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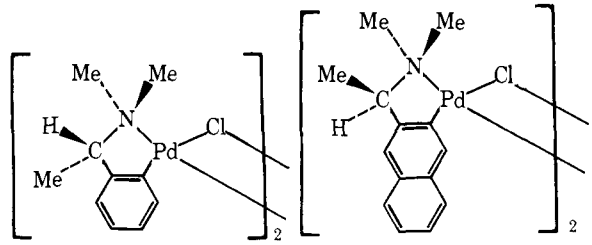
Chiral Metal Complexes. 4.[1] Resolution of Racemic Tertiary Phosphines with Chiral Palladium(II) Complexes. The Chemistry of Diastereomeric Phosphine Pd(II) Species in Solution, and the Absolute Configuration of [(*S*)-Isopropyl-*tert*-butylphenylphosphine]-[(*R*)-*N,N*-dimethyl-α-(2-naphthyl)-ethylamine-3*C,N*]chloropalladium(II) Determined by X-Ray Diffraction

K. Tani,[2a] Leo D. Brown,[2b] Jamil Ahmed,[2b] James A. Ibers,*[2b] M. Yokota,[2a] A. Nakamura,[2a] and S. Otsuka*[2a]

Contribution from the Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan 560, and the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received March 25, 1977*

Abstract: Resolution of racemic tertiary phosphines of the types $PAr^1Ar^2Ar^3$ (**P**^{1}*) and $PArR^1R^2$ (**P**^{2}*) have been achieved with chloro-bridged chiral Pd(II) complexes, (+)-di-μ-chloro-bis[(*S*)-*N,N*-dimethyl-α-phenylethylamine-2*C,N*]dipalladium (**1**) ([(*S*)-**Pd**^{1}]$_2$), and (−)-di-μ-chloro-bis[(*R*)-*N,N*-dimethyl-α-(2-naphthyl)ethylamine-3*C,N*]dipalladium (**2**) ([(*R*)-**Pd**^{2}]$_2$), or with (+)-*cis*-dichlorobis[(*S*)-*sec*-butyl isocyanide]palladium (**3**) by virtue of the solubility difference between diasteromeric monophosphine compounds, [(*S*)-**Pd**^{1}-**P**^{1}*], [(*R*)-**Pd**^{2}-**P**^{2}*], or (RNC)(**P**^{1}*)$PdCl_2$. Racemic phospholene, PhPCH=C(Me)CH_2CH_2 (**P**^{3}*), was resolved via the bisphospholene complex, [(*R*)-**Pd**^{2}-(**P**^{3}*)$_2$]. Addition of the achiral diphos, $Ph_2PCH_2CH_2PPh_2$, caused the preferential crystallization of one diastereomeric complex leaving one enantiomeric phospholene ligand in solution. Chiral tertiary phosphines thus obtained are (optical purity and resolving agent) PPh(*t*-Bu)Me (77.8%, **2**); PPh(*t*-Bu)(i-Pr) (~100%, **2**), PhPCH=C(Me)CH_2CH_2 (43.6%, **2**), PPh(α-Naph)-(*p*-PhC_6H_4) (—, **3**), PPh(α-Naph)(*p*-$MeOC_6H_4$) (—, **3**), P(α-Naph)Ph(*o*-MeC_6H_4) (—, **1**), and PPh(α-Naph)(*p*-$EtOC_6H_4$) (—, **1**). The molecular structure and absolute configuration of [(*S*)-isopropyl-*tert*-butylphenylphosphine][(*R*)-*N,N*-dimethyl-α-(2-naphthyl)ethylamine-3*C,N*]chloropalladium(II) has been determined by single-crystal x-ray diffraction methods. The compound crystallizes in the monoclinic space group C_2^2-$P2_1$ with two molecules in the unit cell of dimensions a = 10.409 (4) Å, b = 10.094 (4) Å, c = 13.151 (5) Å, β = 109.38 (2)°, and V = 1303.5 Å^3; ρ_{calcd} = 1.397 and ρ_{obsd} = 1.39 g cm^{-3}. The full-matrix least-squares refinement of the structure resulted in a final agreement index of 0.037 for the 3756 independent data for which $F_o^2 > 3\sigma(F_o^2)$. The palladium complex has a distorted square-planar geometry. The tertiary phosphine is coordinated trans to the amine nitrogen atom while the chloro ligand (Pd–Cl = 2.404 (2) Å) is opposite the ortho-metalated naphthyl ring (Pd–C = 2.049 (2) Å). The Pd–P and Pd–N bond distances are 2.286 (2) and 2.167 (4) Å, respectively. The absolute configuration of the coordinated tertiary phosphine is *S*, thus confirming the predicted configuration based upon stereochemical correlations.

In the last decade catalytic asymmetric syntheses of various types have been achieved with transition metal catalysts containing chiral phosphines.[3] The importance of a chiral center at the phosphorus atom was recognized for some instances of catalytic asymmetric hydrogenation[4] and alkylation.[5] Tedious steps are required to obtain phosphines with a chiral phosphorus atom.[6-11] Previously,[12] we have briefly reported the use of a chiral chelate palladium complex **1** for optical resolution of various triarylphosphines. We have found that **1** is not effective for resolution of tertiary phosphines other than triarylphosphines. Fortunately two other palladium complexes (**2**, **3**) were found to be effective for resolution of tertiary phosphines. The efficiency of each compound, however, varies depending upon the type of phosphines. Therefore, we are interested in elucidating factors determining the resolution efficiency. In this paper we report some details of the



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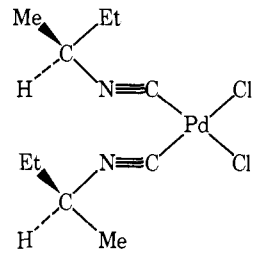

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reaction of **1–3** with tertiary phosphines in solution in order to determine the cause of effective resolution.

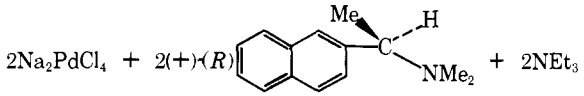
In principle, we should be able to determine the absolute configuration of a tertiary phosphine from stereochemical correlations with the absolute configuration of (+)-(*S*)-methyl-*n*-propylphenylbenzylphosphonium bromide, which was established earlier[13] by x-ray analysis.[9,10,14] However, the determination for PPh(*t*-Bu)R is not possible by this chemical correlation method because *tert*-butyl bromide forms quaternary phosphonium salts with difficulty. An x-ray analysis is thus required to elucidate the absolute configuration of tertiary phosphines containing a *t*-Bu substituent, such as PPh(*t*-Bu)R. In the course of our study, Behrens[15a] reported optical resolution of phosphines of types $PArR^1R^2$ and $PR^1R^2R^3$ by using (+)-(1*R*,5*R*)-π-pinenylnickel halides as the resolving agents. He predicted the absolute configuration of PPh(*t*-Bu)(*i*-Pr) by means of the stereochemical correlation with that of PPh(*t*-Bu)(Me), whose absolute configuration had been determined from an x-ray analysis of (+)-(1*R*,5*R*)-π-pinenylnickel bromide-(*S*)-*tert*-butylmethylphenylphosphine.[15b] Our structural results confirm the predicted absolute configuration.

Results

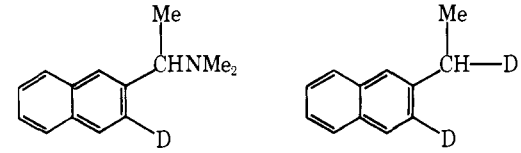
Preparation and Structure of the Resolving Agents. The preparation of (+)-di-μ-chloro-bis[(*S*)-*N*,*N*-dimethyl-α-phenylethylamine-2*C*,*N*]dipalladium(II) (**1**) has been given previously,[12] except for the use of triethylamine as an acceptor of hydrogen chloride. Similarly, (−)-di-μ-chloro-bis[(*R*)-

$$2Na_2PdCl_4 + 2(-)\text{-}(S)\text{-}PhCH(Me)NMe_2 + 2NEt_3 \xrightarrow{\text{in MeOH}} (+)\text{-}\mathbf{1} + 2Et_3N{\cdot}HCl$$

N, *N*-dimethyl-α-(2-naphthyl) ethylamine-3*C*, *N*] dipalladium(II) (**2**) was obtained as pale yellow crystals containing 1



mol of benzene solvent by treating sodium tetrachloropalladate with a 1:1 mixture of (+)-(*R*)-*N*,*N*-dimethyl-α-(2-naphthyl)ethylamine and triethylamine. Degradative deuteration of the complex **2** with $LiAlD_4$ produced β-deuterated naphthalene derivatives (see below) indicative of C-metalation at

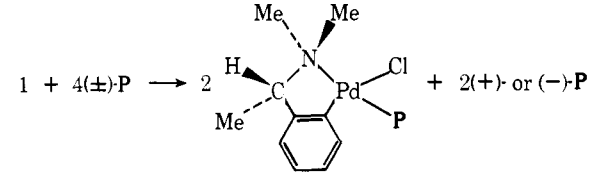


the β carbon atom. A molecular model indicates considerable steric congestion in the α-C-palladated compound. The exclusive formation of **2**, which was confirmed by NMR analysis, probably is the result of steric effects.

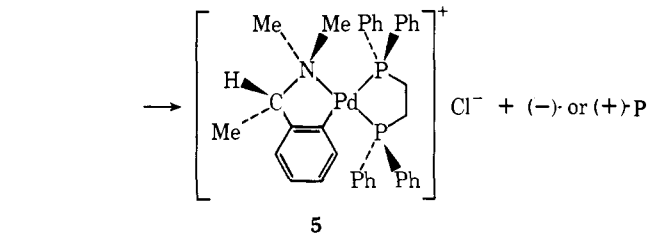
(+)-*cis*-Bis[(*S*)-(*sec*-butyl isocyanide)]dichloropalladium (**3**), prepared from $PdCl_2(NCPh)_2$ and 2 mol of (+)-(*S*)-*sec*-butyl isocyanide, served as another resolving agent. The cis configuration was inferred from the IR spectrum, which contains two Pd–Cl and two N≡C stretching bands.

$$PdCl_2(NCPh)_2 + 2(+)\text{-}(S)\text{-}sec\text{-}BuNC \xrightarrow{\text{benzene}} (+)\text{-}\mathbf{3} + 2PhCN$$

Resolution of Racemic Tertiary Phosphines. As reported previously the formation of less soluble mononuclear phosphine complexes **4** provides a convenient method for resolution of racemic triarylphosphines.[12] A benzene suspension of complex **1** was treated with 4 mol of a racemic phosphine at ambient temperature to form a pale yellow solution. The concentration of the phosphine complex **4** in the homogeneous benzene or toluene solution was adjusted prior to addition of a poor solvent (hexane in most cases) so that upon addition of the solvent (benzene:solvent ca. 1:1 v/v) a slow precipitation of complex **4** ensues. The slow crystallization of **4** leads to the efficient resolution. Thus the partial resolution of PPh(α-Naph)(*o*-MeC_6H_4) and PPh(α-Naph)(*p*-$EtOC_6H_4$) was achieved with **1**.[12] However, the efficiency for resolution of aryldialkylphosphines, e.g., PPh(*t*-Bu)Me, is very low. This appears to result from the comparable solubilities of both of the diastereomeric phosphine complexes in ordinary organic solvents, as will be discussed below. Treatment of **4** with diphos ($Ph_2PCH_2CH_2PPh_2$) in benzene at ambient temperature precipitated the ionic complex **5** almost quantitatively, liberating an optically active phosphine with rotation opposite to that of the phosphine remaining in solution.



4a, P = PPh(α-Naph)(*o*-MeC_6H_4)
b, P = PPh(α-Naph)(*p*-$EtOC_6H_4$)
c, P = PPh(*t*-Bu)Me



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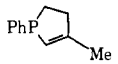
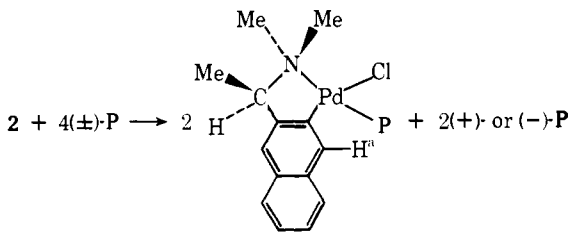
The binuclear palladium complex **2** is a far better resolving agent than **1**, particularly for aryldialkylphosphines such as PPh(*t*-Bu)Me and PPh(*t*-Bu)(*i*-Pr) (see Table I). Upon treating **2** with 4 mol of a racemic phosphine in a fashion similar to that described above, **6** is obtained as insoluble crystals and 2 mol of the resolved phosphine is left in solution.

Table I. Optical Resolution of Tertiary Phosphines[a]

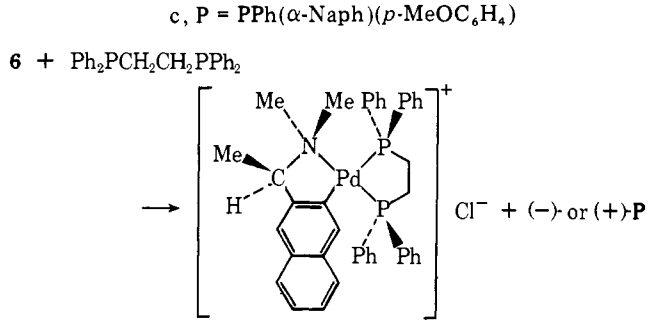
Racemic phosphine	Resolving agent[b]	Isolated yield of phosphine complex, %	Phosphine recovered from complexes $[\alpha]_D$ (t, °C)	OP, %	Yield,[h] %	Unreacted phosphine $[\alpha]_D$ (t, °C)	OP, %	Yield,[i] %
PPh(t-Bu)Me	(+)-(S)-**1**		+0.24° (21)	0.5 (R)[c]	36[j]	−2.0° (23)	3.9 (S)[c]	11
	(−)-(R)-**2**	99	−39.7° (24)	77.8 (S)[c]	71	+36.6° (28)	70.5 (R)[c]	66
	(+)-(S)-**3**	74	0° (20)	0	31	0° (25)	0	52
PPh(t-Bu)(i-Pr)	(−)-(R)-**2**	86	+33.4° (24)	107.3 (R)[d]	76	−19.5° (20)	62.7 (S)[d]	58
	(−)-(R)-**2**	35[j]	−133.3° (24)	43.6[e,k]	21			0
PPh(α-Naph)(p-PhC$_6$H$_4$)	(+)-(S)-**3**	100	+28.2° (23.5)	(R)[f]	54	−27° (32)	(S)[f]	74
PPh(α-Naph)(p-MeOC$_6$H$_4$)	(+)-(S)-**1**	27				0° (24)		56
	(−)-(R)-**2**	75	0° (20)		79	0° (26)		72
	(+)-(S)-**3**	51	+2.7° (25)	[g]	55	−3.5 (28)	[g]	24

[a] Four moles (for **1** and **2**) or 2 mol (for **3**) of phosphine per mol of resolving agent were used. [b] (+)-(S)-**1**, op 95.1%; (−)-(R)-**2**, op 99.5%; (+)-(S)-**3**, op 92.7%. [c] Calculated from the absolute rotation, $[\alpha]^{20}_D \pm 51.1°$ (ref 15a). [d] Calculated from the absolute rotation, $[\alpha]^{20}_D \pm 31.1°$ (ref 15a). [e] Optical rotation reported in the literature: $[\alpha]^{25}_D -32.1°$ (ref 18). [f] Optical rotation reported in the literature: $[\alpha]^{25.4}_{578} +8.7°$ (ref 19). [g] Optical rotation reported in the literature: $[\alpha]_D +2.9°$ (ref 7). [h] Based on the phosphine complex. [i] Based on the starting racemic phosphine. [j] Bisphosphine complex, **8a**. [k] Calculated from ^{1}H NMR spectrum.

The trans alignment of the phosphine ligand to the nitrogen ligand in complex **6** is inferred from the presence of the long-range coupling between the N-methyl protons and the phosphorus atom (see Experimental Section). The α-proton (H^a) signal at the C-4 position of the naphthalene ring appears as a doublet with a coupling constant of ~6 Hz, an unusually large value for a long-range magnetic interaction with the phosphorus atom; the coupling probably results from a "direct" through-space interaction. The optical rotation of the free phosphine is opposite to that of the phosphine liberated upon formation of complex **7** from **6** and diphos. The optical rotation of the PPh(t-Bu)(i-Pr) recovered from the corresponding mononuclear complex **6b** exceeds the maximum reported value.[15a]



6a, P = PPh(t-Bu)Me
b, P = PPh(t-Bu)(i-Pr)
c, P = PPh(α-Naph)(p-MeOC$_6$H$_4$)



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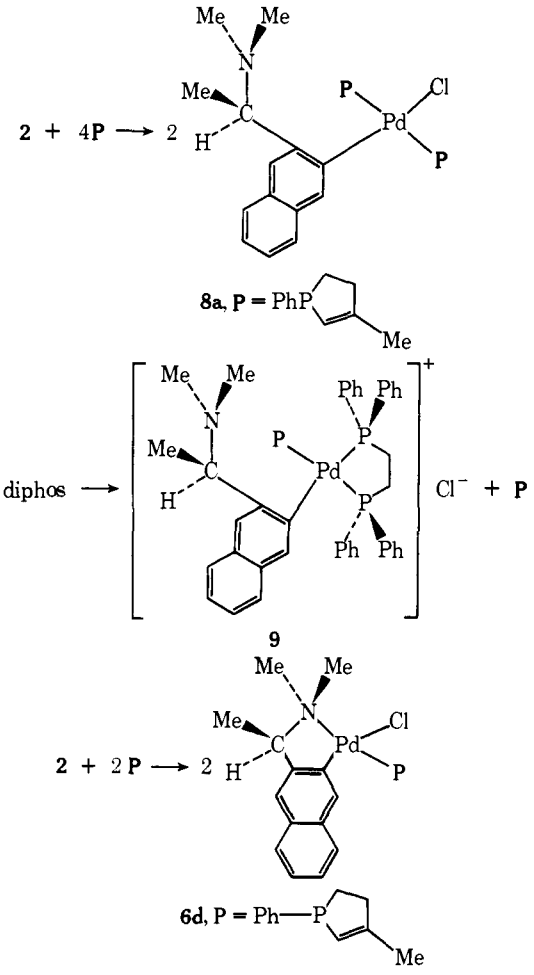
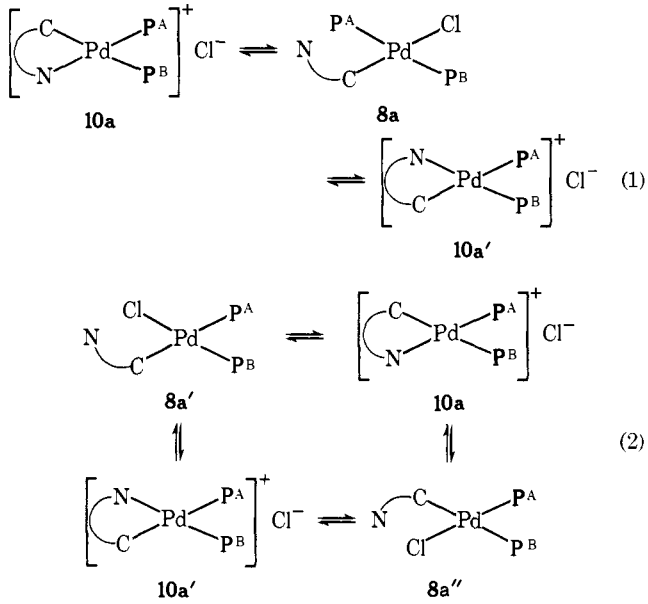
The ^{1}H NMR spectrum of complex **6a** formed in situ from 1 mol of (−)-(R)-**2** with 2 mol of partially resolved (−)-(S)-PPh(t-Bu)Me shows a pair of signals from two diastereomeric complexes, one containing the (S)-phosphine and the other containing the (R)-phosphine. The ratio (3.15:1) of these diastereomers found in the ^{1}H NMR peak assignable to, e.g., CH_3CHN, coincides well with the S/R ratio of the starting phosphine, i.e., 54% optical purity.

The compound 1-phenyl-3-methyl-2-phospholene can also be resolved with **2.** In the reaction mixture of **2** and 4 mol of the phospholene in benzene, free phosphine was not found. All the phospholene molecules coordinate to Pd(II) yielding a rather soluble bisphosphine complex **8a.** Addition of 2 mol of the phospholene to **2** results in a homogeneous solution. Upon concentration a monophosphine complex **6d** was isolated as a mixture of 1:1 diastereomers, which was confirmed by the ^{1}H NMR spectrum. Thus, no preferential coordination of one enantiomeric phospholene takes place in the formation of **6d.** The molecular structure of **6d** is readily established as analogous to those of **6a–c** from the similarity in the ^{1}H NMR spectra. The complex **8a** is characterized by elemental analyses, conductivity measurements, and its ^{1}H NMR spectrum. The molecular structure of **8a** was assumed tentatively to involve a trans alignment of phospholene ligands in view of the established structure of an analogous complex, *trans*-cholorobis(triethylphosphine)[2-phenylazo)phenyl]-palladium(II).[16] A dichloromethane solution of **8a** shows a small molar conductance which is much lower than that expected for a 1:1 electrolyte, such as the ionic complexes **7** or **9.** The ^{1}H NMR spectrum of **8a** shows a reversible temperature dependence. The olefinic proton signals of the coordinated phospholene ligands appear as a very broad doublet ($J_{PH} \cong$ 32 Hz) at δ 5.64 at 35 °C which gives rise at −50 °C to two doublets at δ 5.88 (J_{PH} = 32 Hz) and 6.03 (J_{PH} = 32 Hz) and additional broad signals spreading from δ 4.30 to δ 5.56. The spectral change suggests the presence of a few species of unknown structure at low temperature. Several mechanisms are conceivable for the phosphine ligand equilibration. If **8a** assumes a trans structure as shown, then the equilibration could be achieved through the formation of ionic compounds **10a** and **10a'** (eq 1), or by an S_Ni mechanism postulated for the equilibration in an analogous Pt(II) compound, *trans*-chloro-



bis(methyldiphenylphosphine)[2-(phenylazo)phenyl]platinum(II).[17] If **8a** assumes a cis structure, the equilibration would take place through the route shown in eq 2.



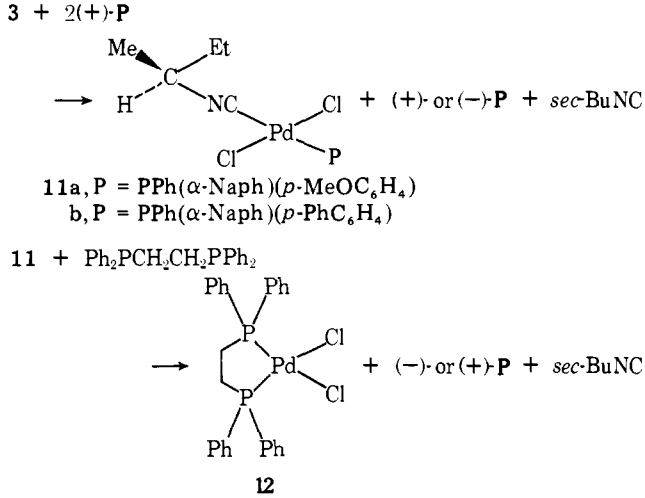
The reaction of **8a** with 1 mol of **2** gives 2 mol of a monophosphine complex **6d.**

$$\mathbf{8a} + \mathbf{2} \rightarrow 2\ \mathbf{6d}$$

The ^{1}H NMR spectrum of **6d** shows two sets of olefinic, *N*-methyl, and *C*-methyl proton signals of equal intensity, indicative of the presence of two diastereomeric complexes in a 1:1 ratio. This implies no preference in configuration of the two phospholene ligands for the formation of **8a.** Hence, the enantiomeric phospholene ligands in **8a** are present in equal amounts. Nevertheless the phospholene liberated from **8a** by treating with diphos is optically active. This is rather surprising.

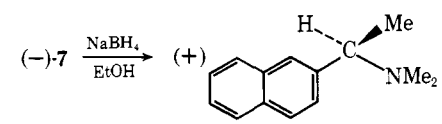
Treatment of **8a** with diphos in benzene at ambient temperature causes slow precipitation of an ionic complex **9** as colorless crystals, and only 1 mol of the two phospholene ligands is liberated. Remarkably, the liberated phospholene shows much higher optical rotation, $[\alpha]^{23}_D$ −133.3° (C_6H_6, *c* 0.83), than the reported value, $[\alpha]^{25}_D$ +32.1° (neat).[18] Unfortunately, the isolated yield is very low owing to polymerization of the phospholene during isolation. The ^{1}H NMR spectrum of the monophospholene complex, **6d,** prepared from (−)-(*R*)-**2** and 2 mol of the optically active phospholene (resolved as above) shows two diastereomeric complexes in a ratio of 1:2.6. This means that the optical purity of the resolved phospholene is 44%. Consistently, the ionic complex **9** that is precipitated from the mixture of **8a** and diphos is also present as a mixture of an essentially similar molar ratio of the two diastereomers, as deduced from the ^{1}H NMR spectrum.

Unexpectedly, **2** is not effective for resolution of triarylphosphines, e.g., PPh(α-Naph)(*p*-PhC_6H_4) and PPh(α-Naph)(*p*-$MeOC_6H_4$). The third resolving agent, (+)-*cis*-bis[(*S*)-*sec*-butyl isocyanide]dichloropalladium (**3**), proved to be a powerful resolving agent for triarylphosphines. The cis isocyanide complex **3,** when treated with an excess of a triarylphosphine, produces exclusively a trans isocyanide–phosphine mixed ligand complex (**11**); a bisphosphine complex was



not formed. The optical rotations ($[\alpha]^{23.5}_D$ +28.2° or $[\alpha]^{32}_D$ −27°) of the resolved (+)- or (−)-PPh(α-Naph)(*p*-PhC_6H_4) are very high in view of the reported value, $[\alpha]^{25.4}_{578}$ +8.7°.[19] The optical rotations of (+)- or (−)-PPh(α-Naph)(*p*-$MeOC_6H_4$) ($[\alpha]^{25}_D$ +2.7 and $[\alpha]^{28}_D$ −3.5°, respectively) are also comparable with the reported rotation, $[\alpha]_D$ +2.9°.[7] The efficiency of a particular resolving agent varies drastically with the type of tertiary phosphine.

Degradative hydrogenation of the diphosphine complex, **7,** with $NaBH_4$ liberates the starting amine ligand in good yield without loss of optical purity. Therefore, the recovered amine can be used repeatedly for the resolution.



Molecular Structure of [(*S*)-Isopropyl-*tert*-butylphenylphosphine][(*R*)-*N,N*-dimethyl-α-(2-naphthyl)ethylamine-3*C,N*]chloropalladium(II) (6b). The structure consists of two

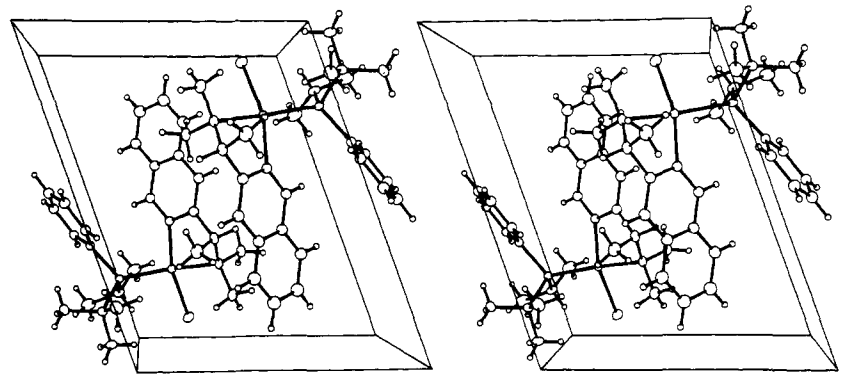


Figure 1. A stereoscopic drawing of the unit cell of $PdCl(C_{14}H_{16}N)(PPh(t\text{-}Bu)(i\text{-}Pr))$. The y axis is perpendicular to the plane of the paper going away from the reader; the z axis is approximately vertical, and the x axis is horizontal and to the right. The thermal ellipsoids are drawn at the 20% probability level. For clarity the hydrogen atoms have been arbitrarily assigned a small thermal parameter of 1 Å^2.

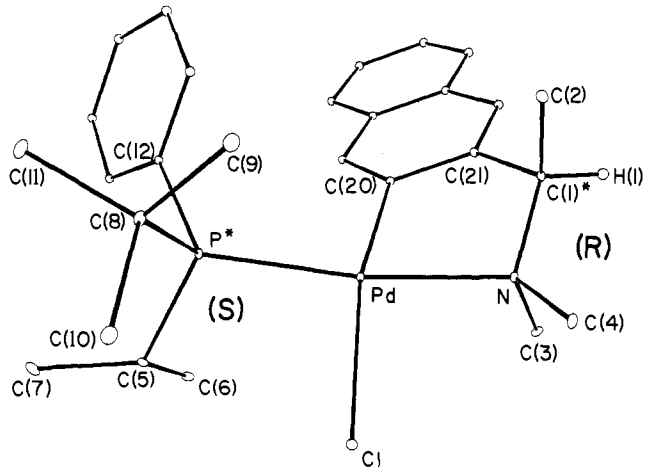


Figure 2. A perspective view of the palladium complex. In order to emphasize the absolute configuration of the complex, the atoms are shown only at the 1% probability contour of thermal motion. The asterisks denote the two asymmetric centers.

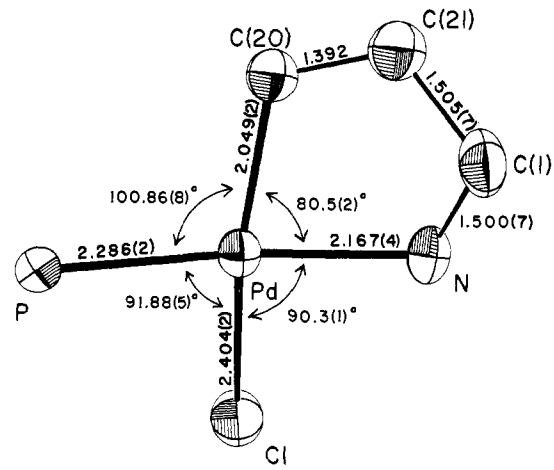


Figure 3. View of the inner coordination geometry about the palladium atom. The thermal ellipsoids are drawn at the 50% probability level.

discrete molecules of **6b** per unit cell as shown in the stereoview of the molecular packing in Figure 1. The four-coordinate palladium(II) complex has square-planar geometry. The amine ligand is attached to the metal center by the nitrogen atom and an ortho-metalated carbon atom on the naphthyl ring. The tertiary phosphine ligand is coordinated trans to the nitrogen atom while the chloro ligand is opposite the naphthyl carbon atom as predicted from the ^1H NMR study. An overall view of the complex emphasizing the absolute configuration is given in Figure 2. A view of the inner coordination sphere of the palladium complex is given in Figure 3. Bond distances and angles in the complex, along with standard deviations as estimated from the inverse matrix, are listed in Table II. Torsion angles within the five-membered Pd-N-C(1)-C(21)-C(20) ring are also given in Table II. The significant deviation of the palladium complex from planar geometry is shown in Table III in which selected least-squares planes are presented.

The structural results show that the absolute configuration of the complex is S for the phosphine center and R about the asymmetric carbon atom of the amine ligand. The complex comprised of the resolving agent, (−)-(R)-**2**, and the (R)-PPh(t-Bu)(i-Pr) tends to precipitate from benzene–n-hexane leaving the (S)-PPh(t-Bu)(i-Pr) in solution.[20]

Discussion

The extent of chiral recognition upon coordination of tertiary phosphines in solution may be examined by means of ^1H NMR spectra. The ^1H NMR spectrum of a mixture of 1 mol of (−)-(R)-**2**, abbreviated as [(R)-**M**]$_2$, and 2 mol of (±)-PPh(t-Bu)Me ((R)- and (S)-**P**) in $CDCl_3$ shows the presence of the two diastereomeric complexes (R)-**M**[(R)-**P**] and (R)-**M**[(S)-**P**] in an equimolar amount, as detected by the intensities of signals at P–CH_3, C–CH_3, –CH–, etc. No other signals ascribable to **2** and the free phosphine can be detected. This indicates (1) large formation constants for both diastereomeric isomers and (2) the absence of rapid phosphine ligand exchange between these two diastereomeric complexes in a solution containing no free phosphine.

$$[(R)\text{-}\mathbf{M}]_2 + (R)\text{-}\mathbf{P} + (S)\text{-}\mathbf{P} \rightleftharpoons (R)\text{-}\mathbf{M}[(R)\text{-}\mathbf{P}] + (R)\text{-}\mathbf{M}[(S)\text{-}\mathbf{P}] \quad (3)$$

With respect to the chiral recognition upon complexation of the phosphine, there may be some difference in the rates of formation of the two diastereomers (R)-**M**[(R)-**P**] and (R)-**M**[(S)-**P**]. Owing to the rapid rate of formation, NMR methods do not provide kinetic information on chiral recognition. That the formation constants are large is consistent with the observation that two diastereomeric complexes of **6**, formed from 1 mol of **2** and 2 mol of an optically active phosphine, exist in solution in a ratio, as determined from ^1H NMR spectra, that reflects the enantiomeric excess of the added phosphine, $PPhR_1R_2$. The large formation constant for (R)-**M**[(R)-**P**] or (R)-**M**[(S)-**P**] appears at first sight to be inconsistent with the finding of a large excess of one enantiomeric phosphine in the solution prepared from **2** and 4 mol of free racemic phosphine. Rapid ligand exchange in the presence of excess phosphine must be postulated to account for the preferential crystallization of one diastereomer (R)-**M**[(R)-**P**] or (R)-**M**[(S)-**P**] upon addition of a poor solvent.

Table II. Selected Bond Distances (Å) and Angles (deg) in $PdCl(C_{14}H_{16}N)(PPh(t\text{-}Bu)(i\text{-}Pr))$

Atoms	Distance	Atoms	Distance
Pd-Cl	2.404 (2)	N-C(4)	1.480 (7)
Pd-P	2.286 (2)	C(1)-C(2)	1.506 (9)
Pd-N	2.167 (4)	C(1)-C(21)	1.505 (7)
Pd-C(20)	2.049 (2)	C(5)-C(6)	1.520 (10)
P-C(5)	1.861 (6)	C(5)-C(7)	1.518 (9)
P-C(8)	1.905 (5)	C(8)-C(9)	1.512 (10)
P-C(12)	1.850 (4)	C(8)-C(10)	1.535 (8)
N-C(1)	1.500 (7)	C(8)-C(11)	1.537 (8)
Atoms	**Angle**	**Atoms**	**Angle**
Cl-Pd-P	91.88 (5)	N-C(1)-C(21)	106.3 (4)
Cl-Pd-N	90.3 (1)	C(2)-C(1)-C(20)	105.2 (4)
P-Pd-C(20)	100.86 (9)	C(2)-C(1)-C(21)	109.9 (5)
N-Pd-C(20)	80.5 (2)	P-C(5)-C(6)	109.6 (4)
P-Pd-N	166.6 (1)	P-C(5)-C(7)	117.7 (5)
Cl-Pd-C(20)	161.37 (8)	C(6)-C(5)-C(7)	113.3 (5)
Pd-P-C(5)	109.9 (2)	P-C(8)-C(9)	108.5 (3)
Pd-P-C(8)	107.5 (2)	P-C(8)-C(10)	110.8 (5)
Pd-P-C(12)	118.3 (1)	P-C(8)-C(11)	112.2 (4)
C(5)-P-C(8)	108.8 (3)	C(9)-C(8)-C(10)	108.0 (5)
C(5)-P-C(12)	108.4 (2)	C(9)-C(8)-C(11)	109.8 (6)
C(8)-P-C(12)	103.5 (2)	C(10)-C(8)-C(11)	107.5 (4)
C(1)-N-Pd	104.8 (3)	C(13)-C(12)-P	122.4 (2)
C(3)-N-Pd	108.3 (4)	C(17)-C(12)-P	117.5 (3)
C(3)-N-C(1)	110.8 (4)	C(19)-C(20)-Pd	127.3 (2)
C(4)-N-Pd	113.7 (3)	C(21)-C(20)-Pd	112.2 (2)
C(4)-N-C(1)	111.2 (4)	C(20)-C(21)-C(1)	117.7 (2)
C(4)-N-C(3)	108.1 (4)	C(22)-C(21)-C(1)	122.2 (3)
N-C(1)-C(2)	113.9 (4)		
	Torsion Angles		
Pd-N-C(1)-C(21)	−44.5 (3)	C(21)-C(20)-Pd-N	−13.8 (2)
N-C(1)-C(21)-C(20)	37.9 (4)	C(20)-Pd-N-C(1)	33.0 (3)
C(1)-C(21)-C(20)-Pd	−9.3 (4)		

Table III. Selected Weighted Least-Squares Planes in $PdCl(C_{14}H_{16}N)(PPh(t\text{-}Bu)(i\text{-}Pr))$

	$Ax + By + Cz = D$[a]			
Plane	*A*	*B*	*C*	*D*
1	1.559	−9.327	3.712	0.916
2	1.813	−9.185	3.910	0.863
3[b]	6.991	−7.457	−2.223	1.012

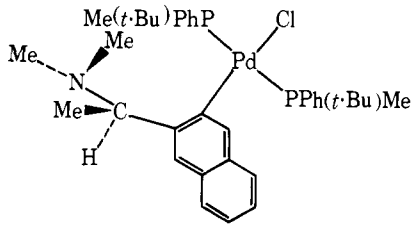
Distance (Å) of Various Atoms from the Planes

Atom	Plane 1	Plane 2	Plane 3
Pd	0.093	0.0004 (1)	−0.239
Cl	−0.074 (2)[c]	−0.120 (2)	−1.249
P	0.046 (1)	0.025 (1)	0.827
N	0.635 (4)	0.475 (4)	−0.800
C(20)	−0.235 (3)	−0.381 (3)	0.000

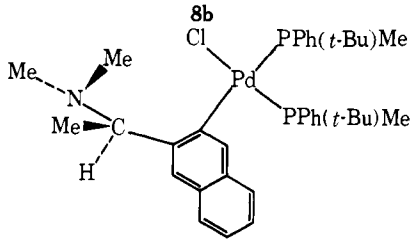
Dihedral Angles between Planes
Plane 1-plane 2 = 2.1°
Plane 1-plane 3 = 36.6°
Plane 2-plane 3 = 35.8°

[a] Monoclinic coordinates. [b] Plane of the naphthyl ring. [c] Numbers with estimated standard deviations given in parentheses indicate the atoms which determined each of the least-squares planes.

The solution species involved in the mixture of 1 mol of (−)-(*R*)-**2** and 4 mol of racemic PPh(*t*-Bu)Me in $CDCl_3$ (35 °C) was investigated by ^1H NMR methods. The spectrum does not contain signals assignable to **6a** or the free phosphine; instead it shows quantitative formation of **8b** (see Experimental Section). Two inequivalent *t*-Bu proton signals observed at



8b

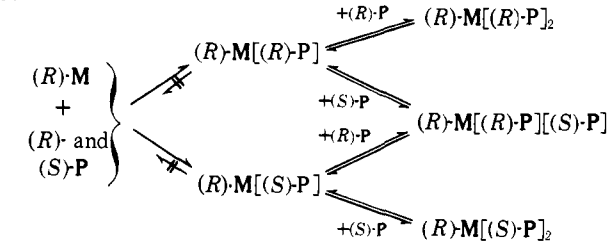


8b′

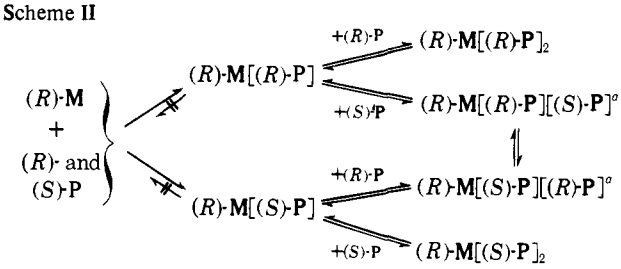
8b or **8b′** ⇌ **6a** + PPh(*t*-Bu)Me (4)

room temperature are consistent with the cis structure (**8b′**). The spectrum, however, is also consistent with the trans structure (**8b**) containing the two diastereotopic phosphines. Thus, a choice between **8b** and **8b′** cannot be made using the present ^1H NMR data. A sharp singlet for *N*-methyl groups indicates that the nitrogen atom is not coordinated. Three diastereomers are possible for complex **8b** with racemic phosphines, while four diastereomers are possible for **8b′**. In the absence of rapid ligand exchange these should be distinguishable, in principle, by ^1H NMR methods. For example, *t*-Bu groups should give rise to four doublet signals for **8b** and eight doublet signals for **8b′**. Clearly the observed spectrum lacks such splittings. The very broad complex signals, observed at −60°, again suggest a rapid exchange of phosphine ligands. These results suggest equilibria involving a ligand exchange, Scheme I for **8b** or Scheme II for **8b′**. No predominant species

Scheme I



Scheme II



[a] These two could be geometrical isomers.

was detected in solution. However, upon precipitation, either by cooling or by adding portions of a poor solvent such as *n*-hexane, the crystalline compound formed consists of only one diastereomer of **6a**. After complete precipitation of the diastereomer of **6a** the free optically active phosphine can be recovered from the solution. The equilibrium 4 in solution ap-

parently shifts toward the right upon precipitation of the less soluble diastereomer leaving the enantiomeric phosphine in solution. Consequently, the efficiency of this resolution depends on the solubility difference between the complexes (*R*)-**M**[(*R*)-**P**] and (*R*)-**M**[(*S*)-**P**].

A similar argument is possible for the resolution of 1-phenyl-3-methyl-2-phospholene with (−)-(*R*)-**2.** Here also no preferential coordination of one enantiomer of the phospholene in the formation of the bis(phospholene) complex **8a** was found from ^{1}H NMR spectra. A question then arises as to the reason why we have a successful optical resolution of the phospholene through the monophospholene(diphos) complex **9.** In order to solve this problem, the complex **9** was prepared by the reaction of the ionic diphos complex **7** with the racemic phospholene. The ^{1}H NMR ($CDCl_3$) spectrum was then examined. The presence of two diastereomeric complexes of **9** in an equimolar amount was clearly indicated since the two methyl signals of the coordinated phospholene ligand show equal intensity. Thus the diastereomers are formed in solution in approximately equal amounts and the efficiency of the resolution depends on the solubility difference between the complexes, (*R*)-**M**[(*R*)-**P**](diphos) and (*R*)-**M**[(*S*)-**P**](diphos). Alternatively, the following explanation is conceivable. Chiral recognition is a factor, with preferred formation of one diastereomer of **6d** as the initial step. The complex **6d** then exerts stereochemical recognition in the binding of the second phosphine. (If the latter is of opposite sense to the first one then it would appear that a racemic mixture binds indiscriminately.) The reaction with diphos should lead to preferential cleavage of one phospholene which in turn results in partial resolution. This explanation seems totally unreasonable since no preferential coordination of one enantiomeric phospholene is observed in the reaction with **2.** Moreover, in the formation of **9** no chiral recognition was found; hence there is no preferential cleavage of one phospholene in the reaction of **8a** with diphos.

The same phosphines, PPh(*t*-Bu)Me and PPh(*t*-Bu)(*i*-Pr), have been resolved also by use of (+)-(1*R*,5*R*)-π-pinenylnickel halides as resolving agents.[15a] As a resolving agent, the palladium complex **2** has several advantages compared with the nickel complexes. The air stability of **2** facilitates the manipulation required for the resolution. The rapid crystallization of the phosphine adduct of **2** compared with the nickel–phosphine complexes is a time-saving feature. The efficiency of the resolution depends on the phosphines in both cases. The phosphine PPh(*t*-Bu)(*i*-Pr), $[\alpha]^{24}_D$ +33.4°, resolved with (−)-(*R*)-**2** shows a higher enantiomeric excess, while the phosphine resolved with the nickel complex shows an optical rotation of $[\alpha]^{20}_D$ −21.9° (cf. the reported maximum optical rotation for the phosphine, $[\alpha]^{20}_D$ ±31.1°).[15a] Yet the phosphine PPh(*t*-Bu)Me resolved with (−)-(*R*)-**2** shows an optical purity of 77.8%, while the phosphine resolved with the nickel complex shows an optical purity of 96.6%, based on the reported maximum rotation, $[\alpha]^{20}_D$ ±51.1°.[15a]

One of the most conspicuous features of the molecular structure of **6b** is the proximity of the two aromatic rings. This type of nonbonded attraction between aromatic groups was observed in M[PPh(*t*-Bu)$_2$]$_2$[21] and MO_2[PPh(*t*-Bu)$_2$]$_2$ (M = Pd, Pt).[22] The molecular model of **6b** indicates that the phenyl plane must be oriented as found (Figure 1), so as to avoid contact with the naphthyl ring. Consistently the naphthyl α proton of **6b** shows an extraordinary high field resonance (δ 6.49). The appearance of two resonances (δ 6.55 and 6.49) in the ^{1}H NMR spectrum of a diastereomeric mixture of **6b** indicates that the proximity of the phenyl and the naphthyl rings is retained in solution for both diastereomeric complexes **6b** at ambient temperature. Assuming the proximity of the two aromatic rings, we may fix the direction of the phenyl–P bond with respect to the molecular plane of the diastereomers **6a** and **6b.** We may then examine the effect of the relative size of the two alkyl substituents of the chiral phosphorus atom on the molecular structure. Any significant difference in compactness of the molecular structure is hardly discernible between (*R*)-**M**[(*S*)-**P**] and (*R*)-**M**[(*R*)-**P**]. At least the molecular structure of **6b** (**P** = PPh(*t*-Bu)(*i*-Pr)), as determined by the x-ray analysis, does not provide an obvious reason for a solubility difference between the (*R*)- and (*S*)-*tert*-phosphine containing complexes. In fact, the two phosphines, PPh(*t*-Bu)Me and PPh(*t*-Bu)(*i*-Pr), liberated from the corresponding palladium complex are of opposite absolute configuration, *S* and *R*, respectively. This clearly indicates that slight differences in the steric and electronic properties of phosphine ligands cause a marked difference in the efficiency for packing of these molecules in the solid state. The relative efficiency of **1** and **2** as resolving agents also suggests the importance of lattice energy in the present optical resolution tactics.

Although the present systems lack a chiral recognition ability in solution, it may not be impossible to gain such ability by a suitable modification of the molecular structure.

Experimental Section

All preparations and resolutions were carried out under an atmosphere of nitrogen. Melting points were measured with a Yanagimoto MP-2 micromelting-point apparatus. All IR, ^{1}H NMR spectra, and optical rotations were recorded on a Hitachi Perkin-Elmer 225, a JEOL JNM 4H-100, or a JEOL JNM C-60HL, and a Jasco automatic polarimeter DIP-SL, respectively.

(−)-(*S*)-*N,N*-Dimethyl-α-phenylethylamine, bp 85–88 °C (26 mm), $[\alpha]^{24}_D$ −68.3° (neat),[23] and (+)-(*R*)-*N,N*-dimethyl-α-(2-naphthyl)ethylamine, bp 113–116 °C (2 mm), $[\alpha]^{28}_D$ +49.9° (*c* 3.28, EtOH), were prepared by methylation[24] of (−)-(*S*)-α-phenylethylamine, $[\alpha]^{25}_D$ −32.9° (*c* 3.3, C_6H_6),[25] and (+)-(*R*)-α-(2-naphthyl)ethylamine, $[\alpha]^{24}_D$ +18.9° (*c* 1.60, EtOH),[26] respectively. (+)-(*S*)-*sec*-Butyl isocyanide, $[\alpha]^{20}_D$ +39.7° (*c* 8.0, $CHCl_3$), was prepared from (+)-(*S*)-*sec*-butylamine, $[\alpha]^{20}_D$ +6.9° (neat), by a known method.[27] Racemic 1-phenyl-3-methyl-2-phospholene [bp 90–95 °C (2 mm)],[28] *p*-methoxyphenyl-α-naphthylphenylphosphine,[7] α-naphthylphenyl-*o*-tolylphosphine (mp 109–111 °C),[7] *p*-ethoxyphenyl-α-naphthylphenylphosphine (mp 148–150 °C),[7] and *p*-biphenyl-α-naphthylphenylphosphine (mp 195–196 °C)[7] were prepared according to known methods. Racemic *tert*-butylmethylphenylphosphine [bp 108–110 °C (10 mm)] and *tert*-butylphenylisopropylphosphine [bp 96–97 °C (5 mm)] were prepared from *tert*-butylchlorophenylphosphine according to literature methods.[29]

(+)-Di-μ-chloro-bis[(*S*)-*N,N*-dimethyl-α-phenylethylamine-2*C*,*N*]dipalladium (1). A mixture of Na_2PdCl_4 (0.02 mol), (−)-(*S*)-*N,N*-dimethyl-α-phenylethylamine (0.02 mol), and triethylamine (0.02 mol) in methanol (100 mL) was stirred at room temperature for 2 h. The solid obtained by filtration was washed with methanol, dried in vacuo, and recrystallized from benzene to give **1** in 65% yield as pale yellow crystals: mp 186–189 °C dec; $[\alpha]^{26}_D$ +72.1° (*c* 0.36, C_6H_6); IR (Nujol) 295 cm^{-1} (Pd–Cl).

Anal. ($C_{20}H_{28}Cl_2N_2Pd_2$) C, H, N, Cl.

(−)-Di-μ-chloro-bis[(*R*)-*N,N*-dimethyl-α-(2-naphthyl)ethylamine-3*C*,*N*]dipalladium (2). Compound **2** containing 1 mol of benzene was prepared similarly from Na_2PdCl_4 (0.029 mol), (+)-(*R*)-*N,N*-dimethyl-α-(2-naphthyl)ethylamine (0.03 mol), and triethylamine (0.03 mol) as pale yellow crystals (C_6H_6) in 65% yield: mp 201.5–203 °C dec; $[\alpha]^{30}_D$ −12.9° (*c* 0.85, $CHCl_3$); IR (Nujol) 265 and 312 cm^{-1} (Pd–Cl); NMR ($CDCl_3$) δ 1.68 (d, *J* = 6.5 Hz, 6, CCH_3), 2.95 (s, 6, NCH_3), 3.98 (q, *J* = 6.5 Hz, 2, –CH–), 7.15–7.85 (m, 18, aromatic).

Anal. ($C_{28}H_{32}Cl_2N_2Pd_2 \cdot C_6H_6$) C, H, N, Cl.

(+)-*cis*-Dichlorobis[(*S*)-*sec*-butyl isocyanide]palladium (3). To a benzene solution (30 mL) of $PdCl_2(NCPh)_2$ (3.0 mmol) was added 0.66 mL (6.0 mmol) of (+)-(*S*)-*sec*-butyl isocyanide. The reddish-brown mixture was stirred at room temperature to give a pale yellow solution. A routine workup gave complex **3** as colorless crystals, 0.95 g (91%): mp 165–168 °C; $[\alpha]^{26}_D$ +33.0° (*c* 2.56, $CHCl_3$); IR (Nujol) 2260, 2240 (N≡C), and 337, 318 cm^{-1} (Pd–Cl); NMR ($CDCl_3$) δ 1.10 (t, *J* = 7.5 Hz, 3, CH_2CH_3), 1.58 (d, *J* = 6.0 Hz, 3, $-CHCH_3$), 1.78 (m, *J* = 7.5 Hz, 2, $-CH_2-$), 4.00 (m, 1, –CH–).

Anal. ($C_{10}H_{18}Cl_2N_2Pd$) C, H, N, Cl.

Resolution of Tertiary Phosphines. We give as a typical example the resolution of *tert*-butylmethylphenylphosphine with the complex (−)-(*R*)-**2**. To a benzene suspension (100 mL) of the palladium complex (−)-(*R*)-**2** (13.9 mmol) was added a benzene solution (100 mL) of (±)-*tert*-butylmethylphenylphosphine (28.4 mmol) and the reaction mixture was stirred at room temperature for 1 h. After some decomposition products were removed by filtration, the filtrate was condensed in vacuo to ca. 20 mL volume. Then 30 mL of *n*-hexane was added and the solution was left undisturbed overnight at room temperature. Yellow crystals of **6a** [P = PPh(*t*-Bu)Me] precipitated in 99% yield (7.16 g): mp 213–215 °C dec; $[\alpha]^{24}_D$ +88.7° (*c* 1.82, C_6H_6); IR (Nujol) 290 cm^{-1} (Pd–Cl).

Anal. ($C_{25}H_{33}ClNPPd$) C, H, N, Cl.

Upon distillation of the mother liquor in vacuo, 1.71 g (65.7%) of PPh(*t*-Bu)Me was recovered in an optically active form: bp 30 °C (10^{-4} mm); $[\alpha]^{28}_D$ +36.6° (*c* 3.34, C_6H_6).

Treatment of the complex **6a** [P = PPh(*t*-Bu)Me] (11.6 mmol) with bis(diphenylphosphino)ethane (12.7 mmol) in benzene (45 mL), followed by addition of *n*-hexane (20 mL), gave 8.10 g (94.5%) of colorless powder of **7** containing 2 mol of water of crystallization: mp 202–203 °C dec; $[\alpha]^{22}_D$ −27.0° (*c* 1.11, $CHCl_3$); Λ_M (molar conductance, 1.48 × 10^{-2} mol L^{-1} in CH_2Cl_2, 25 °C) 34.4 ohm^{-1} cm^2.

Anal. ($C_{40}H_{40}ClNP_2Pd{\cdot}2H_2O$) C, H, N, Cl.

From the mother liquor (−)-(*S*)-*tert*-butylmethylphenylphosphine was isolated by vacuum distillation, 1.48 g (71%): bp ~30 °C (10^{-4} mm); $[\alpha]^{24}_D$ −39.7° (*c* 4.88, C_6H_6). The optical purity (77.8%) of the phosphine, liberated from the complex **6a**, is slightly lower than that expected from the ^1H NMR spectra of **6a**, probably because of racemization during the isolation process.

Similarly (−)-(*R*)-**2 and** (±)-**PPh(*t*-Bu)(*i*-Pr)** gave **6b** [P = Ph(*t*-Bu)(*i*-Pr)] as pale yellow crystals [mp 219–222 °C; $[\alpha]^{24}_D$ −174° (*c* 0.53, $CHCl_3$); IR (Nujol) 284 cm^{-1} (Pd–Cl)] and (−)-PPh(*t*-Bu)(*i*-Pr), bp 40 °C (10^{-4} mm).

Anal. ($C_{27}H_{37}ClNPPd$, **6b**) C, H, N, Cl.

From the amine–phosphine complex (−)-**6b**, (+)-PPh(*t*-Bu)(*i*-Pr) was liberated.

(−)-(*R*)-**2 and** (±)-**PPh(α-Naph)(*p*-MeOC$_6$H$_4$)** gave **6c** [P = Ph(α-Naph)(*p*-$MeOC_6H_4$)]: mp 203–207 °C; $[\alpha]^{26}_D$ −5.19° (*c* 7.52, C_6H_6); IR (Nujol) 288 cm^{-1} (Pd–Cl).

Anal. ($C_{37}H_{35}ClNOPPd$) C, H, N, Cl.

The excess phosphine, recovered from the mother liquor, is optically inactive, probably owing to an insufficient solubility difference between the two diastereomers of **6c**.

Resolution of (±)-1-Phenyl-3-methyl-2-phospholene with (−)-(*R*)-2. To a stirred toluene suspension (50 mL) of the complex (−)-(*R*)-**2** (26.2 mmol) was added the phospholene (52.7 mmol) and stirring was continued for 1 h at room temperature to give a pale reddish brown solution. After addition of *n*-hexane (40 mL) the solution was kept at ca. −20 °C for a few days. Almost colorless crystals of the bisphosphine complex, **8a**, were isolated after recrystallization from a toluene–*n*-hexane mixture in 35.2% yield (6.41 g): mp 143–146 °C; $[\alpha]^{26}_D$ −19.7° (*c* 1.47, $CHCl_3$); IR (Nujol) 298, 286 cm^{-1} (Pd–Cl); Λ_M (1.51 × 10^{-2} mol L^{-1} in CH_2Cl_2, 25 °C) 11.7 ohm^{-1} cm^2.

Anal. ($C_{36}H_{42}ClNP_2Pd$) C, H, N, Cl.

From the mother liquor, free phospholene could not be isolated at all by distillation in vacuo. Treatment of the complex **8a** (7.88 mmol) with bis(diphenylphosphino)ethane (7.89 mmol) in benzene (150 mL), followed by addition of hexane (50 mL), gave 6.07 g (82.6%) of a colorless, crystalline powder of **9** containing 1 mol of water of crystallization: mp 104–107 °C; $[\alpha]^{25}_D$ −52.3° (*c* 1.58, $CHCl_3$); Λ_M (1.16 × 10^{-2} mol L^{-1} in CH_2Cl_2, 25 °C) 35.6 ohm^{-1} cm^2.

Anal. ($C_{51}H_{53}ClNP_3Pd{\cdot}H_2O$) C, H, N, Cl.

From the mother liquor (−)-1-phenyl-3-methyl-2-phospholene was isolated by vacuum distillation, 0.30 g (21.4%): bp ~30 °C (10^{-4} mm); $[\alpha]^{23}_D$ −133.3° (*c* 0.83, C_6H_6).

(−)-(*R*)-**2 and 2 mol of** (±)-**1-phenyl-3-methyl-2-phospholene** gave **6d** as almost colorless crystals, mp 177–179 °C, in 70% yield after recrystallization from a toluene–*n*-hexane mixture. The ^1H NMR spectrum showed that the complex is present as a 1:1 diastereomeric mixture: $[\alpha]^{24}_D$ −28.4 (*c* 1.19, $CHCl_3$); IR (Nujol) 296, 280 cm^{-1} (Pd–Cl).

Anal. ($C_{25}H_{29}ClNPPd$) C, H, N, Cl.

The ^1H NMR spectrum of a reaction mixture prepared from **9** and (−)-(*R*)-2 (1:1 molar ratio) in $CDCl_3$ also showed the presence of **6d** in a 1:1 diastereomeric mixture.

(+)-(*S*)-**1 and** (±)-**PPh(α-Naph)(*o*-MeC$_6$H$_4$)** gave, similarly, the phosphine–amine complex **4a** [P = PPh(α-Naph)(*o*-MeC_6H_4)] as pale yellow crystals and (+)-PPh(α-Naph)(*o*-MeC_6H_4).

Anal. ($C_{33}H_{33}ClNPPd$, **4a**) C, H, N, Cl. C: calcd, 64.30; found, 65.22.

Treatment of the complex **4a** with diphos produced (−)-PPh(α-Naph)(*o*-MeC_6H_4) and the ionic complex **5**.

Anal. ($C_{36}H_{38}ClNP_2Pd$) C, H, N, Cl. C: calcd, 63.68; found, 62.80.

(+)-(**S**)-**1 and** (±)-**PPh(α-Naph)(p-EtOC$_6$H$_4$)** gave **4b** [P = PPh(α-Naph)(*p*-$EtOC_6H_4$)] and (−)-PPh(α-Naph)(*p*-$EtOC_6H_4$).

Anal. ($C_{34}H_{35}ClNOPPd$, **4b**) C, H, N, Cl.

(+)-PPh(α-Naph)(*p*-$EtOC_6H_4$) was liberated from the complex **4b**.

(+)-(**S**)-**1 and** (±)-**PPh(α-Naph)(p-MeOC$_6$H$_4$)** gave similarly **4c** [P = PPh(α-Naph)(*p*-$MeOC_6H_4$)]: mp 199–201 °C; $[\alpha]^{24}_D$ +59.8° (*c* 1.61, C_6H_6); IR (Nujol) 292 cm^{-1} (Pd–Cl).

Anal. ($C_{33}H_{33}ClNOPPd$) C, H, N, Cl.

Both of the phosphines recovered from the mother liquor and from the phosphine–amine complex, **4c**, are optically inactive.

Resolution with (+)-(*S*)-3. To a stirred benzene solution (55 mL) of the complex (+)-(*S*)-**3** (1.60 mmol) was added slowly a benzene solution (30 mL) of (±)-PPh(α-Naph)(*p*-$MeOC_6H_4$) (3.20 mmol) at 5–10 °C to give a pale yellow precipitate of the complex **11a** [P = PPh(α-Naph)(*p*-$MeOC_6H_4$)]: mp 121–125 °C; $[\alpha]^{26}_D$ −13.8° (*c* 1.96, $CHCl_3$); IR (Nujol) 2225 (N≡C) and 335 cm^{-1} (Pd–Cl).

Anal. ($C_{28}H_{28}Cl_2NOPPd$) C, H, N, Cl. C: calcd, 55.79; found, 56.26.

Chromatographic purification of the mother liquor on Florisil with benzene eluent gave (−)-PPh(α-Naph)(*p*-$MeOC_6H_4$) in 24% yield, mp 116–119 °C. A mixture of the complex **11a** (0.73 mmol) and a slight excess of diphos (1.10 mmol) was suspended in benzene (25 mL) and stirred at room temperature for 1 day. After removal of the precipitate of the diphosphine complex **12**, the mother liquor was purified by chromatography on a Florisil column to give (+)-PPh(α-Naph)(*p*-$MeOC_6H_4$) in 55% yield, mp 119–121 °C.

(+)-(**S**)-**3 and** (±)-**PPh(α-Naph)(p-PhC$_6$H$_4$)** gave similarly the phosphine–isocyanide complex, **11b** [P = PPh(α-Naph)(*p*-PhC_6H_4)] as pale yellow crystals [mp 150–159 °C; $[\alpha]^{23}_D$ +10.2° (*c* 1.49, $CHCl_3$); IR (Nujol) 2222 (N≡C) and 333 cm^{-1} (Pd–Cl)] and (−)-PPh(α-Naph)(*p*-PhC_6H_4), mp 191–193 °C, $[\alpha]^{32}_D$ −27.0° (*c* 2.50, $CHCl_3$).

Anal. ($C_{33}H_{30}Cl_2NPPd$) C, H, N, Cl. C: calcd, 61.08; found, 61.86. Cl: calcd, 10.93; found, 9.72.

(+)-PPh(α-Naph)(*p*-PhC_6H_4) was liberated from the complex **9b** in 54% yield, mp 193–196 °C.

(+)-(**S**)-**3 and** (±)-**PPh(*t*-Bu)Me** gave similarly the phosphine–isocyanide mixed complex, **11c** [P = PPh(*t*-Bu)Me] in 74% yield, mp 193–195 °C, $[\alpha]^{24}_D$ +8.36° (*c* 3.47, $CHCl_3$).

Anal. ($C_{16}H_{26}Cl_2NPPd$) C, H, N, Cl.

Both of the phosphines, recovered from the mother liquor and from the complex **11c**, are optically inactive.

^1H NMR Study of a Mixture of (−)-(*R*)-2 and (±)-PPh(*t*-Bu)Me in $CDCl_3$. The spectrum of a 1:2 mixture of (−)-(*R*)-**2** and (±)-PPh(*t*-Bu)Me showed signals at δ 1.31[a,b] (d, J_{PH} = 15.0 Hz, 9, *t*-Bu), 1.70[a] (d, J_{PH} = 9.0 Hz, 1.5, PCH_3), 1.76[b] (d, *J* = 6.0 Hz, 1.5, C-CH_3), 1.86[b] (d, J_{PH} = 9.0 Hz, 1.5, PCH_3), 1.86[a] (d, *J* = 6.0 Hz, 1.5, CCH_3), 2.51[a,b] (m, 3, NCH_3), 2.75[a,b] (m, 3, NCH_3), 3.62[a] (m, 0.5, >CH–), 4.07[b] (m, 0.5, >CH–), 6.49[a] (d, J_{PH} = 6.0 Hz, 0.5, α-H at C-4 position of naphthalene ring), 6.55[b] (d, J_{PH} = 6.0 Hz, 0.5, α-H at C-4 position of naphthalene ring), 6.86–8.08[a,b] (m, 10, aromatic) (The peaks marked (a) are assigned to the complex **6a** containing (*R*)-amine and (*S*)-phosphine; those marked with (b) are assigned to the complex containing (*R*)-amine and (*R*)-phosphine.)

The spectrum of a 1:4 mixture of (−)-(*R*)-**2** and (±)-PPh(*t*-Bu)Me gave signals at δ 1.16 (d, J_{PH} = 14 Hz, 9, *t*-Bu), 1.19 (d, J_{PH} = 14 Hz, 9, *t*-Bu), 1.50 (br d, J_{PH} = 3 Hz, 6, PCH_3), 1.77 (d, *J* = 7 Hz, 3, CCH_3), 2.63 (s, 6, NCH_3), 3.87 (m, 1, >CH–), 6.58 (s, 1, α-H at C-4 of the naphthalene ring), 6.89–7.90 (m, 15, aromatic).

Degradative Deuteration of the Complex 2. The complex **2** (272 mg, 0.72 mmol) was treated at room temperature with $LiAlD_4$ (19 mg, 0.45 mmol) for 20 min in 5 mL of tetrahydrofuran. After removal of the solvent, colorless liquid was collected by vacuum distillation. GLC analysis showed that the distillate contains 2-(α-*N,N*-dimethylaminoethyl)-3-*d*-naphthalene and 2-(α-*d*-ethyl)-3-*d*-naphthalene in about 1:1.3 ratio. The two components were purified by preparative GLC

and examined by ^1H NMR methods. The NMR spectrum (CCl_4) of 2-(α-*N,N*-dimethylaminoethyl)-3-*d*-naphthalene: δ 1.37 (d, J = 7.5 Hz, 3, $CHCH_3$), 2.17 (s, 6, NCH_3), 3.29 (q, J = 7.5 Hz, 1, -CH-), 7.17-7.52 (m, 2, β protons of naphthalene), and 7.60-7.88 (m, 4, α protons of naphthalene). The NMR spectrum (CCl_4) of 2-(α-*d*-ethyl)-3-*d*-naphthalene: δ 1.20-1.44 (m, 3, $-CDHCH_3$), 2.93-2.60 (m, 1.12, $-CDH-$), 7.10-7.45 (m, 2, β protons of naphthalene), 7.50 (s, 1, α proton of naphthalene), 7.60-7.97 (m, 3, α protons of naphthalene).

Recovery of (−)-(*R*)-*N,N*-Dimethyl-α-(2-naphthyl)ethylamine from the Complex 7. An ethanol solution (30 mL) of the ionic diphosphine complex **7** ($[\alpha]^{32}_D$ −27.0° (*c* 1.11, $CHCl_3$), 4.0 g, 5.4 mmol) was heated under reflux with $NaBH_4$ (0.6 g, 16 mmol) for 2 h. After normal workup, 443 mg (41%) of the amine was recovered: bp 150 °C (2 mm); $[\alpha]^{22}_D$ +51.8° (*c* 3.81, EtOH).

^1H NMR Data of Complexes ($CDCl_3$, 35 °C). 6a (isolated in the resolution study, containing (*R*)-amine and (*S*)-PPh(*t*-Bu)Me): δ 1.31 (d, J_{PH} = 15.0 Hz, 9, *t*-Bu), 1.70 (d, J_{PH} = 9.0 Hz, 3, PCH_3), 1.86 (d, J = 6.0 Hz, 3, $-CHCH_3$), 2.51 (br s, 3, NCH_3), 2.75 (br s, 3, NCH_3), 3.62 (m, J = 6.0 Hz, 1, -CH-), 6.49 (d, J_{PH} = 6.0 Hz, 1, α-H of naphthalene), 6.86-8.08 (m, 10, aromatic).

6b (isolated in the resolution study, containing (*R*)-amine and (*R*)-PPh(*t*-Bu)(*i*-Pr)): δ 1.45 (dd, J = 7.2, J_{PH} = 13.2 Hz, 3, $PCHCH_3$), 1.55 (d, J_{PH} = 14.0 Hz, 9, *t*-Bu), 1.79 (dd, J = 7.2, J_{PH} = 17.0 Hz, 3, $PCHCH_3$), 1.89 (d, J = 7.1 Hz, 3, $-CHCH_3$), 2.70 (d, J_{PH} = 2.0 Hz, 3, NCH_3), 2.75 (d, J_{PH} = 3.0 Hz, 3, NCH_3), 3.19 (m, J = 7.2 Hz, 1, PCH), 3.84 (m, J = 7.1 Hz, 1, -CH-), 6.52 (d, J_{PH} = 6.0 Hz, 1, α-H of naphthalene), 6.80-7.85 (m, 10, aromatic).

6b (prepared from (−)-(*R*)-**2** and 2 mol of (±)-PPh(*t*-Bu)(*i*-Pr) in solution): δ 1.13[b] (dd, J = 7.0, J_{PH} = 12.0 Hz, 1.5, $PCHCH_3$), 1.45[a] (dd, J = 7.2, J_{PH} = 13.2 Hz, 1.5, $PCHCH_3$), 1.55[a] (d, J = 14.0 Hz, 4.5, *t*-Bu), 1.62[b] (dd, J = 7.0, J_{PH} = 1.20 Hz, 1.5, $PCHCH_3$), 1.67[b] (d, J = 14.0 Hz, 4.5, *t*-Bu), 1.79[a] (dd, J = 7.2, J_{PH} = 17.0 Hz, 1.5, $PCHCH_3$), 1.83[b] (d, J = 7.1 Hz, 1.5, $-CHCH_3$), 1.89[a] (d, J = 7.1 Hz, 1.5, $-CHCH_3$). 2.70[a] (d, J_{PH} = 2.0 Hz, 1.5, NCH_3), 2.72[b] (d, J_{PH} = 3.0 Hz, 1.5, NCH_3), 2.75[a] (d, J_{PH} = 3.0 Hz, 1.5, NCH_3), 2.78[b] (d, J_{PH} = 2.0 Hz, 1.5, NCH_3), 3.19[a,b] (m, 1, PCH), 3.84[a,b] (m, 1, >CH-), 6.52[a] (d, J_{PH} = 6.0 Hz, 0.5, α-H of naphthalene), 6.59[b] (d, J_{PH} = 6.0 Hz, 0.5, α-H of naphthalene), 6.80-7.85[a,b] (m, 10, aromatic). (The peaks marked (a) are assigned to the complex containing (*R*)-amine and (*R*)-PPh(*t*-Bu)(*i*-Pr); those marked (b) are assigned to the complex containing (*R*)-amine and (*S*)-PPh(*t*-Bu)(*i*-Pr).)

6c: δ 1.87 (d, J = 6.0 Hz, 3, $-CHCH_3$), 2.75 (s, 3, NCH_3), 2.78 (s, 3, NCH_3), 3.73 (s, 3, OCH_3), 3.87 (q, 1, J = 6.0 Hz, >CH-), 6.61-8.00 (m, 21, aromatic), 9.00-9.10 (m, 1, aromatic).

6d (a 1:1 mixture of diastereomers): δ 1.69 (d, J = 6.0 Hz, 1.5, $-CHCH_3$), 1.74 (d, J = 6.0 Hz, 1.5, $-CHCH_3$), 1.97 (br s, 3, $C{=}CCH_3$), 2.10-3.35 (br m, 4, $-CH_2CH_2-$), 2.62 (d, J_{PH} = 3.0 Hz, 1.5, NCH_3), 2.72 (d, J_{PH} = 3.0 Hz, 1.5, NCH_3), 2.73 (d, J_{PH} = 2.5 Hz, 1.5, NCH_3), 2.84 (d, J_{PH} = 2.5 Hz, 1.5, NCH_3), 3.85 (q, J = 6.0 Hz, 0.5, -CH-), 4.05 (q, J = 6.0 Hz, 0.5, -CH-), 6.03 (d, J_{PH} = 33.0 Hz, 0.5, C=CH), 6.15 (d, J_{PH} = 33.0 Hz, 0.5, C=CH), 7.05-8.25 (m, 22, aromatic).

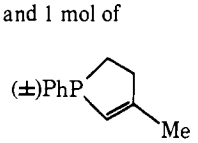
7: δ 1.83 (d, J = 6.0 Hz, 3, CCH_3), 2.12 (br s, 4, H_2O), 2.60 (br d, 6, NCH_3), 2.28-3.05 (br complex, 4, $-CH_2CH_2-$), 4.02 (m, J = 6.5 Hz, 1, >CH-), 6.94-8.19 (m, 26, aromatic).

8a: δ 1.59 (br d, J = 6 Hz, 3, $-CHCH_3$), 1.90 (s, 6, $C{=}CCH_3$), 2.60 (br s, 6, NCH_3), 1.72-2.84 (complex m, 4, $-CH_2-$), 3.97 (q, J = 6 Hz, 1, >CH-), 5.64 (br d, J_{PH} = 32 Hz, 2, C=CH), 7.10-7.90 (m, 16, aromatic).

8a (−50 °C): ~δ 1.72 (br a, $-CHCH_3$), ~1.92 (br b, $C{=}CCH_3$), 1.50-3.12 (br, c, $-CH_2CH_2-$), ~2.68 (br, d, NCH_3) (a + b + c + d = 19), 3.80 (br, 1, >CH-), 4.30-5.56 (br, 1, C=CH), 5.88 (d, J_{PH} ≅ 32 Hz, 0.5, C=CH), 6.03 (d, J_{PH} = 32 Hz, 0.5, C=CH), 6.68-8.08 (m, 16, aromatic).

9 (isolated in the resolution study): δ ~0.90 (br d, J = 7 Hz, 3, $-CHCH_3$), 1.40-3.16 (m, a, $-CH_2CH_2-$), 1.83 (s, b, $C{=}CCH_3$), 1.90 (s, c, $C{=}CCH_3$), 2.06 (s, d, NCH_3), 2.82 (br, e, H_2O) (a + b + c + d + e = 19; b:c ≅ 1:2.5), 3.68 (q, J = 7.0 Hz, 1, >CH-), 5.18 (br, 1, C=CH), 6.80-8.10 (m, 31, aromatic).

9 (prepared from **7** and 1 mol of



in solution); δ ~1.0 (br d, J = 7 Hz, 3, $-CHCH_3$), 1.47-3.00 (br m, a, $-CH_2CH_2-$), 1.83 (s, b, $C{=}CCH_3$), 1.91 (s, c, $C{=}CCH_3$), 2.20 (s, d, NCH_3), 2.67 (br, e, H_2O) (a + b + c + d + e = 21; b:c = 1:1), 3.76 (q, J ≅ 7 Hz, 1, >CH-), 5.19 (br, 1, C=CH), 6.80-8.10 (m, 31, aromatic).

11a: δ 0.58 (t, J = 6.0 Hz, 3, $-CH_2CH_3$), 0.58 (d, J = 6.0 Hz, 3, $-CHCH_3$), 0.91 (q, J = 6.0 Hz, 2, $-CH_2-$), 2.88 (m, J = 6.0 Hz, 1, >CH-), 3.82 (s, 3, OCH_3), 6.83-8.42 (m, 16, aromatic).

11b: δ 0.59 (t, J = 6.0 Hz, 3, $-CH_2CH_3$), 0.60 (d, J = 6.0 Hz, 3, $-CHCH_3$), 0.95 (m, 2, $-CH_2-$), 2.92 (m, 1, >CH-), 7.15-8.42 (m, 21, aromatic).

11c: δ 0.96 (t, J = 7.8 Hz, 3, $-CH_2CH_3$), 1.29 (d, J_{PH} = 17.7 Hz, 9, *t*-Bu), 1.28 (d, 3, $-CHCH_3$), 1.58 (m, 2, $-CH_2-$), 2.00 (d, J_{PH} = 12 Hz, 3, PCH_3), 3.70 (m, 1, >CH-), 7.26-7.89 (m, 5, aromatic).

Table IV. Summary of Crystal Data and Intensity Collection

Compd	$PdCl((CH_3)_2NCHCH_3C_{10}H_6)(P(CH(CH_3)_2)(C(CH_3)_3)(C_6H_5))$
Formula weight	548.43
Formula	$C_{27}H_{37}ClNPPd$
a	10.409 (4) Å
b	10.094 (4) Å
c	13.151 (5) Å
β	109.38 (2)°
V	1303.5 Å^3
Z	2
Density	1.397 g/cm^3 (calcd) 1.39 g/cm^3 (exptl)
Space group	C_2^2-$P2_1$
Crystal dimensions	0.59 × 0.94 × 0.19 mm
Crystal volume	9.54 × 10^{-2} mm^3
Crystal shape	Monoclinic prism plate with {10$\bar{1}$}, {100}, {001}, and {01$\bar{1}$} faces.
Radiation	Cu Kα_1 (λ = 1.540562 Å) prefiltered with 1-mil Ni foil
Absorption coefficient, μ	75.3 cm^{-1}
Transmission factors	0.042-0.359
Receiving aperture	4.0 mm wide by 5.0 mm high
Takeoff angle	4.0°
2θ scan speed	2.0°/min
Background counting	10 s
Scan range	0.9° below Kα_1 and 1.0° above Kα_2 (bisecting mode) 0.9° below Kα_1 and 1.5° above Kα_2 (parallel mode)
2θ limits	5-125° (bisecting), 125-160° (parallel)
Data collected	$\pm h, \pm k, \pm l$ 2θ < 90° $\pm h, -k, +l$ 90° < 2θ < 160°

X-Ray Structure Determination of Compound 6b. Examination of the pale yellow crystals of **6b** by precession and Weissenberg film methods revealed that they belong to the monoclinic space group C_2^2-$P2_1$. Whereas the photographic results could not rule out the centric space group C_{2h}^2-$P2_1/m$, the fact that the compound is optically active eliminates this possibility. The data crystal was mounted on a glass fiber roughly along the *b* axis. The final lattice constants were determined by a least-squares analysis[30] of the angle settings of 19 hand-centered reflections on the Picker FACS-I diffractometer. The refined cell constants and other descriptive information concerning the data crystal and collection of intensity data are given in Table IV.

The intensity data were processed as previously described;[30] the parameter *p* was chosen to be 0.04. An absorption correction was applied[31] to the data before proceeding with any calculations owing to the large range of the transmission factors (see Table IV). The symmetry equivalent data were subsequently averaged into the two sets of $+k$ and $-k$ reflections. The total number of independent data with $I > 3\sigma(I)$ was 3756. Only the $-k$ data were used in the solution and preliminary refinement of the structure.

The palladium atom was easily located from a Patterson synthesis. A subsequent structure factor calculation[31] followed by a Fourier synthesis revealed the positions of a number of atoms, including the

Table V. Positional and Thermal Parameters for the Nongroup Atoms of [(*S*)-Isopropyl-*tert*-butylphenylphosphine] [(*R*)-*N*,*N*-dimethyl-α-(2-naphthyl)ethylamine-3*C*,*N*] chloropalladium(II)

ATOM	X[A]	Y	Z	B11[B]	B22	B33	B12	B13	B23
PD	-0.237528(24)	-1/4	-0.256357(18)	55.34(33)	73.39(42)	40.77(21)	-7.75(31)	16.19(18)	-2.38(21)
CL	-0.23575(14)	-0.16375(17)	-0.085494(95)	109.6(14)	146.9(19)	54.55(78)	-32.3(13)	35.99(76)	-26.45(93)
P	-0.01433(11)	-0.19390(14)	-0.221881(77)	60.8(10)	84.5(12)	33.19(53)	-14.36(89)	14.96(55)	1.37(64)
N	-0.42952(38)	-0.34848(43)	-0.27721(31)	57.7(36)	84.2(42)	59.1(22)	-13.7(32)	24.3(22)	-0.2(26)
C(1)	-0.44289(48)	-0.44901(57)	-0.36411(43)	63.9(44)	90.9(59)	67.8(33)	-24.7(42)	22.0(31)	-11.1(34)
C(2)	-0.35551(68)	-0.57013(60)	-0.32630(53)	124.9(69)	80.3(59)	93.9(43)	-17.5(51)	44.6(43)	-6.7(41)
C(3)	-0.53951(46)	-0.24911(87)	-0.31242(44)	65.9(40)	141.5(68)	77.2(36)	29.6(67)	29.8(32)	-13.6(59)
C(4)	-0.43664(56)	-0.41193(66)	-0.17774(43)	87.1(55)	135.1(67)	76.9(32)	-31.1(50)	36.9(33)	8.2(40)
C(5)	0.01799(63)	-0.02502(58)	-0.16212(39)	117.1(67)	94.2(58)	43.1(25)	-34.9(48)	37.2(33)	-20.4(31)
C(6)	-0.07686(85)	0.07370(69)	-0.23812(49)	204.(10)	99.2(64)	72.3(37)	-22.8(68)	60.8(48)	-20.3(42)
C(7)	0.16463(84)	0.02205(77)	-0.11839(54)	173.(10)	149.9(88)	69.9(41)	-89.6(80)	32.9(51)	-32.3(48)
C(8)	0.09376(50)	-0.31779(63)	-0.11977(36)	76.3(46)	129.5(63)	46.4(25)	11.0(47)	17.3(27)	30.7(36)
C(9)	0.02450(77)	-0.45145(70)	-0.14210(59)	128.9(84)	95.3(75)	98.7(52)	24.7(65)	33.8(53)	50.6(52)
C(10)	0.10582(59)	-0.27693(89)	-0.00456(40)	116.9(59)	202.(12)	45.6(27)	7.5(73)	27.2(33)	29.3(52)
C(11)	0.23887(57)	-0.32898(90)	-0.12464(43)	77.4(53)	231.(11)	64.5(32)	42.5(65)	20.2(33)	31.4(53)

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: EXP[-(B11H^2+B22K^2+B33L^2+2B12HK+2B13HL+2B23KL)]. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^4.

Table VI. Derived Parameters for the Rigid Group Atoms of [(*S*)-Isopropyl-*tert*-butylphenylphosphine] [(*R*)-*N*,*N*-dimethyl-α-(2-naphthyl) ethylamine-3*C*,*N*] chloropalladium(II)

ATOM	X	Y	Z	B, Å^2	ATOM	X	Y	Z	B, Å^2
C(12)	0.35581(30)	-0.20265(26)	-0.33385(20)	2.54(6)	C(20)	-0.29656(26)	-0.28907(27)	-0.41828(13)	2.71(7)
C(13)	0.11182(31)	-0.09311(23)	-0.36790(21)	2.88(7)	C(21)	-0.40337(27)	-0.37956(28)	-0.45062(16)	3.18(8)
C(14)	0.15601(33)	-0.10345(25)	-0.45656(23)	3.16(7)	C(22)	-0.46672(25)	-0.40645(27)	-0.55964(17)	3.46(8)
C(15)	0.14418(35)	-0.22333(30)	-0.51116(21)	3.62(9)	C(23)	-0.42325(26)	-0.34294(22)	-0.63632(14)	3.48(8)
C(16)	0.18817(35)	-0.33267(24)	-0.47711(24)	3.61(9)	C(24)	-0.48660(28)	-0.36973(31)	-0.74534(15)	4.38(11)
C(17)	0.04399(31)	-0.32253(25)	-0.38845(24)	3.28(8)	C(25)	-0.44314(33)	-0.30612(35)	-0.82201(13)	4.65(11)
C(18)	-0.31644(19)	-0.25235(21)	-0.60397(13)	3.19(6)	C(26)	-0.33632(33)	-0.21563(34)	-0.78967(16)	4.62(11)
C(19)	-0.25313(23)	-0.22546(25)	-0.49495(14)	3.02(8)	C(27)	-0.27298(27)	-0.18875(29)	-0.68065(17)	3.82(9)

RIGID GROUP PARAMETERS

GROUP	x_C[A]	y_C	z_C	OELTA[B]	EPSILON	ETA
RING 1	0.10030(20)	-0.21299(21)	-0.42251(16)	-0.2801(19)	-3.1267(15)	-1.2448(19)
RING 2	-0.36985(18)	-0.29760(20)	-0.62014(13)	-0.8543(16)	-3.10108(93)	1.4008(10)

[A] x_C, y_C, AND z_C ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. [B] THE RIGID GROUP ORIENTATION ANGLES OELTA, EPSILON, AND ETA(RADIANS) HAVE BEEN DEFINED PREVIOUSLY: S.J. LA PLACA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511(1965).

phosphorus and chlorine atoms for which there were two possible locations (i.e., the two mirror images of the complex). A consistent set of atoms belonging to one of the possible solutions was chosen arbitrarily. Subsequent least-squares refinements and difference Fourier syntheses revealed the locations of the remaining nonhydrogen atoms. The function minimized in the least-squares refinements was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and $w = 4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors used were those of Cromer and Waber.[32] Anomalous dispersion terms were not applied at this stage of the refinement. The ring carbon atoms for both the phenyl and naphthyl rings were refined as rigid groups.[33] For both groups an ideal C–C distance of 1.397 Å was used. For the phenyl ring ideal D_{6h} symmetry was assumed. For the naphthyl ring D_{6h} symmetry for each half of the ring was used. Each of the group atoms was refined with an individual isotropic temperature factor. With all of the nonhydrogen atoms included with isotropic thermal parameters, the structure refined to $R = 0.071$ and $R_w = 0.124$ where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$.

At this point in the refinement a test was made to determine the absolute configuration of the molecule. Two separate least-squares calculations were carried out in which all of the 15 nongroup atoms were allowed to refine anisotropically; in addition, the anomalous dispersion terms for Pd, P, and Cl were introduced.[34] For all of the subsequent refinements the independent $+k$ and $-k$ reflection sets were used. In the first calculation the original configuration refined to $R = 0.067$ and $R_w = 0.108$. The same least-squares calculation was made for the opposite configuration; this model refined to $R = 0.048$ and $R_w = 0.075$. The dramatic difference in the agreement indices clearly favored the latter configuration, and it was used in the final refinements. In a subsequent difference Fourier map all of the hydrogen atoms were located. These 37 hydrogen atoms were included as a fixed contribution in the subsequent least-squares calculations. The positions of the phenyl and naphthyl hydrogen atoms were uniquely determined from the ring carbon positions assuming ideal geometry and a C–H distance of 0.95 Å. The methylene and methine hydrogen atoms were also ideally located based on the positions of the adjacent atoms. The hydrogen atoms of the eight methyl groups were ideally placed by a least-squares fit based upon the positions of the peaks found in the difference Fourier map. Each of the hydrogen atoms was assigned an isotropic thermal parameter 1 Å^2 greater than the carbon atom to which it is attached.

After two additional least-squares cycles (3756 observations and 164 variables), the structure had converged to final agreement indices of $R = 0.037$ and $R_w = 0.055$. The error in an observation of unit weight is 2.62 electrons. The largest peaks in the final difference Fourier synthesis are approximately 1.0 (1) e Å^{-3} (equivalent to 25% the height of a carbon atom) and are associated with the isotropically refined carbon atoms of the naphthyl group. Of the 13 unobserved reflections, none was found to have $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$.

To substantiate further that the absolute configuration chosen is the correct one, a comparison of Friedel pairs was made. Of the 963 Friedel pairs collected, 243 (for which $F_c \geq 20e$ and $|F_c(hkl) - F_c(\overline{hkl})|/|F_c(hkl)| > 0.05$) were compared. Of this number only eight pairs disagreed with the trend in the observed values vs. $F_c(hkl)$ and $F_c(\overline{hkl})$. This result provides overwhelming confirmation of the

configuration finally adopted. The final positional and thermal parameters for the nongroup atoms along with their estimated standard deviations are given in Table V. Table VI lists the derived positions of the 16 group atoms belonging to the phenyl and naphthyl rings. The root mean square amplitudes of vibration for the anisotropic atoms are given in Table VII.[35] Table VIII lists the idealized positions of the hydrogen atoms.[35] A listing of the structure amplitudes ($10|F_o|$ vs. $10|F_c|$) is also available.[35]

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Supplementary Material Available: Table VII, the root mean square amplitudes of vibration, Table VIII, the idealized positions of the hydrogen atoms, and a listing of the observed and calculated structure amplitudes (15 pages). Ordering information is given on any current masthead page.

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The Probable Existence of a Triple Bond between Two Vanadium Atoms

F. Albert Cotton* and Michelle Millar

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. *Received June 17, 1977*

Abstract: A recent report of the preparation of a compound to which the formula V_2(2,6-dimethoxyphenyl)$_4$·THF was assigned, and for which a structure having as its key component a triple bond between the vanadium atoms was proposed, has prompted us to investigate this substance by x-ray crystallography. We find that the solid actually contains two molecules of THF, which are not coordinated and therefore are easily lost. The actual structure differs in detail from that suggested but does contain a V–V triple bond, with d_{V-V} = 2.200 (2) Å. The essential symmetry of the molecular structure is C_{2h}. The two vanadium atoms and two of the $(MeO)_2C_6H_3$ groups are coplanar, and each of these groups is bound through C(1) to one V atom and through one oxygen atom to the other, and so arranged as to conform to C_{2h} symmetry. The other two $(MeO)_2C_6H_3$ groups are placed above and below this plane and perpendicular to it with their common plane including the V atoms and with their C(1) atoms over the midpoint of the V–V bond. They each interact through both oxygen atoms with the vanadium atoms. The compound, $V_2(C_8H_9O_2)_4$·$2C_4H_8O$, crystallizes in space group $P2_1/c$ with unit cell dimensions a = 13.804 (3) Å, b = 12.308 (3) Å, c = 23.456 (4) Å, β = 102.35 (1)°, and V = 3893 (1) Å^3, with Z = 4. It was necessary to collect data at −70 °C to prevent the crystals from disintegrating by solvent loss, a process which occurs quickly at ambient temperature even in a sealed capillary.

The existence of triple bonds between transition metal atoms is now very well established. Aside from those between atoms of rhenium in $Re_2Cl_5(CH_3SCH_2CH_2SCH_3)_2$,[1] $La_4Re_2O_{10}$,[2] and $Re_2Cl_4(PR_3)_4$,[3,4] there is an extensive series of M_2X_6 compounds[5] formed by the elements Mo and W, in which X groups may be alkyl, R_2N, or RO, as well as related compounds such a $M_2(NR_2)_4X_2$ where X represents Cl, Br, or I. In the first transition series, there are several structurally