Department of Health, Education and Welfare and Faculty Development Grant 7590 from Northeastern University (to G.D.), which are gratefully acknowledged.

**Registry No.** $(tmpd)_2Cu_2Cl_2CO_3$, racemic form, 80225-06-5; $[(DENC)CuCl]_4(CO_3)_2$, 80105-81-3; $[(DENC)CuCl]_4O_2$, 80105-85-7; DENC, 59-26-7; $CO_2$, 124-38-9; $O_2$, 7782-44-7.

**Supplementary Material Available:** Tables of observed and calculated structure factor amplitudes and of least-squares planes (Table VIII) (14 pages). Ordering information is given on any current masthead page.

Contribution from the Research School of Chemistry, The Australian National University, Canberra, A.C.T., 2600, Australia

# Resolutions Involving Metal Complexation. Preparation and Resolution of (*R*,*S*)-Methylphenyl(8-quinolyl)phosphine and Its Arsenic Analogue. Crystal and Molecular Structure of $(+)_{589}$-[(*R*)-Dimethyl(1-ethyl-α-naphthyl)aminato-$C^2$,$N$]-[(*S*)-methylphenyl(8-quinolyl)phosphine]palladium(II) Hexafluorophosphate

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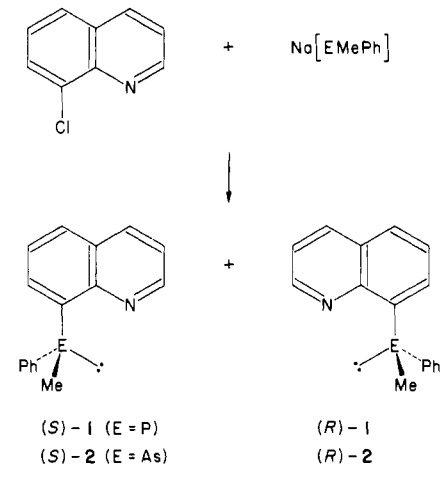
The asymmetric bidentates (*R*,*S*)-methylphenyl(8-quinolyl)phosphine and (*R*,*S*)-methylphenyl(8-quinolyl)arsine have been prepared in high yield from 8-chloroquinoline and the respective substituted phosphide or arsenide anion in tetrahydrofuran at −78 °C. Both compounds are air-stable crystalline solids. An efficient and large-scale resolution of both substances is described, which is based upon the fractional crystallization of a pair of internally diastereoisomeric palladium(II) complexes containing the chiral chelating ligand and an optically active ortho-metalated dimethyl(1-ethyl-α-naphthyl)amine. The optically pure enantiomers of the tertiary phosphine have $[\alpha]_D$ ±107° (mp 98 °C) and the corresponding arsine $[\alpha]_D$ ±115° (mp 75–76 °C) in diethyl ether solution. The molecular structure and absolute configuration of $(+)_{589}$-[(*R*)-dimethyl-(1-ethyl-α-naphthyl)aminato-$C^2$,$N$][(*S*)-methylphenyl(8-quinolyl)phosphine]palladium(II) hexafluorophosphate has been determined by a single-crystal X-ray analysis. The complex crystallizes in space group $P2_12_12_1$ with $a$ = 25.784 (5) Å, $b$ = 19.159 (3) Å, $c$ = 12.277 (2) Å, and $Z$ = 8. The structure was solved by heavy-atom methods and refined by least-squares methods to an $R$ of 0.079 and $R_w$ of 0.047 for 2955 reflections. The tertiary phosphine liberated from this complex, $[\alpha]_D$ −107° (diethyl ether), accordingly has the *R* absolute configuration.

## Introduction

Recent work in our laboratory has shown that palladium(II) complexes containing optically active ortho-metalated dimethyl(α-methylbenzyl)amines are exceedingly effective resolving agents for dissymmetric di(tertiary phosphines[1] and arsines[2]). For bidentates of lower symmetry, however, the existence of cis–trans isomerism within the internally diastereoisomeric complexes is a potential drawback to the generality of the method. In this article we describe the synthesis and resolution of the asymmetric bidentate (*R*,*S*)-methylphenyl-(8-quinolyl)phosphine and its arsenic analogue, symmetrical counterparts of which have been known for some time.[3] Chiral bidentates of this type, which are unsymmetrical with respect to the arrangement of donor atoms, are of considerable synthetic interest because of the potential of their metal chelates to exercise an electronic, as well as steric, control over the asymmetric synthesis of a chiral molecule from an appropriate coordinated substrate. Moreover, in view of our earlier results concerning the dynamic properties of certain square-planar and square-pyramidal complexes of bivalent nickel,[4] palladium, and platinum containing[5] dissymmetric di(tertiary phosphines and arsines), it was appropriate to investigate the behavior of related compounds containing asymmetric bidentates.

Scheme I




The present article describes a direct and efficient synthesis of (*R*,*S*)-methylphenyl(8-quinolyl)phosphine, and its arsenic analogue, as well as the resolution of both compounds, which in each case was based upon the fractional crystallization of a pair of internally diastereoisomeric palladium(II) complexes containing the appropriate bidentate and an optically active ortho-metalated dimethyl(1-ethyl-α-naphthyl)amine.

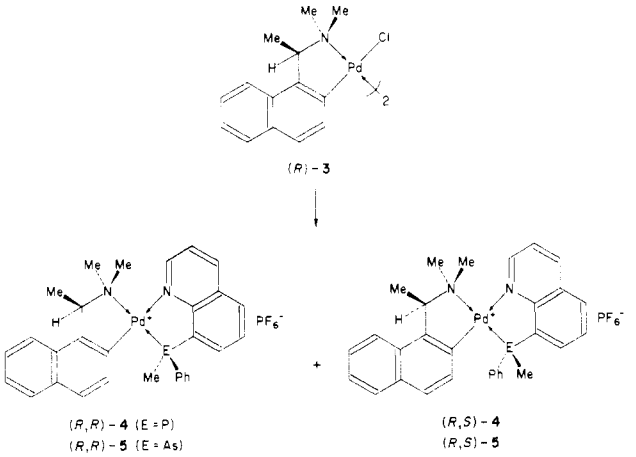
## Results and Discussion

Methylphenyl(8-quinolyl)phosphine, (*R*,*S*)-**1**, and its arsenic analogue, (*R*,*S*)-**2**, were prepared from 8-chloroquinoline and the respective anion in tetrahydrofuran at −78 °C (Scheme I). They distilled as high-boiling viscous oils and were sub-

(1) Roberts, N. K.; Wild, S. B. *J. Am. Chem. Soc.* **1979**, *101*, 6254.
(2) Roberts, N. K.; Wild, S. B. *J. Chem. Soc., Dalton Trans.* **1979**, 2015.
(3) Barclay, G. A.; Harris, C. M.; Kingston, J. V. *Chem. Ind. (London)* **1965**, 227. Hudali, H. A.; Kingston, J. V.; Tayim, H. A. *Inorg. Chem.* **1979**, *18*, 1391. Issleib, K.; Haftendorn, M. *Z. Anorg. Allg. Chem.* **1970**, *376*, 79.
(4) Roberts, N. K.; Wild, S. B. *Inorg. Chem.* **1981**, *20*, 1892.
(5) Roberts, N. K.; Wild, S. B. *Inorg. Chem.* **1981**, *20*, 1900.

0020-1669/82/1321-1007$01.25/0 

Scheme II



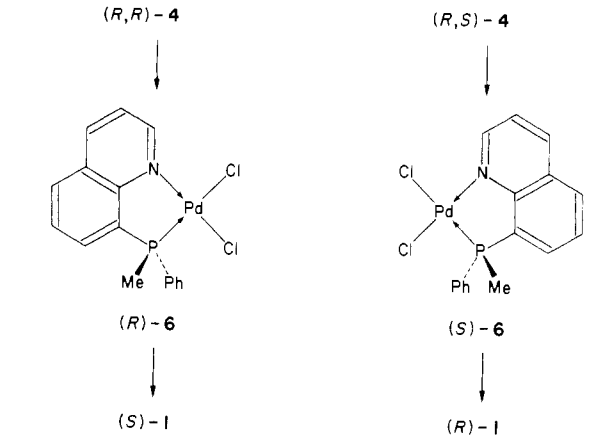

sequently crystallized from boiling methanol. The tertiary phosphine was isolated as pale yellow prisms, mp 111–112 °C, and the arsine as white needles, mp 82–83 °C. Yields in both cases were ca. 80%.

The resolutions of (*R*,*S*)-**1** and (*R*,*S*)-**2** were based upon the separation of a pair of internally diastereoisomer palladium(II) complexes derived from the resolving agent $(+)_{589}$-di-$\mu$-chloro-bis[(*R*)-dimethyl(1-ethyl-$\alpha$-naphthyl)-aminato-$C^2$,*N*]dipalladium(II), (*R*)-**3**. The latter was obtained in 95% yield from $(+)_{589}$-(*R*)-dimethyl(1-ethyl-$\alpha$-naphthyl)-amine and lithium tetrachloropalladate(II) in methanol. The corresponding derivatives of the more readily available optically active dimethyl($\alpha$-methylbenzyl)amines were not found suitable for the resolution of (*R*,*S*)-**1** or (*R*,*S*)-**2** although they were most effective for the resolution of (*RR*,*SS*)-*o*-phenylenebis(methylphenylphosphine)[1] and its arsenic analogue.[2] The partial resolution of certain unidentate mono(tertiary phosphines) has been achieved by use of an analogous palladium(II) complex containing dimethyl(1-ethyl-$\beta$-naphthyl)amine, however.[6]

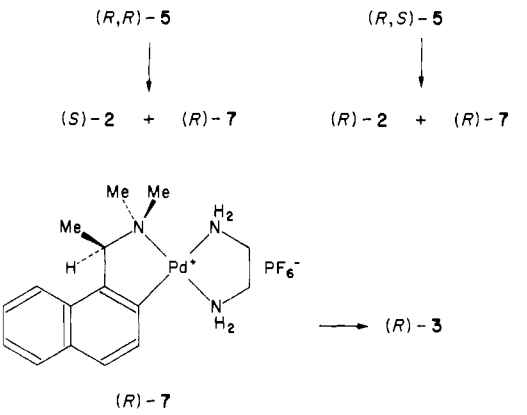
The resolutions were performed as illustrated in Schemes II–IV. The initial step involved the formation of the internally diastereoisomeric palladium(II) complexes as shown in Scheme II. The appropriate racemic bidentate was stirred with a suspension of the chloro-bridged dimer (*R*)-**3** in methanol, giving, in a short time, a pale yellow solution of the expected cationic chlorides. The addition of an excess of $NH_4PF_6$ to either of the solutions precipitated the respective mixtures of internally diastereoisomeric hexafluorophosphate salts in high yield. For both ligands the mixture could be satisfactorily separated by fractional crystallization from acetone. The less soluble salts (*R*,*R*)-**4** and (*R*,*R*)-**5** crystallized as fine white needles having $[\alpha]_D$'s of −346 and −334° in acetone, respectively. The mother liquors were then evaporated to dryness and the residues dissolved in ethyl methyl ketone. The careful addition of diethyl ether to one or other of these solutions led to the precipitation of the more soluble components of the mixtures, viz., (*R*,*S*)-**4** and (*R*,*S*)-**5**. Both salts crystallized as methyl ethyl ketone solvates in the form of pale yellow prisms. A solution of the tertiary phosphine complex in acetone had $[\alpha]_D$ +14° and the corresponding arsenic compound gave −34° in the same solvent. The fractional crystallization procedure was carried out twice more to give a ca. 90% overall recovery of the respective internally diastereoisomeric salts. Recrystallization of the ethyl methyl ketone solvates from acetone by the addition of water afforded the solvent free complexes.

(6) Tani, K.; Brown, L. D.; Ahmed, J.; Ibers, J. A.; Yokota, M.; Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 7876.

Scheme III




Scheme IV




The liberation of the resolved tertiary phosphines from (*R*,*R*)-**4** and (*R*,*S*)-**4** was accomplished as shown in Scheme III. The complexes were treated with sulfuric acid (70%), the reaction mixture was hydrolyzed, and lithium chloride was added. This formed the square-planar complexes (*R*)-**6** and (*S*)-**6**. (The optically active amine was recovered from the mother liquor in each case by neutralization and extraction into diethyl ether.) Removal of the resolved ligands from the dichloropalladium(II) complexes was fulfilled by treating a dichloromethane solution of the appropriate optically active complex with aqueous potassium cyanide. The pure methylphenyl(8-quinolyl)phosphines were then isolated from the organic layer and recrystallized from dichloromethane–methanol mixture. They formed pale yellow prisms, mp 98 °C, with $[\alpha]_D$'s of −107° and +107° (diethyl ether) for the *R* and *S* enantiomers, respectively.

The liberation of the resolved tertiary arsine from (*R*,*R*)-**5** or (*R*,*S*)-**5** was achieved by a method which enabled recovery of the resolving agent (*R*)-**3** rather than the free amine (Scheme IV). Thus, treatment of a dichloromethane solution of either of the pure diastereoisomeric complexes with diamino-1,2-ethane precipitated the salt (*R*)-**7**. The free arsines were then isolated from the mother liquor and recrystallized from methanol. The optically pure tertiary arsines (*R*)-**2** and (*S*)-**2**, mp 75–76 °C, had $[\alpha]_D$'s of −115 and +115° (diethyl ether), respectively. Conversion of (*R*)-**7** into the resolving agent (*R*)-**3** took place upon the addition of concentrated hydrochloric acid to a solution of the former in acetone.

**Crystal and Molecular Structure of (*R*,*S*)-4. Absolute Configuration of $(-)_{589}$-(*R*)-1.** So that the absolute configuration of $(-)_{589}$-**1** could be established, an X-ray crystal structure determination of $(+)_{589}$-(*R*,*S*)-**4** was undertaken. A suitable crystal for the analysis was obtained by dissolving the ethyl ketone solvate of (*R*,*S*)-**4** in acetone and reprecipitating

Table I. Bond Distances (A) with Estimated Standard Deviations (in Parentheses)

| | a | b | | a | b |
|---|---|---|---|---|---|
| Pd-P(1) | 2.202 (5) | 2.216 (6) | C(12)-C(13) | 1.40 (3) | 1.34 (5) |
| N(1) | 2.20 (2) | 2.18 (2) | C(13)-C(14) | 1.37 (3) | 1.37 (4) |
| N(2) | 2.17 (2) | 2.19 (2) | C(15)-C(16) | 1.38 (2) | 1.38 (3) |
| C(6) | 1.99 (2) | 1.99 (2) | C(20) | 1.39 (2) | 1.36 (3) |
| P(1)-C(15) | 1.80 (2) | 1.84 (2) | C(16)-C(17) | 1.41 (3) | 1.43 (3) |
| C(24) | 1.78 (2) | 1.76 (2) | C(17)-C(18) | 1.34 (3) | 1.27 (3) |
| C(30) | 1.83 (2) | 1.79 (2) | C(18)-C(19) | 1.37 (3) | 1.33 (3) |
| N(1)-C(1) | 1.48 (3) | 1.52 (3) | C(19)-C(20) | 1.45 (3) | 1.42 (3) |
| C(2) | 1.52 (3) | 1.47 (3) | C(21) | 1.39 (3) | 1.35 (4) |
| C(3) | 1.54 (3) | 1.51 (3) | C(21)-C(22) | 1.35 (3) | 1.27 (4) |
| N(2)-C(20) | 1.39 (2) | 1.37 (2) | C(22)-C(23) | 1.36 (3) | 1.38 (3) |
| C(23) | 1.35 (3) | 1.33 (3) | C(24)-C(25) | 1.39 (3) | 1.41 (3) |
| C(3)-C(4) | 1.53 (3) | 1.52 (3) | C(29) | 1.39 (3) | 1.39 (3) |
| C(5) | 1.49 (3) | 1.48 (3) | C(25)-C(26) | 1.33 (3) | 1.43 (3) |
| C(5)-C(6) | 1.43 (3) | 1.41 (3) | C(26)-C(27) | 1.37 (3) | 1.39 (3) |
| C(10) | 1.43 (3) | 1.54 (3) | C(27)-C(28) | 1.27 (4) | 1.34 (3) |
| C(6)-C(7) | 1.43 (3) | 1.46 (3) | C(28)-C(29) | 1.44 (4) | 1.36 (3) |
| C(7)-C(8) | 1.34 (3) | 1.36 (3) | P(2)-F(1) | 1.53 (2) | 1.54 (2) |
| C(8)-C(9) | 1.32 (3) | 1.22 (4) | F(2) | 1.50 (2) | 1.54 (2) |
| C(9)-C(10) | 1.38 (3) | 1.45 (4) | F(3) | 1.53 (2) | 1.60 (2) |
| C(11) | 1.48 (3) | 1.56 (4) | F(4) | 1.46 (2) | 1.57 (2) |
| C(10)-C(14) | 1.41 (3) | 1.47 (3) | F(5) | 1.49 (2) | 1.51 (2) |
| C(11)-C(12) | 1.40 (3) | 1.34 (4) | F(6) | 1.46 (2) | 1.56 (2) |

the complex with water. Under these conditions pure (*R,S*)-**4** crystallized as colorless prisms.

The asymmetric unit of the crystal consists of a pair of cations (a and b in Tables I and II) and associated hexafluorophosphate anions. There are no significant differences in the structure of the two complex cations. The stereochemical arrangement of the atoms in the cation is depicted in Figure 1, and the corresponding distances and angles for both cations and anions are presented in Tables I and II. The

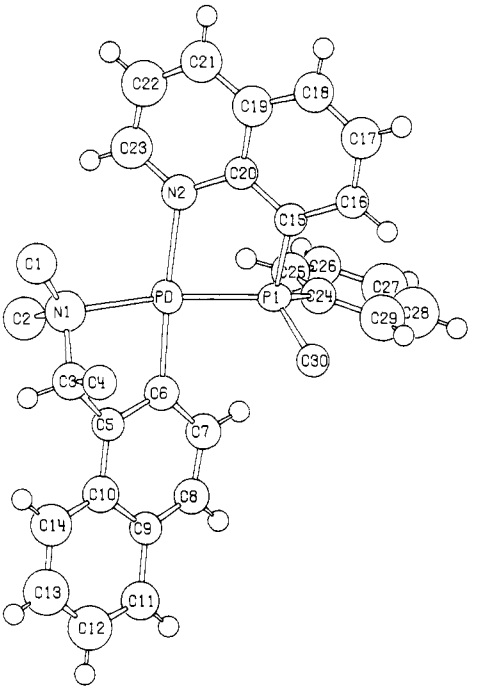



**Figure 1.** Molecular geometry and absolute configuration of $(+)_{589}$-(*R,S*)-**4**.

Table II. Selected Bond Angles (Deg) with Estimated Standard Deviations (in Parentheses)

| | a | b | | a | b |
|---|---|---|---|---|---|
| P(1)-Pd-N(1) | 161.8 (5) | 165.2 (4) | C(12)-C(13)-C(14) | 119 (2) | 114 (3) |
| N(2) | 83.6 (4) | 82.3 (4) | C(13)-C(14)-C(10) | 119 (2) | 116 (2) |
| C(6) | 92.9 (5) | 95.2 (6) | P(1)-C(15)-C(16) | 122 (1) | 124 (2) |
| N(1)-Pd-N(2) | 101.2 (6) | 100.9 (6) | C(20) | 117 (1) | 116 (1) |
| C(6) | 82.5 (7) | 81.0 (7) | C(16)-C(15)-C(20) | 119 (2) | 120 (2) |
| N(2)-Pd-C(6) | 176.3 (7) | 176.7 (7) | C(15)-C(16)-C(17) | 118 (2) | 118 (2) |
| Pd-P(1)-C(15) | 100.3 (6) | 99.5 (7) | C(16)-C(17)-C(18) | 121 (2) | 119 (2) |
| C(24) | 120.3 (7) | 120.6 (7) | C(17)-C(18)-C(19) | 123 (2) | 125 (2) |
| C(30) | 115.8 (6) | 118.5 (7) | C(18)-C(19)-C(20) | 116 (2) | 117 (2) |
| C(15)-P(1)-C(24) | 106.3 (9) | 106.0 (9) | C(21) | 127 (2) | 129 (2) |
| C(30) | 106.5 (8) | 107.0 (9) | C(20)-C(19)-C(21) | 116 (2) | 113 (2) |
| C(24)-P(1)-C(30) | 106.4 (9) | 103.8 (9) | C(19)-C(20)-C(15) | 121 (2) | 120 (2) |
| Pd-N(1)-C(1) | 118 (1) | 119 (1) | N(2) | 120 (2) | 120 (2) |
| C(2) | 108 (1) | 112 (1) | C(15)-C(20)-N(2) | 118 (2) | 121 (2) |
| C(3) | 99 (1) | 98 (1) | C(19)-C(21)-C(22) | 119 (2) | 128 (2) |
| C(1)-N(1)-C(2) | 112 (2) | 108 (2) | C(21)-C(22)-C(23) | 125 (2) | 119 (2) |
| C(3) | 113 (2) | 107 (2) | C(22)-C(23)-N(2) | 118 (2) | 119 (2) |
| C(2)-N(1)-C(3) | 106 (2) | 113 (2) | P(1)-C(24)-C(25) | 122 (2) | 119 (2) |
| Pd-N(2)-C(20) | 116 (1) | 114 (1) | C(29) | 121 (2) | 124 (2) |
| C(23) | 124 (1) | 124 (1) | C(25)-C(24)-C(29) | 117 (2) | 116 (2) |
| C(20)-N(2)-C(23) | 120 (2) | 121 (2) | C(24)-C(25)-C(26) | 125 (2) | 121 (2) |
| N(1)-C(3)-C(4) | 113 (2) | 120 (2) | C(25)-C(26)-C(27) | 115 (2) | 116 (2) |
| C(5) | 110 (2) | 107 (2) | C(26)-C(27)-C(28) | 125 (2) | 123 (2) |
| C(4)-C(3)-C(5) | 111 (2) | 111 (2) | C(27)-C(28)-C(29) | 120 (2) | 120 (2) |
| C(3)-C(5)-C(6) | 115 (2) | 116 (2) | C(28)-C(29)-C(24) | 117 (2) | 123 (2) |
| C(10) | 128 (2) | 129 (2) | F(1)-P(2)-F(2) | 88 (1) | 91 (1) |
| C(6)-C(5)-C(10) | 117 (2) | 115 (2) | F(3) | 92 (1) | 86 (1) |
| Pd-C(6)-C(5) | 113 (1) | 111 (1) | F(4) | 96 (1) | 87 (1) |
| C(7) | 128 (1) | 126 (1) | F(5) | 85 (1) | 90 (1) |
| C(5)-C(6)-C(7) | 119 (2) | 122 (2) | F(6) | 176 (1) | 178 (1) |
| C(6)-C(7)-C(8) | 119 (2) | 119 (2) | F(2)-P(2)-F(3) | 179 (1) | 178 (1) |
| C(7)-C(8)-C(9) | 124 (2) | 121 (3) | F(4) | 89 (1) | 90 (1) |
| C(8)-C(9)-C(10) | 120 (2) | 129 (3) | F(5) | 94 (1) | 91 (1) |
| C(11) | 121 (2) | 128 (3) | F(6) | 91 (1) | 91 (1) |
| C(10)-C(9)-C(11) | 119 (2) | 102 (2) | F(3)-P(2)-F(4) | 92 (1) | 90 (1) |
| C(9)-C(10)-C(5) | 120 (2) | 113 (2) | F(5) | 85 (1) | 89 (1) |
| C(14) | 124 (2) | 133 (2) | F(6) | 89 (1) | 92 (1) |
| C(5)-C(10)-C(14) | 116 (2) | 114 (2) | F(4)-P(2)-F(5) | 177 (1) | 177 (1) |
| C(9)-C(11)-C(12) | 114 (2) | 120 (2) | F(6) | 87 (1) | 92 (1) |
| C(11)-C(12)-C(13) | 125 (2) | 134 (3) | F(5)-P(2)-F(6) | 91 (1) | 91 (1) |

Table III. Selected $^1H$ and $^{13}C$ NMR Data for the Diastereoisomeric Salts

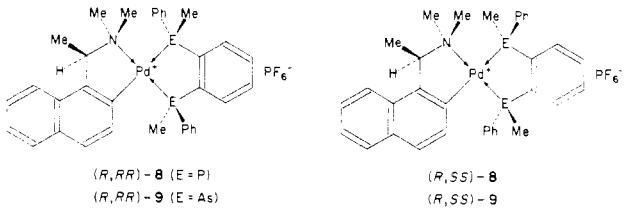
| | $^1H$ NMR Spectra[a] | | | $^{13}C$ NMR Spectra[a] | | |
|---|---|---|---|---|---|---|
| compd | δ(E*Me*) | δ(C*Me*) | δ(N*Me*) | δ(E*Me*) | δ(E*Me*) | δ(N*Me*) |
| (*R*,*R*)-4 | 2.40 (10) | 1.74 (6) | 2.87,[b] 3.00 (4) | 11.63 (29) | 23.91 | 46.91, 51.07 |
| (*R*,*S*)-4 | 2.42 (10) | 1.82 (6) | 2.93,[b] 3.00 (4) | 9.94 (37) | 24.04 | 46.91, 50.81 |
| (*R*,*R*)-5 | 2.39 | 1.82 (6) | 2.97, 3.02 | 9.62 | 24.04 | 47.30, 51.59 |
| (*R*,*S*)-5 | 2.38 | 1.86 (6) | 3.05[b] | 7.54 | 24.17 | 47.30, 50.59 |
| (*R*,*RR*)-8 | 2.42 (10), 2.62 (10) | 1.77 (6) | 2.48, 2.95[b] | 10.59 (33), 12.47 (43) | 25.21 | 51.07 (15.6) |
| (*R*,*SS*)-8 | 2.49 (10)[c] | 1.60 (6) | 2.82[c] | 10.07 (33), 11.89 (45) | 23.26 | 51.07 (15.6) |
| (*R*,*RR*)-9 | 2.36[b] | 1.88 (6) | 2.72, 3.16 | 9.88[b] | 24.82 | 52.76[b] |
| (*R*,*SS*)-9 | 2.34[b] | 1.72 (6) | 2.86, 3.00 | 8.32, 10.14 | 24.56 | 52.63[b] |

[a] Measured in $Me_2SO$-$d_6$ at 34 °C. Chemical shifts are quoted relative to $Me_4Si$ as internal standard; coupling constants in Hz are given in parentheses. [b] Resonance was observed as a broad singlet. [c] Broad doublet.

square-planar coordination geometry of the palladium atoms is distorted by the stereochemical constraints of the chelating ligands and the methyl group substituents on N(1).[6,7] The absolute configuration of the phosphorus atom is *S* and of the asymmetric carbon atom of the ortho-metalated tertiary amine is *R*. The liberation of the tertiary phosphine from (*R*,*S*)-**4** is stereospecific (giving (*R*)-**1**)[8] as verified by repreparing the diastereoisomer from the liberated phosphine. In the $^1H$ NMR spectrum of (*R*,*S*)-**4**, but not (*R*,*R*)-**4** (and stereochemically related compounds), the proton attached to C(7) is strongly shielded by the phenyl group attached to the adjacent phosphorus or arsenic atom (vide infra). The closest point of contact between H(7) and the aromatic ring involves C(24) ($l_a$ = 2.86, $l_b$ = 3.04 Å). The strong shielding effect is also evident in related compounds of dimethyl(1-ethyl-β-naphthyl)amine.[6] However, when chiral unidentate tertiary phosphines are present in the diastereoisomeric complexes, the shielding effect of the phosphorus–phenyl group on the nearest hydrogen on the ortho-metalated naphthyl ring (α-hydrogen in this case) is observed for both absolute configurations of the tertiary phosphine,[6] presumably due to the free rotation about the metal–phosphorus bond. Nevertheless, the presence or absence of this type of shielding in diastereoisomers containing an ortho-metalated naphthyl ring appears to be a generally useful means of assigning absolute configurations to phenyl-substituted tertiary phosphorus or arsenic atoms in chelate rings. The effect cannot be used to this advantage in the corresponding derivatives of dimethyl(α-methylbenzyl)amine, however.

**NMR Spectra.** The $^1H$ and $^{13}C$ NMR spectra of the internally diastereoisomeric complex cations in solution can be rationalized in terms of the structure of (*R*,*S*)-**4** in the solid state (Figure 1). The NMR data corresponding to the methyl groups in the various complexes are summarized in Table III. It is evident from these data that the solid-state coordination geometry is retained in solution: the nitrogen atoms are cis to one another in both phases. The NMe groups are nonequivalent in both (*R*,*R*)-**4** and (*R*,*S*)-**4** and coupled to the phosphorus atom trans to them. A noteworthy feature of the $^1H$ NMR spectra of (*R*,*S*)-**4** and -**5** is the high-field aromatic proton resonance at ca. δ 7, which we have assigned in both cases to the proton on C(7). When the neighboring phosphorus or arsenic atom has the *S* absolute configuration, the phenyl substituent strongly shields the γ-hydrogen of the naphthyl ring (Figure 1). Consistent with this assignment, the corresponding resonance in (*R*,*R*)-**4** and (*R*,*R*)-**5** could not be identified within the broad manifold of aromatic resonances. Furthermore, the resonance due to the proton attached to C(7) in (*R*,*S*)-**4** occurs as a doublet of doublets. The additional coupling ($J_{PH}$ = 6 Hz) probably results from a through-space interaction involving the phosphorus atom. In a related compound containing an ortho-metalated β-naphthyl ring, a coupling constant of the same magnitude was also observed, which was attributed to a long-range magnetic interaction of this type.[6] The profiles of the NMe resonances in (*R*,*S*)-**4** and (*R*,*R*)-**4** are similar in shape, and the absorptions occur in the same position. It is noteworthy that the coupling of the trans phosphorus atom extends to the methine proton of the organometallic ring ($^4J_{PH}$).

We have also prepared the corresponding complexes containing (*RR*)- and (*SS*)-*o*-phenylenebis(methylphenylphosphine), and their arsenic analogues, viz., (*R*,*RR*)- and (*R*,*SS*)-**8** and **9**. The NMR data for the di(tertiary) phosphine and arsine derivatives are also presented in Table I. The complexes were prepared in bridge-splitting reactions involving (*R*)-**3** and the appropriate enantiomer of the di(tertiary) ligand, followed by precipitation of the respective cations with $NH_4PF_6$. Except for (*R*,*RR*)-**8**, the $^1H$ NMR signals due to




(*R*,*RR*)-**8** (E = P)
(*R*,*RR*)-**9** (E = As)
(*R*,*SS*)-**8**
(*R*,*SS*)-**9**

the nonequivalent PMe or AsMe groups could not be resolved. However, the $^{13}C$ NMR spectra were more informative, separate resonances being observed for the PMe and AsMe groups in (*R*,*RR*)-**8**, (*R*,*SS*)-**8**, and (*R*,*SS*)-**9**. The signal to lower field in each case was assigned to the PMe or AsMe group adjacent to the $NMe_2$ moiety. Comparison of the $^{13}C$ NMR chemical shift data for the PMe groups in (*R*,*S*)-**4** and (*R*,*SS*)-**8** (and (*R*,*R*)-**4** and (*R*,*RR*)-**8**) supports the structural assignment of (*R*,*S*)-**4** and (*R*,*R*)-**4** in solution, which had hitherto been based upon the observation of a strong coupling between the $NMe_2$ protons and the trans phosphorus atom in the derivatives of (*R*)- and (*S*)-**1**. A similar relationship existed between the spectra of the corresponding arsenic compounds, viz., (*R*,*S*)-**5** and (*R*,*SS*)-**9**, (*R*,*R*)-**5** and (*R*,*RR*)-**9**. Again, the resonance due to the proton on C(7) of the naphthalene ring in (*R*,*SS*)-**8** and **9** but not (*R*,*RR*)-**8** and **9** was strongly shielded by the phenyl group on the neighboring phosphorus or arsenic donor atom. The proton on C(7) (γ-H of naphthalene ring) in (*R*,*SS*)-**8** resonated as a multiplet due to through-space coupling with the adjacent phosphorus atom being superimposed upon the doublet of doublets arising from direct proton and trans phosphorus coupling interactions.

## Experimental Section

All reactions involving air-sensitive compounds were performed under an argon atmosphere by use of the Schlenk technique. Proton NMR spectra were recorded at 34 °C by use of Jeolco MH-100 or Varian HA 100 spectrometers and $^{13}C$ NMR spectra by use of a Jeolco

(7) Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1980**, 1556.
(8) The apparent inversion which takes place upon liberation of the tertiary phosphine is consistent with the specification of Cahn et al. for absolute configurations.[9]
(9) Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

FX-60 instrument operating at 15.04 MHz. Optical rotations were measured on solutions in a 1-dm cell thermostated to 20 °C by use of a Perkin-Elmer Model 241 polarimeter. Elemental analyses were performed by staff within the school.

**(*R*,*S*)-Methylphenyl(8-quinolyl)phosphine, (*R*,*S*)-1.** Methylphenylphosphine (35.5 g) was reduced by sodium (foil, 7 g) in tetrahydrofuran (300 mL). After 2 h of stirring, the reaction mixture was heated under reflux for 30 min and then filtered to remove excess sodium. The filtrate, which contained Na[PMePh], was then slowly added to a solution of 8-chloroquinoline (49 g) in tetrahydrofuran (400 mL) at −78 °C. When the addition was complete, the reaction mixture was allowed to warm to room temperature and stirred overnight. It was finally heated under reflux for 30 min and the solvent distilled off at atmospheric pressure. The residue was cooled, and water (400 mL), followed by dichloromethane (400 mL), was added. The organic layer was separated and the aqueous layer extracted with dichloromethane (2 × 50 mL). The combined organic extracts were dried ($MgSO_4$) and filtered, and the solvent was removed. The product distilled as a viscous yellow oil: bp 158–160 °C (0.05 mmHg): 56 g (78%). The oil was taken up in boiling methanol (300 mL) and the solution filtered. Upon cooling, the filtrate deposited pale yellow prisms of the pure product, mp 111–112 °C. Anal. Calcd for $C_{16}H_{14}NP$: C, 76.5; H, 5.6; N, 5.6. Found: C, 76.2; H, 5.7; N 5.6. $^1H$ NMR ($CDCl_3$): δ 1.73 (d, 3, $J$ = 3Hz, PMe), 7.4–10.2 (br m, 11, aromatics).

**(*R*,*S*)-Methylphenyl(8-quinolyl)arsine, (*R*,*S*)-2.** This compound was prepared in much the same way as its phosphorus analogue. A solution containing Na[AsMePh] was generated from PhMeAsH (54 g) and sodium (foil, 7.5 g) in tetrahydrofuran (600 mL) by stirring the mixture for 1 h. After brief heating (30-min reflux), the reaction mixture was cooled and filtered to remove unreacted sodium. The clear orange filtrate was then slowly added to a solution of 8-chloroquinoline (52 g) in tetrahydrofuran (400 mL) at −78 °C. The reaction mixture was then stirred overnight with the source of cooling removed and finally heated under reflux for 30 min. The workup at this point followed the procedure outlined for (*R*,*S*)-1. The product was obtained as a pale yellow viscous oil, bp 154–156 °C (0.05 mmHg), 76 g (81%), which was subsequently isolated as white needles from boiling methanol (300 mL), mp 82–83 °C. Anal. Calcd for $C_{16}H_{14}AsN$: C, 65.1; H, 4.8; N, 4.7. Found: C, 64.9; H, 4.8; N, 4.7. $^1H$ NMR ($CDCl_3$): δ 1.58 (s, 3, AsMe), 7.1–9.0 (br m, 11, aromatics).

**$(+)_{589}$-Di-μ-chloro-bis[(*R*)-dimethyl(1-ethyl-α-naphthyl)aminato-$C^2$,$N$]dipalladium(II), (*R*)-3.** Palladous chloride (36.5 g) was dissolved in methanol (400 mL) containing lithium chloride (18 g), and the solution was filtered. To the filtrate was slowly added $(+)_{589}$-(*R*)-dimethyl(1-ethyl-α-naphthyl)amine (82.2 g). After 6 h of stirring, the reaction mixture was filtered and the yellow solid isolated. It was washed with cold methanol and diethyl ether and then dried in vacuo (68.3 g, 97% yield). Recrystallization of this material from dichloromethane–methanol mixture afforded the product as fine orange-yellow crystals, mp 183 °C dec (62.7 g, 89%). Anal. Calcd for $C_{28}H_{32}Cl_2N_2Pd_2$: C, 49.4; H, 4.7; N, 4.1. Found: C, 49.4; H, 4.7; N, 4.1. $^1H$ NMR ($Me_2SO$-$d_6$): δ 1.78, (d, 6, $J$ = 6 Hz, CH*Me*), 2.69 (s, 6, NMe), 2.72 (s, 6, NMe), 4.42 (g, 2, $J$ = 6 Hz, C*H*Me), 7.1–7.7 (br m, 14, aromatics). $[\alpha]_D$ −172° (*c* 0.49, $CH_2Cl_2$). The second equivalent of amine per palladium atom acted as a base to remove the HCl liberated in the reaction. This was recovered in 62% yield from the filtrate (after removal of the product) by adding an excess of 18 M NaOH and extracting the tertiary amine into dichloromethane.

**Resolution of (*R*,*S*)-1: Formation and Separation of Internal Diastereoisomers. $(-)_{589}$-*cis*-[(*R*)-Dimethyl(1-ethyl-α-naphthyl)-aminato-$C^2$,$N$][(*R*)-methylphenyl(8-quinolyl)phosphine]palladium(II) Hexafluorophosphate, (*R*,*R*)-4.** A mixture of (*R*,*S*)-1 (10 g) and (*R*)-3 (13.5 g) in methanol (160 mL) was stirred until the solids had dissolved. The reaction mixture was then filtered and an excess of $NH_4PF_6$ (13 g) in water (20 mL) slowly added to the filtrate. This precipitated the diastereoisomeric cations as hexafluorophosphate salts. Complete precipitation of the mixture was ensured by the addition of a further quantity of water (250 mL). The product was separated, washed with water, aqueous methanol (1:1), methanol–diethyl ether (1:4), and diethyl ether, and dried in vacuo (25 g, 89%): $[\alpha]_D$ −150° (*c* 1.01, acetone). The mixture was separated in a series of fractional recrystallizations involving acetone and ethyl methyl ketone. The first crop of almost pure (*R*,*R*)-4 was obtained by taking up the mixture in boiling acetone (150 mL) and allowing it to cool. The filtrate was then concentrated to ca. 120 mL and the solution stood aside. More of the same diastereoisomer crystallized in an impure state. At this stage, the filtrate was evaporated to dryness and the residue dissolved in boiling ethyl methyl ketone (200 mL). From this solution almost pure (*R*,*S*)-4 crystallized as an ethyl methyl ketone solvate. After this material had been separated, the filtrate was taken to dryness and the residue redissolved in boiling acetone (100 mL) and the whole process repeated. Additional quantities of each diastereoisomer were thus obtained. Altogether three cycles were performed producing, after a final recrystallization from acetone, a 90% yield of pure (*R*,*R*)-4: mp 234 °C dec; $[\alpha]_D$ −346° (*c* 0.92, acetone). Anal. Calcd for $C_{30}H_{30}F_6N_2P_2Pd$: C, 51.4; H, 4.3; N, 4.0. Found: C, 51.4; H, 4.4; N, 4.0. $^1H$ NMR ($Me_2SO$-$d_6$): δ 1.74 (d, 3, $J$ = 6 Hz, CH*Me*), 2.40 (d, 3, $J$ = 10 Hz, PMe), 2.87 (br s, 3, NMe), 3.00 (d, 3, $J$ = 4 Hz, NMe), 4.62 (m, 1, C*H*Me), 7.2–9.5 (br m, 17, aromatics). $^{13}C$ NMR ($Me_2SO$-$d_6$): δ 11.63 (d, 1, $J$ = 29.3 Hz, PMe), 23.91 (s, 1, CH*Me*), 46.91 (s, 1, NMe), 51.07 (s, 1, NMe), 72.90 (s, 1, CH), 123–154 (m, 25, aromatics). $\Lambda_M$ = 40.5 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ ($10^{-3}$ M in $CH_2Cl_2$ at 20 °C).

**$(+)_{589}$-*cis*-[(*R*)-Dimethyl(1-ethyl-α-naphthyl)aminato-$C^2$,$N$][(*S*)-methylphenyl(8-quinolyl)phosphine]palladium(II) Hexafluorophosphate–Ethyl Methyl Ketone Solvate, (*R*,*S*)-4·EtMeCO.** A single recrystallization of the combined crude (*R*,*S*)-4·EtMeCO from an ethyl methyl ketone–diethyl ether mixture afforded the pure solvate as pale yellow prisms: mp 227.5 °C dec; 12.4 g, 90%; $[\alpha]_D$ +14° (*c* 0.96, acetone). Anal. Calcd for $C_{34}H_{38}F_6N_2OP_2Pd$: C, 52.8; H, 5.0; N, 3.6. Found: C, 52.5; H, 5.0; N, 3.6. $^1H$ NMR ($Me_2CO$-$d_6$): δ 0.93 (t, 3, $J$ = 7.5 Hz, $CH_3COCH_2CH_3$), 1.91 (d, 3, $J$ = 6 Hz, CH*Me*), 2.01 (s, 3, $CH_3COCH_2CH_3$), 2.42 (g, 2, $J$ = 7.5 Hz, $CH_3COCH_2CH_3$), 2.45 (d, 3, $J$ = 10 Hz, PMe), 3.00 (br s, 3, NMe), 3.13 (d, 3, $J$ = 4 Hz, NMe), 4.67 (m, 1, C*H*Me), 7.07 (d of d, 1, $J_{HH}$ = 9 Hz, $J_{PH}$ = 6 Hz, γ-H), 7.2–9.7 (br m, 16, aromatics). $^{13}C$ NMR ($Me_2SO$-$d_6$): δ 7.54 (s, 1, $CH_3COCH_2CH_3$), 9.94 (d, 1, $J$ = 37.1 Hz, PMe), 24.04 (s, 1, CH*Me*), 29.24 (s, 1, $CH_3COCH_2CH_3$), 35.74 (s, 1, $CH_3COCH_2CH_3$), 46.91 (s, 1, NMe), 50.81 (s, 1, NMe), 72.90 (s, 1, CHMe), 123–154 (br m, 25, aromatics), 208.70 (s, 1, $CH_3COCH_2CH_3$), $\Lambda_M$ = 40.0 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ ($10^{-3}$ M in $CH_2Cl_2$ at 20 °C).

**$(+)_{589}$-*cis*-[(*R*)-Dimethyl(1-ethyl-α-naphthyl)aminato-$C^2$,$N$][(*S*)-methylphenyl(8-quinolyl)phosphine]palladium(II) Hexafluorophosphate, (*R*,*S*)-4.** The compound (*R*,*S*)-4·EtMeCO was dissolved in acetone and reprecipitated with water. Pure (*R*,*S*)-4 formed white needles: mp 138 °C dec: $[\alpha]_D$ +15.2° (*c* 0.88, acetone). Anal. Calcd for $C_{30}H_{30}F_6N_2P_2Pd$: C, 51.4; H, 4.3; N, 4.0. Found: C, 51.4; H, 4.5; N, 3.8. $^1H$ NMR ($Me_2SO$-$d_6$): δ 1.82 (d, 3, $J$ = 6 Hz, CH*Me*), 2.42 (d, 3, $J$ = 10 Hz, PMe), 2.93 (br s, 3, NMe), 3.00 (d, 3, $J$ = 4 Hz, NMe), 4.66 (q, 1, $J$ = 6 Hz, C*H*Me), 6.90 (d of d, 1, $J_{HH}$ = 9 Hz, $J_{PH}$ = 6 Hz, γ-H), 7.3–9.6 (br m, 16, aromatics).

**$(+)_{589}$-Dichloro[(*R*)-methylphenyl(8-quinolyl)phosphine]palladium(II), (*R*)-6.** The complex (*R*,*R*)-4 (2 g) was dissolved in sulfuric acid (70%, 15 mL) and the solution poured on to ice (ca. 20 g). Lithium chloride (3.6 g) was then added and the mixture stirred, giving a clear yellow solution that was extracted with dichloromethane (3 × 20 mL). The organic layer was separated and dried ($MgSO_4$) and the crude product isolated by removal of the solvent. A recrystallization from boiling methanol (100 mL) gave the pure enantiomer as yellow plates: mp 263–264 °C (1.04 g, 85%): $[\alpha]_D$ +88° (*c* 0.66, $CH_2Cl_2$). Anal. Calcd for $C_{16}H_{14}Cl_2NPPd$: C, 44.8; H, 3.3;, N, 3.3. Found: C, 44.4; H, 3.2; N, 3.2. $^1H$ NMR ($Me_2SO$-$d_6$): δ 2.45 (d, 3, $J$ = 13.4 Hz, PMe), 7.4–10.2 (m, 11, aromatics). The optically active amine was recovered from the neutralized aqueous layer by extraction into diethyl ether and subsequent distillation.

**$(-)_{589}$-Dichloro[(*S*)-methylphenyl(8-quinolyl)phosphine]palladium(II), (*S*)-6.** Decomposition of (*R*,*S*)-4·EtMeCO (2 g) with concentrated sulfuric acid by the procedure described above gave the enantiometric complex (*S*)-6 as yellow plates: mp 263–264 °C (0.95 g, 85%); $[\alpha]_D$ −88° (*c* 0.71, $CH_2Cl_2$). Anal. Calcd for $C_{16}H_{14}Cl_2NPPd$: C, 44.8; H, 3.3; N, 3.3. Found: C, 44.8; H, 3.6; N, 3.1. $^1H$ NMR ($Me_2SO$-$d_6$): identical with that of its enantiomorph.

**$(-)_{589}$-(*R*)-Methylphenyl(8-quinolyl)phosphine, (*R*)-1.** The complex (*S*)-6 (2 g) was dissolved in dichloromethane (100 mL), and a solution of potassium cyanide (2.4 g) in water (20 mL) was added. After several minutes of stirring, the organic layer was almost colorless and was separated. The aqueous portion was washed several times with dichloromethane, and the combined organic extracts were dried

($MgSO_4$), filtered, and evaporated. The residue was extracted with diethyl ether and the solution filtered. The ether was removed and the residue taken up in the minimum of dichloromethane. The addition of methanol to this solution produced pure (*R*)-**1**, as pale yellow prisms: mp 98 °C (1.07 g, 92%); $[\alpha]_D$ −107° (*c* 0.69, diethyl ether). Anal. Calcd for $C_{16}H_{14}PN$: C, 76.5; H, 5.6; N, 5.6. Found: C, 76.2; H, 5.5; N, 5.4. $^1H$ NMR ($CDCl_3$): δ 1.73 (d, 3, *J* = 3 Hz, PMe), 7.2–8.9 (m, 11, aromatics).

**$(+)_{589}$-(*S*)-Methylphenyl(8-quinolyl)phosphine, (*S*)-1.** This was liberated from (*R*)-**6** in the same way as its enantiomorph: yield 91%, mp 98 °C, $[\alpha]_D$ +107° (*c* 0.76, diethyl ether); $^1H$ NMR ($CDCl_3$) identical with that of (*R*)-**1**.

**Resolution of (*R*,*S*)-2: Formation and Separation of Internal Diastereoisomers. $(-)_{589}$-*cis*-[(*R*)-Dimethyl(1-ethyl-α-naphthyl)aminato-$C^2$,*N*][(*R*)-methylphenyl(8-quinolyl)arsine]palladium(II) Hexafluorophosphate, (*R*,*R*)-5.** The compounds (*R*,*S*)-**2** (10 g) and (*R*)-**3** (11.5 g) were suspended in methanol (160 mL), and the mixture was stirred until complete dissolution had occurred. The reaction mixture was then filtered and a solution of $NH_4PF_6$ (12 g) in water (20 mL) slowly added to the filtrate. A further 250 mL of water was added and the precipitate isolated, washed, and dried as described in the resolution of (*R*,*S*)-**1** (22.4 g, 89%); $[\alpha]_D$ −184.5° (*c* 1.03, acetone). The mixture of (*R*,*R*)-**5** and (*R*,*S*)-**5** was then dissolved in hot acetone (200 mL) and the solution allowed to cool slowly. A quantity of almost pure (*R*,*R*)-**5** crystallized (6.5 g, 29%). This was collected, and the filtrate was evaporated to dryness. The residue was taken up in hot acetone (100 mL) and the solution cooled to produce a further crop of (*R*,*R*)-**5** (2 g). This was separated and the solvent removed. The residue was taken up in boiling ethyl methyl ketone (120 mL). Upon cooling to room-temperature, large pale yellow prisms of (*R*,*S*)-**5** deposited as the ethyl methyl ketone solvate (5.7 g, 25%). The whole cycle was repeated by using smaller volumes of solvents and the combined separated diastereoisomers once again recrystallized from the respective solvents. Altogether, 10.1 g (90%) of pure (*R*,*R*)-**5** was obtained: mp 217.5 °C dec; $[\alpha]_D$ −337° (*c* 1.06, acetone). Anal. Calcd for $C_{30}H_{30}AsF_6N_2PPd$: C, 48.4; H, 4.1; N, 3.8. Found: C, 48.2; H, 4.2; N, 3.7. $^1H$ NMR ($Me_2SO$-$d_6$): δ 1.82 (d, 3, *J* = 6 Hz, CH*Me*), 2.39 (s, 3, AsMe), 2.97 (s, 3, NMe), 3.02 (s, 3, NMe), 4.65 (q, 1, *J* = 6 Hz, C*H*Me), 7.0–9.3 (br m, 17, aromatics). $^{13}C$ NMR ($Me_2SO$-$d_6$): δ 9.62 (s, 1, AsMe), 24.04 (s, 1, CH*Me*), 47.30 (s, 1, NMe), 51.59 (s, 1, NMe), 73.81 (s, 1, *C*HMe), 123–155 (br, m, 25, aromatics). $\Lambda_M$ = 43.1 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ ($10^{-3}$ M in $CH_2Cl_2$ at 20 °C).

**$(-)_{589}$-*cis*-[(*R*)-Dimethyl(1-ethyl-α-naphthyl)aminato-$C^2$,*N*][(*S*)-methylphenyl(8-quinolyl)arsine]palladium(II) Hexafluorophosphate Ethyl Methyl Ketone Solvate, (*R*,*S*)-5·EtMeCO.** The pure solvate was obtained after a final recrystallization of the combined second fractions from ethyl methyl ketone: mp 211 °C (11.2 g, 91%); $[\alpha]_D$ −34° (*c* 1.12, acetone). Anal. Calcd for $C_{34}H_{38}AsF_6NOPPd$: C, 50.0; H, 4.7; N, 3.4. Found: C, 49.8; H, 4.6; N, 3.4. $^1H$ NMR ($Me_2SO$-$d_6$): δ 0.93 (t, 3, *J* = 7.5 Hz, $CH_3COCH_2CH_3$), 1.86 (d, 3, *J* = 6 Hz, CH*Me*), 2.06 (s, 3, $CH_3COCH_2CH_3$), 2.38 (s, 3, AsMe), 2.45 (q, 2, *J* = 7.5 Hz, $CH_3COCH_2CH_3$), 3.05 (br s, 6, $NMe_2$), 4.73 (q, 1, *J* = 6 Hz, C*H*Me), 7.07 (d, 1, *J* = 9 Hz, γ-H), 7.3–9.5 (br m, 16, aromatics). $^{13}C$ NMR ($Me_2SO$-$d_6$): δ 7.54 (s, 1, $CH_3COCH_2CH_3$), 7.54 (s, 1, AsMe), 24.17 (s, 1, CH*Me*), 29.24 (s, 1, $CH_3COCH_2CH_3$) 35.87 (s, 1, $CH_3COCH_2CH_3$), 47.30 (s, 1, NMe), 50.59 (s, 1, NMe), 73.94 (s, 1, *C*HMe), 123–155 (br, m, 25, aromatics), 208.82 (s, 1, $CH_3COCH_2CH_3$). $\Lambda_M$ = 42.0 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ ($10^{-3}$ M in $CH_2Cl_2$ at 20 °C).

**$(-)_{589}$-[(*R*)-Dimethyl(1-ethyl-α-naphthyl)aminato-$C^2$,*N*](diamino-1,2-ethane)palladium(II) Hexafluorophosphate, (*R*)-7.** The pure diastereoisomer (*R*,*R*)-**5** (10.72 g) was dissolved in dichloromethane (300 mL), and diamino-1,2-ethane (4.8 mL) was added with stirring. Diethyl ether (200 mL) was then added and the reaction mixture stirred for a further 30 min. The resulting white precipitate was filtered off, washed with diethyl ether, and dried (7.3 g, 99%). The pure salt was obtained mp 218.5 °C dec: $[\alpha]_D$ −69° (*c* 0.87, acetone). Anal. Calcd for $C_{16}H_{24}F_6N_3PPd$: C, 37.7; H, 4.8; N, 8.2. Found: C, 37.7; H, 4.9; N, 8.3. $^1H$ NMR ($Me_2SO$-$d_6$): δ 1.62 (d, 3, *J* = 6 Hz, CH*Me*), 2.58 (s, 3, NMe), 2.64 (s, 3, NMe), 2.97 (br s, 2, $NH_2$), 4.60 (br s, 2, $NH_2$), 4.67 (q, 1, *J* = 6 Hz, C*H*Me), 6.5–7.3 (m, 6, aromatics) (ethylenic resonances obscured by NMe absorptions).

**$(+)_{589}$-(S)-Methylphenyl(8-quinolyl)arsine, (*S*)-2.** The mother liquor from the precipitation and isolation of (*R*)-**7** contained the resolved arsine. The solvent was evaporated to dryness and the residue taken up in diethyl ether (200 mL). The solution was filtered and washed with water (2 × 100 mL). The organic layer was then dried ($MgSO_4$), filtered, and evaporated to dryness. The residue was dissolved in boiling methanol (30 mL) and the solution slowly cooled: white flakes of optically pure (*S*)-**2** crystallized: mp 75–76 °C (3.86 g, 91%), $[\alpha]_D$ +115° (*c* 1.07, diethyl ether). Anal. Calcd for $C_{16}H_{14}AsN$: C, 65.1; H, 4.8; N, 4.7. Found: C, 65.1; H, 4.8; N, 4.6. $^1H$ NMR ($CDCl_3$): δ 1.58 (s, 3, AsMe), 7.1–9.0 (br m, 11, aromatics). The optical purity of (*S*)-**2** was established by re-preparing (*R*,*R*)-**7** from (*R*)-**3** and the liberated tertiary arsine. The $^1H$ NMR spectrum and optical rotation of the reprepared material were identical with those of the pure separated diastereoisomer.

**$(-)_{589}$-(*R*)-Methylphenyl(8-quinolyl)arsine, (*R*)-2.** A 90% yield of optically pure (*R*)-**2** was obtained from (*R*,*S*)-**7**·EtMeCO by treatment with diamino-1,2-ethane by use of the procedure described for its enantiomer. It crystallized from hot methanol as white flakes: mp 75–76 °C: $[\alpha]_D$ −115° (*c* 0.74, diethyl ether). $^1H$ NMR ($CDCl_3$): identical with that of (*S*)-**2**. Pure (*R*,*S*)-**5** was re-prepared from (*R*)-**3** and (R)-**2**, establishing the optical purity of the latter.

The resolving agent (*R*)-**3** can be regenerated from (*R*)-**7** by cautious reaction with 10 M HCl. Thus, (*R*)-**7** (4 g) in acetone (100 mL) upon treatment with 10 M HCl (7 mL) resulted in the precipitation of the crude dimer (2.6 g, 96%), which was purified by recrystallization from a dichloromethane–methanol mixture.

**$(-)_{589}$-[(*R*)-Dimethyl(1-ethyl-α-naphthyl)aminato-$C^2$,*N*][(*RR*)-*o*-phenylenebis(methylphenylphosphine)]palladium(II) Hexafluorophosphate, (*R*,*RR*)-8, and Its Diastereoisomer, (*R*,*SS*)-8.** These were prepared in high yield from (*R*)-**3** and the respective enantiomer of the di(tertiary phosphine)[1] in the usual way. The compound (*R*,*RR*)-**8** crystallized from acetone as white needles of the monoacetone solvate: mp 252 °C dec: $[\alpha]_D$ −445° (*c* 0.54, $Me_2SO$). Anal. Calcd for $C_{37}H_{42}F_6NOP_3Pd$: C, 53.5; H, 5.1. Found: C, 53.5; H, 5.2. $^1H$ NMR ($Me_2SO$-$d_6$): δ 1.77 (d, 3, *J* = 6 Hz, CH*Me*), 2.07 (s, 6, $Me_2CO$), 2.42 (d, 3, *J* = 10 Hz, PMe), 2.62 (d, 3, *J* = 10 Hz, PMe), 2.48 (s, 3, NMe), 2.95 (br s, 3, NMe), 4.63 (m, 1, C*H*Me), 7.3–8.1 (br, m, 20, aromatics). $^{13}C$ NMR ($Me_2SO$-$d_6$): δ 10.59 (d, 1, *J* = 33.2 Hz, PMe), 12.47 (d, 1, *J* = 43.0 Hz, PMe), 25.21 (s, 1, CH*Me*) 51.07 (d, 2, *J* = 15.6 Hz, NMe), 73.42 (s, 1, *C*HMe), 123–155 (br m, 28, aromatics). The $Me_2CO$ resonance is obscured by solvent absorption. The diastereoisomer (*R*,*SS*)-**8** crystallized from acetone–diethyl ether mixture as white plates: mp 244 °C dec: $[\alpha]_D$ +292° (*c* 0.95, acetone); $^1H$ NMR ($Me_2SO$-$d_6$) δ 1.60 (d, 3, *J* = 6 Hz, CH*Me*), 2.49 (br d, 6, *J* = 10 Hz, PMe), 2.51 (s, 3, NMe), 2.82 (br s, 3, NMe), 4.62 (q, 1, *J* = 6 Hz, C*H*Me), 6.97 (m, 1, γ-H), 7.3–8.4 (br m, 19, aromatics); $^{13}C$ NMR ($Me_2SO$-$d_6$) δ 10.07 (d, 1, *J* = 33.2 Hz, PMe), 11.89 (d, 1, *J* = 44.9 PMe), 23.26 (s, 1, CH*Me*), 51.07 (d, 2, *J* = 15.6 Hz, NMe), 73.94 (s, 1, *C*HMe), 123–163 (br m, 28, aromatics). $\Lambda_M$ = 46.0 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ ($10^{-3}$ M in $CH_2Cl_2$ at 20 °C).

**$(-)_{589}$-[(*R*)-Dimethyl(1-ethyl-α-naphthyl)aminato-$C^2$,*N*][(*RR*)-*o*-phenylenebis(methylphenylarsine)]palladium(II) Hexafluorophosphate, (*R*,*RR*)-9, and Its Diastereoisomer, (*R*,*SS*)-9.** Both compounds were prepared from (*R*)-**3** and respective enantiomer of the di(tertiary arsine)[2] by the usual method. Diastereoisomer (*R*,*RR*)-**9** was isolated from an acetone–diethyl ether mixture as pale yellow needles: mp 236–237 °C; $[\alpha]_D$ −384° (*c* 0.53, $Me_2SO$); 95% yield. Anal. Calcd for $C_{34}H_{36}As_2F_6NPPd$: C, 47.5; H, 4.2. Found: C, 47.6; H, 4.2. $^1H$ NMR ($Me_2SO$-$d_6$): δ 1.88 (d, 3, *J* = 6 Hz, CH*Me*), 2.36 (s, 6, AsMe), 2.72 (s, 3, NMe), 3.16 (s, 3, NMe), 4.72 (q, 1, *J* = 6 Hz, C*H*Me), 7.2–8.0 (br m, 20, aromatics). $^{13}C$ NMR ($Me_2SO$-$d_6$): δ 9.88 (br s, 2, AsMe), 24.82 (s, 1, CH*Me*), 52.76 (br s, 2, NMe), 74.20 (s, 1, *C*HMe), 123–155 (br, m, 28, aromatics). The diastereoisomer (*R*,*SS*)-**9** crystallized from acetone–diethyl ether as pale yellow prisms: mp 224 °C: $[\alpha]$ +214° (*c* 0.88, acetone); 95% yield; $^1H$ NMR ($Me_2SO$-$d_6$) δ 1.72 (d, 3, *J* = 6 Hz, CH*Me*), 2.34 (s, 6, AsMe), 2.86 (s, 3, NMe), 3.00 (s, 3, NMe), 4.69 (q, 1, *J* = 6 Hz, C*H*Me), 6.97 (d, 1, *J* = 9 Hz, γ-H), 7.3–8.1 (br m, 19, aromatics); $^{13}C$ NMR ($Me_2SO$-$d_6$) δ 8.32 (s, 1, AsMe), 10.13 (s, 1, AsMe), 24.56 (s, 1, CH*Me*), 52.63 (br s, 2, NMe), 74.07 (s, 1, *C*HMe), 123–154 (br m, 28, aromatics). $\Lambda_M$ = 46.0 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ ($10^{-3}$ M in $CH_2Cl_2$ at 20 °C).

**Collection of X-ray Intensity Data and Solution and Refinement of the Structure of $(+)_{589}$-(*R*,*S*)-4.** Crystal data for $(C_{30}H_{30}N_2PPd)(PF_6)$: $M_r$ = 700.9; orthorhombic; space group $P2_12_12_1$ with *a* = 25.784 (5), *b* = 19.159 (3), *c* = 12.277 (2) Å; *V* = 6064.8 Å$^3$; *Z* = 8; $D_m$ = 1.52, $D_c$ = 1.535 Mg m$^{-3}$; *F*(000) = 2832; λ(Mo Kα) = 0.7107 Å; μ(Mo Kα) = 0.765 mm$^{-1}$; *t* = 21 ± 1 °C.

Table IV. Final Atomic Coordinates and Isotropic Thermal Parameters for $(+)_{589}$-(*R*,*S*)-4

| atom | *x/a* | *y/b* | *z/c* | $B_{iso}$, Å$^2$ |
|---|---|---|---|---|
| PdA | 0.1488 (1) | 0.0321 (1) | 0.2180 (1) | |
| PdB | 0.8308 (1) | 0.8982 (1) | 0.1342 (1) | |
| P(1A) | 0.2340 (2) | 0.0374 (3) | 0.2256 (5) | |
| P(1B) | 0.8906 (2) | 0.8237 (3) | 0.0771 (5) | |
| P(2A) | 0.0657 (3) | 0.0530 (4) | 0.5839 (7) | |
| P(2B) | 0.3880 (3) | 0.3807 (4) | 0.0077 (8) | |
| F(1A) | 0.0126 (6) | 0.0391 (10) | 0.6359 (15) | |
| F(2A) | 0.0400 (6) | 0.1062 (10) | 0.5127 (16) | |
| F(3A) | 0.0919 (7) | −0.0020 (10) | 0.6552 (18) | |
| F(4A) | 0.0809 (9) | 0.1093 (12) | 0.6575 (17) | |
| F(5A) | 0.0524 (7) | −0.0068 (11) | 0.5116 (18) | |
| F(6A) | 0.1150 (6) | 0.0636 (10) | 0.5276 (15) | |
| F(1B) | 0.3879 (8) | 0.3227 (10) | 0.0949 (18) | |
| F(2B) | 0.4433 (5) | 0.4032 (10) | 0.0401 (16) | |
| F(3B) | 0.3305 (6) | 0.3552 (7) | −0.0222 (14) | |
| F(4B) | 0.4115 (7) | 0.3254 (9) | −0.0724 (17) | |
| F(5B) | 0.3645 (6) | 0.4310 (8) | 0.0886 (15) | |
| F(6B) | 0.3867 (7) | 0.4372 (9) | −0.0836 (14) | |
| N(1A) | 0.0694 (6) | 0.0183 (9) | 0.1566 (14) | 5.8 (4) |
| N(2A) | 0.1596 (6) | −0.0639 (7) | 0.3087 (11) | 4.3 (4) |
| N(1B) | 0.7628 (6) | 0.9472 (8) | 0.2076 (14) | 5.0 (4) |
| N(2B) | 0.8901 (6) | 0.9225 (9) | 0.2558 (13) | 4.9 (4) |
| C(1A) | 0.0490 (7) | −0.0538 (10) | 0.1475 (17) | 5.7 (5) |
| C(2A) | 0.0338 (8) | 0.0647 (10) | 0.2235 (18) | 6.3 (6) |
| C(3A) | 0.0748 (8) | 0.0546 (11) | 0.0457 (17) | 4.7 (5) |
| C(4A) | 0.1013 (7) | 0.0090 (9) | −0.0401 (15) | 4.1 (5) |
| C(5A) | 0.1024 (7) | 0.1225 (9) | 0.0593 (15) | 3.6 (5) |
| C(6A) | 0.1435 (7) | 0.1219 (9) | 0.1374 (16) | 4.2 (4) |
| C(7A) | 0.1745 (7) | 0.1831 (10) | 0.1504 (15) | 4.3 (5) |
| C(8A) | 0.1647 (8) | 0.2387 (9) | 0.0877 (15) | 4.3 (5) |
| C(9A) | 0.1297 (7) | 0.2400 (10) | 0.0096 (16) | 3.6 (5) |
| C(10A) | 0.0959 (7) | 0.1848 (11) | −0.0040 (17) | 4.6 (5) |
| C(11A) | 0.1247 (8) | 0.3015 (10) | −0.0629 (18) | 5.0 (6) |
| C(12A) | 0.0863 (9) | 0.2949 (11) | −0.1431 (20) | 6.8 (6) |
| C(13A) | 0.0537 (9) | 0.2370 (13) | −0.1569 (19) | 7.2 (7) |
| C(14A) | 0.0581 (8) | 0.1816 (11) | −0.0870 (19) | 5.9 (6) |
| C(15A) | 0.2489 (7) | −0.0517 (9) | 0.2609 (14) | 3.6 (4) |
| C(16A) | 0.2989 (6) | −0.0774 (9) | 0.2596 (14) | 3.7 (4) |
| C(17A) | 0.3074 (8) | −0.1460 (11) | 0.2979 (17) | 5.7 (5) |
| C(18A) | 0.2698 (9) | −0.1823 (10) | 0.3467 (19) | 5.5 (5) |
| C(19A) | 0.2197 (8) | −0.1596 (11) | 0.3533 (19) | 5.6 (5) |
| C(20A) | 0.2096 (7) | −0.0909 (10) | 0.3089 (15) | 3.7 (5) |
| C(21A) | 0.1788 (9) | −0.1911 (11) | 0.4083 (18) | 6.0 (6) |
| C(22A) | 0.1321 (9) | −0.1594 (13) | 0.4107 (20) | 7.1 (7) |
| C(23A) | 0.1212 (7) | −0.0971 (13) | 0.3630 (19) | 6.0 (5) |
| C(24A) | 0.2651 (7) | 0.0905 (10) | 0.3252 (15) | 4.4 (5) |
| C(25A) | 0.2404 (7) | 0.1100 (11) | 0.4212 (18) | 5.1 (5) |
| C(26A) | 0.2622 (8) | 0.1462 (11) | 0.5015 (17) | 5.3 (5) |
| C(27A) | 0.3124 (10) | 0.1661 (12) | 0.4840 (20) | 7.4 (7) |
| C(28A) | 0.3382 (10) | 0.1544 (13) | 0.3976 (23) | 8.9 (8) |
| C(29A) | 0.3158 (9) | 0.1137 (12) | 0.3108 (18) | 7.2 (6) |
| C(30A) | 0.2669 (6) | 0.0549 (9) | 0.0966 (15) | 3.7 (5) |
| C(1B) | 0.7623 (7) | 0.9594 (11) | 0.3298 (17) | 6.2 (6) |
| C(2B) | 0.7492 (7) | 1.0131 (10) | 0.1538 (15) | 4.2 (5) |
| C(3B) | 0.7240 (7) | 0.8899 (11) | 0.1852 (16) | 4.2 (5) |
| C(4B) | 0.7246 (6) | 0.8239 (10) | 0.2544 (15) | 4.3 (5) |
| C(5B) | 0.7273 (8) | 0.8728 (10) | 0.0682 (18) | 5.0 (5) |
| C(6B) | 0.7778 (7) | 0.8703 (10) | 0.0244 (17) | 4.7 (5) |
| C(7B) | 0.7874 (7) | 0.8544 (9) | −0.0901 (17) | 4.4 (5) |
| C(8B) | 0.7466 (10) | 0.8391 (13) | −0.1563 (21) | 7.8 (7) |
| C(9B) | 0.7024 (10) | 0.8377 (12) | −0.1208 (23) | 6.8 (6) |
| C(10B) | 0.6836 (8) | 0.8523 (10) | −0.0116 (18) | 5.0 (5) |
| C(11B) | 0.6516 (12) | 0.8197 (13) | −0.1841 (21) | 9.4 (8) |
| C(12B) | 0.6057 (11) | 0.8220 (14) | −0.1324 (26) | 8.7 (8) |
| C(13B) | 0.5917 (13) | 0.8319 (17) | −0.0284 (29) | 11.2 (10) |
| C(14B) | 0.6317 (11) | 0.8518 (12) | 0.0379 (20) | 7.6 (7) |
| C(15B) | 0.9291 (7) | 0.8156 (10) | 0.2024 (17) | 4.2 (5) |
| C(16B) | 0.9628 (8) | 0.7615 (11) | 0.2234 (21) | 6.8 (6) |
| C(17B) | 0.9926 (8) | 0.7639 (12) | 0.3217 (19) | 6.3 (6) |
| C(18B) | 0.9875 (9) | 0.8158 (13) | 0.3856 (20) | 6.7 (6) |
| C(19B) | 0.9563 (8) | 0.8704 (12) | 0.3687 (20) | 5.6 (5) |
| C(20B) | 0.9244 (7) | 0.8690 (10) | 0.2742 (17) | 3.9 (4) |
| C(21B) | 0.9507 (9) | 0.9291 (14) | 0.4286 (21) | 7.8 (7) |
| C(22B) | 0.9206 (10) | 0.9804 (13) | 0.4103 (21) | 7.6 (7) |
| C(23B) | 0.8892 (8) | 0.9788 (12) | 0.3191 (19) | 6.0 (6) |
| C(24B) | 0.9347 (7) | 0.8476 (10) | −0.0259 (16) | 3.7 (5) |
| C(25B) | 0.9336 (7) | 0.9160 (10) | −0.0671 (16) | 4.5 (5) |
| C(26B) | 0.9695 (8) | 0.9386 (11) | −0.1487 (19) | 6.3 (6) |
| C(27B) | 1.0077 (8) | 0.8912 (12) | −0.1782 (16) | 6.3 (6) |
| C(28B) | 1.0123 (7) | 0.8282 (10) | −0.1321 (18) | 4.5 (5) |
| C(29B) | 0.9756 (8) | 0.8057 (10) | −0.0606 (17) | 4.6 (5) |
| C(30B) | 0.8708 (8) | 0.7374 (10) | 0.0395 (16) | 4.7 (5) |

**Data Collection.** Clear, colorless crystals suitable for data collection were obtained by slow recrystallization from acetone water mixture. The diffraction symmetry and systematic absences uniquely define the orthorhombic space group $P2_12_12_1$ ($D_2^4$; No. 19). Diffraction data were collected on a Philips PW1100/20 automatic four-circle diffractometer using graphite-monochromated Mo K$\alpha$ radiation. Unit cell dimensions and their estimated standard deviations were determined by least-squares analysis of the setting angles (measured on a Picker FACS-1 diffractometer) of 12 carefully centered reflections having $2\theta$ values between 36 and 43°. Dimensions of the specimen crystal were 0.23 by 0.15 by 0.13 mm. Reflection intensities were measured in the $\theta/2\theta$ scan mode with a scan velocity ($2\theta$) of 2° min$^{-1}$ and scan width of (1.6 + 0.68 tan $\theta$)°. Stationary crystal–stationary counter backgrounds of 10-s duration were measured at each extreme of the scan width and assumed to vary linearly between these extremes. Intensities of three standard reflections (400, 040, and 002) were monitored regularly throughout data collection and did not exhibit any significant variations in their intensities during the course of the experiment. Data within the range $3 < 2\theta$ (Mo K$\alpha_1$) $< 50°$ and spanning one unique octant of reciprocal space ($+h,+k,+l$) were collected. Of the 5952 reflections measured (excluding standards), only 2955 (50%) for which $I > 1.5\sigma(I)$ were accepted as being significantly above background and only these were used in subsequent calculations. Intensities were reduced to structure amplitudes in the usual way. The data were not corrected for absorption as the maximum relative error in $F$ was estimated to be only 4%. The statistical residual, $R_s$ ($=\sum\sigma/\sum|F_o|$ (where $\sigma$ is the error contribution to $F_o$ from counting statistics alone)), for this data set is 0.077. In the calculation of $\sigma_2$ values, an experimental uncertainty factor of $p = 0.04$ was assumed.[10,11]

**Structural Analysis.** The structure was solved on the basis of two independent molecules per asymmetric unit by conventional heavy-atom techniques. Hydrogen atom positions (except those on methyl carbons) were calculated from a C–H bond length of 0.95 Å and assigned isotropic thermal parameters 10% greater than those of the carbons to which they are bonded. These hydrogen atoms were then included as fixed-atom contributors in least-squares refinement with their positions and thermal parameters being recalculated before each cycle. In the terminal scattering model the Pd, P, and F atoms were refined with anisotropic thermal parameters and the N and C atoms with isotropic parameters. This model refined by full-matrix least squares to an $R$ of 0.079 and $R_w$ of 0.0473 (where $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o^2|]^{1/2}$) for 2955 observations and 419 variables. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = \sigma_2^{-2}$. Atomic scattering factors and corrections for anomalous dispersion were taken from ref 12a. On the final cycle of refinement no parameter shifted by more than $0.01\sigma$. An analysis of the weighting scheme showed no systematic trends. The standard deviation of an observation of unit weight was 1.70. There were only two peaks (of 1.3 and 0.8 e Å$^{-3}$) in the final difference map greater than the general background level of ±0.6 e Å$^{-3}$. Each of these was associated with a Pd atom. So that the absolute configuration could be checked, all positional coordinates and related thermal parameters were changed in sign. Refinement as before converged at $R = 0.080$ and $R_w = 0.0488$. According to Hamiltonian's $R$ factor test,[12b] the probability that the original configuration is the correct one is greater than 99.5%. Final atomic coordinates are listed in Table IV, and the atom nomenclature is shown in Figure 1.

(10) Busing, W. R.; Levy, H. A. *J. Chem. Phys.* **1957**, *26*, 563.

(11) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.

(12) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) pp 99, 149; (b) p 288.

**Computer Programs.** The ANUCRYS structure determination package[13,14] was used for all aspects of the crystal structure analysis.

**Registry No.** (*R,S*)-**1**, 80127-37-3; (*R*)-**1**, 80183-96-6; (*S*)-**1**, 80183-97-7; (*R,S*)-**2**, 80127-38-4; (*R*)-**2**, 80183-98-8; (*S*)-**2**, 80183-99-9; (*R*)-**3**, 80145-77-3; (*R,R*)-**4**, 80226-02-4; (*R,S*)-**4**, 80145-79-5; (*R,R*)-**5**, 80226-04-6; (*R,S*)-**5**, 80145-81-9; (*R*)-**6**, 80145-82-0; (*S*)-**6**, 80225-16-7; (*R*)-**7**, 80146-04-9; (*R,RR*)-**8**, 80160-35-6; (*R,SS*)-**8**, 80286-60-8; (*R,RR*)-**9**, 80146-06-1; (*R,SS*)-**9**, 80286-62-0; methylphenylphosphine, 6372-48-1; 8-chloroquinoline, 611-33-6; PhMeAsH, 53979-86-5.

**Supplementary Material Available:** Tables of anisotropic thermal parameters (Table V), calculated hydrogen atom parameters (Table VI), and observed and calculated structure factor amplitudes (Table VII) (12 pages). Ordering information is given on any current masthead page.

(13) McLaughlin, G. M.; Taylor, D.; Whimp, P. O. "The ANUCRYS Structure Determination Package"; Research School of Chemistry, The Australian National University: Canberra, A.C.T., Australia 2600.
(14) Ferguson, J.; Mau, A. W.-H.; Whimp, P. O. *J. Am. Chem. Soc.* **1979**, *101*, 2363.

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# Synthesis and Characterization of Sterically Hindered $CuN_4$ Complexes of Tripod Ligands[1]

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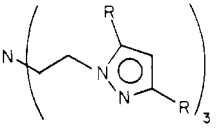
The synthesis of tris[2-(1-pyrazolyl)ethyl]amine (trpyn) and its 3,5-dimethylpyrazolyl and 3,5-di-*tert*-butylpyrazolyl derivatives is described. The ligands form trigonal-pyramidal Cu(I) and square-pyramidal Cu(II) complexes, which show unusual electrochemistry as a result of pronounced environmental effects. The $E_{1/2}$ values for the three Cu(I) complexes are 0.49, 0.67, and 0.94 V vs. SCE, respectively. The last is the highest potential ever recorded for a $CuN_4$ complex and results because the alkyl groups on the pyrazole rings form a nonpolar pocket, protecting the copper atom from approach of the solvent or a counterion that would stabilize the 2+ valence. The compounds reported here also represent the first structurally characterized copper complexes of tripod ligands having three-atom bridges between ligating termini. Crystal data for $[Cu(trpyn)H_2O][BF_4]_2$: triclinic, $a$ = 9.9673 (57) Å, $b$ = 12.9565 (28) Å, $c$ = 9.4734 (33) Å, $\alpha$ = 91.2446 (258)°, $\beta$ = 103.4556 (422)°, $\gamma$ = 106.7023 (261)°, $V$ = 1134.36 Å$^3$, space group $P\bar{1}$, $Z$ = 2. Crystal data for $[Cu(trpynMe_6)]BF_4$: orthorhombic, $a$ = 16.904 (8) Å, $b$ = 16.985 (6) Å, $c$ = 17.407 (16) Å, $V$ = 4997.87 Å$^3$, space group *Pbca*, $Z$ = 8.

Interest in modeling "blue-copper" proteins has focused mainly on their unusual spectroscopic and structural properties.[2] Of fundamental importance, however, is the ability of those proteins to shuttle electrons in biological systems at essentially diffusion-controlled rates.[3] The distorted geometry of the active site,[4] which also apparently governs the EPR and near-IR spectral parameters,[5] is thought to play a key role in the electron transfer since no molecular reorganization is required during the redox process.[6] The high reduction potential for blue-copper proteins[7] is another puzzling feature which has been difficult to explain; however, it is generally accepted that the nonplanar geometry of the copper ion or the nature of the ligands bound to copper is important in that regard.[7,8]

In this paper we describe the synthesis and characterization of a series of copper complexes of ligands **1-3** which display very high reduction potentials due to pronounced environmental effects. The compounds reported here also represent the first structurally characterized copper complexes of tripod ligands having three-atom bridges between ligating termini.



**1**, R = H (trpyn)
**2**, R = $CH_3$ ($trpynMe_6$)
**3**, R = *t*-$C_4H_9$ ($trpynBu_6$)

## Experimental Section

All reagents and solvents were purchased from commercial sources and used as received, unless noted otherwise. The following solvents were distilled: *N,N*-dimethylformamide (DMF), from sodium hydride under reduced pressure; tetrahydrofuran (THF), from sodium-benzophenone ketyl under nitrogen; methanol, from $Mg(OCH_3)_2$ under nitrogen. 3,5-Dimethylpyrazole and 3,5-di-*tert*-butylpyrazole were prepared by literature methods.[9] Melting points were obtained with use of a Fisher-Johns apparatus and are uncorrected. Microanalyses were performed by Integral Microanalytical Laboratories, Inc., Raleigh, NC, and by Galbraith Laboratories, Inc., Knoxville, TN.

$^1$H NMR spectra were recorded on a Varian XL-100 instrument operating in the FT mode at 100.1 MHz. All chemical shifts are relative to an internal standard of $Me_4Si$. EPR spectra on samples frozen in a glass of 1:1 methanol-THF at 77 K were obtained with use of a Varian E-3 spectrometer, calibrated with DPPH. Electronic spectra were taken on a Cary 17 spectrophotometer.

**Tris[2-(1-pyrazolyl)ethyl]amine (1).** Under a nitrogen atmosphere, 6.7 g (0.1 mol) of pyrazole was added slowly to a suspension of 2.4 g (0.1 mol) of NaH in 130 mL of dry DMF. The solution was allowed to stir at 60 °C for 3 h, and then an additional 0.75 g of NaH was added. To the resulting suspension was added, in small portions, 6.03

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