Stereochemical Investigation of Bis(bidentate)–Palladium(II) Complexes. Transmission of Ring Chiralities between Chelating Amine Ligands via Their Prochiral N-Methyl Substituents

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Three diastereomeric palladium(II) complex cations containing the orthometalated (S)-dimethyl(1-(α-naphthyl)-ethyl)amine together with the (R,R)-, (S,S)- and (R,S)- forms of N,N,N',N'-tetramethyl-2,3-butanediamine have been prepared separately as their perchlorate salts. The (S,R,R) isomer with $[\alpha]_D$ +167° (c 1.0, CH$_2$Cl$_2$) crystallizes in the space group P2$_1$2$_1$2$_1$ with a = 7.872 (3) Å, b = 15.843 (5) Å, c = 20.273 (6) Å, Z = 4, and R = 0.0372. The square-planar geometry around palladium is slightly distorted. The (S,S,S) isomer with $[\alpha]_D$ +87° (c 1.0, CH$_2$Cl$_2$) crystallizes in the space group P2$_1$ with a = 7.978 (2) Å, b = 20.856 (2) Å, c = 15.218 (2) Å, β = 90.06 (2)°, Z = 4, and R = 0.0362. The coordination geometry around palladium is distorted seriously from square-planar due to severe ligand–ligand interactions. The (S,R,S) isomer with $[\alpha]_D$ +158° (c 1.0, CH$_2$Cl$_2$) crystallizes stereoselectively as a sole conformer in the space group P2$_1$ with a = 11.661 (3) Å, b = 9.982 (2) Å, c = 13.227 (4) Å, β = 105.29 (2)°, Z = 2, and R = 0.0319. In solution, the diamine ligands of these complexes are found to be labile under ambient conditions, as evidenced by facile intermolecular ligand redistributions between diastereomers. For the (S,R,S) isomer, a marked temperature dependent asymmetric equilibration occurred between two possible internal diastereomeric structures. Furthermore, it has been shown that although steric factors govern the relative thermodynamic stabilities in this series of complexes, these effects are frequently outweighed by lattice effects in isolated solids, where a sterically unfavorable isomer can be isolated readily from a diastereomeric equilibrium mixture in the crystallization process.

Introduction

Enantiofacial recognition is one of the fundamental requirements in the design of metal-based auxiliaries for asymmetric synthesis.[1] To date, most of the excellent work in asymmetric catalysis involves optically active diphosphines with prochiral substituents borne on the phosphorus donor atoms while the chirality of the bidentate resides in the carbon skeleton.[2] The spectacular success of such asymmetric controllers is partly attributed to the great ability of the prochiral groups in projecting chirality to the center of reaction. Several diamines with similar molecular architecture are also found to be impressive external chiral inducing agents.[3]

We are interested in developing the enantiomerically pure forms of the square-planar palladium(II) complex, **1**, into efficient catalysts for asymmetric synthesis. The compound is selected because it meets the following stereochemical requirements. First, the rigidity of the 5-membered chiral organometallic ring is well established in which a particular skew configuration is adopted with the methyl substituent on the α-carbon invariably taking up an *axial* position, presumably due to repulsive forces between the methyl groups on the α-carbon and on nitrogen.[4] Hence, the λ

configuration will always be observed for the chelate ring when the absolute configuration of the carbon stereocenter is S. With this constraint, the chiral induction cannot be dissipated by rotameric conformations. Second, the prochiral N–Me groups, which are located next to the carbon stereocenter, are expected to project the chirality of the asymmetric chelate ring to the site of reaction. Third, the organometallic chelation has been found to be kinetically and thermodynamically stable. Indeed, the 5-membered ring remained unchanged after being treated with hydrochloric acid, and in a few cases, it can even be recovered from the reaction with aqueous cyanide.[4,5] Fourth, both enantiomeric forms of the naphthylamine ligands are commerically available and the method for the synthesis of **1** is highly efficient.[5] Fifth, the weakly coordinated acetonitrile ligands are readily displaced by most substrates. Finally, the compound is soluble in most common organic solvents, such as benzene and dichloromethane, which are generally suitable for asymmetric synthesis. Indeed, with these outstanding physical and chemical properties, it is unsurprising that Wild and co-workers have already developed an analogous dimeric compound, bis(μ-chloro)bis[(R/S)-[1-(dimethylamino)ethyl]naphthalenyl-C,N]dipalladium(II), as an efficient inorganic resolving agent for bidentate ligands containing tertiary phosphorus and arsenic stereocenters.[4] Recently, we have reported the use of **1** for the optical resolution of two chelating sulfoxides[5] and their application as diamagnetic NMR chiral shift reagents for some functionalized diamines.[6]

The distinct electronic directing effects originating from the organometallic ring in **1** have been reported previously.[4,7] In this paper we show the diastereotopic interactions between the prochiral NMe groups in the product complexes, **2**, where the acetonitrile ligands in (S)-1 are displaced by the (R,R), (S,S) and (R,S) forms of N,N,N',N'-tetramethyl-2,3-butanediamine.

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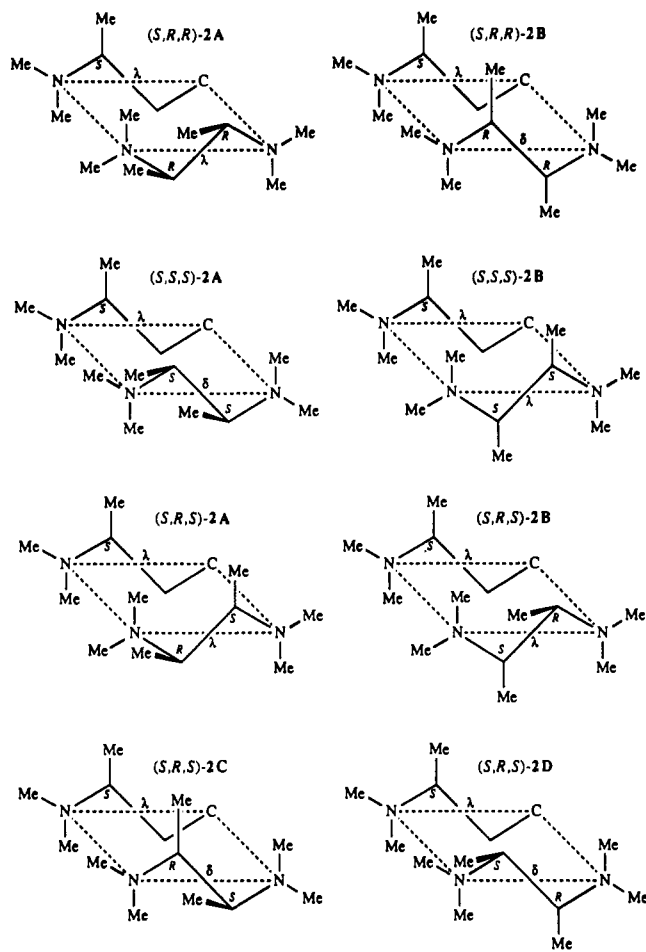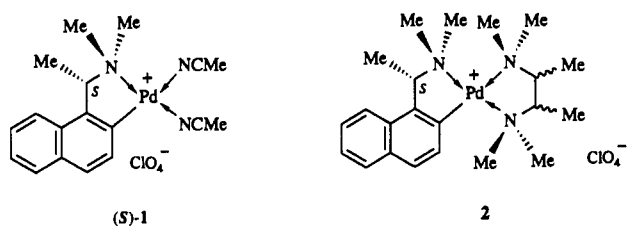
Figure 1. Possible square-planar palladium(II) diastereomers of **2**.

In subsequent work, it will be shown that the information obtained in this model study is crucial to the rational utilization of the stereoelectronic properties of **1** in some stereochemically highly demanding organic reactions.

Results

Stereochemical Considerations. As outlined in the Introduction, the 5-membered ring in (S)-**1** adopted stereospecifically the λ configuration. The same stereochemistry is expected for the organometallic rings in all the isomers of **2**. Accordingly, when an optically active form of the C_2-symmetric N,N,N',N'-tetramethyl-2,3-butanediamine bidentate ligand is used, the sole source of diastereomerism in the resulting complex will be from the absolute conformation adopted by the nonplanar diamine chelate. Therefore there are two possible diastereomeric conformers each for (S,R,R) and (S,S,S)-**2** (Figure 1). Structure (S,R,R)-**2A**, with the λλ ring configurations, has the four adjacent cis N–Me groups (two each from the organometallic and the diamine rings) in staggered orientation together with both C–Me groups of the diamine chelate ring occupying equatorial positions. Due to the δλ configuration in structure (S,R,R)-**2B**, however, all the C–Me groups in the complex cation are axial and the cis N–Me groups are in eclipsed form. It is well known that C–Me

substituted 5-membered chelate rings always adopt a single static chiral conformation with the C–Me groups equatorially disposed.[8] This literature finding, taken in conjunction with the sterically favorable staggered orientation of the neighboring N–Me groups, predicts that isomer (S,R,R)-**2A** is energetically favorable. On the other hand, the axial dispositions of the C–Me groups in isomer (S,R,R)-**2B** are favorable only if enormous internal equatorial–equatorial repulsive forces exist between the methyl groups within the chelating diamine ring, as in the case of its neighboring 5-membered organometallic counterpart.

In isomer (S,S,S)-**2A**, both C–Me groups on the diamine chelate ring are equatorially disposed. The neighboring prochiral N–Me groups are, however, orientated in eclipsed positions. Dreiding models indicated that these methyl groups are suffering from severe steric constraints and, indeed, a square-planar model of (S,S,S)-**2A** could not be constructed when normal bond distances and bond angles were considered. The adoption of the λλ configurations as in isomer (S,S,S)-**2B**, on the other hand, would markedly relieve the interchelate eclipsed N–Me interactions, but both C–Me groups on the diamine skeleton have to be axially located. In this arrangement, however, the classic 1,3-diaxial repulsion occurs between the C-methyl group and one of the N-methyl groups within the diamine ring. It is not possible, therefore, to apply model studies and literature data to track the steric interactions and to identify the more stable isomer in (S,S,S)-**2**. This type of structural dilemma can only be resolved through experimental investigations.

In contrast to the (S,R,R) and (S,S,S) diastereomers, the coordination of the originally centrosymmetric *meso*-diamine ligand to the asymmetrical (S)-**1** can, in principle, lead up to four stereochemically distinct isomers in (S,R,S)-**2** (Figure 1). In all four isomers, one of the C–Me groups on the diamine ring is equatorially disposed while its adjacent counterpart occupies an axial position. The equitable axial–equatorial distribution of the C–Me groups in this chelate ring remits any internal conformational preference. The absolute chirality of the 5-membered diamine ring should therefore be solely governed by the diastereotopic interactions with the stereochemically rigid organometallic system, obviously, via their cis prochiral N–Me groups. Structures (S,R,S)-**2A** and -**2B** have these methyl groups in staggered form while structures (S,R,S)-**2C** and -**2D** have them in eclipsed arrangements. Given the choices of the four (S,R,S) conformers, model studies clearly indicated that the unbearable torsional strains will preclude the formation of **2C** and **2D**. Interestingly, both of the sterically more favorable structures **A** and **B** adopt the λλ absolute ring configurations. These two structures are, however, diastereomeric due to the divergence in the relative axial-equatorial dispositions of the substituents at the carbon stereocenters in the diamine ring. The chiral array of the N–Me groups on the organometallic ring is therefore expected to exercise a discriminating effect on the relative populations of these two stereochemically nonequivalent cations. Structural investigations of (S,R,S)-**2** in the solid state and in solution would therefore directly evaluate the chiral inductive effect from the N-methyl groups of the orthometalated dimethyl-(1-(α-naphthyl)ethyl)amine ring.

Formation and Structural Analysis of Diastereomers. The various diastereomers of **2** were obtained directly as their perchlorate salts in high yields from the reaction between (S)-**1** and the appropriate forms of the N-methyl-substituted diamine in dichloromethane. All three complexes are highly crystalline and pale yellow in color. Selected NMR data for the complexes are given in Table 1. In acetone, they behave as 1:1 electrolytes. In contrast to the analogous water soluble palladium complex containing ethylenediamine,[4] the perchlorate salts of **2** are soluble

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Table 1. Selected ¹H NMR Data for the Diastereomeric Complexes[a]

	(S,R,R)-2	(S,S,S)-2	(S,R,S)-2	
			major isomer	minor isomer
δ CMe[b]	1.08 (6.4)	1.08 (6.7)	1.24 (6.8)	1.42 (6.8)
	1.09 (6.4)	1.11 (6.6)	1.63 (7.0)	1.50 (7.0)
	2.14 (6.3)	2.06 (6.3)	2.17 (6.3)	2.21 (6.3)
δ NMe[c]	2.60[d]	2.65	2.57[d]	2.57
	2.74	2.71	2.62	2.69
	2.84	2.73	2.76	2.80
	2.87	2.76	2.89	2.85
	2.96	2.78	3.24	2.89
		3.13		2.95

[a] 300 MHz ¹H NMR spectra chemical shift values in ppm for CDCl₃ solutions measured at 25 °C. [b] Resonance signals appeared as doublets (³J_{HH} values are given in parentheses). [c] Sharp singlets. [d] Two NMe resonances occurred at the same chemical shift.

Table 2. Crystal Data for Three Diastereomeric Complexes

|	(S,R,R)-2	(S,S,S)-2	(S,R,S)-2
chem formula	C₂₂H₃₆ClN₃-O₄Pd	C₂₂H₃₆ClN₃-O₄Pd	C₂₈H₄₂ClN₃-O₄Pd
fw	548.4	548.4	626.5
cryst system	orthorhombic	monoclinic	monoclinic
space group	P2₁2₁2₁	P2₁	P2₁
a, Å	7.872(3)	7.978(2)	11.661(3)
b, Å	15.843(5)	20.856(2)	9.982(2)
c, Å	20.273(6)	15.218(2)	13.227(4)
β, deg	–	92.06(2)	105.29(2)
V, Å³	2528.6(14)	2530.4(8)	1485.2(7)
Z	4	4	2
D_c, g cm⁻³	1.440	1.439	1.401
D_m, g cm⁻³	1.426	1.452	1.390
F(000)	1136	1136	652
μ, mm⁻¹	0.87	0.87	0.75
no. of data colld	2584	4986	2934
no. of data refined[a]	2295	3973	2659
GOF	1.30	0.86	1.12
R[b]	0.0372	0.0362	0.0319
R_w[c]	0.0435	0.0465	0.0443

[a] $[F > 3\sigma(F)]$. [b] $R = \Sigma|F_o - F_c|/\Sigma(F_o)$. [c] $R_w = \{[\Sigma w|F_o - F_c|^2]/[\Sigma w(F_o)^2]\}^{1/2}$.

in organic solvents. The structures of all diastereomers in the solid state were characterized by X-ray crystallography. In all the diastereomers, the 5-membered organometallic ring adopted the predicted λ configuration. In solution, the geometries of the diamine rings were assigned by ¹H NMR spectroscopy.

It should be noted that, interestingly, all forms of **2** could be prepared only from **1**. Attempts to prepare these diastereomeric cations from the analogous dimeric complex, bis(μ-chloro)bis-[(S)-[1-(dimethylamino)ethyl]naphthalenyl-C,N]dipalladium-(II) were unsuccessful. NMR studies of samples containing the various forms of the diamine and 0.5 equiv of the dimeric complex in CDCl₃ confirmed that the bidentate ligand remained uncoordinated in solution.

(a) The (S,R,R) Diastereomer.[9] Pale yellow crystals of (S,R,R)-**2** suitable for X-ray crystallography were grown from a mixture of benzene/dichloromethane solution. Crystallographic data are given in Table 2 and positional and thermal parameters are given in Table 3. The structure of the complex cation is shown in Figure 2. It is clearly evident that both rings adopted the λ configuration as depicted by structure (S,R,R)-**2A** in Figure 1. The palladium center is slightly distorted from the ideal square planar geometry (Table 4). As predicted, the C-methyl groups of the diamine ring occupy the equatorial sites while that of the

(9) In this series of compounds, each diastereomeric complex contains three carbon stereocenters. For clarity, the first descriptor always refers to the absolute configuration at the carbon center in the organometallic ring. The second and third descriptors refer to the chirality of the diamine carbon centers. For racemic mixtures, the R* and S* descriptors refer to the relative configurations of the stereocenters.
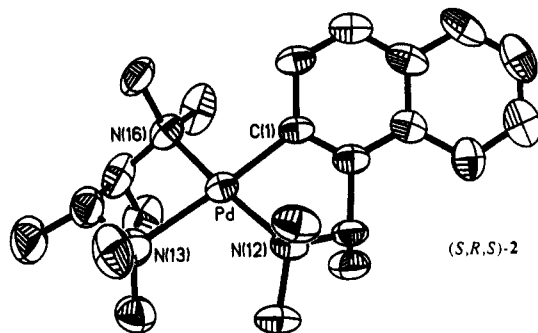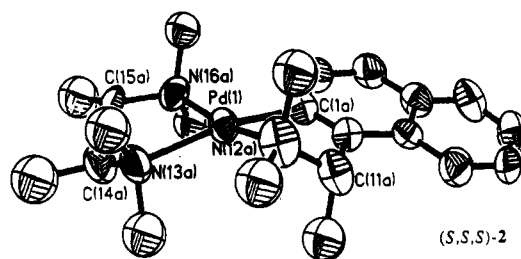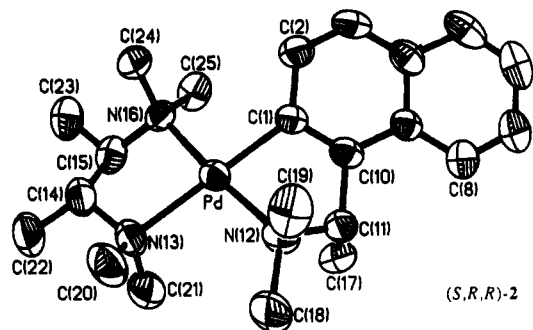
Figure 2. ORTEP plot of the three diastereomeric complex cations showing the labeling scheme for non-hydrogen atoms.

organometallic ring takes up the axial position. The two adjacent C–Me carbons are only 0.11 and 0.36 Å from the mean C(1)–N(12)–N(13)–N(16) plane. It is noted, with interest, that the bond lengths C(11)–N(12), C(14)–N(13), and C(15)–N(16) are similar in magnitude. This observation suggests that repulsion between the methyl group on C(11) and N(12) alone may not be the dictatorial force for the C-methyl group to assume the axial position.[10] Other steric forces must be at work. We believe that severe unfavorable interactions exist between the proton borne on C(8) of the strictly planar naphthalene ring and any equatorially disposed steric substituent at the C(11) stereocenter.

The 300-MHz ¹H NMR spectrum of the complex in CDCl₃ contained sharp singlets and doublets for the nonequivalent N–Me and C–Me groups indicating only one isomer is present in solution. Resonance signal for the benzylic proton in the organometallic system was observed at δ 4.12 as a simple quartet (³J_{HH} = 6.2 Hz). Two sets of distinct doublet of quartet patterns occurring at δ 3.17 (³$J_{HH'}$ = 11.2 Hz, ³J_{HMe} = 6.5 Hz) and 3.27 (³$J_{HH'}$ = 11.2 Hz, ³J_{HMe} = 6.4 Hz) were assigned to the two vicinal protons at the carbon stereocenters in the diamine chelate. The chemical shifts and the vicinal coupling constant of these signals are in good agreement with the axial dispositions of both protons with a HCC'H' dihedral angle of ca. 180° in the λ orientation of the bidentate ligand.[11] Furthermore, when the spectrum of the complex was measured in dichloromethane-d_2 down to –80 °C,

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Table 3. Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{Å}^2 \times 10^3$)

	x	y	z	U(eq)ᵃ		x	y	z	U(eq)ᵃ
					(S,R,R)-2				
Pd	9727(1)	5565(1)	1162(1)	43(1)	C(17)	12175(10)	4569(6)	29(4)	69(3)
C(1)	8363(8)	4693(4)	666(3)	44(2)	C(18)	11921(15)	6370(6)	0(5)	104(5)
C(2)	6832(9)	4273(5)	846(3)	56(2)	C(19)	8906(13)	6311(5)	-132(5)	80(4)
C(3)	6162(9)	3662(5)	469(4)	57(2)	C(20)	10966(12)	7369(4)	1470(4)	78(3)
C(4)	6896(9)	3416(4)	-125(4)	54(2)	C(21)	13095(10)	6263(6)	1645(5)	76(3)
C(5)	6256(11)	2729(5)	-526(4)	69(3)	C(22)	11943(12)	6861(6)	2895(4)	84(3)
C(6)	7043(11)	2509(5)	-1089(4)	72(3)	C(23)	9910(11)	5395(5)	3314(3)	74(3)
C(7)	8510(11)	2943(5)	-1310(4)	64(3)	C(24)	7324(8)	5498(5)	2270(4)	60(2)
C(8)	9129(10)	3584(4)	-960(3)	58(2)	C(25)	9042(11)	4243(4)	2178(4)	63(3)
C(9)	8385(8)	3846(4)	-354(3)	45(2)	Cl	6066(3)	8677(1)	2115(1)	72(1)
C(10)	9028(8)	4493(5)	61(3)	46(2)	O(1)	6160(10)	8962(5)	2776(4)	113(2)
C(11)	10579(9)	5006(4)	-157(3)	52(2)	O(2A)	4413(22)	8664(11)	1793(8)	112(5)
N(12)	10338(9)	5856(3)	167(3)	62(2)	O(3A)	7216(19)	9053(9)	1670(7)	96(4)
N(13)	11263(7)	6500(4)	1708(3)	57(2)	O(4A)	6539(27)	7785(13)	2042(9)	134(6)
C(14)	10704(10)	6449(4)	2417(3)	59(3)	O(2B)	7513(35)	8224(16)	2031(11)	171(8)
C(15)	10354(9)	5525(4)	2585(3)	55(2)	O(3B)	4568(31)	8291(15)	2103(11)	157(8)
N(16)	9049(7)	5170(3)	2116(3)	47(2)	O(4B)	6151(19)	9468(10)	1783(7)	100(4)
					(S,S,S)-2				
Pd(1)	7840(1)	195	5242(1)	54(1)	C(9B)	5844(10)	4403(4)	8885(5)	57(3)
C(1A)	9206(9)	-329(4)	4401(4)	50(2)	C(10B)	6290(10)	3901(4)	9495(5)	54(3)
C(2A)	10514(10)	-138(4)	3836(5)	62(3)	C(11B)	7707(12)	3989(4)	10163(6)	65(3)
C(3A)	11236(11)	-563(4)	3281(6)	68(3)	N(12B)	7363(11)	3525(4)	10903(5)	74(3)
C(4A)	10664(10)	-1208(4)	3192(5)	58(3)	N(13B)	8377(8)	1956(4)	10930(4)	64(2)
C(5A)	11337(13)	-1634(5)	2601(7)	78(4)	C(14B)	8213(12)	1362(5)	10384(6)	67(3)
C(6A)	10679(13)	-2235(5)	2487(6)	81(4)	C(15B)	6407(12)	1237(5)	10162(6)	67(3)
C(7A)	9409(13)	-2434(4)	3008(7)	82(4)	N(16B)	5617(8)	1811(3)	9732(4)	53(2)
C(8A)	8762(11)	-2047(4)	3628(6)	64(3)	C(17B)	9391(12)	3878(6)	9775(7)	85(4)
C(9A)	9370(9)	-1412(3)	3727(5)	48(2)	C(18B)	5815(17)	3732(6)	11371(7)	98(5)
C(10A)	8677(10)	-954(4)	4343(5)	48(2)	C(19B)	8710(18)	3568(6)	11576(7)	109(5)
C(11A)	7361(12)	-1170(4)	4942(6)	67(3)	C(20B)	7904(14)	1838(6)	11849(6)	87(4)
N(12A)	7494(11)	-748(4)	5734(5)	77(3)	C(21B)	10146(11)	2166(6)	10893(7)	88(4)
N(13A)	5959(9)	747(4)	5950(5)	79(3)	C(22B)	9044(16)	761(5)	10821(8)	101(5)
C(14A)	5932(12)	1400(5)	5543(6)	76(4)	C(23B)	6070(15)	618(5)	9647(7)	87(4)
C(15A)	7699(15)	1611(6)	5420(8)	88(4)	C(24B)	5843(13)	1793(4)	8767(5)	68(3)
N(16A)	8620(9)	1125(3)	4884(4)	62(2)	C(25B)	3814(2)	1804(1)	9944(1)	71(3)
C(17A)	5597(13)	-1120(6)	4487(8)	93(4)	Cl(1)	10905(1)	655(1)	8096(1)	77(1)
C(18A)	6124(18)	-910(6)	6333(8)	110(5)	O(11A)	10870	725	7183	174(6)
C(19A)	9073(18)	-897(6)	6238(7)	100(5)	O(12A)	12440	441	8379	185(7)
C(20A)	6305(16)	747(6)	6904(6)	108(5)	O(13A)	9674	195	8275	152(5)
C(21A)	4238(12)	459(7)	5782(8)	105(5)	O(14A)	10475	1230	8470	150(5)
C(22A)	4912(20)	1874(8)	6053(11) ·	148(7)	O(11B)	11425	489	8941	72(6)
C(23A)	7805(17)	2299(5)	5077(9)	109(5)	O(12B)	9625	1106	8133	83(7)
C(24A)	8292(13)	1248(5)	3913(5)	73(3)	O(13B)	12237	924	7665	105(9)
C(25A)	10422(1)	1200(1)	5096(1)	77(3)	O(14B)	10334	121	7643	194(21)
Pd(2)	6688(1)	2656(1)	10268(1)	50(1)	Cl(2)	3110(2)	2141(1)	3186(1)	99(1)
C(1B)	5524(1)	3310(1)	9482(1)	51(2)	O(21A)	1662	2449	3319	155(5)
C(2B)	4122(1)	3241(1)	8873(1)	67(3)	O(22A)	3022	1501	3404	198(8)
C(3B)	3604(12)	3719(5)	8316(6)	73(3)	O(23A)	4394	2427	3690	221(9)
C(4B)	4484(10)	4304(4)	8288(5)	58(3)	O(24A)	3494	2199	2303	181(6)
C(5B)	4051(12)	4781(5)	7672(6)	75(3)	O(21B)	3110	2237	4085	105(9)
C(6B)	4937(14)	5348(5)	7634(6)	82(4)	O(22B)	2115	1614	2959	72(6)
C(7B)	6290(13)	5453(4)	8249(6)	74(3)	O(23B)	4736	2025	2940	211(25)
C(8B)	6692(12)	4991(4)	8854(6)	69(3)	O(24B)	2479	2677	2755	164(15)
					(S,R,S)-2				
Pd	3612(1)	2613	911(1)	43(1)	C(19)	1610(6)	1065(8)	-420(6)	63(2)
C(1)	3722(4)	2945(5)	-560(4)	45(2)	C(20)	2727(7)	2784(13)	3044(5)	80(3)
C(2)	4744(4)	2721(11)	-962(4)	52(2)	C(21)	3120(8)	586(8)	2457(6)	82(3)
C(3)	4688(5)	2974(6)	-1975(5)	60(2)	C(22)	5008(9)	1988(12)	4334(5)	107(4)
C(4)	3647(5)	3477(6)	-2674(5)	56(2)	C(23)	4987(8)	4586(8)	3001(7)	90(3)
C(5)	3584(8)	3826(7)	-3719(6)	73(3)	C(24)	6186(6)	1787(8)	1610(6)	68(3)
C(6)	2580(8)	4311(8)	-4376(5)	80(3)	C(25)	5950(7)	4146(8)	1290(7)	77(3)
C(7)	1574(9)	4458(8)	-4030(6)	75(3)	C(26)	770(7)	8081(9)	-3836(7)	88(3)
C(8)	1565(6)	4104(7)	-3029(5)	60(2)	C(27)	613(9)	9220(12)	-3300(7)	99(4)
C(9)	2608(5)	3637(5)	-2311(4)	49(2)	C(28)	1006(9)	10382(10)	-3516(8)	95(4)
C(10)	2698(4)	3333(5)	-1237(4)	45(2)	C(29)	1578(10)	10491(11)	-4269(10)	105(5)
C(11)	1624(5)	3460(7)	-798(4)	52(2)	C(30)	1759(8)	9351(13)	-4856(8)	102(4)
N(12)	1812(3)	2422(6)	56(3)	47(2)	C(31)	1307(8)	8146(10)	-4600(7)	91(3)
N(13)	3512(5)	1993(6)	2531(4)	62(2)	Cl	1939(1)	7084(2)	2332(2)	74(1)
C(14)	4812(7)	2071(8)	3172(5)	70(2)	O(1)	2307(7)	7475(15)	1434(7)	150(3)
C(15)	5439(7)	3189(8)	2805(6)	74(2)	O(2)	2951(6)	7238(8)	3171(5)	107(2)
N(16)	5416(4)	2968(5)	1673(4)	56(2)	O(3)	1399(8)	5832(11)	2106(7)	139(3)
C(17)	1536(6)	4874(8)	-416(6)	70(3)	O(4)	1110(9)	8013(12)	2504(8)	153(4)
C(18)	888(4)	2619(12)	639(4)	66(2)					

ᵃ Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

**Table 4.** Selected Bond Lengths (Å) and Angles (deg) in the Three Diastereomeric Complexes

	(S,R,R)-2	(S,S,S)-2[a]	(S,R,S)-2
Pd–C(1)	2.017(6)	2.030(7)	2.010(5)
		2.018(1)	
Pd–N(12)	2.123(6)	2.127(8)	2.114(4)
		2.115(8)	
Pd–N(13)	2.209(6)	2.203(8)	2.262(5)
		2.206(7)	
Pd–N(16)	2.101(5)	2.114(7)	2.109(4)
		2.108(6)	
N(12)–C(11)	1.510(8)	1.492(12)	1.505(8)
		1.517(11)	
N(13)–C(14)	1.505(9)	1.497(13)	1.532(8)
		1.494(12)	
N(16)–C(15)	1.509(8)	1.509(14)	1.506(9)
		1.494(12)	
C(1)–Pd–N(12)	78.3(2)	78.6(3)	78.7(2)
		78.2(2)	
C(1)–Pd–N(13)	178.8(2)	168.6(3)	173.6(2)
		168.1(2)	
C(1)–Pd–N(16)	96.8(2)	99.3(3)	97.2(2)
		99.5(2)	
N(12)–Pd–N(13)	101.9(2)	102.2(3)	101.0(2)
		102.5(3)	
N(12)–Pd–N(16)	174.8(2)	169.3(3)	174.4(2)
		170.3(3)	
N(13)–Pd–N(16)	83.0(2)	81.9(3)	83.5(2)
		81.7(3)	
distortn (θ)[b]	1.9	16.5	7.9
		16.9	

[a] Two figures are given for (S,S,S)-2 since there are two pairs of distinct molecules in the unit cell. The first figure refers to the molecule depicted in Figure 2. [b] As illustrated in Figure 3.

no changes attributable to the freezing out of conformation interconversion were observed. We therefore deduced that (S,R,R)-2 exists exclusively, both in the solid state and in solution, as the λλ conformer.

(b) The (S,S,S) Diastereomer. The synthesis of this sterically ambiguous diastereomer is, surprisingly, efficient with 76% isolated yield using the method described. The cation is stable indefinitely in solid state and in organic solutions. The diastereomer crystallizes as two pairs of two crystallographically distinct molecules in the unit cell. However, they are of identical stereochemistries and differ only slightly in bond distances and angles (Table 4). For clarity, only one molecule of (S,S,S)-2 is depicted in Figure 2. The ORTEP plot of another molecule has been deposited as supplementary material.

In Figure 2, the molecule has the δλ ring conformation together with the two C–Me groups of the diamine in equatorial positions as represented by structure (S,S,S)-2A in Figure 1. Obviously, the tendency for the two C–Me groups to be in equatorial positions is indeed enormous. This tendency, however, is not sufficient to lock the adjacent N–Me groups in the energetically unfavorable eclipsed orientation as depicted in Figure 1. Balancing the two contradicting forces as well as accommodating the requirement of efficient packing in the solid state results in the serious tetrahedral distortion in the coordination geometry around palladium (Figure 3). Distortion angles of 16.5 and 16.9° were observed for the two crystallographically distinguishable molecules. Obviously, this geometrical adjustment is crucial for the solid state stability of the δλ helices in structure 2A as it allows the neighboring N–Me groups to be orientated into an energetically acceptable pseudostaggered form. In consistency with this argument, the distortion angle in the sterically favored (S,R,R) diastereomer was found to be only 1.9° (Table 4). The structural compromise is also reflected in the N(13)–C(14)–C(15)–N(16) torsion angle, with a value of –56.6° for (S,R,R)-2 and a value of –60.5° for (S,R,S)-2 but values of 55.7 and 54.7° for the two independent molecules in (S,S,S)-2. The directions of the tetrahedral distortion with respect to the horizontal C(1)–Pd–
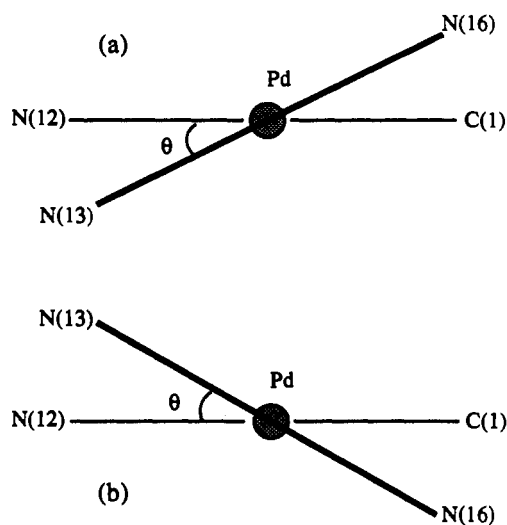

Figure 3. Tetrahedral distortion of the diastereomers at the palladium-(II) center. The absolute configurations of distortion are depicted (a) for (S,R,R)- and (S,R,S)-2 and (b) for (S,S,S)-2. The distortion angle, θ, of each isomer is given in Table 4.

N(12) plane is thus opposite for (S,S,S)-2 on the one hand and (S,R,R)-2 and (S,R,S)-2 on the other. In the case of (S,R,R)-2, the N(13) donor atom takes up a position below the trigonal plane (as defined in Figure 3a) while N(16) is above. In (S,S,S)-2, the N(13) donor is above the trigonal plane and N(16) is below (Figure 3b). It appears that in both cases the direction of distortion are governed by similar steric repulsive forces between the equatorially disposed methyl substituent on N(16) and the proton borne on C(2) which is adjacent to the metalated carbon in the naphthylene ring. Due to the rigid skew λ conformation of the organometallic ring and the strict planar naphthylene structure, this aromatic proton is protruding uncompromisingly toward the space just below N(16). Thus, greater steric interactions are expected between this aromatic proton and any substituent on N(16) located below the trigonal plane than that of its counterpart located above. In (S,R,R)-2, the λ configuration of the diamine ring directs the equatorial N-methyl group concerned to project slightly above the trigonal plane. A minor distortion of this methyl group along the same direction further reduces the steric interactions with the protruding aromatic proton. In (S,S,S)-2, however, the δ configuration of the diamine ring locks the equatorial methyl substituent on N(16) into a sterically unfavorable position below the trigonal plane. To minimize the repulsive forces from the protruding aromatic proton as well as to adopt a pseudo staggered orientation for the neighboring N–Me₂ groups, N(16) must be adjusted substantially below the horizontal C(1)–Pd–N(12) plane. In agreement with our observation in this series of compounds, the C(2) proton of the organometallic ring has indeed been reported to show high sensitivities toward the stereochemical environment of its cis-donor atom in similar square-planar complex systems.[4–6]

NMR studies of (S,S,S)-2 in CDCl₃ clearly indicated that only one isomer was present, and the δ configuration of the diamine ring remained unchanged in solution. Two sets of well-resolved doublet of quartet pattern for the vicinal protons at the diamine stereocenters were observed at δ 2.99 ($^3J_{HH'}$ = 11.5 Hz, $^3J_{HMe}$ = 6.4 Hz) and 3.25 ($^3J_{HH'}$ = 11.5 Hz, $^3J_{HMe}$ = 6.5 Hz). The chemical shifts and the vicinal coupling constant of these signals are consistent with the axial dispositions of both protons as depicted in structure (S,S,S)-2A. Similar to its (S,R,R) analogue, the spectrum of the strained complex was unchanged when it was measured at –90 °C in dichloromethane-d₂. Undoubtedly, (S,S,S)-2 exists solely as its δλ conformer.

A dynamic NMR experiment[12] was carried out in order to compare the stabilities of the strained and the sterically favored

Scheme 1

(*R,R,R*)-2   1 : 1   (*S,S,S*)-2

(major)   (minor)

(*R,S,S*)-2   1 : 1   (*S,R,R*)-2
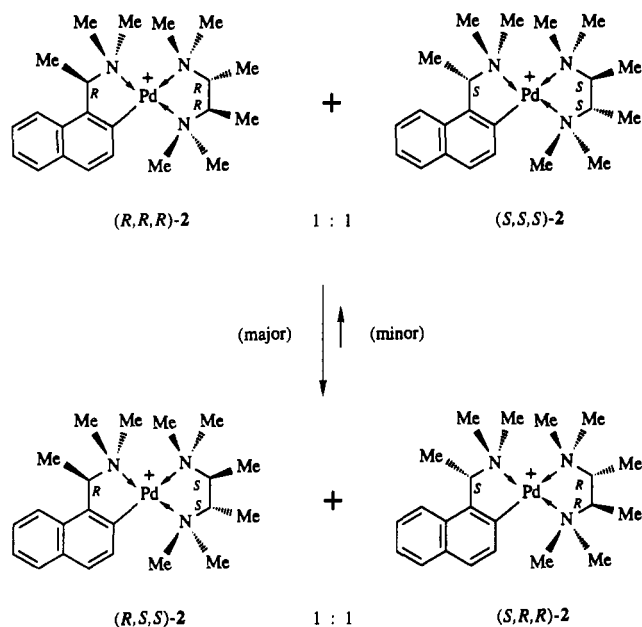
diastereomers in solution (Scheme 1). In this study, the enantiomeric form of the strained molecule, (*R,R,R*)-2 was first prepared from the equally accessible (*R*)-1 and (*R,R*)-*N,N,N',N'*-tetramethyl-2,3-butanediamine. Under normal conditions, (*R,R,R*)- and (*S,S,S*)-2 exhibit identical NMR signals in achiral solvents and their spectra remained unchanged over a 7-day period. However, after equal amounts of the pure enantiomorphic optically active complexes in CDCl$_3$ were mixed at 25 °C, signals due to racemic-(*R*,S*,S**)-2 emerged immediately. Over a period of 24 h, the sample rearranged into a diastereomeric mixture of equilibrium composition of racemic-(*R*,R*,R**):racemic-(*R*,S*,S**) = 1:19. The observation of such an asymmetric transformation between diastereomers of 2 revealed that intermolecular redistribution of the diamine ligands is kinetically facile in solutions under ambient conditions. Furthermore, from the proportions of the two diastereomers present in the equilibrium solution, it is clear that the sterically favored (*R*,S*,S**) cation is indeed thermodynamically more stable.

The correlation between the internal steric interactions and the relative population of the two diastereomers in solutions undoubtedly suggests that, (*S*)-1 favors (*R,R*)-*N,N,N',N'*-tetramethyl-2,3-butanediamine. In order to investigate if there is a similar correlation in the kinetic energies during the formation of the two diastereomers, a kinetic resolution of the diamine was attempted. In this experiment, 0.5 equiv of (*S*)-1 was treated with 1 equiv of the racemic diamine. The crystalline product obtained, surprisingly, was identified by NMR spectroscopy to be a ca 1:1 mixture of (*S,R,R*)- and (*S,S,S*)-2. Obviously there is no significant difference in the kinetic barriers for the formation of the two isomers. Furthermore, the ratio of diastereomers was not altered by further recrystallizations in various solvent systems. Clearly crystal packing forces must be significant in the isolation of these reaction products. In our judgement, therefore, (*S*)-1 is not an appropriate kinetical and mechanical resolving agent for this family of diamines. It is worth noting, however, that it is often more efficient to prepare an optically active 2,3-butanediamine from the appropriate form of 2,3-butanediol than by physically separating a diastereomeric mixture.[13]

(c) **The (*S,R,S*) Diastereomer.** In contrast to the two diastereomers discussed above, (*S,R,S*)-2 is unstable in polar

solvents such as THF and acetone. It is, however, stable in solid state and in less polar solvents. The perchlorate salt crystallized as a C$_6$H$_6$ solvate from dichloromethane/benzene in 76% yield. X-ray structure determination of the complex showed that the diamine indeed adopted the predicted λ configuration. However, only the cation which has an equatorial C–Me group at C(14) and an axial C–Me group at C(15), that is structure (*S,R,S*)-2A in Figure 1, was observed in the solid state. A tetrahedral distortion of 7.9° was observed around the coordination environment of Pd. As both (*S,R,S*)-2A and (*S,R,R*)-2 have similar λλ ring configurations, the directions of distortion are the same (Figure 3a).

The 300-MHz ^{1}H NMR spectrum of the complex in dichloromethane-d_2 at 25 °C indicated that there are two isomers present in a ratio of 1:6. The equilibrium process was found to be temperature dependent and reversible. Thus when the dichloromethane-d_2 sample was cooled to 0 °C, the minor component diminished to a ratio of 1:7. When the temperature was lowered to –20 °C, only the signals due to the major component were detected. The spectrum then remained unchanged even when it was recorded down to –80 °C. The vicinal proton signals of the major isomer were observed at δ 2.41 ($^3J_{HH'}$ = 3.0 Hz, $^3J_{HMe}$ = 7.0 Hz) and 3.50 ($^3J_{HH'}$ = 3.0 Hz, $^3J_{HMe}$ = 6.9 Hz) and were assigned as occupying an equatorial and axial positions respectively in the five membered chelated ring.[11,14] As the temperature of the solution was raised, signals due to the minor isomer reappeared, and the 1:6 equilibrium ratio was restored at 25 °C. Similar equilibrium ratios were observed for the complex in CDCl$_3$. The percentage of the minor isomer could be increased to 28% at 90 °C in DMSO-d_6, although decomposition of the complex started to occur. No broadening of ^{1}H NMR resonances was observed between –80 and +90 °C. Thus, we deduced that at ambient temperatures, both structures (*S,R,S*)-2A and 2B, as illustrated in Figure 1, were present as an equilibrium mixture in solution although the NMR study alone was inadequate to unequivocably identify the dominant isomer in solution.

A correlation between the X-ray crystallography data and a Dreiding model study provided useful information concerning the stabilities of the two possible diastereomers in solution. Model studies indicated that the diamine chelates in both isomers are suffering from an internal 1,3-diaxial repulsion between the C-methyl group and one of the N-methyl groups on the λ ring configuration. Isomer 2A tolerates such unfavorable steric interaction simply by means of tetrahedral distortion at palladium. Indeed, the angle of distortion in (*S,R,S*)-2A (7.9°) was found to be larger than that in (*S,R,R*)-2 (1.9°), even though both molecules adopted the λλ ring configurations and have their cis N–Me groups orientated in staggered positions. This consideration is also in consistent with a smaller N(13)–C(14)–C(15)–N(16) torsional angle observed in (*S,R,R*)-2. On the other hand, 1,3-diaxial repulsion in (*S,R,S*)-2B occurs below the C(1)–Pd–N(12) trigonal plane. In the tetrahedrally distorted form, the N–Me group involved also suffers from the steric interaction with the protruding aromatic proton borne on C(2) of the naphthylene ring. Although a larger tetrahedral distortion angle at palladium may diminish the above steric problems, the cis NMe$_2$ groups in the molecule will experience enormous equatorial–equatorial repulsion as a result of such a structural adjustment. In the light of these steric considerations, we can unambiguously assign structure (*S,R,S*)-2A as the major and more stable isomer in solution.

Experimental Section

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conductivity meter for 10^{-3} M solutions of the complexes at 25 °C. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry.

The enantiomerically pure forms of bis(acetonitrile)[1-[1-(dimethylamino)ethyl]-2-naphthyl-C,N]palladium(II) perchlorate, **1**,[5] (R,R)-, (S,S)-, and (R^*,S^*)-2,3-butanediamine[13] were prepared from (S,S)-, (R,R)-, and (R^*,S^*)-2,3-butanediol[15] as previously described. (R^*,S^*)-N,N,N',N'-tetramethyl-2,3-butanediamine was prepared according to a modified literature procedure.[17]

Caution! *All the complexes described were isolated as perchlorate salts and should be handled as potentially explosive compounds.*

(S,S)-N,N,N',N'-Tetramethyl-2,3-butanediamine. The optically pure (S,S)-2,3-butanediamine (1.5 g) was added slowly to ice-cooled 98–100% formic acid (10 mL), followed by 37% formaldehyde (8 mL). The reaction flask was then transferred to an oil bath which had been previously heated to 95–100 °C. A vigorous evolution of carbon dioxide began after 2 min. At this stage the flask was removed from the bath until the gas evacuation subsided. The reaction mixture was then refluxed gently for 8 h. The solution was treated with HCl (37%, 5 mL) and then evaporated to dryness under high vacuum. The pale brown syrupy residue was dissolved in a minimal amount of water, and the tetramethylated diamine was liberated by addition of 18 M NaOH solution. After extracted into dichloromethane and dried (MgSO₄), the product was distilled under nitrogen as a colorless oil: bp 153–155 °C; yield 1.6 g (67%); [α]_D +4.61° (c 4.9, C₆H₆). ¹H NMR (CDCl₃): δ 0.85 (d, 6H, $^3J_{HH}$ = 6.3 Hz, CHMe),[18] 2.23 (s, 12H, NMe), 2.48–2.58 (m, 2H, CHMe). Anal. Calcd for C₈H₂₀N₂: C, 66.6; H, 14.0; N, 19.4. Found: C, 66.3; H, 14.4; N, 19.0.

[(S)-1-[1-(Dimethylamino)ethyl]-2-naphthalenyl-C,N][N,N,N',N'-tetramethyl-(R,R)-2,3-butanediamine-N,N']palladium(II) Perchlorate ((S,R,R)-2). (R,R)-N,N,N',N'-Tetramethyl-2,3-butanediamine (0.10 g) in dichloromethane (1 mL) was added to (S)-1 (0.35 g) in dichloromethane (5 mL) and the resulting solution stirred for 3 h. After removal of solvent, the yellow glass was recrystallized from acetone–diethyl ether as pale yellow needles (yield 0.34 g, 86%): mp 170–171 °C; [α]_D +167° (c 1.0, CH₂Cl₂). ¹H NMR (CDCl₃): δ 1.08 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CHMe), 1.09 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CHMe), 2.14 (d, 3H, $^3J_{HH}$ = 6.3 Hz, CHMe), 2.60 (s, 6H, 2NMe), 2.74 (s, 3H, NMe), 2.84 (s, 3H, NMe), 2.87 (s, 3H, NMe), 2.96 (s, 3H, NMe), 3.17 (d of q, 1H $^3J_{HMe}$ = 6.5 Hz, $^3J_{HH'}$ = 11.2 Hz, CHMe), 3.27 (d of q, 1H, $^3J_{HMe}$ = 6.4 Hz, $^3J_{HH'}$ = 11.2 Hz, CHMe), 4.12 (q, 1H, $^3J_{HH}$ = 6.2 Hz, CHMe), 7.36–7.82 (m, 6H, aromatics); ¹H NMR (CD₂Cl₂) δ 1.05 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CHMe), 1.07 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CHMe), 2.01 (d, 3H, $^3J_{HH}$ = 6.3 Hz, CHMe), 2.54 (s, 3H, NMe), 2.57 (s, 3H, NMe), 2.70 (s, 3H, NMe), 2.79 (s, 3H, NMe), 2.84 (s, 3H, NMe), 2.91 (s, 3H, NMe), 3.04 (d of q, 1H $^3J_{HMe}$ = 6.4 Hz, $^3J_{HH'}$ = 11.2 Hz, CHMe), 3.16 (d of q, 1H, $^3J_{HMe}$ = 6.5 Hz, $^3J_{HH'}$ = 11.2 Hz, CHMe), 4.14 (q, 1H, $^3J_{HH}$ = 6.3 Hz, CHMe), 7.37–7.81 (m, 6H, aromatics). Λ_m: 169.1 cm² Ω⁻¹mol⁻¹ (Me₂CO) (1:1). Anal. Calcd for C₂₂H₃₆ClN₃O₄Pd: C, 48.2; H, 6.6; N, 7.7. Found C, 48.5; H, 6.6; N, 7.7.

[(S)-1-[1-(Dimethylamino)ethyl]-2-naphthalenyl-C,N][N,N,N',N'-tetramethyl-(S,S)-2,3-butanediamine-N,N']palladium(II) Perchlorate ((S,S,S)-2). The compound was prepared similarly from (S)-1 (0.35 g) and (S,S)-N,N,N',N'-tetramethyl-2,3-butanediamine (0.10 g): pale yellow needles; mp 162–163 °C; yield 0.30 g (76%); [α]_D +87.0° (c 1.0, CH₂Cl₂). ¹H NMR (CDCl₃): δ 1.08 (d, 3H, $^3J_{HH}$ = 6.7 Hz, CHMe), 1.11 (d, 3H, $^3J_{HH}$ = 6.6 Hz, CHMe), 2.06 (d, 3H, $^3J_{HH}$ = 6.3 Hz, CHMe), 2.65 (s, 3H, NMe), 2.71 (s, 3H, NMe), 2.73 (s, 3H, NMe), 2.76 (s, 3H, NMe), 2.78 (s, 3H, NMe), 2.99 (d of q, 1H, $^3J_{HMe}$ = 6.4 Hz, $^3J_{HH'}$ = 11.5 Hz, CHMe), 3.13 (s, 3H, NMe), 3.25 (d of q, 1H, $^3J_{HMe}$ = 6.5 Hz, $^3J_{HH'}$ = 11.5 Hz, CHMe), 4.11 (q, 1H, $^3J_{HH}$ = 6.2 Hz, CHMe), 7.37–7.81 (m, 6H, aromatics). ¹H NMR (CD₂Cl₂): δ 1.10 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CHMe), 1.12 (d, 3H, $^3J_{HH}$ = 6.5 Hz, CHMe), 2.06 (d, 3H, $^3J_{HH}$ = 6.3 Hz, CHMe), 2.62 (s, 3H, NMe), 2.72 (s, 3H, NMe), 2.73 (s, 3H, NMe), 2.76 (s, 3H, NMe), 2.78 (s, 3H, NMe), 2.93 (d of q, 1H, $^3J_{HMe}$ = 6.5 Hz, $^3J_{HH'}$ = 11.5 Hz, CHMe), 3.13–3.19 (m, 1H, CHMe), 3.14 (s, 3H, NMe), 4.16 (q, 1H, $^3J_{HH}$ = 6.3 Hz, CHMe), 7.41–7.84 (m, 6H, aromatics).

Λ_m: 161.3 cm² Ω⁻¹ mol⁻¹ (Me₂CO) (1:1). Anal. Calcd for C₂₂H₃₆ClN₃O₄Pd: C, 48.2; H, 6.6; N, 7.7. Found: C, 48.3; H, 6.6; N, 7.7.

The (R,R,R) enantiomer was prepared from (R)-1 and (R,R)-N,N,N',N'-tetramethyl-2,3-butanediamine under similar conditions; (R,R,R)-2 had mp 162–163 °C; [α]_D −88.0° (c 0.5, CH₂Cl₂), and Λ_m 157.0 cm² Ω⁻¹ mol⁻¹ (Me₂CO) (1:1). ¹H NMR (CDCl₃ and CD₂Cl₂): identical with that of the corresponding enantiomeric material. Anal. Calcd for C₂₂H₃₆ClN₃O₄Pd: C, 48.2; H, 6.6; N, 7.7. Found: C, 48.3; H, 6.5; N, 7.6.

[(S)-1-[1-(Dimethylamino)ethyl]-2-naphthalenyl-C,N][N,N,N',N'-tetramethyl-(R,S)-2,3-butanediamine-N,N']palladium(II) Perchlorate ((S,R,S)-2). With use of (S)-1 (0.35 g) and (R,S)-N,N,N',N'-tetramethyl-2,3-butanediamine (0.10 g) as starting materials, the compound was prepared under similar conditions as described above. The crude product was crystallized as beautiful pale yellow needles from a mixture of dichloromethane-benzene: mp 118–119 °C; yield 0.343 g (76%); [α]_D +158.3° (c 1.0, CH₂Cl₂). ¹H NMR (CDCl₃): δ 1.24 (d, 2.6H, $^3J_{HH}$ = 6.8 Hz, 0.87CHMe), 1.42 (d, 0.4H, $^3J_{HH}$ = 6.8 Hz, 0.13CHMe), 1.50 (d, 0.4H, $^3J_{HH}$ = 7.0 Hz, 0.13CHMe), 1.63 (d, 2.6H, $^3J_{HH}$ = 7.0 Hz, 0.87CHMe), 2.17 (d, 2.6H, $^3J_{HH}$ = 6.3 Hz, 0.87CHMe), 2.21 (d, 0.4H, $^3J_{HH}$ = 6.3 Hz, 0.13CHMe), 2.50 (d of q, 1H, $^3J_{HMe}$ = 6.8 Hz, $^3J_{HH'}$ = 3.0 Hz, CHMe), 2.57 (s, 5.6H, 1.87NMe), 2.62 (s, 2.6H, 0.87NMe), 2.69 (s, 0.4H, 0.13NMe), 2.76 (s, 2.6H, 0.87NMe), 2.80 (s, 0.4H, 0.13NMe), 2.85 (s, 0.4H, 0.13NMe), 2.89 (s, 3H, 1NMe), 2.95 (s, 0.4H, 0.13NMe), 3.24 (s, 2.6H, 0.87NMe), 3.63(d of q, 1H, $^3J_{HMe}$ = 6.8 Hz, $^3J_{HH'}$ = 3.0 Hz, CHMe), 4.14 (q, 1H, $^3J_{HH}$ = 6.3 Hz), 7.26–7.83 (m, 6H, aromatics), 7.36 (s, 6H, benzene). ¹H NMR (CD₂Cl₂): δ 1.22 (d, 2.6H, $^3J_{HH}$ = 6.9 Hz, 0.86CHMe), 1.38 (d, 0.4H, $^3J_{HH}$ = 6.8 Hz, 0.14CHMe), 1.48 (d, 0.4H, $^3J_{HH}$ = 7.0 Hz, 0.14CHMe), 1.62 (d, 2.6H, $^3J_{HH}$ = 7.0 Hz, 0.86CHMe), 2.15 (d, 2.6H, $^3J_{HH}$ = 6.3 Hz, 0.86CHMe), 2.18 (d, 0.4H, $^3J_{HH}$ = 6.2 Hz, 0.14CHMe), 2.41 (d of q, 1H, $^3J_{HMe}$ = 7.0 Hz, $^3J_{HH'}$ = 3.0 Hz, CHMe), 2.52 (s, 2.6H, 0.86NMe), 2.54 (s, 3H, NMe), 2.60 (s, 2.6H, 0.86NMe), 2.64 (s, 0.4H, 0.14NMe), 2.70 (s, 2.6H, 0.86NMe), 2.73 (s, 0.4H, 0.14NMe), 2.83 (s, 3.4H, 1.14NMe), 2.90 (s, 0.4H, 0.14NMe), 3.17 (s, 2.6H, 0.86NMe), 3.50(d of q, 1H, $^3J_{HMe}$ = 6.9 Hz, $^3J_{HH'}$ = 3.0 Hz, CHMe), 4.14 (q, 1H, $^3J_{HH}$ = 6.3 Hz, CHMe), 7.30–7.82 (m, 6H, aromatics), 7.32 (s, 6H, benzene); ¹H NMR (DMSO-d_6) δ 1.15 (d, 2.55H, $^3J_{HH}$ = 6.8 Hz, 0.85CHMe), 1.31 (d, 0.45H, $^3J_{HH}$ = 6.8 Hz, 0.15CHMe), 1.42 (d, 0.45H, $^3J_{HH}$ = 7.0 Hz, 0.15CHMe), 1.55 (d, 2.55H, $^3J_{HH}$ = 6.9 Hz, 0.85CHMe), 1.83 (d, 0.45H, $^3J_{HH}$ = 6.0 Hz, 0.15CHMe), 2.06 (d, 2.55H, $^3J_{HH}$ = 6.2 Hz, 0.85CHMe), 2.46 (s, 2.55H, 0.85NMe), 2.48 (s, 2.55H, 0.85NMe), 2.54 (s, 2.55H, 0.85NMe), 2.60 (s, 0.45H, 0.15NMe), 2.71 (s, 2.55H, 0.85NMe), 2.73 (s, 0.45H, 0.15NMe), 2.80 (s, 3.45H, 1.15NMe), 2.85 (s, 0.45H, 0.15NMe), 3.15 (s, 2.55H, 0.85NMe), 3.50 (d of q, 1H, $^3J_{HMe}$ = 6.8 Hz, $^3J_{HH'}$ = 2.8 Hz, CHMe), 4.32 (q, 1H, $^3J_{HH}$ = 6.1 Hz, CHMe), 7.36 (s, 6H, benzene), 7.38–7.87 (m, 6H, aromatics). The CHMe and NMe resonances were obscured by the DMSO-d_6 residual signals. Λ_m: 135.2 cm² Ω⁻¹ mol⁻¹ (Me₂CO) (1:1). Anal. Calcd for C₂₂H₃₆ClN₃O₄Pd·C₆H₆: C,53.7; H, 6.7; N, 6.7; Found: C,53.7; H, 6.6; N, 6.9.

Structural Analysis. Pale yellow single crystals suitable for X-ray structural determination were grown from dichloromethane–benzene solutions for (S,R,R)- and (S,R,S)-2 in which the (S,R,S) diastereomer was obtained as mono benzene solvate. Crystals of (S,S,S)-2 were crystallized from a acetone–diethyl ether mixture. The crystals used for analysis is of approximate dimension 0.20 × 0.30 × 0.35, 0.23 × 0.26 × 0.29, and 0.30 × 0.30 × 0.35 mm respectively for (S,R,R)-, (S,S,S)-, and (S,R,S)-2. Unit cell parameters were determined by least-squares refinements of 22, 30, and 30 independent reflections for the three diastereomers in the above order. The reflections for (S,R,R)- and (S,R,S)-2 were obtained by an automated random search routine while those for (S,S,S)-2 were taken from a rotation photograph at room temperature on a Siemens R3m/V four-circle diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Semiempirical absorption corrections were applied; minimum and maximum transmission coefficients were 0.72–0.83, 0.39–0.44, and 0.77–0.85 for (S,R,R)-, (S,S,S)-, and (S,R,S)-2 respectively. Crystallographic data are gathered together in Table 2. The structures were solved by direct methods, and non-hydrogen atoms were located from Fourier difference maps. All the non-hydrogen atoms except the oxygen atoms in the perchlorate anions were refined anisotropically. In (S,R,R)-2 three of the four perchlorate oxygen atoms were given 50% occupancy at the two positions each, while in (S,S,S)-2 all the oxygen atoms were found at two sites with 75% and 25% occupancies and the two perchlorate anions were refined as rigid groups. Hydrogen atoms were introduced at calculated

(15) The procedure for the preparation of (R^*,S^*)-2,3-butanediylbis-(methanesulfonate), an intermediate involved in the synthesis of (R^*,S^*)-2,3-diaminobutane, has been reported recently.[16]

(16) Gugger, P.; Limmer, O.; Watson, A. A.; Willis, A. C.; Wild, S. B. *Inorg. Chem.* **1993**, *32*, 5692–5696.

(17) Conner, J. A.; Lloyd, J. P. *J. Chem. Soc. A* **1970**, *19*, 3237–3242.

(18) The sharp doublet was at the center of a typical AX₃AX₃ (J_{HH} = 2.6 Hz) satellite.[19]

(19) Bothner-By, A. A.; Colin, N. *J. Am. Chem. Soc.* **1962**, *84*, 743–747.

positions from carbon atoms and were assigned fixed thermal parameters. All calculations were performed on a Digital Equipment Corporation MicroVax II computer using the Siemens SHELXTL PLUS software package.

Supplementary Material Available: For all three diastereomers, tables of crystallographic data, final position parameters, bond distances and angles, anisotropic thermal parameters of non-hydrogen atoms and calculated hydrogen parameters and, for (*S,S,S*)-2, a figure showing structural diagram of the second molecule in the unit cell and its atom labeling scheme (27 pages). Ordering information is given on any current masthead page.