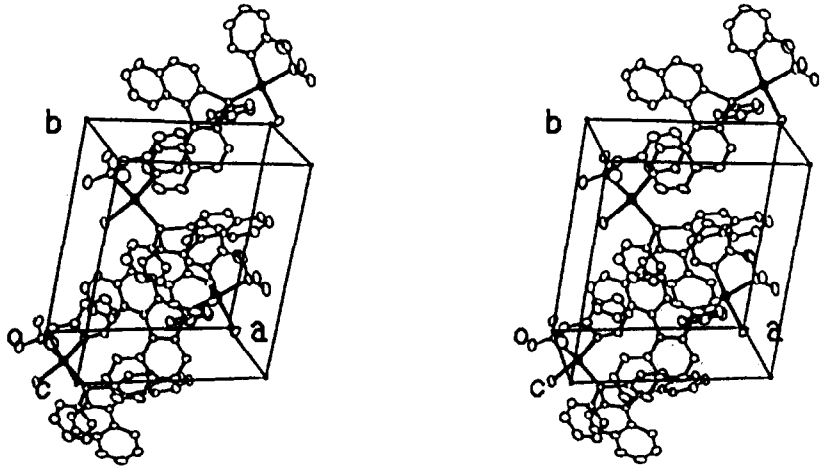


Fig. 3. Stereoscopic drawing of the unit cell of (*S*)(*P*)-**4a**.

TABLE 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^4$) for Pd{(*S*)-$C_6H_4CH(CH_3)N(CH_3)_2$}{(*P*)-PPh($C_{20}H_{12}$)}Cl (**4a**)

Atom	*x*	*y*	*z*	U_{eq} (Å^2) [a]
Pd	7958.6(2)	2500.0	4104.0(3)	400(1)
Cl	8993(1)	1124(1)	5403(2)	763(8)
P	6711(1)	1455(1)	2613(1)	349(5)
N	9283(3)	3491(4)	4847(7)	676(25)
C(1)	7218(3)	3800(3)	3412(5)	410(20)
C(2)	6185(3)	4049(4)	3323(5)	429(21)
C(3)	5846(4)	5041(4)	3118(6)	528(28)
C(4)	6531(5)	5774(4)	2946(7)	651(29)
C(5)	7556(5)	5535(4)	3054(8)	699(33)
C(6)	7916(4)	4565(3)	3302(7)	544(24)
C(7)	9045(4)	4292(4)	3550(9)	715(32)
C(8)	9249(6)	3967(7)	1983(12)	1001(52)
C(9)	9293(6)	3940(6)	6443(11)	856(42)
C(10)	10344(4)	3041(7)	5047(17)	976(54)
C(11)	6223(3)	351(3)	3421(5)	350(19)
C(12)	6847(4)	−426(3)	4304(5)	440(22)
C(13)	6378(4)	−1280(3)	4580(5)	482(22)
C(14)	5297(4)	−1430(3)	3887(5)	435(20)
C(15)	4813(4)	−2373(4)	4029(6)	568(26)
C(16)	3800(4)	−2555(5)	3247(6)	674(27)
C(17)	3198(5)	−1852(4)	2202(8)	589(30)
C(18)	3597(4)	−925(3)	2030(6)	480(23)
C(19)	4652(3)	−675(3)	2943(5)	394(19)
C(20)	5126(3)	280(3)	2829(5)	350(19)
C(21)	4631(3)	1186(3)	1968(5)	346(18)
C(22)	3562(3)	1512(3)	1599(5)	396(19)
C(23)	2817(3)	1150(3)	2395(6)	471(22)
C(24)	1799(4)	1487(4)	1979(8)	638(28)
C(25)	1462(4)	2204(4)	745(9)	747(33)
C(26)	2160(3)	2595(5)	17(7)	627(25)
C(27)	3235(3)	2306(3)	460(5)	443(21)
C(28)	3988(4)	2802(3)	−143(5)	453(21)
C(29)	5041(3)	2604(4)	450(4)	396(18)
C(30)	5365(3)	1803(3)	1530(5)	351(18)
C(31)	7267(3)	920(3)	1056(5)	380(18)
C(32)	6618(3)	338(3)	−190(6)	484(23)
C(33)	7020(4)	−72(4)	−1362(7)	574(27)
C(34)	8048(4)	106(4)	−1352(7)	629(30)
C(35)	8685(5)	684(5)	−144(8)	710(33)
C(36)	8303(4)	1082(4)	1053(8)	610(28)

[a] Anisotropically refined atoms as given in the isotropic equivalent thermal parameters, defined as $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (a_i a_j)$.

245). Solvents were distilled under Ar from appropriate drying agents prior to use. Racemic 2,2'-dibromo-1,1'-binaphthyl and butyllithium were a generous gift from Takasago Research Institute Co. Ltd. and Nippon Alkylaluminum Co. Ltd. respectively. μ-Dichlorobis[*N*,*N*-dimethylbenzylamine-2*C*,*N*]dipalladium (**3b**) [10] and μ-dichlorobis[(*S*)-*N*,*N*-dimethyl-α-phenethylamine-2*C*,*N*]dipalladium ((*S*)-**3a**) [4] were prepared according to the literature. Other chemicals were of reagent grade.

TABLE 3. Selected bond distances (Å) and angles (°) for Pd{(*S*)-$C_6H_4CH(CH_3)N(CH_3)_2$}{(*P*)-PPh($C_{20}H_{12}$)}Cl (**4a**)

Bond distances			
Pd–Cl	2.378(2)	Pd–P	2.261(1)
Pd–N	2.143(6)	Pd–C(1)	2.009(5)
P–C(11)	1.828(4)	P–C(30)	1.814(4)
P–C(31)	1.833(4)	H(18)···H(23)	2.36(8)
Bond angles			
Cl–Pd–P	90.40(6)	Cl–Pd–N	92.0(2)
Cl–Pd–C(1)	168.9(1)	P–Pd–N	162.6(2)
P–Pd–C(1)	99.3(1)	N–Pd–C(1)	80.3(2)
Pd–P–C(11)	124.8(1)	Pd–P–C(30)	125.2(1)
Pd–P–C(31)	106.0(1)	Pd–N–C(7)	104.2(5)
Pd–N–C(9)	108.7(5)	Pd–N–C(10)	116.1(7)
Pd–C(1)–C(2)	128.0(4)	Pd–C(1)–C(6)	112.8(3)
Pd–C(1)–C(7)	80.5(2)	C(11)–P–C(30)	90.2(2)
C(11)–P–C(31)	102.0(2)	C(30)–P–C(31)	105.4(2)
P–C(11)–C(12)	126.2(2)	P–C(11)–C(20)	111.0(3)
P–C(30)–C(21)	111.1(3)	P–C(30)–C(29)	127.2(3)
P–C(31)–C(32)	119.1(2)		

3.1. 7-Phenyldinaphtho[2,1-b;1',2'-d]phosphole (1)

To a cooled solution (−78°C) of 2,2'-dibromo-1,1'-binaphthyl (0.63 g, 1.5 mmol) in 10 ml of dry tetrahydrofuran (THF) was added butyllithium (3.7 ml of 1.35 M in hexane, 5.0 mmol) dropwise over 5 min. The reaction mixture was stirred for 2 h at this temperature, and a yellowish green slurry was obtained. The cooling bath was removed and the temperature was allowed to warm to room temperature. Evaporation of the solvents *in vacuo* gave a yellowish green solid residue, which was washed with hexane (10 ml) in order to remove excess butyllithium. THF (10 ml) was added to the solid residue, and the mixture was cooled in a dry-ice acetone bath. A solution of dichlorophenylphosphine (0.24 g, 1.3 mmol) in THF (10 ml) was added dropwise over 10 min to the yellowish green

TABLE 4. Dihedral angles (°) of least-squares planes [a] with estimated standard deviations in parentheses for Pd{(*S*)-$C_6H_4CH(CH_3)N(CH_3)_2$}{(*P*)-PPh($C_{20}H_{12}$)}Cl (**4a**) and (*P*)-P($C_{20}H_{12}$)(C_6H_5) (**1**) [3]

Plane	4a	1	Plane	4a	1
pl 1–pl 2	160.8(2)		pl 6–pl 7	8.7(2)	12.2(2)
pl 2–pl 3	24.0(2)		pl 8–pl 9	10.5(2)	9.6(1)
pl 3–pl 4	41.7(1)		pl 6–pl 8	24.1(2)	18.7(2)
pl 1–pl 5	37.09(9)		pl 7–pl 9	41.3(3)	38.2(2)
pl 4–pl 5	144.9(1)		pl 5–pl 10	90.8(2)	92.9(2)
pl 5–pl 6	12.0(2)	6.67(9)	pl 4–pl 10	106.5(2)	
pl 5–pl 8	12.4(1)	12.03(9)	pl 11–pl 12	32.4(1)	28.7(1)

[a] The least-squares planes of **4a** are as follows. pl 1: Pd, Cl, P; pl 2: Pd, N, C(1); pl 3: C(1)–C(6); pl 4: P, Cl, N, C(1); pl 5: P, C(11), C(20), C(21), C(30); pl 6: C(11)–C(14), C(19), C(20); pl 7: C(14)–C(19); pl 8: C(21), C(22), C(27)–C(30); pl 9: C(22)–C(27); pl 10: C(31)–C(36); pl 11: C(11)–C(20); pl 12: C(21)–C(30).

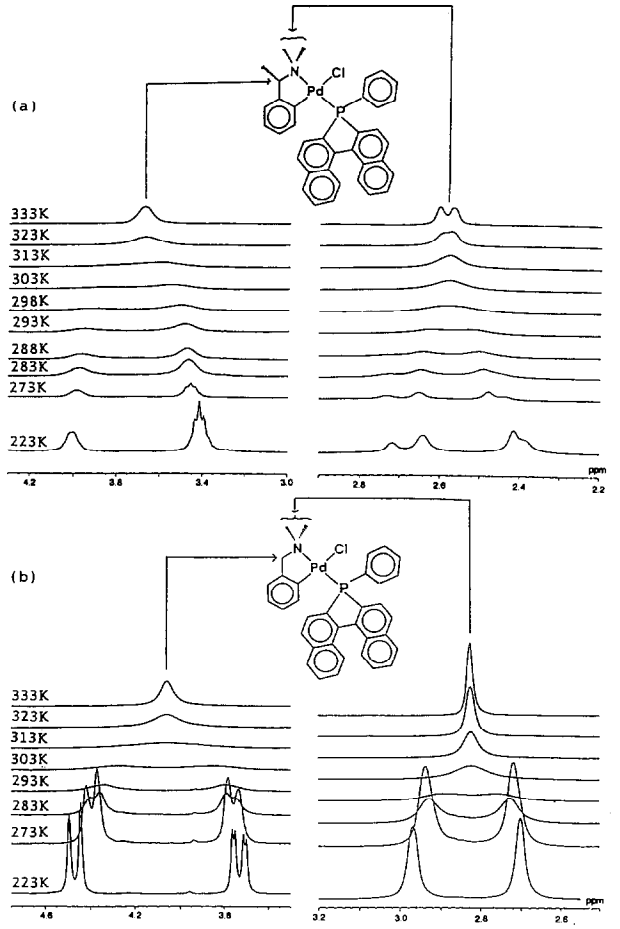


Fig. 4. Temperature-dependent ^1H NMR spectra (270.05 MHz): (a) for NMe_2 and CH protons of (*S*)(*P*)-**4a**; (b) for NMe_2 and CH_2 protons of **4b**. In $CDCl_3$.

suspension and the mixture was stirred for 1 h at this temperature. The initial yellowish green slurry changed to a yellow slurry and then to a yellow solution when the reaction mixture was allowed to warm to room temperature. The solution was stirred overnight (12 h), the solvent was removed under reduced pressure and the solid residue was extracted with benzene. The benzene extract was condensed to approximately 5 ml and purified by column chromatography (silica gel, benzene under Ar). The first running band was collected and recrystallized from ethanol to give the phosphole as pale yellow crystals (0.29 g, 60%), m.p. 157.5–159.0°C. Anal. Calc. for $C_{26}H_{17}P$: C, 86.65; H, 4.75. Found: C, 85.90; H, 4.93. HRMS (EI). Calc. for $C_{26}H_{17}P$: $[M^+]$ *m/z* 360.1068. Found: 360.1056. ^1H NMR (500 MHz, $CDCl_3$, 35°C): δ 7.17–7.32 (m, 5H, *Ph*), 7.47 (t, 2H, H_2, H_{12}), 7.52 (t, 2H, H_3, H_{11}), 7.77 (m, 2H, H_6, H_8), 7.84 (d, 2H, H_5, H_9), 7.93 (d, $J = 8.0$ Hz, 2H, H_4, H_{10}), 8.46 (d, $J = 8.0$ Hz, 2H, H_1, H_{13}). $^{13}C\{^1H\}$ NMR (125.65 MHz, $CDCl_3$, 35°C): δ 124.64 (*C*-7, *C*-7′ of Np), 125.85 (*C*-6, *C*-6′ of Np), 126.36 (br d, $J_{PC} = 22.4$ Hz, *C*-3, *C*-3′ of Np), 127.55 (*C*-8, *C*-8′ of Np), 128.14 (d, $J_{PC} = 9.5$ Hz, *C*-4, *C*-4′ of Np), 128.49 (*C*-5, *C*-5′ of Np), 128.77 (*m-Ph*), 129.67 (*p-Ph*), 129.90, 133.45 (br d, $J_{PC} = 19.9$ Hz, *o-Ph*), 134.49, 134.73, 140.89, 142.73. (−50°C): δ 124.62 (*C*-7 or *C*-7′ of Np), 124.70 (*C*-7′ or *C*-7). $^{31}P\{^1H\}$ NMR (109.25 MHz, $CDCl_3$, 35°C): δ −8.34 (s). IR (KBr tablet, cm^{-1}): 3050(s), 2950(m), 1960(w), 1820(w), 1760(w), 1610(w), 1580(m), 1560(w), 1505(s), 1480(s), 1450(m), 1440(s), 1260(w), 1230(s), 1310(w), 1260(s), 1210(m), 1185(w), 1145(s), 1090(s), 1030(s), 1000(s), 960(s), 875(m), 860(s), 850(m), 810(s), 770(s), 745(s), 695(s), 655(s), 625(s), 610(m), 540(s), 515(s), 465(s), 425(w), 400(s). UV ($CHCl_3$) λ_{max} nm (log ϵ): 358.0 (4.1), 287.4sh (4.2), 275.6 (4.5), 230.2 (4.9).

3.2. *7-Oxo-7-phenyldinaphtho[2,1-b;1',2'-d]phosphole (2)*

To a solution of phosphole **1** (0.39 g, 1.1 mmol) in acetone (20 ml) was added 30% hydrogen peroxide (10 ml) dropwise under ice cooling and the reaction mixture was stirred overnight at room temperature. After concentration, water (70 ml) was added and the resulting pale yellow precipitate was collected, washed several times with water and dried in air. The crude products were purified by column chromatography (silica gel, ethyl acetate–CH_2Cl_2 (1 : 1)). Successive recrystallization from ethyl acetate gave **2** as yellow crystals (0.25 g, 62% yield), m.p. 263.2–264.2°C. Anal. Calc. for $C_{26}H_{17}PO$: C, 82.97; H, 4.55. Found: C, 82.89; H, 5.10. ^1H NMR (500 MHz, $CDCl_3$, 35°C): δ 7.34 (dt, 2H, H_6, H_8), 7.46 (dt, 1H, *p-Ph*), 7.54 (t, 2H, H_2, H_{12}), 7.60–7.66 (m, 4H, H_3, H_{11}, *o-Ph*), 7.83 (dd, 2H, H_6, H_8), 7.97 (br d, 4H, H_4, H_{10}, H_5, H_9), 8.22 (d, $J = 8.1$ Hz, 2H, H_1, H_{13}). $^{13}C\{^1H\}$ NMR (125.65 MHz, $CDCl_3$, 35°C): δ 124.22 (d, $J_{PC} = 10$ Hz, *C*-3, *C*-3′ of Np), 125.64 (*C*-7, *C*-7′ of Np), 127.47 (*C*-6, *C*-6′ of Np), 127.85 (*C*-8, *C*-8′ of Np), 128.62 (d, $J_{PC} = 12.2$ Hz, *m-Ph*), 128.62 (*C*-5, *C*-5′ of Np), 130.39 (br, *C*-4, *C*-4′ of Np), 130.28 (d, $J_{PC} = 102.9$ Hz, *ipso-Ph*), 130.89 (d, $J_{PC} = 10.8$ Hz, *o-Ph*), 132.04 (d, $J = 3$ Hz, *p-Ph*), 137.15 (d, $J_{PC} = 1.5$ Hz, *C*-4a, *C*-4a′), 141.64 (br, *C*-1, *C*-1′ of Np). (−50°C): δ 125.70 (*C*-7 or *C*-7′ of Np), 125.82 (*C*-7′ or *C*-7 of Np). IR (KBr tablet, cm^{-1}): 3000(br w), 1437(m), 1335(m), 1258(w), 1205(s), 1192(sh s), 1153(s), 1110(m), 1020(w), 880(m), 860(m), 820(s), 780(w), 752(s), 720(s), 695(m), 656(s), 618(m), 561(m), 530(s), 485(m), 402(w). UV ($CHCl_3$) λ_{max} nm (log ϵ): 387 (3.7), 351 (3.6), 337 (3.5), 284 (4.4), 257 (4.5), 249 (4.5), 231 (4.9).

3.3. *$Pd\{C_6H_4CH_2N(CH_3)_2\}\{PPh(C_{20}H_{12})\}Cl$ (4b)*

A mixture of μ-dichlorobis[*N*,*N*-dimethylbenzylamine-2*C*,*N*]dipalladium (**3b**) (0.12 g, 0.22 mmol) and

the dinaphthophosphole **1** (0.16 g, 0.44 mmol) was dissolved in 10 ml of dichloromethane and the resulting solution was stirred overnight at room temperature. The solvent was removed under reduced pressure to give a yellow powder. Recrystallization of the yellow powder from acetone gave the pure complex **4b** as yellow crystals containing two moles of solvated acetone (0.19 g, 58%), m.p. 209.5°C (decomp.). Anal. Calc. for $C_{35}H_{29}ClNPPd \cdot 2C_3H_6O$: C, 65.43; H, 5.49; N, 1.86; Cl, 4.71. Found: C, 65.64; H, 5.52; N, 2.00; Cl, 4.76. ^1H NMR (270 MHz, $CDCl_3$, 25°C): δ 2.18 (s, *acetone*), 2.80 (br s, N*Me*$_2$), 3.80 (br, CH_2), 4.34 (br, CH_2), 6.35–8.40 (m, *arom.*); (−50°C): δ 2.70 (s, N*Me*), 2.97 (s, N*Me*), 3.73 (dd, $J_{HH} = 13.6$ Hz, $J_{PH} = 3.5$ Hz, CH_2), 4.47 (d, $J = 13.6$ Hz, CH_2), 6.35–8.48 (m, *arom.*); (60°C): δ 2.83 (s, N*Me*$_2$), 4.06 (s, CH_2), 6.30–8.40 (m, *arom.*). $^{31}P\{^1H\}$ NMR (202.35 MHz, $CDCl_3$, 30°C): δ 37.46 (s); (−50°C): 38.48 (s). IR (CsI tablet, cm^{-1}): 3040(br m), 2875(br m), 1730(br m), 1610(w), 1580(s), 1500(w), 1450(s), 1433(s), 1400(w), 1358(w), 1330(s), 1300(s), 1290(w), 1262(sh w), 1255(m), 1210(w), 1170(sh w), 1150(m), 1092(m), 1047(w), 1020(s), 992(s), 970(m), 912(w), 861(s), 841(s), 820(s), 778(w), 750(sh s), 736(s), 701(m), 689(m), 650(s), 630(m), 580(w), 532(s), 487(m), 470(w), 452(m), 431(w), 401(w), 390(w), 285(m).

3.4. *Pd{(S)-$C_6H_4CH(CH_3)N(CH_3)_2$}{(P)-PPh($C_{20}H_{12}$)}Cl ((S)(P)-4a)*

A solution of (±)-7-phenyldinaphtho[2,1-*b*;1',2'-*d*]phosphole (0.12 g, 0.34 mmol) in benzene (3 ml) was added dropwise to a stirred solution of μ-dichlorobis [(*S*)-*N*,*N*-dimethyl-α-phenethylamine-2*C*,*N*]dipalladium ((*S*)-**3a**) (0.10 g, 0.17 mmol) in benzene (3 ml) and the resulting yellow solution was stirred at room temperature for several hours. On evaporation of the solvent *in vacuo* a yellow solid was obtained. Recrystallization of the crude solid from acetone gave the pure product as yellow crystals (0.18 g, 80%), m.p. 171–173°C (decomp.). Anal. Calc. for $C_{36}H_{31}ClNPPd$: C, 66.47; H, 4.80; N, 2.15; Cl, 5.45. Found: C, 66.50; H, 4.82; N, 2.12; Cl, 5.45. ^1H NMR (270 MHz, $CDCl_3$, 30°C): δ 1.62 (br s, C*Me*, 2.58 (br s, N*Me*$_2$), 3.56 and 3.90 (br, C*H*Me), 6.14–8.22 (m, *arom.*); (−50°C): δ 1.46 (br d, $J = 7.2$ Hz, C*Me* minor), 1.73 (br d, $J = 7.2$ Hz, C*Me* major), 2.38 (br s, N*Me* minor), 2.42 (br s, N*Me* major), 2.64 (br s, N*Me* major), 2.72 (br s, N*Me* minor), 3.41 (br q, C*H*, major), 4.01 (br, C*H*, minor), 5.90–8.40 (m, *arom.*); (60°C): δ 1.64 (d, $J = 6.4$ Hz, C*Me*), 2.57 (br d, $J \approx 2.3$ Hz, N*Me*), 2.61 (s, N*Me*), 3.68 (br, C*H*), 6.13–8.23 (m, *arom.*). $^{31}P\{^1H\}$ NMR (109.25 MHz, $CDCl_3$, 35°C): δ 31.74 (br s, minor), 33.27 (br s, major); (55°C): δ 32.37 (s). IR (Nujol, cm^{-1}): 3070(m), 3050(m), 1715(m), 1580(s), 1380(s), 1330(s), 1255(m), 1210(m), 1090(s), 1010(s), 940(s), 870(m), 820(s), 750(s), 730(s), 685(s), 655(s), 630(s), 530(s), 480(s), 425(m), 405(m), 380(m), 290(w). UV (dioxane) λ_{max} nm (log ϵ): 380 (4.06), 350 (4.21), 338 (4.10), 290 (4.58), 266 (4.80), 252 (4.86), 228 (5.16).

3.5. *Crystal structure determination of Pd{(S)-$C_6H_4CH(CH_3)N(CH_3)_2$}{(P)-PPh($C_{20}H_{12}$)}Cl ((S)(P)-4a)*

Yellow crystals were grown from an acetone solution. A suitable crystal for X-ray analysis was fixed on the end of a glass fiber with cyanoacrylate adhesives. The crystal data and the conditions used for the data collection are summarized in Table 1. The positional parameters for non-hydrogen atoms were determined using direct methods (MULTAN 78 [11]) from 2227 reflections ($k \geq 0$). The number of reflections used in the refinements was 3840; $-14 \leq h \leq +14$, $-15 \leq k \leq +15$, $0 \leq l \leq +9$, $8.0\sigma(F_o) < F_o$ and $0.05 < \sin\theta/\lambda$. All H atoms were located in the difference Fourier map. The absolute configuration of the C(7) atom of the amine ligand was determined to be *S* based on the known chirality of (−)(*S*)-*N*,*N*-dimethylphenethylamine [12]. The refinements of the atomic parameters were carried out by full-matrix techniques (ANYBLK [13]). Least-squares calculations were carried out by allowing all non-hydrogen and hydrogen atoms to refine anisotropically and isotropically respectively; in addition, the anomalous dispersion terms for Pd, P and Cl were introduced [14]. The above configuration refined to $R = 0.0242$, $wR = 0.0312$. The calculation was also made for the opposite configuration; this model refined to $R = 0.0630$ and $wR = 0.0927$. The difference in the agreement indices also confirmed the absolute configuration. The largest peak in the final difference Fourier synthesis is approximately 0.96 e Å^{-3} and is located near the Pd atom (1.02 Å). All calculations were carried out on an NEC ACOS 930S computer at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University. The fractional parameters are given in Table 2 and selected bond distances and angles are listed in Table 3. Further crystallographic details (fractional coordinates and isotropic thermal parameters of H atoms, anisotropic thermal parameters, complete interatomic distances and angles, details of computation of dihedral angles between the least-squares planes and structure factors) have been deposited with the Cambridge Crystallographic Data Centre.

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References and notes

1 K. Tani, H. Tashiro and T. Yamagata, *Abstracts of Symposium on Organometallic Chemistry, Japan*, 1992, Kinki Chemical Society, Division of Organometallic Chemistry, Japan, 1992, pp. 178–180.
2 (a) A.A. Watson, A.C. Willis and S.B. Wild, *J. Organomet. Chem., 445* (1993) 71; (b) A. Dore, D. Fabbri, S. Gladiali and O. De Lucchi, *J. Chem. Soc., Chem. Commun.*, (1993) 1124.
3 K. Tani, T. Yamagata and H. Tashiro, *Acta Crystallogr., Sect. C*, in press.
4 (a) S. Otsuka, A. Nakamura, T. Kano and K. Tani, *J. Am. Chem. Soc., 93* (1971) 4301; (b) K. Tani, L.D. Brown, J. Ahmed, J. Ibers, M. Yokota, A. Nakamura and S. Otsuka, *J. Am. Chem. Soc., 99* (1977) 7876.
5 (a) A. Miyashita, A. Yasuda, H. Takaya, K. Toriumi, T. Ito, T. Souchi and R. Noyori, *J. Am. Chem. Soc., 102* (1980) 7932; (b) A. Miyashita, H. Takaya, T. Souchi and R. Noyori, *Tetrahedron, 40* (1984) 1245.
6 N.K. Roberts and S.B. Wild, *J. Am. Chem. Soc., 101* (1979) 6254.
7 C.K. Johnson, ORTEP-II. *A FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations, ORNL-5138*, Oak Ridge National Laboratory, March, 1976.
8 A.C.T. North, D.C. Phillips and B.W. Mathew, *Acta Crystallogr., Sect. A, 24* (1968) 351.
9 (a) J. Sandström, *Dynamic NMR Spectroscopy*, Academic Press, London, 1982; (b) H. Shanan-Atidi and K.H. Bar-Eli, *J. Phys. Chem., 74* (1970) 961.
10 A.C. Cope and E.C. Friedrich, *J. Am. Chem. Soc., 90* (1968) 909.
11 P. Main, S.E. Hull, L. Lessinger, G. Germain, J.-P. Declercq and M.M. Woolfson, *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*, MULTAN 78, University of New York, 1978.
12 A.C. Cope, *J. Am. Chem. Soc., 71* (1949) 3929.
13 H. Imoto, ANYBLK(1990). *Program for Least-squares Refinement* Department of Chemistry, The University of Tokyo, Japan, p. 113.
14 D.T. Cromer and J.A. Ibers, *International Tables for X-ray Crystallography*, Vol. IV, Kynoch, Birmingham, 1974, Table 2.3.1.