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Self-Assembly of Homochiral Double Helix and Side-by-Side Helix Conformers of Double-Stranded Disilver(I)− and Digold(I)−Tetra(tertiary phosphine) Helicates

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The enantiomers of the (R^*,R^*)-(±) diastereomer of the chelating C_2-tetra(tertiary phosphine) (R^*,R^*)-(±)-1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane, (R^*,R^*)-(±)/(R^*,S^*)-**1**, spontaneously self-assemble into homochiral double-stranded disilver(I) and digold(I) helicates of the type $[\mathrm{M_2(tetraphos)_2}]\mathrm{X_2}$ upon reaction with appropriate silver(I) and gold(I) salts. The corresponding copper(I) complex is mononuclear. Crystal and molecular structures of Δ-(−)-$[\mathrm{Cu}\{(R,R)\text{-}\mathbf{1}\}]\mathrm{PF_6{\cdot}EtOH}$, Λ-(−)-$[\mathrm{Ag_2}\{(R,R)\text{-}\mathbf{1}\}_2](\mathrm{PF_6})_2$, and Λ-(−)-$[\mathrm{Au_2}\{(R,R)\text{-}\mathbf{1}\}_2](\mathrm{PF_6})_2{\cdot}\mathrm{CH_2Cl_2}$ are reported. The structure determinations on the silver and gold complexes are the first to be performed on enantiomerically pure dimetal helicates with chiral ligands. The dinuclear silver complex crystallizes with one molecule each of the left-handed (Λ) D_2-double helix and C_2-side-by-side helix conformers of the cation and associated anions in each unit cell, whereas crystals of the analogous gold complex contain only the side-by-side helix and associated anions. The absolute configuration(s) of the metal stereocenter(s) in each complex is *S*. Conductance measurements in acetonitrile indicated considerable rearrangement of the mononuclear copper complex into the dinuclear helicate complex, whereas the silver and gold complexes conducted as di-univalent salts under similar conditions. Energy minimization calculations of the structures of the disilver complex cation with use of the program SPARTAN 3.0 predicted the structures observed with considerable accuracy, especially the conformations of the chiral central ten-membered ring in the complex and the relationship of the helicity of this ring to the stereoselective formation of the double helix and side-by-side helix structures. The resolution of (R^*,R^*)-(±)-**1** is the first on a tetra(tertiary phosphine). The more-soluble (R^*,R^*)-(±) form of the ligand was separated in high yield from the less-soluble (R^*,S^*) form by selective extraction with tetrahydrofuran, whereupon it was resolved by the method of metal complexation with the readily prepared homochiral complex (+)-di(μ-chloro)bis[(R)-1-[1-(dimethylamino)ethyl]-2-phenyl-C^2,N]dipalladium(II)−1-dichloromethane, (R)-**2**·$\mathrm{CH_2Cl_2}$. The enantiomers of the phosphine were obtained by liberation from the diastereomeric complexes (R_C),(R_P,R_P)- and (R_C),(S_P,S_P)-**3** ($X = \mathrm{PF_6}$) and brought to optical purity by crystallization from acetone−ethanol, giving colorless needles having mp 88 °C and $[\alpha]^{21}_\mathrm{D}$ +20.5 (c 1.0, $\mathrm{CH_2Cl_2}$) (*S*,*S* enantiomer) and $[\alpha]^{21}_\mathrm{D}$ −20.5 (c 1.0, $\mathrm{CH_2Cl_2}$) (*R*,*R* enantiomer). The crystal and molecular structures of (R_C),(R_P,R_P)-**3** ($X = \mathrm{PF_6}$) have been determined. The complete optical purity of each enantiomer of the tetra(tertiary phosphine) was confirmed in each case by the quantitative repreparation of the diastereomeric palladium complex from which it was liberated.

Introduction

Although an important feature of biology, the self-assembly of molecules into larger supramolecular structures can now be mimicked by a variety of inorganic coordination complexes. Thus, the spontaneous synthesis of double- or triple-stranded polynuclear metal helices[1] (and molecular links and knots[2]) from semirigid oligo-2,2′-bipyridines and related ligands has aroused considerable interest. In general, the double-stranded metal helices (also termed double-stranded helicates[3]) have been prepared from achiral ligands and isolated as racemic mixtures or as conglomerates (separated in one instance[4]) with little work being directed towards the stereoselective synthesis of polynuclear helices from homochiral ligands.[5] In an investigation related to the generation of artificial ion channels, however, diastereomeric diiron(III) helices were generated from a triple-stranded tripodal ligand containing L-leucine amide and hydroxamate groups, which acted as ligands and H-bonding groups, respectively.[6] In other work, tricopper(I) and trisilver(I) double helices were synthesized from appropriate metal salts and a tris(2,2′-bipyridine) ligand containing a pair of homochiral α-methyl-2-pyridinemethanol spacer groups; circular dichroism measurements indicated 95% helical induction in the complex by the homochiral ligand.[7] Recently the resolution of a triple-stranded dicobalt(III) helix was achieved by elution of the racemate on a column of Sephadex SP-C25 ion exchange resin with sodium antimonyl-D-tartrate.[8]

The object of this project was to investigate by chemical synthesis and molecular modeling calculations interactions between the individual enantiomers of the linear C_2-tetra(tertiary phosphine) (R^*,R^*)-(±)-$\mathrm{Ph_2PCH_2CH_2P(Ph)CH_2CH_2P(Ph)CH_2CH_2PPh_2}$, ($R^*$,$R^*$)-(±)-**1**, and the univalent ions of copper, silver, and gold with the view to the self-assembly and rationalization of structures of homochiral dinuclear metal helices of the type $[\mathrm{M_2(tetraphos)_2}]^{2+}$. Previous work in our

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(1) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304. Constable, E. C. *Tetrahedron* **1992**, *48*, 10013.

(2) Dietrich-Buchecker, C; Sauvage, J.-P. *Bull. Soc. Chim. Fr.* **1992**, *129*, 113.

(3) Lehn, J.-M; Rigault, A.; Siegel, J.; Harrowfield, J.; Chevrier, B.; Moras, D. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 2565.

(4) Kramer, R.; Lehn, J.-M.; De Cian, A.; Fischer, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 703.

(5) van Stein, G. C.; van Koten, G.; Vrieze, K.; Brevard, C.; Spek, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 4486. van Stein, G. C.; van Koten, G.; Vrieze, K.; Brevard, C. *Inorg. Chem.* **1984**, *23*, 4269.

(6) Libman, J; Tor, Y.; Stanzer, A. *J. Am. Chem. Soc.* **1987**, *109*, 5880.

(7) Zarges, W.; Hall, J.; Lehn, J.-M; Bolm, C. *Helv. Chim. Acta* **1991**, *74*, 1843.

(8) Charbonniere, L. J.; Bernardinelli, G.; Piguet, C.; Sargeson, A. M.; Williams, A. F. *J. Chem. Soc., Chem. Commun.* **1994**, 1419.

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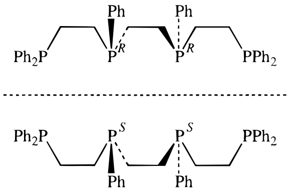
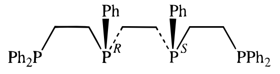
laboratory had indicated that tetrahedral complexes of these metals of the type $[M(diphos)_2]^+$ underwent rapid rearrangements between diastereomers, with redistribution rates for complexes of the bis(tertiary phosphine) 1,2-phenylenebis(methylphenylphosphine) increasing in the order gold(I) < copper(I) < silver(I). Moreover, metal stereocenter inversion barriers were low for complexes of this type with stabilities decreasing in the order copper(I) > gold(I) > silver(I).[9] Thus, the self-assembly of homochiral dinuclear helicates of the type $[M_2(tetraphos)_2]^{2+}$, perhaps in equilibrium with the mononuclear species $[M(tetraphos)]^+$, was anticipated for the reactions of the individual enantiomers of (R^*,R^*)-(±)-**1** with appropriate salts of these metals. Despite extensive work on the synthesis and resolution of chiral unidentate and bidentate bis(tertiary phosphines)[10] and arsines[11] for use as stereochemical probes of intra- and intermolecular rearrangements in coordination complexes[12] and as auxiliaries for transition-metal-mediated organic asymmetric synthesis,[13] little work has been directed toward the isolation of similar ligands of higher denticity in stereochemically homogeneous form. To our knowledge, the only linear C_2-quadridentate of this type to be separated into stereoisomeric forms is the tetra(tertiary arsine) (R^*,R^*)-(±)/(R^*,S^*)-1,1,12,-12-tetramethyl-5,8-diphenyl-1,5,8,12-tetraarsadodecane, which was separated into diastereomers and resolved via dichlorocobalt(III) complexes.[14] Fourteen-membered cyclic *trans*-As_2S_2 and *trans*-As_2N_2 quadridentates have also been isolated in stereochemically pure forms.[15] Here we report the separation into diastereomers and resolution of commercially available or readily prepared[16] (R^*,R^*)-(±)/(R^*,S^*)-**1** and the use of the enantiomers of the (R^*,R^*)-(±) form of the ligand for the self-assembly of homochiral dinuclear metal helicates of the type $[M_2(tetraphos)_2]^{2+}$. Partial separation of the diastereomers of **1** has been achieved previously,[17,18] and a number of reactions of the (R^*,R^*)-(±)/(R^*,S^*) mixture (including a compound of the type $[Pt_2(tetraphos)_2]$[16]) and the individual diastereomers have been noted,[17−19] but the resolution of the (R^*,R^*)-(±) diastereomer has not been accomplished hitherto. Preliminary accounts of parts of this work have been published.[20]

Results and Discussion

Separation of Diastereomers of (R^*,R^*)-(±)/(R^*,S^*)-1. The compound (R^*,R^*)-(±)/(R^*,S^*)-**1** was synthesized and isolated as an equimolar mixture of the two diastereomers by the base-catalyzed addition of diphenylvinylphosphine to 1,2-bis(phenylphosphino)ethane.[16] (A procedure giving the bis(secondary phosphine) in 65% yield from 1,2-bis(diphenylphosphino)ethane is described here.) Commercial **1** contains an excess of the less-soluble (R^*,S^*) diastereomer—one shipment had (R^*,R^*)-(±):(R^*,S^*) ca. 1:4.[21] An unequal mixture of the diastereomers of **1,** however, can be equilibrated into a 1:1 mixture by heating at 200 °C for 2 h [E_{inv} ca. 31 kcal mol^{-1} for phosphines of the type (±)-$PArR_1R_2$[22]]. The equimolar mixture of (R^*,R^*)-(±)/(R^*,S^*)-**1** can then be separated by selective extraction with tetrahydrofuran. Thus, 33 g of a 1:1 mixture of the diastereomers of **1** was suspended in tetrahydrofuran (400 mL), and the mixture was stirred for 12 h and then filtered; 13.3 g of pure (R^*,S^*)-**1** having mp 183 °C (lit.[16] mp 187 °C) was thus isolated as a colorless microcrystalline solid. The mother liquor was concentrated in vacuo to ca. 150 mL and diluted with methanol (400 mL); 15.6 g of pure (R^*,R^*)-(±)-**1** of mp 115−116 °C (lit.[16] mp 117−117.5 °C) crystallized from this solution over 2 days. The $^{31}P\{^1H\}$ NMR data for the two diastereomers agreed with those given in ref 17. The (R^*,S^*) diastereomer was converted into an (R^*,R^*)-(±):(R^*,S^*) = 1:1 mixture by being heated as described above and recycled into the (R^*,R^*)-(±) form.



(R^*,R^*) - (±) – **1**



(R^*,S^*) – **1**

Resolution of (R^*,R^*)-(±)-1. (R^*,R^*)-(±)-**1** was resolved by the formation and fractional crystallization of diastereomeric palladium(II) complexes containing ortho-metalated (*R*)-(+)-*N*,*N*-dimethyl-α-methylbenzylamine, as indicated in Scheme 1. In a completely regioselective bridge-splitting reaction, 1 equiv of (R^*,R^*)-(±)-**1** reacted quantitatively with 2 equiv of (*R*)-**2**·CH_2Cl_2[23] in methanol to give an almost colorless solution of the diastereomeric *chlorides* $(R_C),(R_P,R_P)/(R_C),(S_P,S_P)$-**3** (X = Cl), which were precipitated with aqueous ammonium hexafluorophosphate as the *hexafluorophosphates* $(R_C),(R_P,R_P)/(R_C),(S_P,S_P)$-**3** (X = PF_6) in 92% yield. The $^{31}P\{^1H\}$ NMR spectrum of the mixture of hexafluorophosphates in dichloromethane-d_2 exhibited peaks at δ 64.37, 65.9, and 43.25 with intensities 1:1:2 due to overlap of the lower-field resonance corresponding to the outer-phosphorus nuclei of each diastereomer. In the ^1H NMR spectra in the same solvent, the methine proton resonance of the chiral auxiliary in each diastereomer provided the most convenient indicator of purity of the diastereomeric mixture.

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(9) Salem, G.; Schier, A.; Wild, S. B. *Inorg. Chem.* **1988**, *27,* 3029.

(10) Pietrusiewicz, K. M.; Zablocka, M. *Chem. Rev.* **1994**, *94*, 1375.

(11) Wild, S. B. In *The Chemistry of Arsenic, Antimony and Bismuth Compounds*; Patai, S., Ed.; Wiley: Chichester, 1994; Chapter 3.

(12) Salem, G; Wild, S. B. *Inorg. Chem.* **1992**, *31*, 581 and references cited therein.

(13) Brunner, H. *Top. Stereochem.* **1988**, *18*, 129; *Synthesis* **1988**, 645. Noyori, K. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994.

(14) Bosnich, B.; Jackson, W. G.; Wild, S. B. *J. Am. Chem.* Soc. **1973**, *95*, 8269. Bosnich, B.; Jackson, W. G.; Wild, S. B. *Inorg. Chem.* **1974**, *13*, 1121.

(15) Kerr, P. G.; Leung, P. -H.; Wild, S. B. *J. Am. Chem.* Soc. **1987**, *109*, 4321. Martin, J. W. L.; Stephens, F. S.; Weerasuria, K. D. V.; Wild, S. B. *J. Am. Chem. Soc.* **1988**, *110***,** 4346.

(16) King, R. B.; Kapoor, P. N. *J. Am. Chem. Soc.* **1969**, *91*, 5191. King, R. B.; Kapoor, P. N. *J. Am. Chem. Soc.* **1971**, *93*, 4158. King, R. B.; Kapoor, P. N. *Inorg. Chem.* **1972**, *11*, 1524. King, R. B.; Heckley, P. R.; Cloyd, J. C. *Z. Naturforsch., B* **1974**, *296*, 574.

(17) Brown, J. M.; Canning, L. R. *J. Organomet. Chem.* **1984**, *267*, 179.

(18) Batista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T. *Can. J. Chem.* **1994**, *72*, 547.

(19) Bacci, M.; Ghilardi, C. A. *Inorg. Chem.* **1974**, *13*, 2398. Ghilardi, C. A.; Midollini, S.; Sacconi, L.; Stoppioni, P. *J. Organomet. Chem.* **1981**, *205*, 193. Brown, J. M.; Chaloner, P. A.; Kent, A. G.; Murrer, B. A.; Nicholson, P. N.; Parker, D.; Sidebottom, P. J. *J. Organomet. Chem.* **1981**, *216*, 263. Brüggeller, P. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1992**, *48*, 445. Brüggeller, P.; Nar, H.; Messerschmidt, A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1992**, *48*, 817. Chen, J. D.; Cotton, F. A.; Hong, B. *Inorg.Chem.* **1993**, *32*, 2343. Dillinger, K.; Oberhauser, W.; Bachmann, C.; Brüggeller, P. *Inorg. Chim. Acta* **1994**, *223*, 13.

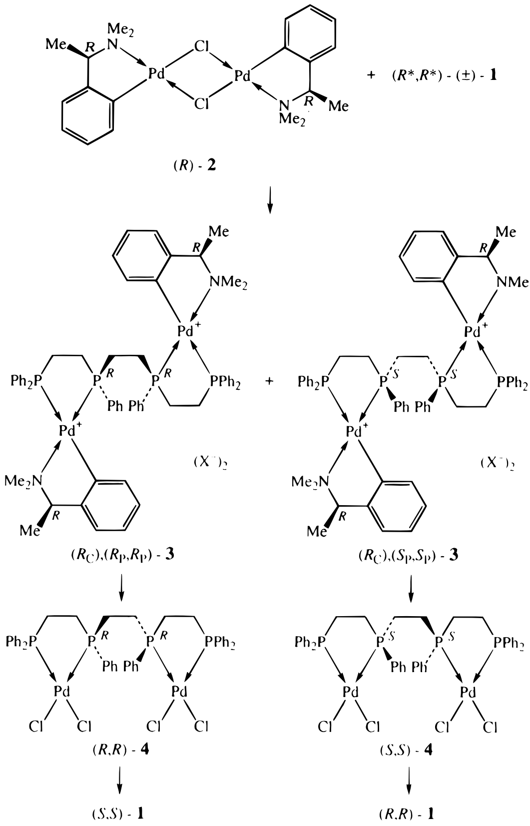
(20) Airey, A. L.; Swiegers, G. F.; Willis, A. C.; Wild, S. B. *J. Chem. Soc., Chem. Commun.* **1995**, 693. Airey, A. L.; Swiegers, G. F.; Willis, A. C.; Wild, S. B. *J. Chem. Soc., Chem. Commun.* **1995**, 695.

(21) Purchased from the Aldrich Chemical Co. Inc., Milwaukee, Wisconsin, 53233.

(22) Mislow, K. *Trans. N.Y. Acad. Sci.* **1973**, *35*, 227.

(23) Allen, D. G.; McLaughlin, G. M.; Robertson, G. B.; Steffen, W. L.; Salem, G.; Wild, S. B. *Inorg.Chem.* **1982**, *21*, 1007. Martin, J. W. L.; Palmer, J. A. L.; Wild, S. B. *Inorg.Chem.* **1984**, *23*, 2664.

Scheme 1



Thus, a single extraction of 30 g of the equimolar mixture (R_C),(R_P,R_P)/(R_C),(S_P,S_P)-**3** (X = PF_6) with chloroform (100 mL) over 2 h brought about ca. 95% separation, according to the intensities of the methine resonances in the ^{1}H NMR spectra of the two fractions. The less-soluble component of the mixture was washed with diethyl ether and dried in vacuo. Dissolution of this fraction in dichloromethane, followed by the gradual addition of ethanol over 2 days, afforded 13.9 g of colorless microcrystalline (R_C),(R_P,R_P)-**3** (X = PF_6) having $[\alpha]_D$ −96 (*c* 1.0, Me_2CO). The crystal and molecular structures of (R_C),(R_P,R_P)-**3** (X = PF_6) were determined (see below). The mother liquor from the initial separation was evaporated to dryness, and the residue was recrystallized from acetone−ethanol and acetone−2-propanol to give pure (R_C),(S_P,S_P)-**3** (X = PF_6) in 64% yield having $[\alpha]_D$ +77 (*c* 1.0, Me_2CO).

The configurationally homogeneous diastereomers of **3** (X = PF_6) were individually converted into the corresponding enantiomeric bis[dichloropalladium(II)] complexes (*R*,*R*)- and (*S*,*S*)-**4** by treatment with concentrated hydrochloric acid in acetone (Scheme 1). Thus, (R_C),(R_P,R_P)-**3** (X = PF_6) gave (*R*,*R*)-**4**, $[\alpha]_D$ −70.1 (*c* 0.1, CH_2Cl_2), and (R_C),(S_P,S_P)-**3** (X = PF_6) gave (*S*,*S*)-**4**, $[\alpha]_D$ +70.1 (*c* 0.1, CH_2Cl_2). Optically pure (*R*)-(+)-*N*,*N*-dimethyl-α-methylbenzylamine was recovered from the mother liquors after neutralization.

The final step of the resolution procedure involved the liberation of the enantiomers of (*R**,*R**)-(±)-**1** from the corresponding bis[dichloropalladium(II)] complexes. This was readily achieved by treating suspensions of the individual palladium complexes in dichloromethane with aqueous sodium cyanide (Scheme 1). After ca. 4 h the complexes had reacted to give clear colorless solutions of the phosphine (dichloromethane) and yellow solutions of tetracyanopalladate(II) (water). Thus, (*R*,*R*)-**4** gave 86% of crystalline (*S*,*S*)-**1**[24] having mp 88 °C from acetone−ethanol and $[\alpha]_D$ +20.5 (*c* 1.0, CH_2Cl_2); (*S*,*S*)-**4** gave a similar yield of (*R*, *R*)-**1** of mp 88 °C and $[\alpha]_D$ −20.5 (*c* 1.0, CH_2Cl_2). The value of $[\alpha]_D$ for (*S*,*S*)-**1** in dichloromethane varies linearly between +19.5 and +24.5 over the temperature range 0−25 °C for *c* = 1. The optical purities of the enantiomers of (*R**,*R**)-(±)-**1** were confirmed by the quantitative in situ regeneration of the respective diastereomers of **3** (X = PF_6) with use of (*R*)-**2**·CH_2Cl_2 in dichloromethane-d_2; in each case, the diastereomers of **3** (X = PF_6) were found to be pure within the limits of detectability of the NMR spectrometer.

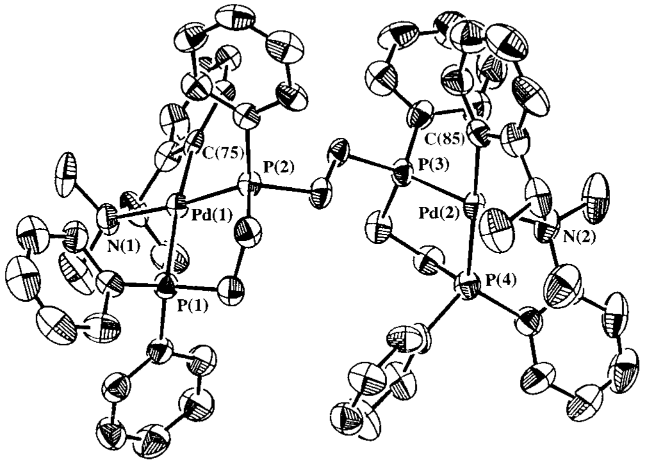


Figure 1. ORTEP view of the cation of (R_C),(R_P,R_P)-(−)-**3** (X = PF_6) with 50% probability ellipsoids.

Absolute Configurations. The molecular structure of the cation of (R_C),(R_P,R_P)-**3** (X = PF_6) is depicted in Figure 1. Crystallographic details are given in Table 1, and important distances and angles for the complex are listed in Table 2. Of particular significance to the present work is the coordination geometry around each palladium, which is [*SP*-4-4] in each case (inner phosphorus *trans* to nitrogen), and the absolute configurations of the inner chiral tertiary phosphine stereocenters (*R*). The longer distances Pd(1)−P(1) and Pd(2)−P(4) [2.363(3) and 2.356(3) Å, respectively] are consistent with the stronger donor capacities of the inner-phosphine groups compared to the terminal phosphine groups of the tetra(tertiary phosphine). It is noteworthy, however, that both *C*-methyl groups of the 1-[1-(dimethylamino)ethyl]phenylamine-C^2,*N* rings in the structure adopt axial dispositions and that both rings have the same helicity (*δ*).[26] The tendency for the organometallic ring to adopt enantiomeric ring conformations in the solid state with axial or equatorial *C*-methyl substituents has been discussed elsewhere.[27]

Syntheses of Complexes. Treatment of $[Cu(NCMe)_4]PF_6$ with an equimolar quantity of (*S*,*S*)-**1** in dichloromethane, followed by the addition of ethanol and cooling, afforded colorless prisms of (−)-[Cu{(*R*,*R*)-**1**}]PF_6 having mp 110−112 °C and $[\alpha]_D$ −101.1 (*c* 1.0, CH_2Cl_2). When recrystallized from neat ethanol, however, (−)-[Cu{(*R*,*R*)-**1**}]PF_6 afforded colorless prisms of the *1-ethanol solvate*. Silver(I) perchlorate, when

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[24] The coordination of the phosphine to the metal is stereospecific with retention of configuration at phosphorus: the apparent inversion upon displacement from the metal is a consequence of the Cahn−Ingold−Prelog rules for assigning absolute configurations.[25]

[25] Cahn, R. S.; Ingold C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

[26] Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1980**, 1556. Dai, L.-x; Zhou, Z.-h.; Zhang, Y.-z.; Ni, C.-z.; Zhang, Z.-m.; Zhou, Y.-f. *J. Chem. Soc., Chem. Commun.* **1987**, 1760. Gladiali, S.; Dore, A.; Fabbri, D.; De Lucchi, O.; Manassero, M. *Tetrahedron: Asymmetry* **1994**, *5*, 511. Schmid, R.; Foricher, J.; Cereghetti, M.; Schönholzer, P. *Helv. Chim. Acta* **1991**, *74*, 370.

[27] Alcock, N. W.; Holmes, D. I.; Brown, J. M. *J. Chem. Soc., Chem. Commun.* **1995**, 395.

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

	(R_C),(R_P,R_P)-**3** (X = PF_6)	[Cu{(*R*,*R*-**1**}]PF_6·EtOH	[Ag_2{(*R*,*R*)-**1**}$_2$](PF_6)$_2$	[Au_2[(*R*,*R*)-**1**]$_2$]PF_6·CH_2Cl_2
molecular formula	$C_{62}H_{70}F_{12}N_2P_6Pd_2$	$C_{42}H_{42}CuF_6P·C_2H_5OH$	$C_{84}H_{84}Ag_2F_{12}P_{10}$	$C_{84}H_{84}Au_2F_{12}P_{10}·CH_2Cl_2$
fw, g mol^{-1}	1469.89	925.27	1847.06	2110.17
space group	$P2_1$ (No. 4)	$P4_3$ (No. 78)	$P1$ (No. 1)	$P2_12_12_1$ (No. 19)
crystal system	monoclinic	tetragonal	triclinic	orthorhombic
a, Å	10.841(3)	10.435(2)	12.420(4)	15.924(5)
b, Å	13.668(2)		12.641(4)	18.392(7)
c, Å	22.330(3)	41.040(4)	27.270(9)	29.384(7)
α, deg			92.59(3)	
β, deg	103.09(1)		94.82(3)	
γ, deg			99.15(3)	
V, Å^3	3222.8(10)	4469.0(7)	4204(2)	8605(4)
Z	2	4	2	4
D_{calc}, g cm^{-3}	1.515	1.375	1.459	1.629
crystal size, mm	0.17 × 0.18 × 0.20	0.09 × 0.10 × 0.37	0.05 × 0.17 × 0.24	0.08 × 0.12 × 0.21
μ, cm^{-1}	7.8	28.79	7.2	37.4
instrument	Philips PW1100/20	Rigaku AFC6R	Philips PW1100/20	Philips PW1100/20
radiation	Mo Kα	Cu Kα	Mo Kα	Mo Kα
no. of unique reflcns	5941	3414	10999	6230
no. of reflcns obsd	4418 ($I > 3\sigma(I)$)	3072 ($I > 3\sigma(I)$)	6123 ($I > 3\sigma(I)$)	4349 ($I > 3\sigma(I)$)
2*θ* range, deg	4−50	4−120.2	4−45	4−45
scan technique	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$	ω
scan width (deg)	1.0 + 0.35 tan *θ*	1.1 + 0.3 tan *θ*	0.9 + 0.35 tan *θ*	1.0 + 0.35 tan *θ*
temperature (°C)	20(1)	−60(1)	20(1)	20(1)
structural refinement	XTAL3.2[47]	teXsan[48]	XTAL3.2[47]	XTAL3.2[47]/teXsan[48]
final *R*, R_w	0.036, 0.033	0.030, 0.034	0.070, 0.066	0.035, 0.022

Table 2. Selected Bond Distances (Å) and Angles (deg) for (R_C),(R_P,R_P)-(−)-**3** (X = PF_6)

Bond Distances (Å)			
Pd(1)−P(1)	2.363(3)	Pd(1)−P(2)	2.247(3)
Pd(1)−N(1)	2.161(9)	Pd(1)−C(75)	2.063(8)
Pd(2)−P(3)	2.227(3)	Pd(2)−P(4)	2.356(3)
Pd(2)−N(2)	2.142(9)	Pd(2)−C(85)	2.06(1)
Bond Angles (deg)			
P(1)−Pd(1)−P(2)	84.97(9)	P(1)−Pd(1)−N(1)	99.3(2)
P(1)−Pd(1)−C(75)	172.3(3)	P(2)−Pd(1)−N(1)	175.3(2)
P(2)−Pd(1)−C(75)	96.0(3)	N(1)−Pd(1)−C(75)	80.0(3)
P(3)−Pd(2)−P(4)	84.7(1)	P(3)−Pd(2)−N(2)	172.6(3)
P(3)−Pd(2)−C(85)	92.5(3)	P(4)−Pd(2)−N(2)	101.6(3)

treated with an equimolar quantity of (*S*,*S*)-**1** in methanol, followed by the addition of a 2-fold excess of ammonium hexafluorophosphate in the same solvent, gave (−)-[Ag_2{(*R*,*R*)-**1**}$_2$](PF_6)$_2$ as colorless needles in 92% yield having mp 194−195 °C and $[\alpha]_D$ −7.5 (*c* 1.0, CH_2Cl_2). Recrystallization of this material from hot methanol gave prisms of the pure material suitable for X-ray crystallography. The analogous gold(I) complex was prepared by reacting (*S*,*S*)-**1** with $Et_4N[AuBr_2]$ in dichloromethane and treating the intermediate with aqueous NH_4PF_6: colorless (−)-[Au_2{(*R*,*R*)-**1**}$_2$](PF_6)$_2$·CH_2Cl_2 was subsequently isolated from the dichloromethane phase and purified by recrystallization from dichloromethane−ethanol, giving colorless needles of mp 228−230 °C and $[\alpha]_D$ −117.7 (*c* 1.0, CH_2Cl_2).

Crystal and Molecular Structures of Copper, Silver, and Gold Complexes. Crystal data, information relating to data collection, and refinement details for Δ-(−)-[Cu{(*R*,*R*)-**1**}]PF_6·EtOH, Λ-(−)-[Ag_2{(*R*,*R*)-**1**}$_2$](PF_6)$_2$, and Λ-(−)-[Au_2{(*R*,*R*)-**1**}$_2$](PF_6)$_2$·CH_2Cl_2 are given in Table 1. Table 2 lists the most important distances and angles for the copper complex employing the atom-labeling scheme given in Figure 2; corresponding data for the silver and gold complexes are given in Tables 3 and 4 and Figures 3 and 4.

The molecular structure of the cation of (−)-[Cu{(*R*,*R*)-**1**}]PF_6·EtOH is depicted in Figure 2. The cation forms a single helix with an idealized C_2 axis bisecting the angle P(1)−Cu−P(4). The configuration of the helix is Δ, as determined by the IUPAC skew-line convention (Figure 5, part a).[28] The five-membered chelate rings in the cation each adopt the *λ* conformation and the inner-*P*-phenyl groups have equatorial dispositions on phosphorus stereocenters of *R* configuration. The Cu−P distances are similar to those in [Cu(dppe)$_2$]X (where dppe = 1,2-bis(diphenylphosphino)ethane),[29] but it is noteworthy that the angle P(1)−Cu−P(4) of 135.91(6)° in (−)-[Cu{(*R*,*R*)-**1**}]PF_6·EtOH indicates considerable strain in the mononuclear metal cation.

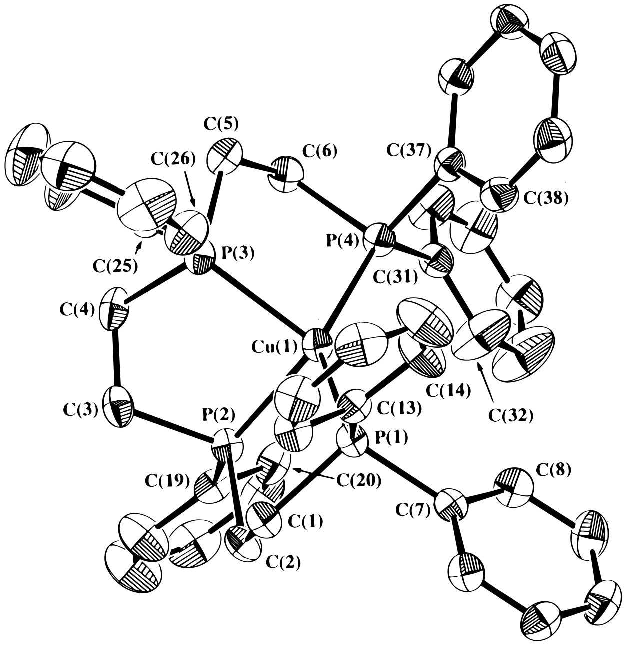

Figure 2. ORTEP view of the cation of Δ-(−)-[Cu{(*R*,*R*)-**1**}]PF_6·EtOH with 50% probability ellipsoids.

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(28) *IUPAC Nomenclature of Inorganic Chemistry (Recommendations 1990)*; Blackwell Scientific Publications: Oxford, 1990.

(29) Camus, A.; Marich, N.; Nardin, G.; Randaccio, L. *Transition Met. Chem.* **1976**, *1*, 205. Doyle, G.; Eriksen, K. A.; Van Engen, D. *J. Am. Chem. Soc.* **1985**, *107*, 7914. Berners-Price, S. J.; Colquhoun, L. A.; Healy, P. C.; Byriel, K. A.; Hanna, J. K. *J. Chem. Soc., Dalton Trans.* **1992**, 3357. Leoni, P.; Pasquali, M.; Ghilardi, C. A. *J. Chem. Soc., Chem. Commun.* **1983**, 240.

Table 3. Selected Bond Distances (Å) and Angles (deg) in Δ-(−)-[Cu{(*R*,*R*)-**1**}]PF$_6$·EtOH

Bond Distances			
Cu(1)−P(1)	2.239(2)	P(2)−C(3)	1.837(6)
Cu(1)−P(2)	2.279(2)	P(2)−C(19)	1.815(6)
Cu(1)−P(3)	2.276(2)	P(3)−C(4)	1.843(6)
Cu(1)−P(4)	2.237(2)	P(3)−C(5)	1.850(6)
P(1)−C(1)	1.839(6)	P(3)−C(25)	1.822(6)
P(1)−C(7)	1.825(6)	P(4)−C(6)	1.848(6)
P(1)−C(13)	1.824(6)	P(4)−C(31)	1.835(6)
P(2)−C(2)	1.844(6)	P(4)−C(37)	1.834(6)

Bond Angles			
P(1)−Cu(1)−P(2)	89.67(6)	P(2)−Cu(1)−P(3)	89.74(6)
P(1)−Cu(1)−P(3)	123.85(7)	P(2)−Cu(1)−P(4)	120.32(7)
P(1)−Cu(1)−P(4)	135.91(6)	P(3)−Cu(1)−P(4)	90.28(6)

Table 4. Selected Bond Distances (Å) and Angles (deg) for the Double Helix and Side-by-Side Helix Conformers in Λ-(−)-[Ag$_2${(*R*,*R*)-**1**}$_2$](PF$_6$)$_2$

Bond Distances			
Double Helix		Side-by-Side Helix	
Ag(1)−P(11)	2.480(8)	Ag(3)−P(31)	2.513(9)
Ag(1)−P(12)	2.525(7)	Ag(3)−P(32)	2.538(8)
Ag(1)−P(21)	2.508(7)	Ag(3)−P(41)	2.520(9)
Ag(1)−P(22)	2.524(8)	Ag(3)−P(42)	2.543(9)
Ag(2)−P(13)	2.524(8)	Ag(4)−P(33)	2.487(9)
Ag(2)−P(14)	2.526(7)	Ag(4)−P(34)	2.509(9)
Ag(2)−P(23)	2.507(8)	Ag(4)−P(43)	2.475(8)
Ag(2)−P(24)	2.501(7)	Ag(4)−P(44)	2.510(8)

Bond Angles (deg)			
Double Helix		Side-by-Side Helix	
P(11)−Ag(1)−P(12)	84.9(2)	P(31)−Ag(3)−P(32)	83.9(3)
P(11)−Ag(1)−P(22)	120.7(3)	P(31)−Ag(3)−P(41)	126.9(3)
P(12)−Ag(1)−P(22)	114.4(2)	P(31)−Ag(3)−P(42)	128.4(3)
P(13)−Ag(2)−P(14)	83.5(2)	P(32)−Ag(3)−P(41)	115.5(3)
P(13)−Ag(2)−P(24)	120.9(2)	P(32)−Ag(3)−P(42)	122.6(3)
P(14)−Ag(2)−P(24)	127.6(3)	P(41)−Ag(3)−P(42)	83.9(3)
		P(33)−Ag(4)−P(34)	84.1(3)
		P(33)−Ag(4)−P(43)	121.8(3)
		P(33)−Ag(4)−P(44)	127.5(3)
		P(34)−Ag(4)−P(43)	132.8(3)
		P(34)−Ag(4)−P(44)	110.5(3)
		P(43)−Ag(4)−P(44)	85.4(3)

Table 5. Selected Bond Distances (Å) and Angles (deg) in Λ-(−)-[Au$_2${(*R*,*R*)-**1**}$_2$](PF$_6$)$_2$·CH$_2$Cl$_2$

Bond Distances			
Au(1)−P(11)	2.406(4)	Au(2)−P(13)	2.417(4)
Au(1)−P(21)	2.419(4)	Au(2)−P(14)	2.421(4)
Au(1)−P(12)	2.394(4)	Au(2)−P(23)	2.394(4)
Au(1)−P(22)	2.379(4)	Au(2)−P(24)	2.447(4)

Bond Angles			
P(11)−Au(1)−P(12)	85.7(1)	P(13)−Au(2)−P(14)	86.1(1)
P(11)−Au(1)−P(21)	119.8(1)	P(13)−Au(2)−P(23)	115.0(1)
P(11)−Au(1)−P(22)	124.1(1)	P(13)−Au(2)−P(24)	128.5(1)
P(12)−Au(1)−P(21)	124.9(1)	P(14)−Au(2)−P(23)	132.8(1)
P(12)−Au(1)−P(22)	120.9(1)	P(14)−Au(2)−P(24)	115.4(1)
P(21)−Au(1)−P(22)	86.0(1)	P(23)−Au(2)−P(24)	85.0(1)

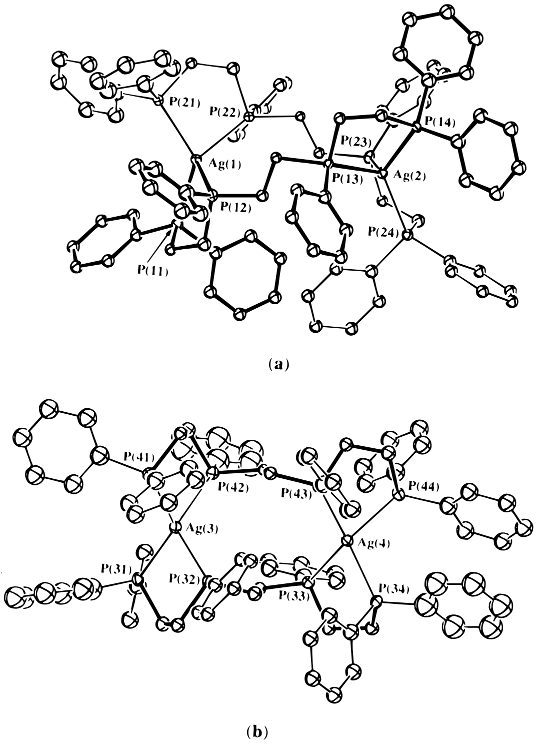

Figure 3. ORTEP view of double helix (a) and side-by-side helix (b) conformers of the cation of Λ-(−)-[Ag$_2${(*R*,*R*)-**1**}$_2$](PF$_6$)$_2$ with 50% probability ellipsoids.

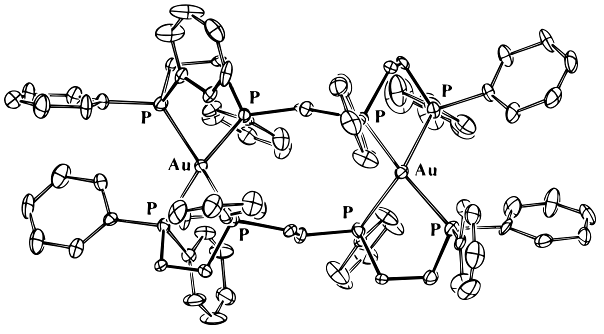

Figure 4. ORTEP view of the cation of Λ-(−)-[Au$_2${(*R*,*R*)-**1**}$_2$]-(PF$_6$)$_2$·CH$_2$Cl$_2$ with 50% probability ellipsoids.

The structural determination of (−)-[Ag$_2${(*R*,*R*)-**1**}$_2$](PF$_6$)$_2$ revealed one molecule each of the double helix and side-by-side helix conformers of the disilver cation and associated anions in each unit cell (Figure 3). The binding of the phosphine ligands to the silver ions is completely stereoselective in each of the conformers giving silver stereocenters of *S* configuration. The essential difference between the two structures lies in the relationship between the helicity of the central ten-membered ring, which has the chiral twist-boat−chair−boat (TBCB) conformation in each structure (Figure 6), rather than the usual achiral BCB conformation of cyclodecane and its derivatives,[30] and the configurations of the chiral inner-phosphorus stereocenters. When the ten-membered ring has the λ conformation, the phenyl groups attached to the inner-phosphorus stereocenters of *R* configuration adopt equatorial dispositions and the axial terminal (diphenylphosphino)ethyl groups are in position to generate the D_2-double helix conformation of the complex; when the central ring has the δ conformation, the terminal (diphenylphosphino)ethyl groups have equatorial dispositions, which results in the tighter turns of the side-by-side helix conformer (Figure 7). The difference between the two conformations of the complex is accordingly reflected in the C−C−P−C torsion angles running from the central carbon−carbon bonds of the ten-membered rings through to the adjacent phosphorus−carbon bonds of the terminal five-membered rings. In the double helix conformer of idealized D_2 symmetry (torsion angles 176−178°, Ag···Ag 6.859(3) Å), each molecule of the tetra(tertiary phosphine) completes a one-half turn of a left-handed or Λ helix (as does the overall complex); in the side-by-side conformer of idealized C_2 symmetry (torsion angles 63−80°, Ag···Ag 6.072(4) Å), each of the ligands completes one and one-half turns of a Λ helix (Figure 5, parts b and c).

The structure of the cation of (−)-[Au$_2${(*R*,*R*)-**1**}$_2$](PF$_6$)$_2$·CH$_2$Cl$_2$ is shown in Figure 4. The side-by-side helix of Λ configuration was again observed, each gold stereocenter having

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(30) Hendrickson, J. B. *J. Am. Chem. Soc.* **1967**, *89*, 7047. Engler, E. M.; Andose, J. D.; von R. Schleyer, P. *J. Am. Chem. Soc.* **1973**, *95*, 8005.

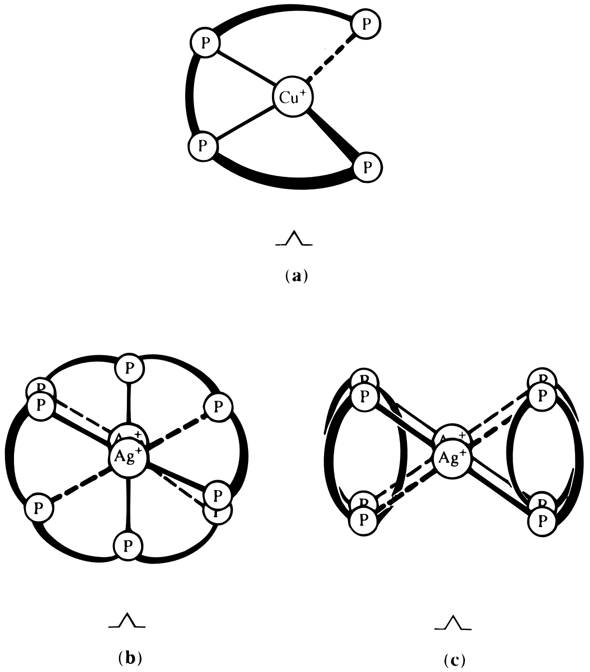

Figure 5. Helical displacements in cations of Δ-(−)-[Cu{(*R*,*R*)-**1**}]-PF_6·EtOH (a) and double-stranded D_2-double helix (b) and D_2-side-by-side helix (c) conformers of Λ-(−)-[Ag_2{(*R*,*R*)-**1**}$_2$]$(PF_6)_2$.

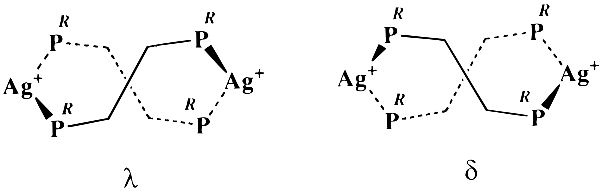

Figure 6. Enantiomorphic TBCB conformations of central ten-membered ring in Λ-(−)-[Ag_2{(*R*,*R*)-**1**}$_2$]$(PF_6)_2$.

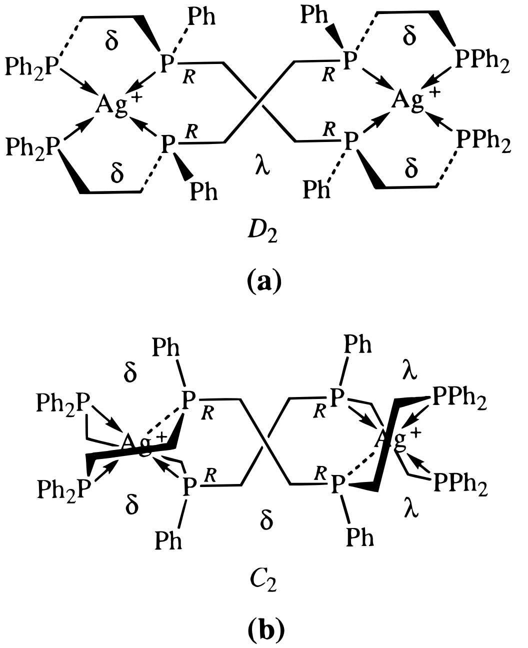

Figure 7. Schematic side elevations of the double-stranded D_2-double helix (a) and C_2-side-by-side helix (b) conformers of the cation of Λ-(−)-[Ag_2{(*R*,*R*)-**1**}$_2$]$(PF_6)_2$.

the *S* configuration with C−C−P−C torsion angles of 63−80° (Au···Au 6.244(2) Å) in the central ten-membered ring of δ conformation. Whereas the corresponding conformer of the silver helicate has idealized C_2 symmetry with a $\delta,\delta,\lambda,\lambda$ arrangement of the terminal five-membered chelate rings, the gold complex has C_1 symmetry because of a $\delta,\delta,\delta,\lambda$ arrangement of the five-membered rings. The side-by-side helical arrangements of the poly(tertiary phosphines) about the univalent silver and gold ions are the structural motifs of the leucine repeat or zipper transcriptional proteins, wherein two polypeptide α-helicies are held together by hydrogen bonding in parallel side-by-side arrangements.[31]

Solution Properties. (a) NMR Spectroscopy. ^{1}H and ^{31}P NMR spectra were recorded on the three complexes in dichloromethane-d_2 at 21 °C. Three broad peaks of nonintegral intensities were observed in the ^{1}H NMR spectra at 21 °C between 1.8 and 2.8 ppm for the methylene protons in each of the complexes, together with multiplets for the aromatic protons. The methylene peak to lowest field was split into two broad resonances of equal intensity at −75 °C for the copper complex, and broadening was observed in the spectra of the silver and gold complexes upon cooling the samples to this temperature. In the ^{31}P NMR spectra at 21 °C, the silver complex exhibited sharp resonances at 5.67 and 3.63 ppm and the copper and gold complexes broad resonances centered at 20.9 and 15.2 ppm (Cu) and 26.0 and 19.6 ppm (Au) for the inner- and outer-phosphorus nuclei. Cooling the samples to −90 °C did not lead to significant sharpening of the broad peaks observed for the copper and gold complexes.

(b) Conductances. The conductances of 10^{-4}−10^{-2} M solutions of the three complexes in highly purified acetonitrile at 21 °C were determined. The Onsager law, $\Lambda_{eq} = \Lambda_o - AC_{eq}^{1/2}$, implies a linear relationship between the equivalent conductance (Λ_{eq}) and the square root of the equivalent concentration of the electrolyte ($C_{eq}^{1/2}$), with the slope *A* being dependent upon the type of electrolyte. Thus, the value of *A* for a given compound can be compared with the values for known electrolytes under similar conditions or with a calculated value by use of an experimentally determined conductance at infinite dilution, Λ_o.[32] For the silver complex, the value for *A* of 794 Ω^{-1} equiv$^{-3/2}$ cm^2 L$^{1/2}$ compares with the calculated values of 890 and 334 Ω^{-1} equiv$^{-3/2}$ cm^2 L$^{1/2}$ in this solvent for 2:1 and 1:1 electrolytes, respectively. For the gold complex, $A = 785$ Ω^{-1} equiv$^{-3/2}$ cm^2 L$^{1/2}$ with the calculated values for the 2:1 and 1:1 electrolyte being 951 and 350 Ω^{-1} equiv$^{-3/2}$ cm^2 L$^{1/2}$, respectively. In the case of the copper complex, the value for *A* of 588 Ω^{-1} equiv$^{-3/2}$ cm^2 L$^{1/2}$ lies between the calculated values of 852 and 324 Ω^{-1} eq$^{-3/2}$ cm^2 L$^{1/2}$. The deviations from calculated values of *A* for all three complexes may reflect uncertainties in the calculations or the existence of monomer−dimer equilibria, although there was no clear evidence for such equilibria in the ^{1}H or ^{31}P NMR spectra. The electrospray mass spectrum of the silver complex at a cone voltage of 25 V, however, displayed a pattern of peaks in the range *m*/*z* 776.7−779.7 because of the isotopes ^{107}Ag (51.35%) and ^{109}Ag (48.65%) that uniquely identify the disilver cation $[M + 2H]^{2+}$, along with a smaller peak for the monosilver cation $[M + H]^+$. The digold(I) complex exhibited an ion at *m*/*z* 866.8, but because gold is monoisotopic this peak could not be assigned to the mononuclear or dinuclear gold cation. The copper complex contained peaks in the range *m*/*z* 732.7−736.7 (^{63}Cu (69.09%), ^{65}Cu (30.91%)) for the monomeric cation $[M + H]^+$ only. Electrospray mass spectrometry has been employed previously for the determination of stoichiometry of a series of iron(III) complexes of dihydroxamic acids.[33] It is noteworthy that 2,6-bis(1-methylbenzimadazol-2-yl)pyridine and 1,3-bis-

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[31] O'Shea, E. K.; Rutkowski, R.; Kim, P. S. *Science* **1989**, *243*, 538.

[32] Feltham, R. D.; Hayter, R. G. *J. Chem. Soc.* **1964**, 4587. Bogess, R. K.; Zatko, D. A. *J. Chem. Educ.* **1975**, *52*, 649 and references cited therein.

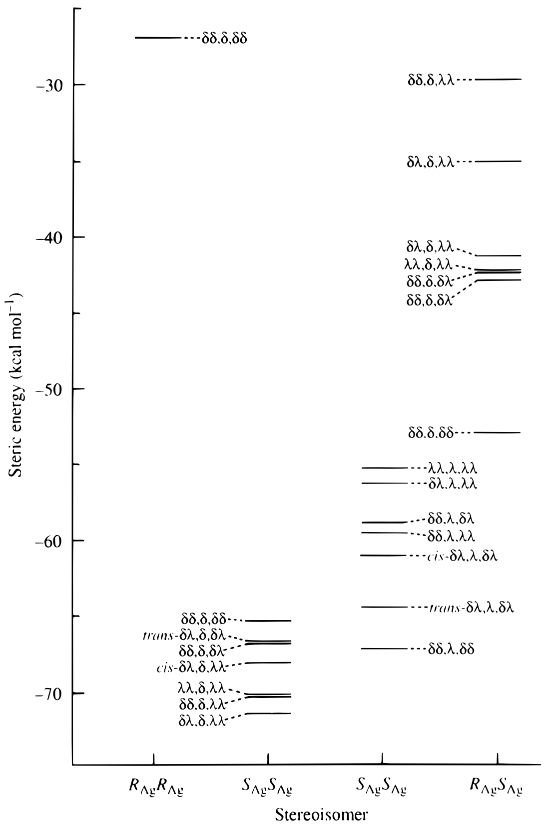

Figure 8. Relative steric energies of stereoisomers of $[Ag_2\{(R,R)\text{-}\mathbf{1}\}_2]^{2+}$.

(1-methylbenzimidazol-2-yl)benzene react with copper(I) to produce double helix and nonhelical side-by-side dicopper complexes, respectively, the structures of which are maintained in each case in polar aprotic solvents.[34]

Molecular Mechanics Calculations. The evaluations of the steric energies for the configurational and conformational isomers of $[Ag_2\{(R,R)\text{-}\mathbf{1}\}_2]^{2+}$ were performed with use of the force field TRIPOS 5.2 in the program SPARTAN 3.0.[35] The starting structures were generated by varying the metal stereocenter configurations, the conformations of the central ten-membered rings containing the two metal ions, and the conformations of the four terminal-puckered five-membered chelate rings in each cation. The calculations indicated that the lowest-energy diastereomers for the complex cation were associated with the (S_{Ag},S_{Ag}) relative configuration of the metal stereocenters in conjunction with a chiral ten-membered ring containing the two metal ions in the TBCB conformation. Moreover, the λ conformation of the ten-membered TBCB ring always generated double helix structures and the δ form side-by-side helix structures for the *R*-tetra(tertiary phosphine). For each of the ten-membered-ring conformations, δ or λ, there are seven different combinations of the four terminal five-membered ring conformations lying between the idealized D_2-double helix (central ring λ, terminal rings $\delta,\delta,\delta,\delta$) and the idealized D_2-side-by-side helix (central ring δ, terminal rings $\lambda,\lambda,\lambda,\lambda$). The energies of the various diastereomers for the disilver cations of the *R*-tetra(tertiary phosphine) are given in Figure 8. The calculations indicated similar energies for the 14 conformers having the (S_{Ag}, S_{Ag}) configuration. Only one high-energy conformer stabilized with the (R_{Ag}, R_{Ag}) configuration of the metal centers from 14 starting geometries. For the (R_{Ag}, S_{Ag}) diastereomer, four conformers stabilized at relatively high energies. For a central ten-membered TBCB ring of δ conformation, five-membered terminal rings of δ conformation appear to favor the double helix structure, whereas two or more five-membered rings of λ conformation stabilize side-by-side helices.

Statistical root mean square (rms) comparisons of observed and calculated structures have been used as measures of accuracy.[36] In an evaluation of results for 76 organic molecules involving the use of the TRIPOS 5.2 force field, rms analyses of carbon atom positions, individual bond lengths, bond angles, and torsion angles gave rms movements of 0.25 Å, 0.025 Å, 2.5°, and 9.6°, respectively.[37] In a recent evaluation of a force field developed to model cyclopentadienyliron complexes, a 10-fold weighting was given to the metal atom coordinates in order to superimpose the structures for atom position comparison.[38] In the present work, hydrogen atoms were not included in the rms comparisons, and equal weighting was given to the "heavy atoms" carbon, phosphorus, and silver when superimposed for atom position analysis. The rms differences between the observed and calculated structures of the side-by-side dimer $[Ag_2\{(R,R)\text{-}\mathbf{1}\}_2]^{2+}$ were determined. The average rms deviation for bond lengths in this conformer was 0.03 Å. A superimposition of the calculated and observed structures led to an rms movement of 0.323 Å for the 34 heavy atom positions describing the core of the helix. The Ag···Ag distance in the side-by-side conformer of 6.07 Å compared with a calculated value of 6.03 Å. Bonded torsion angles involving combinations of carbon, phosphorus, and silver atoms throughout the molecule, and nonbonded intramolecular P−Ag···Ag−P torsion angles, exhibited an average rms movement of 9.8°. The angular rms value of 5.09° was higher than the 2.5° (av) reported for organic molecules,[39] but can be attributed to discrepancies of 5° (av) about the AgP_4 tetrahedral angles and an underestimation of the spread of the Ag−P−C(*ipso*-phenyl) angles, viz. 106−114° (calcd), 116−129° (obsd). The larger spread of the Ag−P−C(*ipso*-phenyl) angles in the solid state appears to be due to supramolecular edge-to-face interactions between the terminal phenyl groups of the two conformers in the lattice. The principal difference between the calculated and observed structure for the side-by-side silver(I) helix is the orientation of two pairs of phenyl groups; these are edge-to-face in the crystal structure, where there appears to be a significant supramolecular interaction, and face-to-face in the calculated structure. The importance of concerted intermolecular edge-to-face attractions between phenyl groups in crystal lattices of triphenylphosphine−metal complexes has been demonstrated elsewhere.[40]

A superimposition of atom positions for the most symmetrical part of the observed C_2-double helix with the equivalent atoms of the calculated D_2 structure led to an average rms movement of 0.285 Å. Average rms bond length differences over the entire molecule were 0.03 Å, and average angular rms movements

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(33) Caudle, M. T.; Stevens, R. D.; Crumbliss, A. L. *Inorg. Chem.* **1994**, *33*, 6111.

(34) Piguet, C.; Bernardinelli, G.; Williams, A. F. *Inorg. Chem.* **1989**, *28*, 2920; Rütimann, S.; Piguet, C.; Bernardinelli, G.; Bocquet, B.; Williams, A. F. *J. Am. Chem. Soc.* **1992**, *114*, 4230.

(35) Energy minimization calculations were performed with use of the program SPARTAN 3.0 (Wavefunction Inc., Irvine, CA, 1992) in conjunction with the force field TRIPOS 5.2 with additional metal parameters from SPARTAN.

(36) Hall, D.; Pavitt, N. *J. Comput. Chem.* **1984**, *5*, 441; Momany, F. A.; Rone, R. *J. Comput. Chem.* **1992**, *13*, 888. Whitlow, M.; Teeter, M. M. *J. Am. Chem. Soc.* **1986**, *108*, 7163.

(37) Clark, M.; Cramer, R. D., III; van Opdenbosch, N. *J. Comput. Chem.* **1989**, *10*, 982.

(38) Doman, T. N.; Hollis, T. K.; Bosnich, B. *J. Am. Chem. Soc.* **1995**, *117*, 1352.

(39) Rabinowitz, R.; Pellon, J. *J. Org. Chem.* **1961**, *26*, 4623. Wu, C.; Welch, F. J. *J. Org. Chem.* **1965**, *30*, 1229.

(40) Dance, I.; Scudder, M. *J. Chem. Soc., Chem. Commun.* **1995**, 1039.

were similar to those calculated for the side-by-side structure (4.98°). The average rms movement for angles of the core atoms for the observed C_2- and calculated D_2-double helix was 3.63°. The P−Ag···Ag−P torsion angles were remarkably accurate in the calculated D_2-double helix structure, with an average rms movement of 7° when compared to the observed C_2 structure.

Conclusion. The (*S*,*S*) enantiomer of the linear tetra(tertiary phosphine) (R*,R*)-(±)-**1** reacts with silver(I) or gold(I) salts containing noncoordinating anions to give homochiral double-stranded disilver(I)− and digold(I)−tetra(tertiary phosphine) helicates of Λ configuration by stereoselective self-assembly. The disilver(I) complex crystallizes as an equimolar compound of the double helix and side-by-side helix conformers of the helicate; the digold(I) helicate crystallizes as the side-by-side conformer. A similar reaction with copper(I) gives a mononuclear metal complex of Δ configuration. Conductance measurements in acetonitrile indicated that the dinuclearity of the silver(I) and gold(I) complexes was retained in solution and that the mononuclear copper(I) complex rearranged considerably into a dinuclear species. Energy minimization calculations on the disilver(I) cation with use of the program SPARTAN 3.0 gave remarkably good agreements with observed structures and were of great assistance in rationalizing the relationships between the configurations of the chiral phosphorus and silver stereocenters and the conformations of the five- and ten-membered rings present.

Experimental Section

Manipulations involving air-sensitive compounds were performed under an inert atmosphere using Schlenk techniques. Tetrahydrofuran was distilled over sodium benzophenone ketyl. ^{31}P, ^{13}C, and ^{1}H NMR spectra were recorded at 21 °C on a Varian VXR 300S spectrometer operating at 299.96 MHz. ^{31}P NMR spectra were referenced to external aqueous H_3PO_4 (85%). Electrospray mass spectra (ES MS) were recorded on acetonitrile solutions on a Quattro II mass spectrometer with a cone potential of 25 V. Optical rotations were measured on the specified solutions in a 1.0 dm cell at 21 °C with use of a Perkin-Elmer Model 241 polarimeter. Elemental analyses were performed by staff within the Research School of Chemistry. Conductance measurements were determined on solutions of the complexes in highly purified acetonitrile using a Radiometer CDC344 immersion electrode. Diphenylvinylphosphine was prepared according to the method given in ref 16. An improved preparation of 1,2-bis(phenylphosphino)ethane is described.[41] The materials $Et_4N[AuBr_2]$ and $[Cu(MeCN)_4]PF_6$ were prepared by the methods given in refs 42 and 43, respectively.

1,2-Bis(phenylphosphino)ethane. The following procedure for the preparation of this compound is based upon that given in ref 16. Finely divided lithium wire (6.0 g, 4.3 equiv) in THF (360 mL) was added to a vigorously stirred solution of 1,2-bis(diphenylphosphino)ethane (80 g) in THF (480 mL). The mixture was heated under reflux for 3 h. The hot solution was separated from excess lithium with use of a cannula. (If the solution is cooled over 12 h, yellow crystals of $[Li(THF)_2]_4[PhPCH_2CH_2PPh]_2$[44] deposit.) The red-brown reaction mixture was treated with ammonium bromide (80 g). The THF was then removed in vacuo, and water (400 mL) and diethyl ether (200 mL) were added to the residue. After three extractions of the aqueous phase with similar quantities of diethyl ether, the combined extracts were dried ($MgSO_4$) and distilled, giving the pure product as a colorless oil: yield 32.2 g (65%), bp 140 °C (0.07 mmHg). ^{31}P{^{1}H} NMR (C_6D_6): δ −46.43, −46.59 ((R*,R*)/(R*,S*)). ^{1}H NMR (C_6D_6): δ 1.80−2.10 (br m, 4 H, CH_2), 3.94 (br m, 1 H, PH), 4.62 (br m, 1 H, PH), 7.27 (br m, 6 H, ArH), 7.48 (br m, 4 H, ArH).

(R*,R*)-(±)/(R*,S*)-1,1,4,7,10,10-Hexaphenyl-1,4,7,10-tetraphosphadecane ((R*,R*)-(±)/(R*,S*)-1). The large-scale synthesis of this compound is based on the method given in ref 16. A solution of diphenylvinylphosphine (93.8 g, 0.44 mol) and 1,2-bis(phenylphosphino)ethane (55.4 g, 0.22 mol) in THF (1 L) was treated with potassium *tert*-butoxide (18.7 g), and the mixture was heated under reflux for 6 h. [The absence of a signal at δ −10.3 (C_6D_6 lock) in the ^{31}P{^{1}H} NMR spectrum of a sample taken from the mother liquor at this stage indicated complete reaction of the diphenylvinylphosphine.] The volume of tetrahydrofuran was reduced to ca. 450 mL by distillation, and degassed methanol (450 mL) was added. A colorless precipitate of the product separated. After ca. 15 h at 0 °C, the mixture was treated with additional methanol (450 mL) and stirred for 1 h. The colorless precipitate was collected and washed with methanol and diethyl ether and dried (60 °C, 0.1 mmHg). Yield: 128.5 g (85%). Additional product was obtained from the mother liquors by concentration and addition of methanol. Overall yield: 99%.

Separation of Diastereomers. (R*,R*)-(±)/(R*,S*)-**1** (20 g) was maintained as a melt at 200 °C for 2 h under an inert atmosphere to ensure a 1:1 mixture of diastereomers. The resulting oil solidified upon cooling, and the solid was stirred in tetrahydrofuran (80 mL) for 2 days, whereupon the sparingly soluble material was filtered off, washed with tetrahydrofuran (25 mL), and dried in vacuo: yield 11.21 g, mp 175−179 °C. Recrystallization of the solid from dichloromethane−ethanol afforded colorless microcrystals of the pure (R*,S*) diastereomer (9.8 g, 97%) having mp 183 °C (lit.[16] mp 187 °C). The solvent was removed from the mother liquor. The resulting oil solidified over 5 days to give 8.5 g (85%) of the pure (R*,R*)-(±) diastereomer having mp 115−116 °C (lit.[16] mp 118 °C). Several recrystallizations of this material from dichloromethane−ethanol did not increase the melting point. **(R*,S*)-1**. Anal. Calcd for $C_{42}H_{42}P_4$: C, 75.2; H, 6.3. Found: C, 75.4; H 6.4. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ_A −12.95 (terminal P; AA′), δ_X −16.42 (internal P; XX′) (AXX′A′; J_{AX} = 28.60 Hz, $J_{AX'}$ = 0.33 Hz, $J_{XX'}$ = 23.79 Hz, $J_{AA'}$ = 0.00 Hz). ^{1}H NMR ($CDCl_3$): δ 1.55−1.70, 1.85−2.00 (br m, 12 H, CH_2), 7.29 (br s, 30 H, ArH). ^{13}C NMR ($CDCl_3$): δ 23.6, 129.1, 133.0. **(R*,R*)-(±)-1**. Anal. Calcd for $C_{42}H_{42}P_4$: C, 75.2; H, 6.3. Found: C, 75.1; H 6.2. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ_A −13.01 (terminal P), δ_X −16.78 (internal P) (AXX′A′; J_{AX} = 28.86 Hz, $J_{AX'}$ = 0.37 Hz, $J_{XX'}$ = 25.29 Hz, $J_{AA'}$ = 0.00 Hz). ^{1}H NMR ($CDCl_3$): δ 1.55−1.70, 1.85−2.00 (br ms, 12 H, CH_2), 7.29 (br s, 30 H, ArH). ^{13}C NMR ($CDCl_3$): δ 23.43, 128.61, 132.60.

Resolution of (R*,R*)-(±)-1. Formation and Separation of Diastereomers [*SP*-4-4-[$(R_C),(R_P,R_P)$]]- and [*SP*-4-4-[$(R_C),(S_P,S_P)$]]-Bis[1-[1-dimethylamino)ethyl]-2-phenyl-C^2,*N*](1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane-*P*,*P*,*P*,*P*)dipalladium(II) Hexafluorophosphate ($(R_C),(R_P,R_P)$- and $(R_C),(S_P,S_P)$-3 (X = PF_6)). A mixture of (R*,R*)-(±)-**1** (67.07 g, 0.1 mol) and (*R*)-**2**·CH_2Cl_2 (58.01 g, 0.18 mol) in methanol (600 mL) reacted to give an almost colorless solution of the diastereomeric chlorides $(R_C),(R_P,R_P)/(R_C),(S_P,S_P)$-**3** (X = Cl), which was treated over 1 h with a solution of NH_4PF_6 (35 g) in water (50 mL). Additional methanol (300 mL) was then added, and the mixture was stirred for 5 h. The colorless precipitate was filtered off, washed with water, aqueous methanol (90%), methanol, and diethyl ether, and dried. The 1:1 mixture of the two diastereomers was thus obtained as a microcrystalline solid in 97% yield (130.0 g) having $[\alpha]_D$ −6.9 (*c* 1.0, Me_2CO). The mixture (30.0 g) was suspended in chloroform (100 mL) and stirred for 15 h. The insoluble material was filtered off, washed with diethyl ether, and dried in vacuo (14.7 g, $[\alpha]_D$ −75.3 (*c* 1.0, CH_2Cl_2)), and the filtrate was evaporated to dryness, leaving a colorless solid (15.3 g, $[\alpha]_D$ +57.9 (*c* 1.0, CH_2Cl_2)). The ^{31}P{^{1}H} and ^{1}H NMR spectra of the two components thus obtained indicated a separation of ca. 95% efficiency. The less-soluble diastereomer (14.7 g) was dissolved in dichloromethane (80 mL), the solution filtered, and the filtrate carefully diluted with ethanol (40 mL) over 2 days. A fraction of the less-soluble diastereomer (10.4 g) having $[\alpha]_D$ −91.6 (*c* 1.0, CH_2Cl_2) was collected. The mother liquor was evaporated to dryness, and the residue was dissolved in dichloromethane (35 mL) and treated with ethanol (20 mL) over 30 min. An additional fraction of the less-soluble diastereomer separated (4.96 g) having $[\alpha]_D$ −76.2 (*c* 1.0, CH_2Cl_2), which was recrystallized similarly from dichloromethane (35 mL)−ethanol (20 mL) to give the almost pure

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(41) Kimpton, B. R.; McFarlane, W.; Muir, A. S.; Patel, P. G.; Bookham, J. L. *Polyhedron* **1993**, *12*, 2525.

(42) Braunstein, P.; Clark, R. J. H. *J. Chem. Soc., Dalton Trans.* **1973**, 1845.

(43) Kubas, G. J. *Inorg. Synth.* **1990**, *28*, 68.

(44) Brooks, P. A.; Gallagher, M. J.; Sarroff, A. *Aust. J. Chem.* **1987**, *40*, 1341 and references therein. Brooks, P.; Craig, D. C.; Gallagher, M. J.; Rae, A. D.; Sarroff, A. *J. Organomet. Chem.* **1987**, *323*, C1.

less-soluble diastereomer (4.13 g) of $[\alpha]_D$ −90.4 (*c* 1.0, CH_2Cl_2). A recrystallization of the combined less-soluble fractions from dichloromethane (70 mL) by the careful addition of ethanol (50 mL) afforded the pure less-soluble diastereomer (R_C),(R_P,R_P)-**3** (X = PF_6) as colorless prisms: mp 233−235 °C dec, 13.9 g (93%), $[\alpha]_D$ −96 (*c* 1.0, Me_2CO). Anal. Calcd for $C_{60}H_{70}F_{12}N_2P_6Pd_2$: C, 50.7; H, 4.8; N, 1.9. Found: C, 50.6; H, 4.8; N, 1.9. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ_A 64.57 (terminal P, AA′), δ_X 43.68 (internal P, XX′) (AXX′A′; J_{AX} = 18.62 Hz, $J_{AX'}$ = 5.95 Hz, $J_{XX'}$ = 53.41 Hz, $J_{AA'}$ = 0.00 Hz), −143.6 (sept, $_1J_{PF}$ = 711.2 Hz, PF_6^-). ^1H NMR (CD_2Cl_2): δ 1.47−2.69 (br m, 30 H, CH_2, CH*Me*, NMe_2), 3.60 (br m, 2 H, C*H*Me), 6.70−7.90 (m, 38 H, ArH). ^{13}C NMR (CD_2Cl_2): δ 26.82, 50.80, 51.93, 78.66, 124.03, 127.10, 130.37, 132.34, 133.64, 134.1, 134.90, 137.00, 157.00. The chloroform was removed from the combined filtrates, the residue dissolved in acetone (40 mL), and the solution diluted with 2-propanol (68 mL) over 2 days. The crystalline product, consisting of almost pure (R_C),(S_P,S_P)-**3** (X = PF_6) (6.97 g) having $[\alpha]_D$ +76 (*c* 1.0, Me_2CO), separated. The mother liquor after evaporation afforded 8.3 g of material that was similarly crystallized from acetone (22 mL)−2-propanol (38 mL) giving an additional more-soluble diastereomer (3.8 g) having $[\alpha]_D$ +56.4 (*c* 1.0, Me_2CO) that was again recrystallized from acetone (10 mL)−2-propanol (22 mL), whereupon material (2.1 g) having $[\alpha]_D$ +72.0 (*c* 1.0, Me_2CO) was obtained. Similar recrystallizations of the more-soluble fractions in mother liquors from small quantities of acetone−2-propanol yielded 1.23 g of complex having $[\alpha]_D$ +70.6 (*c* 1.0, Me_2CO). A final recrystallization of the combined more-soluble fractions (10.3 g) from acetone (30 mL)−2-propanol (70 mL) gave the pure more-soluble diastereomer (R_C),(S_P,S_P)-**3** (X = PF_6) having mp 203−205 °C dec, 9.8 g (64%), $[\alpha]_D$ +77 (*c* 1.0, Me_2CO). Anal. Calcd for $C_{60}H_{70}F_{12}N_2P_6Pd_2$: C, 50.7; H, 4.8; N, 1.9. Found: C, 50.6; H, 5.1; N, 1.7. ^{31}P NMR (CD_2Cl_2): δ_A 65.93 (terminal P, AA′), δ_X 43.13 (internal P, XX′) (AXX′A′; J_{AX} = 17.48 Hz, $J_{AX'}$ = 6.56 Hz, $J_{XX'}$ = 62.15 Hz, $J_{AA'}$ = 0.00 Hz), −143.6 (sept, $^1J_{PF}$ = 711.2 Hz, $PF_6)^-$. ^1H NMR (CD_2Cl_2): δ 1.28−2.57 (br m, 30 H, CH_2, CH*Me*, NMe_2), 3.85 (m, 2 H, C*H*Me), 6.70−7.90 (m, 38 H, ArH). ^{13}C NMR (CD_2Cl_2): δ 11.56, 43.22, 51.46, 73.90, 125.44, 126.71, 130.49, 132.62, 133.99, 134.50, 135.66, 154.28.

[SP-4-[R-(R*,R*)]]-(−)- and [SP-4-[S-(R*,R*)]]-(+)-(1,1,4,7,10,10-Hexaphenyl-1,4,7,10-tetraphosphadecane-P,P,P,P)bis[dichloropalladium(II)] ((R,R)- and (S,S)-4). A solution of (R_C),(R_P,R_P)-**3** (X = PF_6) (10 g) in acetone (200 mL) was treated with hydrochloric acid (20 mL, 10 M), and the mixture was heated under reflux for 30 min. A colorless precipitate of (*R*,*R*)-**4** separated. The reaction mixture was allowed to cool, and water (20 mL) was added. After the mixture was stirred for 1 h, the product was separated by filtration, washed with water, aqueous methanol, methanol, and diethyl ether, and dried. Pure (*R*,*R*)-**4** was thus isolated and was purified by Soxhlet extraction into dichloromethane, giving colorless needles: mp 289 °C, 6.81 g (96%), $[\alpha]_D$ −70.1 (*c* 0.1, CH_2Cl_2). Anal. Calcd for $C_{42}H_{42}Cl_4P_4Pd_2$: C, 49.2; H, 4.1; Found: C, 48.9; H, 4.4. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ_A 72.35, δ_B 66.04 (A_2B_2, J_{AB} = 5.41 Hz). ^1H NMR (CD_2Cl_2): δ 2.11−2.95 (br m, 12 H, CH_2), 7.56 (m, 20 H, ArH), 8.02 (m, 10 H, ArH). MS: *m/z* 988.9 [M^+ − Cl]. The mother liquor was evaporated to dryness, and (*R*)-(+)-PhCH(Me)NMe_2 was recovered from the residue following neutralization with potassium hydroxide (excess), extraction of the amine into diethyl ether, and distillation. Similar decomposition of (R_C),(S_P,S_P)-**3** (X = PF_6) with concentrated HCl afforded pure (*S*,*S*)-**4** in similar yield: mp 289 °C, $[\alpha]_D$ +71.0 (*c* 0.1, CH_2Cl_2). Anal. Calcd for $C_{42}H_{42}Cl_4P_4Pd_2$: C, 49.2; H, 4.1. Found: C, 49.0; H, 4.3. $^{31}P\{^1H\}$ and ^1H NMR (CD_2Cl_2): identical to those of the mirror-image enantiomer under similar conditions.

[R-(R*,R*)]-(−)- and [S-(R*,R*)]-(+)-1,1,4,7,10,10-Hexaphenyl-1,4,7,10-tetraphosphadecane ((R,R)- and (S,S)-1). (*R*,*R*)-**4** (6.81 g) was suspended in dichloromethane (100 mL), and a solution of sodium cyanide (10 g) in water (35 mL) was added. The mixture was stirred vigorously for 6 h, during which time the solid dissolved and the aqueous layer developed a pale yellow color. The yellow organic layer was separated, washed with water (2 × 50 mL), and dried ($MgSO_4$). The solvent was removed leaving a yellow oil, which crystallized. This material was dissolved in acetone−ethanol (3:1, 40 mL), and the solution was concentrated on the steam bath until crystallization commenced. The pure (*S*, *S*) phosphine formed colorless needles: mp 88 °C, 3.21 g (71%), $[\alpha]_D$ +20.5 (*c* 1.0, CH_2Cl_2). The mother liquor, after removal of solvent and purification of the residue on a silica gel column by elution with dichloromethane, afforded an additional 0.86 g of pure (*S*,*S*)-**1** after recrystallization from acetone−ethanol. Combined yield: 4.07 g (90%). Anal. Calcd for $C_{42}H_{42}P_4$: C, 75.2; H, 6.3. Found: C, 75.3; H, 6.6. ^1H and ^{31}P NMR: identical to those of (*R**,*R**)-(±)-**1**. A similar decomposition of (*S*,*S*)-**4** afforded (*R*,*R*)-**1** of similar form and purity having mp 88 °C and $[\alpha]_D$ −20.5 (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{42}H_{42}P_4$: C, 75.2; H, 6.3. Found: C, 75.1; H, 6.5.

[T-4-[(R-(R*,R*)]]-Δ-(−)-(1,1,4,7,10,10-Hexaphenyl-1,4,7,10-tetraphosphadecane)copper(I) Hexafluorophosphate (Δ-(−)-[Cu{(R,R)-1}]PF_6). A solution of (*S*,*S*)-**1** (0.40 g, 0.06 mmol) in dichloromethane (5 mL) was added to a solution of $[Cu(MeCN)_4]PF_6$ (0.19 g, 0.06 mmol) in the same solvent (5 mL). A colorless precipitate formed and redissolved during the addition. The reaction mixture was filtered, and the filtrate was diluted with ethanol (15 mL) and cooled to 5 °C, whereupon colorless needles of the pure product separated: yield 0.47 g (87%) after washing with ethanol and drying in vacuo, mp 110−112 °C, $[\alpha]_D$ −101.1 (*c* 1.0, CH_2Cl_2) Anal. Calcd for $C_{42}H_{42}CuF_6P_5$: C, 57.4; H, 4.8. Found: C, 57.0; H, 4.8. $^{31}P\{^1H\}$NMR (CD_2Cl_2): δ 20.9 (br m), 15.2 (br m), −143.6 (sept, $^1J_{PF}$ = 711.2 Hz, PF_6^-). ^1H NMR (CD_2Cl_2): δ 2.03 (br m, ca. 4 H, CH), 2.50 (br m, ca. 6 H, CH), 2.75 (b, ca. 2 H, CH), 7.17−7.76 (overlapping multiplets, 30 H, ArH). ^{13}C NMR (CD_2Cl_2): δ 24.63, 26.34, 27.95, 129.70, 131.07, 131.49, 131.62, 132.41, 132.51, 132.61, 133.52, 133.63. ES MS: *m/z* 732.7−736.7 ([M + H]$^+$). The mirror-image enantiomer was similarly prepared from (*R*,*R*)-**1**. **Λ-(+)-[Cu{(S,S)-1}]PF_6·EtOH**: yield 0.35 g (70%), mp 110−112 °C, $[\alpha]_D$ +101.1 (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{42}H_{42}CuF_6P_5$: C, 57.4; H, 4.8. Found: C, 57.6; H, 5.0. NMR and mass spectra: identical to those of the mirror-image enantiomer. A small quantity of Δ-(−)-[Cu{*R*,*R*)-**1**}]PF_6, when recrystallized from hot ethanol, yielded colorless prisms of the *1-ethanol solvate*. Anal. Calcd for $C_{44}H_{48}CuF_6OP_5$: C, 57.1; H, 5.2. Found: C, 57.0; H, 5.3.

[T-4-[(R-(R*,R*)]]-Λ-(−)-Bis(1,1,4,7,10,10-Hexaphenyl-1,4,7,10-tetraphosphadecane)disilver(I) Hexafluorophosphate (Λ-(−)-[Ag_2{(R,R)-1}$_2$](PF_6)$_2$). A solution of (*S*,*S*)-**1** (0.5 g, 0.75 mmol) in dichloromethane (5 mL) was added to a solution of silver(I) perchlorate (0.15 g, 0.72 mmol) in methanol (5 mL). The mixture was heated briefly, and then it was evaporated to dryness; the resulting oil was stirred with diethyl ether. The amorphous colorless product was filtered off and dried. Redissolution of this material in methanol (100 mL), followed by the addition of ammonium hexafluorophosphate (0.21 g) in methanol (29 mL), afforded a colorless solution from which colorless needles of the product deposited: yield 0.58 g (92%), mp 194−195 °C, $[\alpha]_D$ −7.5 (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{84}H_{84}Ag_2F_{12}P_{10}$: C, 54.6; H, 4.6. Found: C, 55.0; H, 4.5. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 5.67 (s), 3.63 (s), −143.6 (sept, $^1J_{PF}$ = 711.2 Hz, PF_6^-). ^1H NMR (CD_2Cl_2): δ 2.10 (br m, ca. 4 H, CH_2), 2.40 (br m, ca. 6 H, CH_2), 2.80 (br m, ca. 2 H, CH_2), 7.10 (m, ca. 10 H, ArH), 7.28 (m, ca. 10 H, ArH), 7.45 (m, ca. 10 H, ArH). ^{13}C NMR (CD_2Cl_2): δ 25.30, 27.07, 129.46, 130.94, 131.42, 133.18. ES MS: *m/z* 777.1−781.1 ([M + H]$^+$), 781.6−777.1 ([M + 2H]$^{2+}$). The mirror-image enantiomer, Δ-(+)-[Ag_2{(*S*,*S*)-**1**}$_2$](PF_6)$_2$, was prepared similarly: yield 0.57 g (90%), mp 194−195 °C, $[\alpha]^{21}_D$ +7.5 (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{84}H_{84}Ag_2F_{12}P_{10}$: C, 54.6; H, 4.6. Found: C, 54.2; H, 4.6. NMR and mass spectra: identical to those of Λ-(−)-[Ag_2{(*R*,*R*)-**1**}$_2$](PF_6)$_2$.

[T-4-[(R-(R*,R*)]]-Λ-(−)-Bis(1,1,4,7,10,10-Hexaphenyl-1,4,7,10-tetraphosphadecane)digold(I) Hexafluorophosphate-1-Dichloromethane (Λ-(−)-[Au_2{(R,R)-1}$_2$](PF_6)$_2$·CH_2Cl_2). A solution of $Et_4N[AuBr_2]$ (0.36 g, 0.75 mmol) in dichloromethane (20 mL) was treated with (*S*,*S*)-**1** (0.5 g, 0.75 mmol) in the same solvent (10 mL). After 2 h an aqueous solution of NH_4PF_6 (1.22 g) in water (20 mL) was added. After the solution was stirred vigorously for 2 h, the organic layer was separated, dried over $MgSO_4$, and diluted with ethanol (10 mL). Slow evaporation of the solution on a steam bath afforded colorless prisms of the pure product: yield 0.78 g (99%), mp 228−230 °C, $[\alpha]_D$ −111.7 (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{84}H_{84}Au_2F_{12}P_{10}$·$CH_2Cl_2$: C, 48.4; H, 4.1. Found: C, 48.3; H, 4.0. ^{31}P NMR (CD_2Cl_2): δ 26.0 (br m), 19.6 (br m), −143.6 (sept, $^1J_{PF}$ = 711.2 Hz, PF_6^-). ^1H NMR (CD_2Cl_2): δ 2.10 (br m, ca. 4 H, CH_2), 2.40 (br m, ca. 2 H, CH_2), 2.63 (br m, ca. 6 H, CH_2), 5.33 (s, CH_2Cl_2), 6.95−7.45 (overlapping multiplets, 30 H, ArH). ^{13}C NMR (CD_2Cl_2): δ 26.80, 27.53, 30.89, 129.03, 129.10, 129.16, 124.499, 129.56, 130.82, 130.95, 131.11, 131.35, 132.38, 132.48, 132.58, 132.72, 133.05. ES MS: *m*/*z* 866.8−867.8 ($[M + 2H]^{2+}$). The mirror-image enantiomer of the complex was obtained by a similar procedure with use of (*R*,*R*)-**1**: yield 0.24 g (62%), mp 228−230 °C, $[\alpha]_D$ +111.7 (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{84}H_{84}Au_2F_{12}P_{10}\cdot CH_2Cl_2$: C, 48.4; H, 4.1. Found: C, 48.1; H, 4.4. NMR and mass spectra: identical to those of Λ-(−)-$[Au_2\{(R,R)\text{-}\mathbf{1}\}_2](PF_6)_2\cdot CH_2Cl_2$.

Structural Analyses. Crystallographic parameters and information related to data collection and structural refinements for the complexes are given in Table 1. Data were corrected for decay (when required), absorption, and Lorenz and polarization effects. The structures were solved by heavy-atom and difference Fourier techniques. Hydrogen atoms were placed at calculated positions and included in structure factor calculations; their coordinates were not refined but were periodically recalculated. The least-squares analyses were performed using full-matrix methods. In the structure of Λ-(−)-$[Ag_2\{(R,R)\text{-}\mathbf{1}\}_2](PF_6)_2$, anisotropic displacement factors were used for the Ag and P atoms and the phenyl rings were refined as rigid groups. For the other structures, individual anisotropic displacement factors were used for all non-hydrogen atoms (except for disordered atoms). The absolute configuration of $(R_c),(R_P,R_P)$-**3** ($X = PF_6$) was assigned with use of a Flack enantiomorph−polarity parameter,[45] while that of Δ-(−)-$[Cu\{(R,R)\text{-}\mathbf{1}\}]PF_6\cdot EtOH$ was assigned by comparing the final *R*-factor with that obtained from a refinement in space group $P4_1$ with coordinates transformed by ($-x$, $-y$, $-z$). The absolute configurations of Λ-(−)-$[Ag_2\{(R,R)\text{-}\mathbf{1}\}_2](PF_6)_2$ and Λ-(−)-$[Au_2\{(R,R)\text{-}\mathbf{1}\}_2](PF_6)\cdot CH_2Cl_2$ were assigned on the basis of the known chirality of the ligand. Form factors were taken from standard listings.[46] More detailed descriptions of the refinements are given in the individual structural reports, which are included in the Supporting Information.

Molecular Mechanics Calculations. Calculations were performed using the molecular mechanics module of the commerical program SPARTAN 3.0 and force field parameters and minimization algorithms therein. Starting structures were hand drawn using the molecular builder provided within the program. The backbone stuctures were drawn and minimized using "Minimize+", intitially with hydrogen substituents (500 iterations); these were replaced with methyl substituents (500 iterations) and then phenyl substituents (1000 iterations). All structures minimized with a convergence criterion of 0.05 kcal mol^{-1} $Å^{-1}$. For the (R_{Ag},S_{Ag}) and (R_{Ag}, R_{Ag}) configurational isomers, the starting structures were generated by variation of the helicities of the five- and ten-membered rings and minimized to the conformers shown in Figure 8. Cross-checks, by perturbing the structures at each stage, were made to ensure true convergence. Coordinates of the calculated structures were exported in Sybyl mol 2 format and converted to protein databank format using Chem3D file interpreters[49] for import and superimposition with crystal structure coordinates (in the same format) using the SuprA function of the program Macromodel.[50] Bond, bond angle, and torsion angle rms differences were calculated using ClarisWorks spreadsheet software.[51]

Acknowledgment. We thank Dr. Greg Kilby for recording the electrospray mass spectra of the complexes.

Supporting Information Available: A summary of crystallographic data, atom-labeling diagrams, and tables of fractional coordinates, bond distances and angles, torsion angles, least-squares planes and angles between planes, anisotropic thermal parameters, general displacement parameters for $(R_C),(R_P,R_P)$-**3** ($X = PF_6$), Δ-(−)-$[Cu\{(R,R)\text{-}\mathbf{1}\}]PF_6\cdot EtOH$, Λ-(−)-$[Ag\{(R,R)\text{-}\mathbf{1}\}](PF_6)_2$, and Λ-(−)-$[Au_2[(R,R)\text{-}\mathbf{1}]_2]PF_6\cdot CH_2Cl_2$ (141 pages). Ordering information is given on any current masthead page.

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(45) Flack, H. D. *Acta Crystallogr., Sect. A: Fundam. Crystallogr.* **1983**, *39*, 876.

(46) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99−101, 149−150 (Present distributor: Kluwer Academic Publishers, Dordrecht, The Netherlands).

(47) Hall, S. R.; Flack, H. D.; Stewart, J. M., Eds. *XTAL3.2 Reference Manual*; Universities of Western Australia, Geneva, and Maryland; Lamb: Perth, 1992.

(48) *teXsan: Single Crystal Structure Analysis Software, Version 1.6c*; Molecular Structure Corp.: The Woodlands, TX, 1993.

(49) Chem 3D Plus, Version 3.1.1 1993, Cambridge Scientific Computing Inc., 875 Massachusetts Ave, Sixth Floor, Cambridge, Massachusetts 02139.

(50) Macromodel, Department of Chemisty, Columbia University, New York, 1992.

(51) ClarisWorks 2.0, March 1993, Claris Corporation.