Pergamon

Tetrahedron, Vol. 53, No. 11, pp. 4083-4094, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00019-7

Facile Interconversions Between Diastereomers of Chloro-Bridged Palladium(II) Dimers of Orthometallated (±)-Dimethyl[1-(1-naphthyl)ethyl]amine

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Abstract: The important chloro-bridged dipalladium(II) resolving agents (*R*,*R*)- and (*S*,*S*)-*cis*-di-μ-chlorobis[1-[1-(dimethylamino)-ethyl]-2-naphthalenyl-*C*,*N*]dipalladium, (*R*,*R*)- and (*S*,*S*)-*cis*-**1**, undergo facile rearrangements into unequal mixtures of cis and trans diastereomers upon dissolution in chloroform or dichloromethane, although concentration of the solution in each case affords in high yield the pure cis diastereomer of the dinuclear metal complex as the corresponding mono-solvate in a typical second-order asymmetric transformation. When equimolar solutions of (*R*,*R*)-*cis*- and (*S*,*S*)-*cis*-**1**·CH_2Cl_2 in dichloromethane are mixed together, however, an equilibrium is rapidly established between the cis and trans diastereomers of the (*R**,*R**)-(±) and (*R**,*S**) forms of **1** and from which solution configurationally homogeneous (*R**,*S**)-*trans*-**1**·CH_2Cl_2 crystallizes in high yield by second-order asymmetric transformation. The crystal and molecular structures of (*R*,*R*)-*cis*-**1**·CH_2Cl_2 and (*R**,*S**)-*trans*-**1**·CH_2Cl_2 have been determined. The optical purities of the individual enantiomers of (*R**,*R**)-(±)-**1**·CH_2Cl_2 have been determined by reaction with (1*R*,2*S*,5*R*)-menthyldiphenylphosphine or (1*S*, 2*S*, 5*R*)-neomenthyldiphenylphosphine in chloroform-d_1 and analysis of the $^{31}P\{^1H\}$ NMR spectra of the resulting solutions of the corresponding bridge-split palladium(II)–phosphine epimers.

The complexes (*R*,*R*)- and (S,S)-di-μ-chlorobis[1-[(1-dimethylamino)ethyl]-2-naphthalenyl-C,N]-dipalladium, (*R*,*R*)- and (*S*,*S*)-**1**,[1,2] and the derivatives (*R*)- and (*S*)-bis(acetonitrile)[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*]palladium(II) perchlorate,[4,5] are highly effective resolving agents for chiral ligands that are capable of splitting the chlorine bridges in the former or displacing acetonitrile in the latter.[1–6] The superiority of the naphthalenyl complexes over the analogous [1-(dimethylamino)ethyl]-2-phenyl compounds (*R*,*R*)- and (*S*,*S*)-**2**, which are nevertheless important resolving agents,[7] is due to the rigidity of the five-membered organometallic rings in the naphthalenyl compounds, which have the locked asymmetric envelope conformation. Because of an unfavourable interaction between the carbon–methyl group of the organometallic ring and H(8) of the naphthalenyl ring in the complex, the carbon–methyl group selectively adopts an axial disposition in a ring of δ conformation when the chiratopic carbon to which it is attached has the *R* configuration (Figure 1). All known crystal structures of complexes containing the chiral naphthalenyl-*C*,*N* organometallic ring display this conformational feature, which persists in solution according to 2D ROESY NMR experiments.[8] A consequence of the locked chiral ring in the complex is the helical displacement of H(3) of the naphthalene ring below the C(2)–Pd–N plane and into the face of the ligand attached cis to it and trans to the nitrogen atom. This effect has important ramifications for the use of the naphthalenyl complexes in asymmetric synthesis and for determinations of absolute configurations.[1,2,4–6] The carbon–methyl–H(8) locking mechanism is absent in the analogous benzylamine complexes, and, in the resolution of (±)-1-(2-diphenylphosphino-1-naphthyl)isoquinidine with (*S*,*S*)-**2**, the two diastereomers formed crystallized together as a quasiracemate in which one diastereomer had the (*S*)-δ conformation of the five-membered organometallic ring (equatorial carbon–methyl group) and the other the (*S*)-λ conformation (axial carbon–methyl group).[9]

In fond memory of Professor Arthur Birch

Here we report the hitherto unrecognized interconversion between the cis and trans diastereomers of **1** in solution. The rearrangement between the diastereomers is facile, unlike the exchange of the orthometallated amine ligand in similar complexes with free amines and imines capable of orthometallation, which requires temperatures of 25–118 °C and acidic conditions.[10]

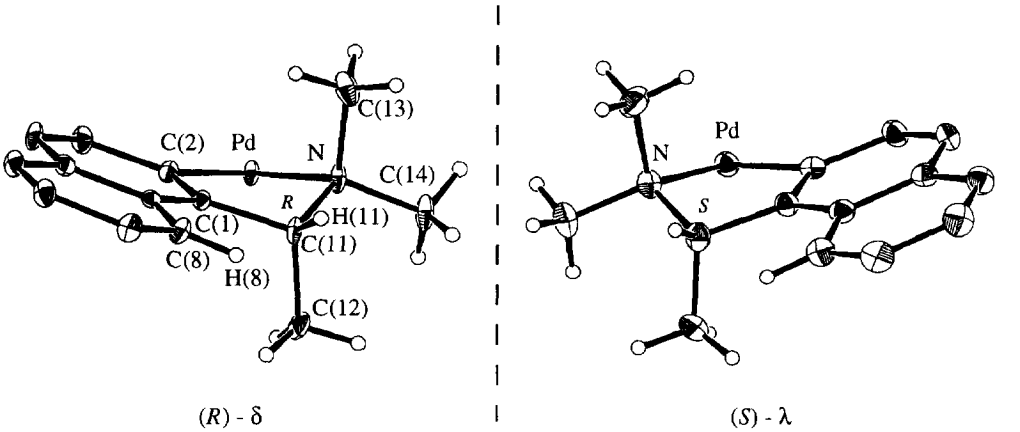
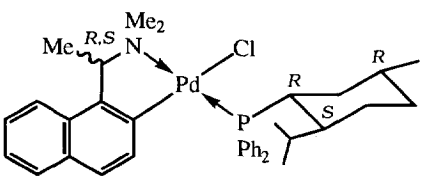


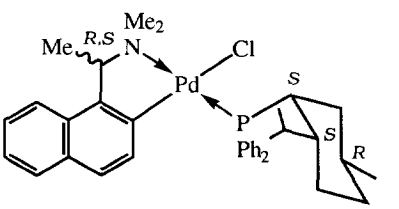
Fig. 1. Enantiomorphic (*R*)-δ and (*S*)-λ conformations of five-membered naphthalenyl-*C,N* ring.

RESULTS AND DISCUSSION

The complexes (*R,R*)- and (*S,S*)-**1** were prepared from the respective enantiomers of (±)-dimethyl[1-(1-naphthyl)ethyl]amine and palladium(II) chloride–lithium chloride in methanol containing triethylamine.[2] The optically active chloro-bridged dipalladium(II) complexes crystallize from the reaction mixtures in high yield as air-stable microcrystalline powders that form highly crystalline mono-solvates when recrystallized from chloroform– or dichloromethane–methanol. Thus, (*S*)-(–)-dimethyl[1-(1-naphthyl)ethyl]-amine having $[\alpha]_D$ –127.6 (neat)[11] furnished (*S,S*)-**1** of $[\alpha]_D$ +185.4 (*c* 1.00, CH_2Cl_2). The optical purity of the crude complex (and indirectly of the free amine) was determined to be 98% by reacting it with (1*R*, 2*S*, 5*R*)-menthyldiphenylphosphine[14] or (1*S*, 2*S*, 5*R*)-neomenthyldiphenylphosphine[15] in chloroform-d_1, and integrating the intensities of the $^{31}P\{^1H\}$ NMR signals for the epimers **3a** and **3b** (menthyl) or **4a** and **4b** (neomenthyl). The identities of the epimers **3a/3b** and **4a/4b** were established by comparisons of the $^{31}P\{^1H\}$ NMR spectra of the above samples with those of authentic specimens prepared directly from (*R,R*)- and (*S,S*)-*cis*-**1**·CH_2Cl_2 and the appropriate phosphine.



3a / 3b



4a / 4b

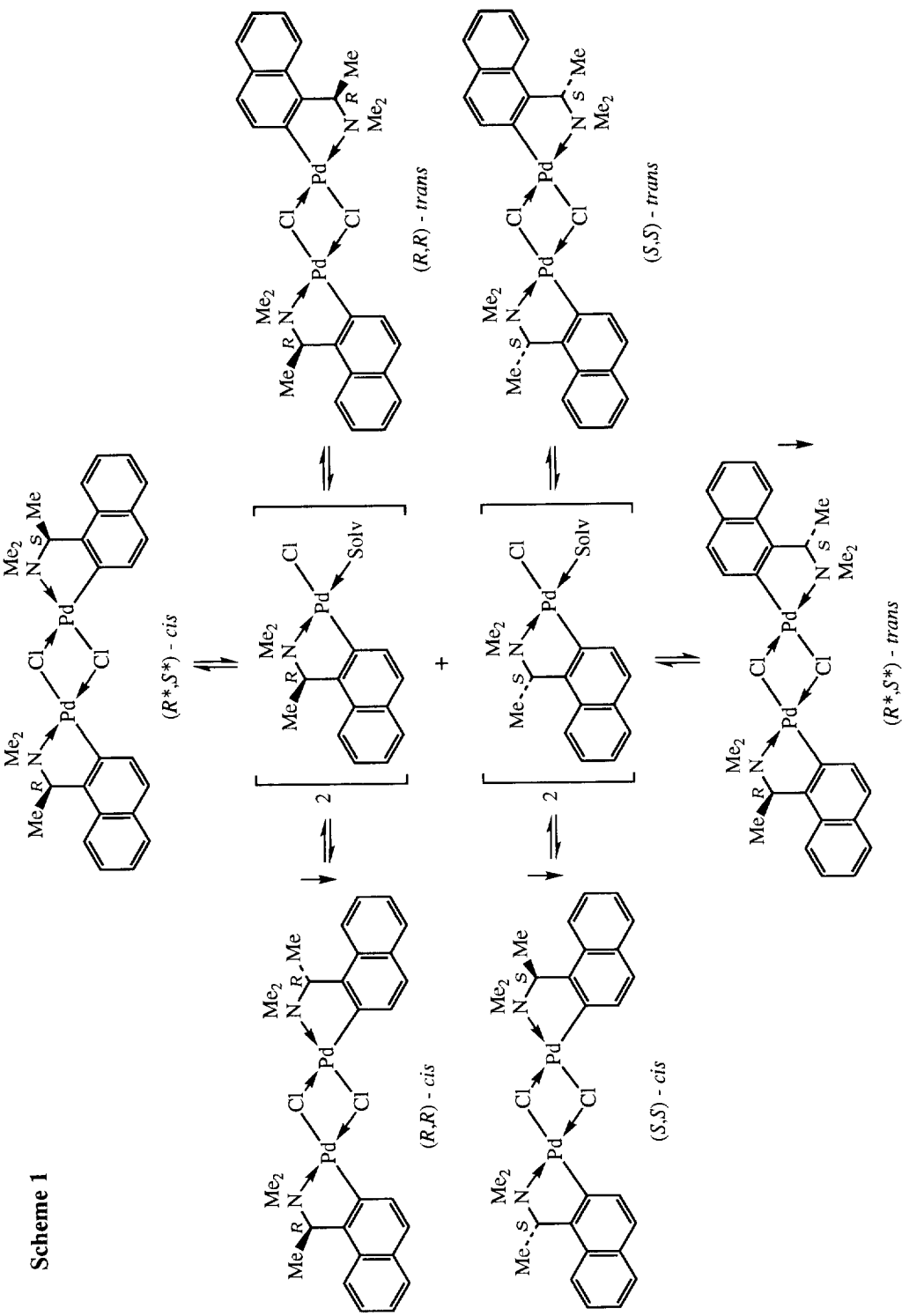
The nitrogen trans to phosphorus geometries for the mononuclear palladium–phosphine epimers were assigned on the basis of the known geometries of similar complexes. The configurational homogeneity of each of the

phosphines was readily established by $^{31}P\{^1H\}$ NMR spectroscopy. (The neomenthylphosphine, mp 96–99 °C, is easier to crystallize than the menthyl compound, which has mp 57.5–58.5 °C.) Recrystallizations of crude (*S*,*S*)-**1** from dichloromethane– or chloroform–methanol gave the corresponding, highly crystalline, solvates (*S*,*S*)-**1**·CH_2Cl_2 or (*S*,*S*)-**1**·$CHCl_3$. If a small quantity of first-formed crystals in either case is separated by decantation of the mother liquor, subsequent crystalline fractions of the solvate have complete optical purity (>99%) according to the $^{31}P\{^1H\}$ NMR spectra of the fractions in the presence of the neomenthyldiphenylphosphine. (*S*,*S*)-**1**·CH_2Cl_2 of this purity has $[\alpha]_D$ +168.8 (*c* 1.00, CH_2Cl_2) and (*S*,*S*)-**1**·$CHCl_3$ has $[\alpha]_D$ +162.4 (*c* 1.00, CH_2Cl_2).

Crystal and Molecular Structure of (R,R)-cis-1·CH_2Cl_2. A suitable crystal of the title compound was obtained by concentration of a solution of the complex in dichloromethane. The unit cell of the crystal consists of four molecules of the dinuclear metal complex and associated solvent molecules. The molecular structure of the complex is depicted in Figure 2. The complex has C_2 symmetry, with each palladium atom having a distorted square-planar geometry. The twisting in each half of the dissymmetric molecule is manifested in the torsion angle Cl(2)–Pd(1)–C(2)–C(3), which is –24.1(1)°. The overall helicity of the molecule is Λ. A ring puckering analysis[16] of the symmetry-related five-membered organometallic rings of δ conformation in the complex using the program PLATON[17] gave a puckering amplitude q_2 of 0.470(11) Å and a phase angle ϕ_2 of 214.9(15)°. The values confirm the δ envelope conformation of the ring, with the *N* atom exhibiting a marked deviation from the plane of the other four atoms (Figure 2). The H(8)–C(12) distance in the complex is 2.696 Å. If C(12) and H(11) are interchanged, as would be the case if the five-membered ring had the λ conformation (methyl group equatorial), the H(8)–C(12) distance becomes 2.059 Å.

Interconversions between diastereomers of 1. The 500 MHz ^1H NMR spectrum of (*S*,*S*)-*cis*-**1**·CH_2Cl_2 in chloroform-d_1 at 25 °C in the N*Me* region is reproduced in Figure 3a. The spectrum consists of two pairs of N*Me* resonances in the ratio ca. 4:3 for the cis and trans diastereomers of the complex. In attempts to assign the resonances in the spectrum, samples of (*S*,*S*)-*cis*-**1**·CH_2Cl_2 were suspended in chloroform-d_1 and dichloromethane-d_2 at –78 °C and the spectra of the mixtures were monitored as the temperature was raised to 25 °C: no discernible selective dissolution of the cis diastereomer was evident in either case. The complex is somewhat more soluble in dichloromethane and a spectrum was obtained at –50 °C, but this consisted of the ca. 4:3 mixture of diastereomers. (The configurational homogeneity of the crystalline cis complex was confirmed by recording the solid state ^{13}C NMR spectrum, which contained the signals of a single diastereomer.) The position of the equilibrium appeared to be identical in chloroform-d_1, dichloromethane-d_2, or acetonitrile-d_3 at 25 °C. On the basis of these data, we propose that (*S*,*S*)-*cis*-**1**·CH_2Cl_2 undergoes a facile bridge-splitting reaction upon dissolution, to give a trace of a highly reactive mononuclear palladium intermediate (undetected) that rapidly dimerises with cis:trans ca. 4:3 diastereoselectivity (Scheme 1).

Scheme 1



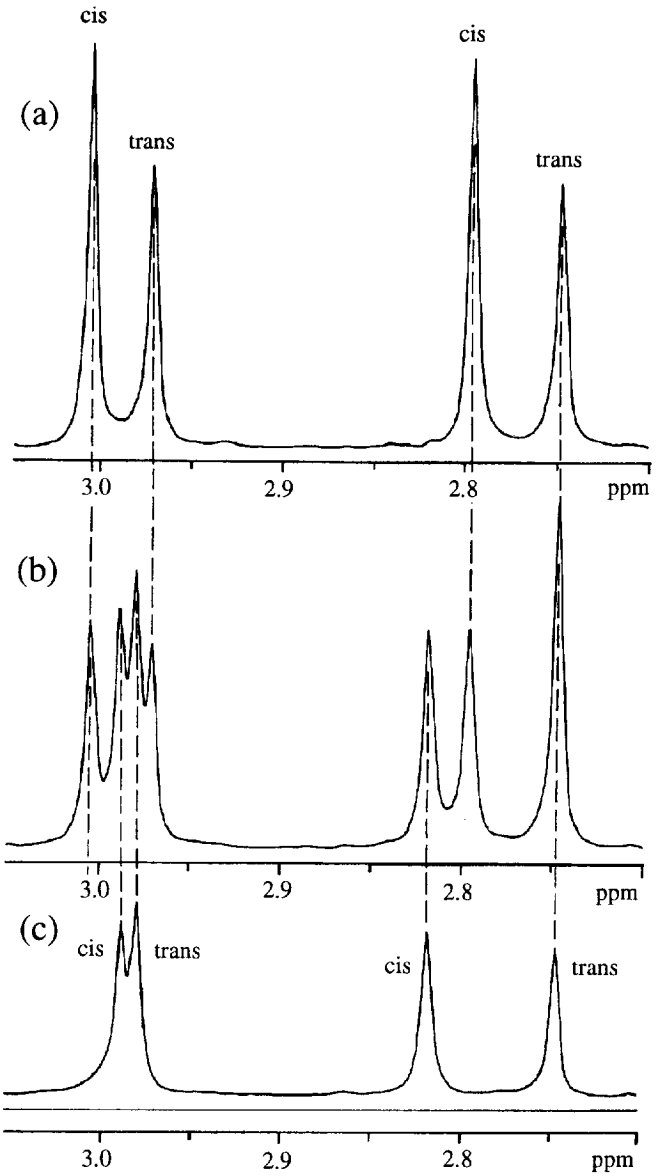


Fig. 3. ^{1}H NMR spectrum of (*S*,*S*)-**1**·CH_2Cl_2 in chloroform-d_1 in the N*Me* region (a) and of an equimolar mixture of (*R*,*R*)-**1**·CH_2Cl_2 and (*S*,*S*)-**1**·CH_2Cl_2 under similar conditions (b). The difference spectrum (c) shows the N*Me* resonances of the cis and trans diastereomers of (R^*,S^*)-**1** at equilibrium. Assignments for cis and trans diastereomers are arbitrary.

When solutions of the complex in chloroform-d_1 or dichloromethane-d_2 were concentrated, the respective mono-solvate crystallized in high yield in a typical second-order asymmetric transformation.[18] The ^{1}H NMR spectrum of the mother liquor in each case exhibited peaks due to the equilibrium cis: trans ca. 4:3 mixture.

When equimolar solutions of (*R*,*R*)-*cis*-**1**·CH_2Cl_2 and (*S*,*S*)-*cis*-**1**·CH_2Cl_2 in chloroform-d_1 were mixed together at 25 °C, the ^1H NMR spectrum obtained in the N*Me* region is shown in Figure 3b. The spectrum consists of four pairs of N*Me* resonances corresponding to an unequal mixture of the cis and trans isomers of (*R**,*R**)-(±)- and (*R**,*S**)-**1**.[19] The spectrum in dichloromethane-d_2 is similar, but there is overlap of two of the four low-field N*Me* peaks. The dichloromethane-d_2 solution of the complexes deposited in high yield sparingly soluble crystals of a complex that was subsequently identified as (*R**,*S**)-*trans*-**1**·CD_2Cl_2 on the basis of a crystal structure determination on (*R**,*S**)-*trans*-**1**·CH_2Cl_2. The ^1H NMR spectrum of the mother liquor was identical with that of the original mixture, thus confirming the second-order asymmetric transformation leading to the single diastereomer of the product. Figure 3c shows the difference ^1H NMR spectrum of the mixture, which corresponds to the N*Me* resonances of the cis and trans diastereomers of (*R**,*S**)-**1**.

Crystal and Molecular Structure of (R,S*)-trans-1·CH2Cl2.* A suitable crystal for X-ray crystallography was selected from a sample of the complex prepared by mixing equimolar solutions of (*R*,*R*)-*cis*-**1**·CH_2Cl_2 and (*S*,*S*)-*cis*-**1**·CH_2Cl_2 in dichloromethane and concentrating the resulting solution. The configurational homogeneity of the product was confirmed by solid-state ^{13}C NMR spectroscopy. The complex crystallizes with two molecules of the centrosymmetrical molecule and associated solvent molecules in the unit cell. The molecular structure of the complex is depicted in Figure 4. The angle of twist in each half of the molecule is 19(6)°, as indicated by the torsion angle Cl(1)–Pd(1)–C(2)–C(3). Ring-puckering analyses on the equivalent five-membered organometallic rings in the complex gave q_2 0.441(4) Å and ϕ_2 213.8(5)°, which confirm the almost identical nature of the rings with those in (*R*,*R*)-*cis*-**1**·CH_2Cl_2.

CONCLUSION

The chloro-bridged palladium(II) dimers of orthometallated (±)-dimethyl[1-(1-naphthyl)ethyl]amine undergo facile rearrangements between cis and trans diastereomers in solution, as evidenced by ^1H NMR spectroscopy. In typical second-order asymmetric transformations, however, cis diastereomers of the palladium(II) dimers selectively crystallize from equilibrium cis–trans mixtures of the individual enantiomers of the complex and the trans diastereomer selectively crystallizes from solutions of the racemate.

EXPERIMENTAL

^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at 25 °C on Varian VXR 500 and Gemini 300 spectrometers, respectively, with resonances being referenced to internal Me_4Si (^1H) and external 85% H_3PO_4 (^{31}P). Optical rotations were measured at 20 °C on the specified solutions in a 1-dm cell with a Perkin Elmer Model 241 spectropolarimeter. Specific rotations were estimated to be within ± 0.05 deg $cm^2\ g^{-1}$. Elemental analyses were determined by staff within the Research School of Chemistry.

(S,S)-(+)-cis-Di-μ-chlorobis[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-C,N]dipalladium(II)–1-Dichloromethane ((S,S)-cis-1·CH2Cl2). The *solvent free* complex was prepared from (*S*)-(–)-dimethyl[1-(1-naphthyl)-ethyl]amine ($[\alpha]_D$ –127.6 (neat)) and lithium tetrachloropalladate(II) in the presence of triethylamine, as described in ref. 3. The crude complex had $[\alpha]_D$ +185.4 (*c* 1.00, CH_2Cl_2); recrystallization of this material from dichloromethane–methanol gave, after removal of a small quantity of crystals, the configurationally homogeneous *dichloromethane solvate* as large yellow prisms: mp 183–185 °C, $[\alpha]_D$ +168.8 (*c* 1.00, CH_2Cl_2). Anal. Calcd for $C_{29}H_{34}Cl_4N_2Pd_2$: C, 45.5; H, 4.5; N, 3.7. Found: C, 45.6; H, 4.7; N, 3.7. ^1H NMR ($CDCl_3$): δ

1.91 (m, CH*Me*), 2.74 (s, N*Me*–(*S,S-trans*), 2.79 (s, N*Me*–(*S,S*)-*cis*), 2.97 (s, N*Me*–(*S,S*)-*trans*), 3.00 (s, N*Me*–(*S,S-cis*), 4.18 (br q, $^3J_{HH}$ = 6.05 Hz, C*H*Me), 5.29 (s, CH_2Cl_2), 7.33–7.78 (m, Ar*H*). (The assignments to the pairs of N*Me* resonances for the cis and trans diastereomers are arbitrary.) Recrystallization of the crude complex from chloroform–methanol afforded yellow prisms of (*S,S*)-*cis*-**1**·$CHCl_3$: mp 175–179 °C, $[\alpha]_D$ + 162.4 (*c* 1.00, CH_2Cl_2). Anal. Calcd for $C_{29}H_{33}Cl_5N_2Pd_2$: C, 43.6; H, 4.2; N, 3.5. Found: C, 43.2; H, 4.0; N, 3.6. A similar preparation with use of (*R*)-(+)-dimethyl[1-(1-naphthyl)ethyl)]amine of $[\alpha]_D$ +127.0 (neat) gave (*R,R*)-**1**·CH_2Cl_2 having $[\alpha]_D$ –168.5 (*c* 1.00, CH_2Cl_2) after recrystallization from dichloromethane–methanol.

(R,S*)-trans-Di-μ-chlorobis[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-C,N]dipalladium(II)–1-Dichloromethane ((R*,S*)-trans-1·CH2Cl2).* A solution of (*R,R*)-*cis*-**1**·CH_2Cl_2 (0.50 g) in dichloromethane (15 mL) was mixed with a similar solution of the mirror-image enantiomer of the complex; pure (*R*,S**)-*trans*-**1**·CH_2Cl_2 crystallized from the resulting solution over 12 h (0.98 g, 98%): mp 211–213 °C. Anal. Calcd for $C_{29}H_{34}Cl_4N_2Pd$: C, 45.5; H, 4.5; N, 3.7. Found: C, 45.6; H, 4.7; N, 3.7. ^{1}H NMR ($CDCl_3$): δ 1.93 (m, CH*Me*), 2.74 (s, N*Me*–(*R*,R**)-*trans*, (*R*,S**)-*trans*), 2.79 (s, N*Me*–(*R*,R**)-*cis*), 2.81 (s, N*Me*–(*R*,S**)-*cis*), 2.97 (s, N*Me*–(*R*,R**)-*trans*), 2.98 (s, N*Me*–(*R*,S**)-*trans*), 2.99 (s, N*Me*–(*R*,S**)-*cis*), 3.00 (s, N*Me*–(*R*,R**)-*cis*), 4.19 (br q, $^3J_{HH}$ = 6.06 Hz, C*H*Me), 5.30 (s, CH_2Cl_2), 7.36–7.79 (m, Ar*H*). Assignments for cis and trans diastereomers are arbitrary.

[SP-4-4-(S)]-(–)-Chloro[1-[1-(dimethylamino)ethyl]naphthalenyl-C,N][(1R, 2S, 5R)-menthyldiphenylphosphine]palladium(II) (3a). A solution of (*S,S*)-**1**·CH_2Cl_2 (1.33 g, 1.74 mmol; $[\alpha]_D$ +172.2 (*c* 1.00, CH_2Cl_2)) in dichloromethane (50 mL) was treated with (1*R*, 2*S*, 5*R*)-menthyldiphenylphosphine (1.13 g, 3.48 mmol). After ca. 30 min, the solvent was removed to leave a yellow glass. (The $^{31}P\{^1H\}$ NMR spectrum of the glass in chloroform-d_1 contained a single peak at δ 43.08.) The crude product was dissolved in dichloromethane (10 mL) and *n*-hexane (30 mL) was added. Careful concentration of this solution in vacuo furnished the pure product as yellow plates (1.76 g, 76%): mp 119–121 °C, $[\alpha]_D$ –157.1 (*c* 1.00, CH_2Cl_2). Anal. Calcd for $C_{36}H_{45}ClNPPd$: C, 65.1; H, 6.8; N, 2.1. Found: C, 64.9; H, 7.2; N, 1.9. ^{1}H NMR ($CDCl_3$): δ 0.48 (d, 3 H, $^3J_{HH}$ = 5.73 Hz, menthyl-CH*Me*), 0.63 (d, 3 H, $^3J_{HH}$ = 6.77 Hz, CH*Me*Me), 0.73–0.93 (m, 3 H, CH_2), 0.87 (d, 3 H, $^3J_{HH}$ = 6.35 Hz, CHMe*Me*), 1.02 –1.15 (m, 1 H, C*H*H), 1.40–1.85 (m, 4 H, menthyl-CH, CH_2), 2.11 (d, 3 H, $^3J_{HH}$ = 6.41 Hz, NCH*Me*), 2.49 (s, 3 H, N*Me*), 2.93 (d, 3 H, $^4J_{PH}$ = 3.35 Hz, N*Me*), 3.16 (m, 1 H, menthyl-C*H*), 3.44 (m, 1 H, menthyl-C*H*), 4.26 (d of q, 1 H, $^3J_{HH}$ = 6.12 Hz, $^4J_{PH}$ = 5.83 Hz, NC*H*Me), 6.67 (d of d, 1 H, $^3J_{HH}$ = 8.52 Hz, $^3J_{HH}$ = 6.01 Hz, Ar*H*-3), 6.96 (d, 1 H, $^3J_{HH}$ = 8.67 Hz, Ar*H*), 7.19–7.71 (m, 12 H, Ar*H*), 8.22–8.29 (m, 2 H, Ar*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 43.08 (s).

[SP-4-4-(R)]-(+)-Chloro[1-[1-(dimethylamino)ethyl]naphthalenyl-C,N][(1R, 2S, 5R)-menthyldiphenylphosphine]palladium(II)-0.5-Dichloromethane (3b·0.5CH2Cl2). This compound was prepared as described above, but with use of (*R,R*)-*cis*-**1**·CH_2Cl_2 and recrystallisation of the crude product from dichloromethane-methanol. Yield: 84%, mp 159–160 °C, $[\alpha]_D$ +136.1 (*c* 1.04, CH_2Cl_2). Anal. Calcd for $C_{36.5}H_{46}Cl_2NPPd$: C, 62.0; H, 6.6, N, 2.0. Found: C, 62.4; H, 6.8; N, 2.0. ^{1}H NMR ($CDCl_3$): δ 0.30–0.78 (m, 3 H, menthyl-CH, CH_2) 0.68 (d, 3 H, $^3J_{HH}$ = 7.02 Hz, menthyl-CH*Me*), 0.71 (d, 3 H, $^3J_{HH}$ = 6.77 Hz, CH*Me*Me), 1.18–1.30 (m, 1 H, C*H*H), 1.25 (d, 3 H, $^3J_{HH}$ = 6.72 Hz, CHMe*Me*), 1.45–1.60 (m, 4 H, menthyl-CH, CH_2), 1.91–1.96 (m, 1 H C*H*H) 2.05 (d, 3 H, $^3J_{HH}$ = 6.35 Hz, NCH*Me*), 2.49 (s, 3 H, N*Me*), 2.90 (d, 3 H, $^4J_{PH}$ = 3.42 Hz, N*Me*),

3.76–3.86 (m, 1 H, menthyl-C*H*), 4.01–4.09 (m, 1 H, menthyl-C*H*), 4.24 (d of q, 1 H, $^3J_{HH}$ = 6.08 Hz, $^4J_{PH}$ = 5.98 Hz, NC*H*Me), 5.29 (s, 1 H, CH_2Cl_2), 6.78 (d of d, 1 H, $^3J_{HH}$ = 8.54 Hz, $^4J_{PH}$ = 5.68 Hz, Ar*H*-3), 7.00 (d, 1 H, $^3J_{HH}$ = 8.67 Hz, Ar*H*), 7.19–7.71 (m, 12 H, Ar*H*), 8.07–8.13 (m, 2 H, Ar*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 35.61 (s).

[SP-4-4-(S)]-(–)-Chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-C,N][(1R, 2S, 5R)-neomenthyldiphenylphosphine]palladium(II)–1-Diethyl Ether (**4a**). This compound was isolated in 90% yield by the above method with use of (*S*)-*cis*-**1**·CH_2Cl_2 and the phosphine: yellow rosettes from diethyl ether – *n*-hexane. Mp 145–147 °C, $[\alpha]_D$ –83.9 (*c* 1.00, CH_2Cl_2). Anal. Calcd for $C_{40}H_{55}ClNOPPd$: C, 65.0; H, 7.5; N, 1.9. Found: C, 63.3; H, 7.4; N, 1.5. ^1H NMR ($CDCl_3$): δ 0.28 (d, 3 H, $^3J_{HH}$ = 6.78 Hz, menthyl-CH*Me*), 1.21 (t, 6 H, $^3J_{HH}$ = 7.14 Hz, $O(CH_2CH_3)_2$),1.08 (d, 6 H, $^3J_{HH}$ = 7.20 Hz, $CHMe_2$), 1.25–1.98 (m, 7 H, menthyl-C*H*, CH_2), 2.10 (d, 3 H, $^3J_{HH}$ = 6.35 Hz, NCH*Me*), 2.59 (s, 3 H, NMe), 2.61–2.66 (m, 1 H, menthyl-C*H*), 2.94 (d, 3 H, $^4J_{PH}$ = 3.29 Hz, NMe), 3.14 (br s, 1 H, menthyl-C*H*), 3.47 (q, 4 H, $^3J_{HH}$ = 7.14 Hz, $O(CH_2CH_3)_2$), 3.82–3.94 (m, 1 H, menthyl-C*H*), 4.29 (d of q, 1 H, $^3J_{HH}$ = 6.08 Hz, $^4J_{PH}$ = 6.02 Hz, NC*H*Me), 6.86 (d of d, 1 H, $^3J_{HH}$ = 8.49 Hz, $^4J_{PH}$ = 5.50 Hz, Ar*H*-3), 7.03 (d, 1 H, $^3J_{HH}$ = 8.66 Hz, Ar*H*), 7.11–7.17 (m, 2 H, Ar*H*), 7.30–7.54 (m, 8 H, Ar*H*), 7.65 (d, 1 H, $^3J_{HH}$ = 8.25 Hz, Ar*H*), 7.72 (d, 1 H, $^3J_{HH}$ = 8.37 Hz, Ar*H*), 8.03–8.09 (m, 2 H, Ar*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 38.75 (s).

[SP-4-4-(R)]-(+)-Chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-C,N][(1S, 2S, 5R)-neomenthyldiphenylphosphine]palladium(II) (**4b**) With use of (*R*)-*cis*-**1**·CH_2Cl_2 and the phosphine by the above method, the product was obtained as yellow needles dichloromethane–methanol with mp 208–210 °C, $[\alpha]_D$ +19.8 (*c* 1.00, CH_2Cl_2). Anal. Calcd for $C_{36}H_{45}ClNPPd$: C, 65.1; H, 6.8; N, 2.1. Found: C, 64.7; H, 6.5; N, 2.0. ^1H NMR ($CDCl_3$): δ 0.92 (d, 6 H, $^3J_{HH}$ = 6.66 Hz, menthyl-CH*Me*, CHMe*Me*), 1.05 (d, 3 H, $^3J_{HH}$ = 7.02 Hz, CH*Me*Me), 1.10 (m, 1 H, CH_2), 1.27–1.35 (m, 2 H, CH_2), 1.49–1.70 (m, 4 H, menthyl-C*H*, CH_2), 2.01 (m, 1 H, CH_2), 2.09 (d, 3 H, $^3J_{HH}$ = 6.31 Hz, NCH*Me*), 2.60 (d, 3 H, $^4J_{PH}$ = 1.71 Hz, NMe), 2.95 (d, 3 H, $^4J_{PH}$ = 3.42 Hz, NMe), 3.17–3.37 (m, 2 H, menthyl-C*H*), 4.29 (d of q, 1 H, $^3J_{HH}$ = 6.15 Hz, $^4J_{PH}$ = 6.10 Hz, NC*H*Me), 6.64 (d of d, 1 H, $^3J_{HH}$ = 8.33 Hz, $^4J_{PH}$ = 5.71 Hz, Ar*H*-3), 6.93 (d, 1 H, $^3J_{HH}$ = 8.67 Hz, Ar*H*), 7.17–7.70 (m, 12 H, Ar*H*), 8.12–8.18 (m, 2 H, Ar*H*). $^3P\{^1H\}$ NMR ($CDCl_3$): δ 40.12 (s).

X-Ray Crystal Structure Determinations. Both structures were solved using direct methods (SIR 92)[20] and expanded using Fourier techniques (DIRDIF 94)[21]. All non-hydrogen atoms were refined anisotropically in both cases. For the trans isomer, the dichloromethane solvate molecule was refined with half occupancy. Hydrogen atoms were included in calculated positions and held fixed. All calculations were performed using the teXsan structure analysis software of Molecular Structure Corporation.[22] Atomic coordinates, bond lengths and angles, and thermal parameters for both complexes have been deposited with the Cambridge Crystallographic Data Centre.

Supplementary Material Available: For (*R,R*)-*cis*-**1**·CH_2Cl_2 and (R^*,S^*)-*trans*-**1**·CH_2Cl_2, text detailing the X-ray analyses, figures showing the structures, and tables of bond distances and angles, and torsion angles have been deposited with the Cambridge Crystallographic Centre (36 pages).

Table 1. Crystal Data and Experimental Parameters for X-ray Structure Analyses

	(*R*, *R*)-*cis*-**1**·CH_2Cl_2	(*R**,*S**)-*trans*-**1**·CH_2Cl_2
formula	$C_{28}H_{32}Cl_2N_2Pd_2 \cdot CH_2Cl_2$	$C_{28}H_{32}Cl_2N_2Pd_2 \cdot CH_2Cl_2$
M_r	765.21	765.21
crystal system	tetragonal	monoclinic
space group	$P4_12_12$ (#92)	$P2_1/n$ (#14)
a (Å)	9.619(1)	9.877(2)
b (Å)		9.056(3)
c (Å)	32.890(3)	16.955(2)
β (°)		94.19(1)
cell volume (Å)	3043.4(9)	1512.4(5)
Z	4	2
D_c (g cm^{-3})	1.670	1.680
F(000)	1528	764
instrument	AFC6R	AFC6S
radiation	Cu Kα	Mo Kα
scan mode	ω–2θ	ω–2θ
θ range for data collection (°)	1.5–60.1	1.5–25
scan angle (°)	(1.2 + 0.3tanθ)	(0.80 + 0.34tanθ)
no. of reflections collected	2629	3037
no. observed $I > 3\sigma(I)$	1317	2301
temperature (K)	213	295
crystal dimensions (mm)	0.28 x 0.28 x 0.24	0.32 x 0.20 x 0.20
μ (cm^{-1})	129.13	15.64
min; max transmission (Ψ)	0.544; 1.000	0.976; 1.000
residual electron density (e Å^{-3})	min −1.14; max 2.14	min −0.34; max 0.62
final R; R_w	0.055; 0.070	0.025; 0.046

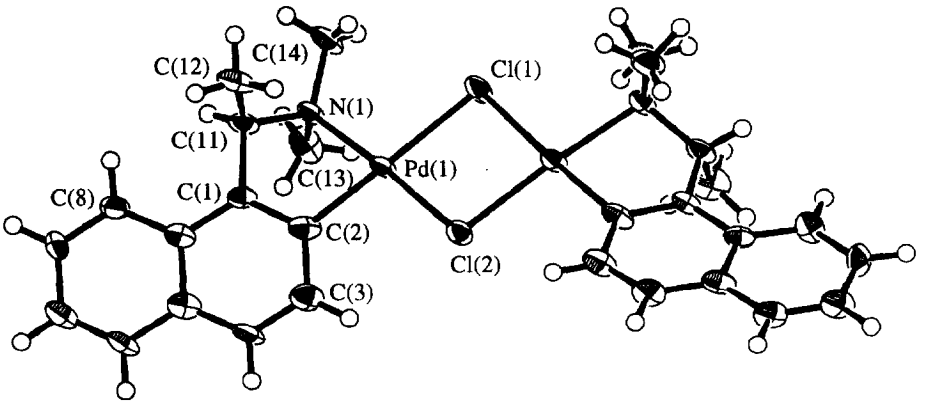


Fig. 2. ORTEP drawing of *(R,R)-cis* - **1**. Selected interatomic distances (Å) and angles (°) in the molecule are as follows: Pd(1)–C(2) 2.352(3), Pd(1)–N(1) 2.09(1), Pd(1)–Cl(1) 2.458(3), Pd(1)–Cl(2) 2.352(3), Cl(1)–Pd(1)–Cl(2) 86.0(1), Cl(1)–Pd(1)–N(1) 97.4(3), C(2)–Pd(1)–N(1) 80.3(4), C(2)–Pd(1)–Cl(2) 96.3(4), Pd(1)–N(1)–C(11) 106.0(7), C(1)–C(11)–N(1) 106(1), C(2)–C(1)–C(11) 116(1), C(2)–Pd(1)–N(1) 80.3(4).

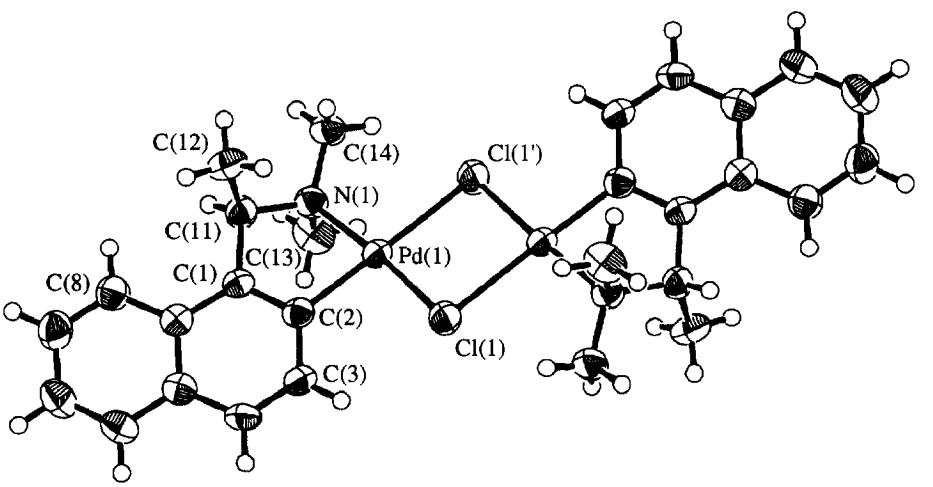


Fig. 4. ORTEP drawing of *(R*,S*)-trans* - **1**. Selected interatomic distances (Å) and angles (°) are as follows: Pd(1)–C(2) 1.967(4), Pd(1)–N(1) 2.072(4), Pd(1)–Cl(1) 2.475(1), Cl(1)–Pd(1)–Cl(1') 86.12(4), Cl(1)–Pd(1)–N(1) 97.9(1), C(2)–Pd(1)–N(1) 80.9(2), C(2)–Pd(1)–Cl(1) 95.1(1), Pd(1)–N(1)–C(11) 107.1(2), C(1)–C(11)–N(1) 105.6(3), C(2)–C(1)–C(11) 116.3(4), C(2)–Pd(1)–N(1) 80.9(2).

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(*Received in UK* 31 *October* 1996; *accepted* 8 *January* 1997)