Photoluminescence properties of four-coordinate gold(I)-phosphine complexes of the types [Au(diphos)2]PF6 and [Au2(tetraphos)2](PF6)2

7 **AUTHORS**, INCLUDING:

Robert Stranger
Australian National University
176 PUBLICATIONS **2,501** CITATIONS

SEE PROFILE

Gerhard (Gerry) F. Swiegers
University of Wollongong
156 PUBLICATIONS **3,288** CITATIONS

SEE PROFILE

Stanley Bruce Wild
Australian National University
182 PUBLICATIONS **3,136** CITATIONS

SEE PROFILE

Inorganic Chemistry

Article

Diastereoselectivity and Molecular Recognition in the Self-Assembly of Double-Stranded Dinuclear Metal Complexes of the Type [M₂{(R*,S*)-tetraphos}₂](PF₆)₂ (M = Ag and Au)

Christopher J. Blake, Vernon C. Cook, Max A. Keniry, Heather J. Kitto, A. David Rae, Gerhard F. Swiegers, Anthony C. Willis, Johann Zank, and S. Bruce Wild*

Research School of Chemistry, Institute of Advanced Studies, Australian National University, Canberra, ACT 0200, Australia

The ligand (R^*,S^*)-Ph₂PCH₂CH₂P(Ph)CH₂CH₂P(Ph)CH₂CH₂PPh₂, (R^*,S^*)-tetraphos, combines with silver(I) and gold-(I) ions in the presence of hexafluorophosphate to diastereoselectively self-assemble the head-to-head (H,H) diastereomers of the double-stranded, dinuclear metal complexes [M₂{(R^*,S^*)-tetraphos}₂](PF₆)₂ in which the two chiral metal centers in the complexes have M (R end of phosphine) and P (S end of phosphine) configurations. The crystal and molecular structures of the compounds have been determined: (H,H)-(M,P) -[Ag₂{(R^*,S^*)-tetraphos}₂]-(PF₆)₂, monoclinic, $P2_1/c$, $a = 10.3784(2)$, $b = 47.320(1)$, $c = 17.3385(4)$ Å, $\beta = 103.8963(5)°$, $Z = 4$; (H,H)-(M,P)-[Au₂{(R^*,S^*)-tetraphos}₂](PF₆)₂, monoclinic, $P..2_1$ (No. 4, c unique axis), $a = 24.385(4)$, $b = 46.175(3)$, $c = 14.820(4)$ Å, $Z = 8$. The complexes crystallize as racemic compounds in which the unit cell in each case contains equal numbers of enantiomorphic molecules of the cation and associated anions. The cations in both structures have similar side-by-side structures of idealized C_2 symmetry, the bulk helicity of each molecule in the solid state being due solely to the twist of the central ten-membered ring containing the two metal ions of opposite configuration, which has the chiral twist-boat–chair–boat conformation. When 1 equiv each of (R^*,S^*)-tetraphos, (R^*,R^*)-(±)-tetraphos, (S,S)-(+)-tetraphos, 2 equiv of Ph₂PCH₂CH₂PPh₂ (dppe), and 7 equiv of [AuCl(SMe₂)] in dichloromethane are allowed to react for several minutes in the presence of an excess of ammonium hexafluorophosphate in water (two phases), the products are the double-stranded digold(I) complexes in which each ligand strand has recognized itself by stereoselective self-assembly, together with [Au(dppe)₂]PF₆.

Introduction

The spontaneous synthesis of stable, di- and oligonuclear metal complexes from bridging ligands and kinetically labile metal ions mimics the assembly in biology of conglomerates of large molecules through dynamic noncovalent bonding.[1] In the inorganic coordination systems, equilibrium is achieved by *dynamic dative bonding* between the components. A wide variety of interesting structural motifs is now available through application of the strategy of self-assembly under equilibrium conditions.[2] With use of semirigid di- and oligo-2,2′-bypyridines and related ligands, for example, in conjunction with copper(I) and silver(I), the self-assembly has

been achieved of helicates, metallocatenanes, rotaxanes, and molecular grids and knots, where the rigidity of chelating entities and flexibility of the spacer groups combine with tetrahedral coordination around the labile metal ions to generate the primary structures of the assemblies.[2,3] For complexes derived from *fully flexible ligands*, however, such as double-stranded di- and trinuclear metal helicates containing linear, aliphatic tetra- and hexatertiary phosphines and univalent Group 11 ions, the configurationally stable, chiral, inner-phosphorus stereocenters in the ligands lead to stereospecific complexation of the metal ions because of the bridging requirements of the ligands.[4–6] The relationships

* Author to whom correspondence should be addressed. E-mail: sbw@rsc.anu.edu.au.
(1) Machado, V. G.; Baxter, P. N.; Lehn, J. M. *J. Braz. Chem. Soc.* **2001**, *12*, 431–462 (review with 377 references). Lehn, J. M. *Supramolecular Chemistry*; VCH: Weinheim, 1995.
(2) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483–3537.

(3) Piguet, C.; Bernardinelli, G.; Hopfgartner, G. *Chem. Rev.* **1997**, *97*, 2005–2062.
(4) Airey, A. L.; Swiegers, G. F.; Willis, A. C.; Wild, S. B. *Inorg. Chem.* **1997**, *36*, 1588–1597.
(5) Cook, V. C.; Willis, A. C.; Zank, J.; Wild, S. B. *Inorg. Chem.* **2002**, *41*, 1897–1906.

between the configurational elements at donor and metal and the helical conformations of the flexible primary and secondary chelate rings determine the overall structures of the helicates. For example, in double-stranded helicates derived from flexible, configurationally pure, linear tetra- and hexatertiary phosphines and univalent Group 11 ions, the sense of the helicity of the conformationally preferred ten-membered, twist-boat−chair−boat rings containing adjacent metal ions determines the relative stabilities of the double α-helix and parallel helix conformers of the configurationally pure helicates.[4−6]

Here we describe our findings concerning the self-assembly of double-stranded disilver(I) and digold(I) complexes of the fully flexible, *achiral*, tetratertiary phosphine (*R**,*S**)-tetraphos. A recent paper describes the synthesis and crystal and molecular structures of *tetra*gold(I) helicates of (*R**,*R**)-(±)- and (*R**,*S**)-tetraphos.[7]

Results and Discussion

Stereochemical Considerations. (a) Configurational Factors. The ligand (*R**,*S**)-tetraphos, which is a constitutionally symmetrical A−B−B−A ligand, functions in double-stranded dinuclear metal complexes of the type [M$_2${(*R**,*S**)-tetraphos}$_2$] as a bridging A−B−C−A tetradentate because of the oppositely chiral (stereoheterotopic) relationship of the pair of inner phosphorus stereocenters. Thus, (*R**,*S**)-tetraphos can form head-to-head (*H,H*) and head-to-tail (*H,T*) diastereomers of complexes of the type [M$_2${(*R**,*S**)-tetraphos}$_2$]. To form these diastereomers it is necessary only that there be no performable symmetry operation (a proper rotation) relating the inner and outer pairs of donor groups.[8] Ligands that fall within this category are henceforth referred to as meso or *R**,*S** tetradentates and are designated A−*R*−*S*−A to distinguish them from their constitutionally unsymmetrical A−B−C−A counterparts, which have no symmetry element relating the donor atoms or groups. The A−*R*−*S*−A ligands can generate isomeric complexes one-for-one but not necessarily in symmetry with those formed by A−B−C−A ligands.

The two highest symmetry, dinuclear metal, chelating conformers of (*R**,*S**)-tetraphos are the chiral synclinal (±sc) and centrosymmetrical antiperiplanar (ap) rotamers shown in Figure 1.[8,9] The relationship between the lone pairs of electrons on the inner pairs of phosphorus atoms in the two comformers is shown in Figure 2. The lone pairs of electrons in the ±sc conformer of the ligand are suitably disposed for chelation to two metal atoms in double-stranded dinuclear metal helicates of the type [M$_2${(*R**,*S**)-tetraphos}$_2$], whereas those in the ap form could generate coordination polymers of the type {[M$_2${(*R**,*S**)-tetraphos}$_2$]}$_\infty$ (Figure 2). Both

(6) Bowyer, P. K.; Cook, V. C.; Gharib-Naseri, N.; Gugger, P. A.; Rae, A. D.; Swiegers, G. F.; Willis, A. C.; Zank, J.; Wild, S. B. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4877−4882.

(7) Schuh, W.; Kopacha, H.; Wurst, K.; Peringer, P. *Eur. J. Inorg. Chem.* **2002**, 2202−2206.

(8) Tapscott, R. E.; Mather, J. D.; Them, T. F. *Coord. Chem. Rev.* **1979**, *29*, 87−127.

(9) Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; John Wiley & Sons: New York, 1994.
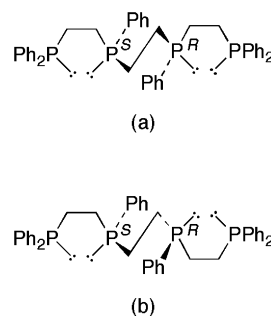
Figure 1. Enantiomers of helicating synclinal (a) and bridging antiperiplanar (b) conformers of (*R**,*S**)-tetraphos.
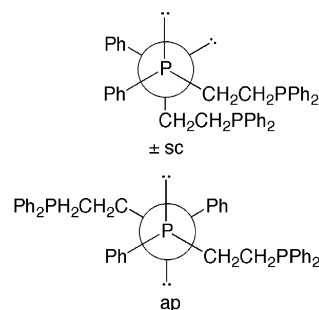

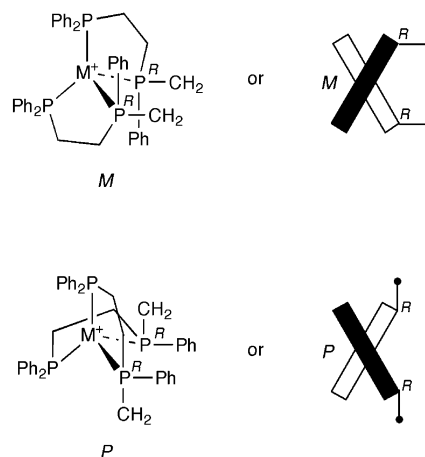**Figure 2.** Dispositions of inner-phosphorus lone pairs in ± sc and ap chelating rotamers of (*R**,*S**)-tetraphos.

Figure 3. Diastereomeric C_2 head (*R* phosphorus) ends of head-to-head diastereomers of the type *(H,H)*-[M$_2${(*R**,*S**)-tetraphos}$_2$]$^{2+}$.

types of complexes have been isolated and structurally characterized for certain silver(I)−tetraimine systems.[10]

The stereochemistries of the head-to-head and head-to-tail diastereomers of a complex of the type [M$_2${(*R**,*S**)-tetraphos}$_2$]$^{2+}$ containing tetrahedrally disposed univalent Group 11 ions can be rationalized by inspection of the hypothetical mononuclear metal units depicted in Figure 3. The mononuclear metal units shown correspond to the two possible ends of the three head-to-head diastereomers of [M$_2${(*R**,*S**)-tetraphos}$_2$]$^{2+}$. (In the structures, the head end of the ligand contains the coordinated phosphorus stereocenters of *R* configuration[11]). It is apparent from Figure 3 that the diastereomeric C_2 unit, in which two inner-phos-

(10) Bowyer, P. K.; Porter, K. A.; Rae, A. D.; Willis, A. C.; Wild, S. B. *Chem. Commun.* **1998**, 1153−1154.

(a)

(b)

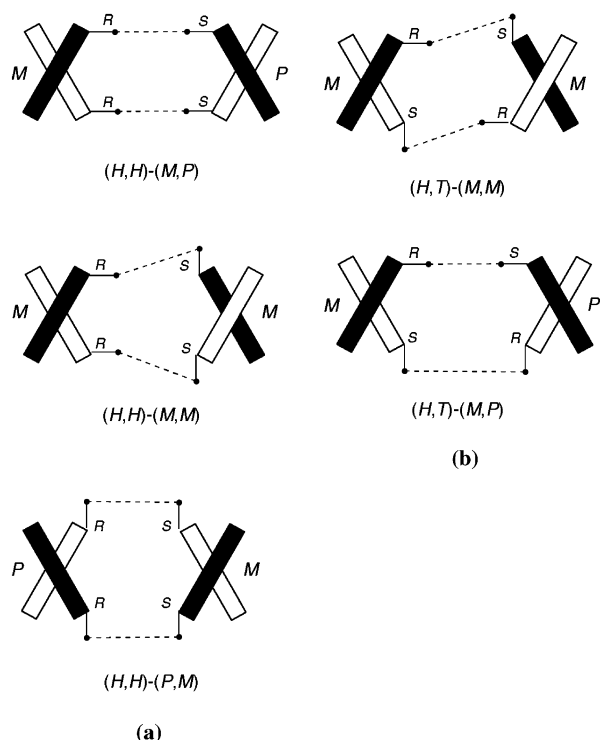**Figure 4.** Configurational diastereomers of (*H*,*H*)-[M$_2${(*R**,*S**)-tetraphos}$_2$]$^{2+}$ ((*H*,*H*)-(*P*,*P*) enantiomer not shown) (a) and (*H*,*T*)-[M$_2${(*R**,*S**)-tetraphos}$_2$]$^{2+}$ ((*H*,*T*)-(*P*,*P*) enantiomer not shown) (b).

phorus donors of *R* configuration combine with a metal center of *M* configuration to give a chiral unit in which each methylene group is equatorially disposed,[12] is ideally suited for dimerization with its enantiomorph (phosphorus centers *S*, metal *R*) to give the head-to-head dimer, viz., (*H*,*H*)-(*M*,*P*)-[M$_2${(*R**,*S**)-tetraphos}$_2$]$^{2+}$ (Figure 4).[13]

Theoretical Modeling. Theoretical modeling of the structure of [Cu$_2${(*R**,*S**)-H$_2$PCH$_2$CH$_2$P(H)CH$_2$CH$_2$P(H)CH$_2$CH$_2$-PH$_2$}$_2$]$^{2+}$, [Cu$_2${(*R**,*S**)-tetraphos*}$_2$]$^{2+}$, was carried out with use of the TRIPOS 5.2 force field in the program SPARTAN 5.0.[14] Starting structures for the calculations included all known, stable conformations of the central 10-membered ring[15] containing the two metal ions and were modified subsequently by consideration of the conformations (δ and λ) of the four terminal 5-membered chelate rings. The
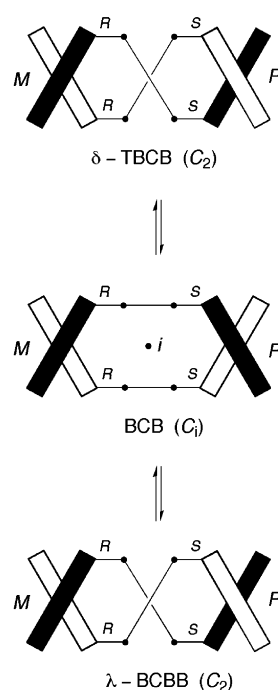
(11) As a consequence of the Cahn−Ingold−Prelog (CIP) rules for specifying absolute configurations, an apparent inversion at phosphorus occurs upon coordination of a *P*-chiral tertiary phosphine to an element of higher atomic number than 12.[12] The use of the relative configuration descriptors (*R**,*R**)-(±)- and (*R**,*S**) for the racemic and meso diastereomers of the tetraphosphine, respectively, conforms with current *Chemical Abstracts* practice and IUPAC recommendations.
(12) Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385−414.
(13) Spirocyclic complexes of the type M(AB)$_2$ may be viewed as helices, and their stereomer may be denoted as *P* (right-handed or clockwise turns of chelate rings when viewed *down* the principal C$_2$ axis, from either end) or *M* (left-handed) or they can be considered to have a chiral center, in which case they may be assigned an *R* (or *aR*) or *S* (*aS*) descriptor, respectively. The correspondence of *R* with *M* and *S* with *P* is general.[9] The *P*,*M* nomenclature is more appropriate for di- and oligonuclear metal helicates of the type considered here because the bulk helicity of a particular helicate, also designated *P* or *M*, is then a direct manifestation of the individual helicities of the chiral components.
(14) *SPARTAN 5.0*; Wavefunction Inc.: Irvine, CA, 1997.
(15) Hendrickson, J. B. *J. Am. Chem. Soc.* **1967**, *89*, 7047−7061.

Figure 5. Inversion of chiral TBCB conformers of (*H*,*H*)-(*M*,*P*)-[M{(*R**,*S**)-tetraphos}$_2$]$^{2+}$.

molecular mechanics-optimized structures for the cation were then refined at the semiempirical PM3(TM) level of theory with use of special parameters for copper.[16] The strain energies calculated for the conformers of the mononuclear metal complex ion [Cu{(*R**,*S**)-tetraphos*}]$^+$ were much greater (ca. 72 kcal mol^{-1}) than those for [Cu{(*S*,*S*)-tetraphos*}]$^+$ (ca. 20 kcal mol^{-1}). (The complex (*M*)-(−)-[Cu{(*R*,*R*)-tetraphos}]PF$_6$ has been isolated and structurally characterized.[4]) Of the five possible configurational diastereomers of the dinuclear metal cation, the most stable was the achiral head-to-head diastereomer (*H*,*H*)-(*M*,*P*)-[Cu$_2${(*R**,*S**)-tetraphos*}$_2$]$^{2+}$ (Figure 4a), which was ca. 10 kcal mol^{-1} more stable than the next most stable species, the almost degenerate head-to-tail diastereomers (*H*,*T*)-(*M*,*M*)- and (*H*,*T*)-(*M*,*P*)-[Cu$_2${(*R**,*S**)-tetraphos*}$_2$]$^{2+}$ (Figure 4b). In the most stable (*H*,*H*)-(*M*,*P*) diastereomer of the complex, the most stable conformations of the central 10-membered ring are the chiral twist-boat−chair−boat (TBCB) and the symmetrical boat−chair−boat (BCB), which have similar energies. The centrosymmetrical form of the complex containing the BCB ring corresponds to the transition structure for racemization of the δ and λ forms of the complex containing the TBCB ring (Figure 5). Since the helicities of the chiral metal centers in the (*H*,*H*)-(*M*,*P*) diastereomer of the complex are opposed to one another, the δ or λ twist of the flexible 10-membered TBCB ring in the dinuclear metal cation is the only contribution to the bulk helicity of the side-by-side helicate.

Synthesis of Metal Complexes. The complex [Ag$_2${(*R**,*S**)-tetraphos}$_2$](PF$_6$)$_2$ was prepared by reacting a solution of (*R**,*S**)-tetraphos (1 equiv) in dichloromethane with an aqueous solution of silver(I) nitrate (1 equiv) containing

(16) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209−220.

Table 1. Crystal Data and Experimental Parameters for X-ray Structure Analyses
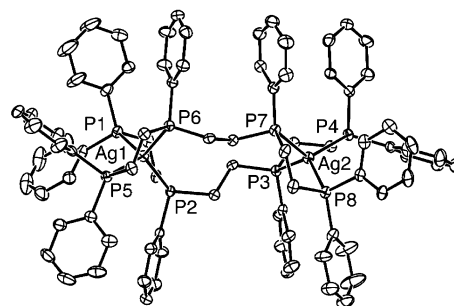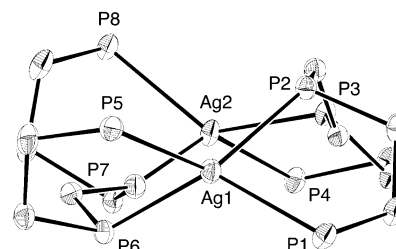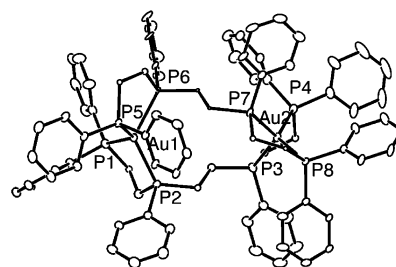
	(H,H)-(M,P)-[Ag$_2${(R*,S*)-tetraphos}$_2$](PF$_6$)$_2$	(H,H)-(M,P)-[Au$_2${(R*,S*)-tetraphos}$_2$](PF$_6$)$_2$
molecular formula	C$_{84}$H$_{84}$Ag$_2$F$_{12}$P$_{10}$	C$_{84}$H$_{84}$Au$_2$F$_{12}$P$_{10}$
fw, g mol^{-1}	1847.04	2154.24
space group	$P2_1/c$	$P..2_1$ (No. 4, c unique axis)
cryst syst	monoclinic	monoclinic
a, Å	10.3784(2)	24.385(4)
b, Å	47.320(1)	46.175(3)
c, Å	17.3385(4)	14.820(4)
β, deg	103.896(1)	
γ, deg		90.0
V, Å^3	8265.8(3)	16687(4)
Z	4	8
D_{calcd}, g cm^{-3}	1.484	1.714
cryst size, mm^3	0.28 × 0.12 × 0.10	0.30 × 0.20 × 0.15
μ, cm^{-1}	7.37	89.3
instrument	Nonius Kappa CCD	Rigaku AFC6R
radiation	Mo Kα	Cu Kα
no. of unique reflns	14494	13497
no. of reflns obsd	7710 ($I > 2\sigma(I)$)	9548 ($I > 3\sigma(I)$)
2θ range, deg	4−50	4−120
scan technique	ϕ and ω	$\omega-2\theta$
temp (°C)	−73	−80
structural refinement	teXsan[23]	teXsan,[23] RAELS[24]
final R, R_w	0.0387, 0.0382	0.085, 0.118

Table 2. Selected Bond Distances (Å) and Angles (deg) in (H,H)-(M,P)-[M$_2${(R*,S*)-tetraphos}$_2$](PF$_6$)$_2$ (M = Ag, Au)

	M = Ag	M = Au (Cation A)
M(1)−P(1)	2.531(2)	2.393(4)
M(1)−P(2)	2.510(2)	2.395(4)
M(1)−P(5)	2.558(2)	2.414(4)
M(1)−P(6)	2.487(2)	2.385(4)
M(2)−P(3)	2.484(2)	2.399(4)
M(2)−P(4)	2.508(2)	2.428(4)
M(2)−P(7)	2.519(2)	2.396(4)
M(2)−P(8)	2.468(1)	2.405(4)
M(1)···M(2)	6.8673(6)	6.483(5)
P(1)−M(1)−P(2)	82.74(5)	87.7(4)
P(1)−M(1)−P(5)	118.03(5)	130.4(4)
P(1)−M(1)−P(6)	125.95(5)	112.3(4)
P(2)−M(1)−P(5)	124.78(5)	123.5(4)
P(2)−M(1)−P(6)	127.29(5)	125.4(4)
P(5)−M(1)−P(6)	83.28(5)	81.9(4)
P(3)−M(2)−P(4)	85.25(5)	84.4(4)
P(3)−M(2)−P(7)	111.65(5)	121.2(4)
P(3)−M(2)−P(8)	130.35(5)	118.4(4)
P(4)−M(2)−P(7)	129.89(5)	118.5(4)
P(4)−M(2)−P(8)	121.45(5)	130.1(4)
P(7)−M(2)−P(8)	83.84(5)	88.4(4)

Figure 6. ORTEP view of cation of (H,H)-(M,P)-[Ag$_2${(R*,S*)-tetraphos}$_2$]-(PF$_6$)$_2$ with 50% probability ellipsoids.

Figure 7. Core structure of cation of (H,H)-(M,P)-[Ag$_2${(R*,S*)-tetraphos}$_2$]-(PF$_6$)$_2$ showing parallel arrangement of ligand strands.

Figure 8. ORTEP view of cation A of (H,H)-(M,P)-[Au$_2${(R*,S*)-tetraphos}$_2$](PF$_6$)$_2$ with 50% probability ellipsoids.

an excess of ammonium hexafluorophosphate. The crude product was isolated from the organic phase and was recrystallized from dichloromethane−diethyl ether, from which it precipitated as colorless prisms suitable for X-ray crystallography. The complex [Au$_2${(R*,S*)-tetraphos}$_2$](PF$_6$)$_2$ was also synthesized by the two-phase method involving 1 equiv each of Me$_2$SAuCl and (R*,S*)-tetraphos in dichloromethane and ammonium hexafluorophosphate in water. A single recrystallization of the crude product from hot ethanol afforded colorless prisms of the pure gold complex.

Crystal and Molecular Structures. Crystal data, information relating to data collection, and refinement details for [Ag$_2${(R*,S*)-tetraphos}$_2$](PF$_6$)$_2$ and the gold analogue are given in Table 1. The silver complex crystallizes in the space group $P2_1/c$ with four molecules of the cation (two enan-

tiomorphic pairs) and associated hexafluorophosphate ions in the unit cell. Table 2 lists the most important distances and angles for the cation of the complex employing the atom-labeling scheme given in Figure 6. The two strands of the A−R−S−B ligand in the disilver cation are arranged in a head-to-head arrangement about the two metal ions of opposite configuration in which the central 10-membered ring containing the two metal ions and the four phosphorus atoms has the chiral TBCB conformation. The parallel arrangement of the two ligand strands about the two metal ions in the side-by-side helicates is shown in Figure 7. There are two molecules of each enantiomer of the cation arranged centrosymmetrically in the unit cell. The Ag−P distances of 2.468(2)−2.558(2) Å in the cation of the side-by-side helix derived from (R*,S*)-tetraphos compare closely with those in (M,M)-(−)-[Ag$_2${(R,R)-tetraphos}$_2$](PF$_6$)$_2$.[4] The Ag···Ag distance of 6.8673(6) Å in the complex the (R*,S*)-tetraphos complex is similar to that in the *double α-helix* conformer of (M,M)-[Ag$_2${(R,R)-tetraphos}$_2$](PF$_6$)$_2$, viz., 6.859(3) Å, but is substantially longer than that in the *parallel helix* conformer of the complex, viz., 6.072(4) Å.[4]

The structure of the cation of [Au$_2${(R*,S*)-tetraphos}$_2$]-(PF$_6$)$_2$ is shown in Figure 8, and important distances and angles in the cation are given in Table 2. The complex
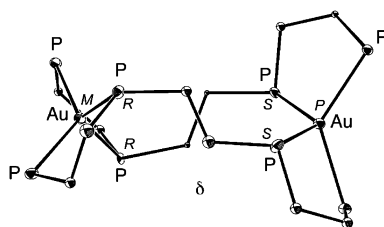
Figure 9. Core structure of cation of (*H*,*H*)-(*M*,*P*)-[Au$_2${(*R**,*S**)-tetraphos}$_2$]-(PF$_6$)$_2$ showing δ-TBCB conformation of central ten-membered ring.

crystallizes in the space group *P*..2$_1$ (No. 4, *c* unique axis) with eight molecules of the cation and associated anions in the unit cell. The structure of the cation is very similar to that of the silver analogue, there being four pairs of enantiomorphic cations arranged pseudo-centrosymmetrically in the unit cell. The twist of each enantiomer of the cation in the structure is due solely to the twist of the central TBCB ring (Figure 9). In contrast, the centrosymmetrical cation of [Au$_4${(*R**,*S**)-tetraphos}$_2$](OTf)$_4$·EtOH contains two pairs of roughly linear P−Au−P interactions (angles: outer 171.0-(2), inner 168.0(2)) between the two ligand strands, which have the head-to-head arrangement.[7] Because of the constraints of the central ten-membered ring in the structure, which has a centrosymmetrical chairlike conformation, the *R* ends of the two phosphine strands generate a terminal ten-membered ring of λ conformation and the *S* ends a ring of δ conformation in the centrosymmetrical cation. The oppositely chiral relationship of these rings corresponds to the oppositely chiral relationships of the chiral metal stereocenters in the digold complex. In the tetragold complex the Au···Au distance in the outer rings is 2.9802(4), which is the optimum equilibrium distance for an aurophilic interaction, viz., ca. 3.0 Å.[17] The distance between the gold atoms in the central ring of the tetragold complex is 4.1062(5) Å. The Au···Au distance of 6.483(5) Å in the digold complex compares with the value of 6.244(2) Å found in (*M*,*M*)-(−)-[Au$_2${(*R*,*R*)-tetraphos}$_2$](PF$_6$)$_2$ (parallel helix conformer).[4]

NMR Spectra. Extensive $^nJ_{PP}$, *J*-coupling in the one-dimensional ^{31}P NMR spectra of the complexes presented difficulties in resolving the resonances associated with the diastereomeric forms of the complexes. The spectra were considerably simplified by recording the 2D *J*-resolved spectra and taking a 45° F2 projection.[18] The resulting spectrum in each case contained only ^{31}P NMR chemical shift information, which allowed ready resolution of the inner and outer phosphorus resonances for the diastereomers of the complexes (Figure 10).

Molecular Recognition. The 2D *J*-resolved ^{31}P NMR spectrum of a CD$_2$Cl$_2$ solution containing an equimolar mixture of (*R**,*S**)- and (*R**,*R**)-(±)-tetraphos after reaction with [AuCl(SMe$_2$)] in the presence of aqueous ammonium hexafluorophosphate indicates that each diastereomer and enantiomer of the tetraphosphine quantitatively recognizes itself by stereoselective self-assembly in the double-stranded dinu-
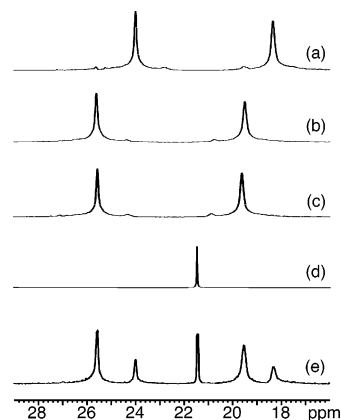

Figure 10. 2D *J*-resolved ^{31}P NMR spectra in CD$_2$Cl$_2$ at 295 K of (*H*,*H*)-(*M*,*P*)-[Au$_2${(*R**,*S**)-tetraphos}$_2$](PF$_6$)$_2$ (a), (*M*,*M*)-[Au$_2${(*R*,*R*)-tetraphos}$_2$]-(PF$_6$)$_2$/(*P*,*P*)-[Au$_2${*S*,*S*}-tetraphos}$_2$](PF$_6$)$_2$ (b), (*M*,*M*)-[Au$_2${(*R*,*R*)-tetraphos}$_2$]-(PF$_6$)$_2$ (c), [Au(dppe)$_2$]PF$_6$ (d), and the mixture, a−d, generated in situ (e).

clear metal complexes (Figure 10). Thus, a CD$_2$Cl$_2$ solution containing (*R**,*S**)-tetraphos (1 equiv) and [AuCl(SMe)] (1 equiv), after exposure to an aqueous solution of ammonium hexafluorophosphate (excess) followed by separation and drying (MgSO$_4$) of the organic phase, contains only (*H*,*H*)-(*M*,*P*)-[Au$_2${(*R**,*S**)-tetraphos}$_2$](PF$_6$)$_2$, which is also the diastereomer isolated by crystallization. Under similar conditions, (*R**,*R**)-(±)-tetraphos and [AuCl(SMe$_2$)] produce only racemic (*P*,*P*)-[Au$_2${(*S*,*S*)-tetraphos}](PF$_6$)$_2$/(*M*,*M*)-[Au$_2${(*R*,*R*)-tetraphos}$_2$](PF$_6$)$_2$ and none of the crossover or *meso* product (*M*,*P*)-[Au$_2${(*R*,*R*)-tetraphos}{(*S*,*S*)-tetraphos}](PF$_6$)$_2$ in solution or by crystallization. The identity of the racemic helicate was confirmed by the comparison of the 2D *J*-resolved ^{31}P NMR spectrum of the (*R**,*R**)-(±)-tetraphos/[AuCl(SMe$_2$)] system with that of enantiomerically pure (*M*,*M*)-(−)-[Au$_2$-{(*R*,*R*)-tetraphos}$_2$](PF$_6$)$_2$,[4] with which it is identical under similar conditions. The mixture of 1 equiv each of (*R**,*S**)-tetraphos, (*R**,*R**)-(±)-tetraphos, and (*S*,*S*)-(+)-tetraphos, and dppe (2 equiv) and [AuCl(SMe$_2$)] (7 equiv) in CD$_2$Cl$_2$/NH$_4$PF$_6$(H$_2$O) similarly showed in the 2D *J*-resolved ^{31}P NMR spectrum only the dinuclear gold(I) products of self-recognition of each tetraphosphine ligand strand for itself, as well as [Au(dppe)$_2$]PF$_6$ (δ$_p$ 21.6) (Figure 10). The ability of (*R**,*S**)-tetraphos to recognize itself by stereoselective self-assembly to give in solution and in the solid state a single diastereomer of the double-stranded digold(I) complex allowed a detailed investigation of the photoluminescence properties of the complex.[19]

Conclusion

The stereoheterotopic ligand (*R**,*S**)-tetraphos combines diastereoselectively with silver(I) and gold(I) ions in the presence of hexafluorophosphate to self-assemble head-to-head diastereomers of the double-stranded dinuclear metal complexes (*H*,*H*)-[M$_2${(*R**,*S**)-tetraphos}$_2$](PF$_6$)$_2$ in which the two tetrahedral metal stereocenters have an oppositely chiral relationship in the formally centrosymmetrical side-by-side complexes. In the solid state, however, the central ten-

(17) Schmidbaur, H.; Graf, W.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 417−419. Schmidbaur, H. *Gold Bull.* **2000**, *33*, 3−10.

(18) Nagayama, K.; Bachmann, P.; Wüthrich, K.; Ernst, R. R. *J. Magn. Reson.* **1978**, *31*, 133−148.

(19) Delfs, C. D.; Kitto, H. J.; Stranger, R.; Swiegers, G. F.; Wild, S. B.; Willis, A. C.; Wilson, G. J. *Inorg. Chem.* **2003**, *42*, 4469−4478.

membered ring containing the two metal centers has the chiral twist-boat−chair−boat conformation, which engenders a helical twist to the cations. The salts, however, crystallize as racemic compounds in which enantiomorphic pairs of the double-stranded dinuclear metal helicate conformers of the cations and associated anions are arranged centrosymmetrically in the achiral unit cells. The molecular recognition of the A-*R*−*S*−A tetraphos for itself in the head-to-head, double-stranded digold(I) complex is quantitative, even in the presence of (*R**,*R**)-(±)-tetraphos and dppe, which similarly recognize themselves by stereoselective self-assembly in the presence of gold(I) ions. The self-recognition of these fully flexible ligands for themselves, especially that of the stereoheterotopic A−*R*−*S*−B ligand, under self-assembly conditions is analogous to molecular recognition displayed in double-stranded polynucleotides.

Experimental Section

One-dimensional and 2D *J*-resolved ^{31}P NMR spectra were recorded at 20 °C on a Varian INOVA 600 MHz spectrometer operating at 242 MHz. The ^{31}P NMR 2D *J*-resolved spectra were acquired with a recycle time of 1.5 s over a sweep width of 4000 Hz using 4 K data points in ω2 and a sweep width of 500 Hz and 128 complex points in ω1. The spectra were processed with Varian VNMR 6.1C software. Elemental analyses were performed by staff within the Research School of Chemistry. The complexes (*M*,*M*)-(−)-[Au$_2$\{(*R*,*R*)-tetraphos\}$_2$](PF$_6$)$_2$[4] and [AuCl(SMe$_2$)][20] were prepared by the literature methods.

(*H*,*H*)-(*M*,*P*)-[Ag$_2$\{(*R**,*S**)-tetraphos\}$_2$](PF$_6$)$_2$. A solution of (*R**,*S**)-tetraphos (0.25 g, 0.37 mmol) in dichloromethane (20 mL) was added to a solution of silver nitrate (0.064 g, 0.37 mmol) and ammonium hexafluorophosphate (0.61 g, 3.7 mmol) in water (30 mL), and the mixture was vigorously stirred for 30 min. The two phases were separated, and the organic phase was dried (MgSO$_4$) and evaporated to dryness. Recrystallization of the residue that remained from dichloromethane−ethanol gave the pure product as colorless needles. Yield: 0.315 g (92%). Mp: 270 °C. Anal. Calcd for C$_{84}$H$_{84}$Ag$_2$P$_{10}$: C, 54.6; H, 4.6. Found: C, 54.7; H, 4.7. ^{31}P NMR (CD$_2$Cl$_2$): δ 3.8 (dd, 8P), −143.7 (sept, 2P, $^1J_{PF}$ = 717.2 Hz, PF$_6$$^-$).

(*H*,*H*)-(*M*,*P*)-[Au$_2$\{(*R**,*S**)-tetraphos\}$_2$](PF$_6$)$_2$. The ligand (*R**,*S**)-tetraphos (1.0 g, 1.5 mmol) and [AuCl(SMe$_2$)] (0.44 g, 1.5 mmol) were dissolved in dichloromethane (20 mL), and the solution was treated with a solution of ammonium hexafluorophosphate (2.18 g, 13.4 mmol) in water (30 mL). The mixture was vigorously stirred for 30 min, the layers were separated, and the organic phase was dried (MgSO$_4$) and evaporated to dryness. The residue was recrystallized by dissolution in dichloromethane and precipitation with diethyl ether. The pure product crystallized as colorless prisms from hot ethanol. Yield: 1.21 g (80%). Mp: 194−196 °C. Anal. Calcd for C$_{84}$H$_{84}$Au$_2$F$_{12}$P$_{10}$: C, 49.2; H, 4.2. Found: C, 49.6; H, 4.1. ^{31}P NMR (CD$_2$Cl$_2$): δ 23.3−25.0 (m, 4P, inner-P), 17.5−19.2 (m, 4P, outer-P), −143.6 (sept, $^1J_{PF}$ = 708.3 Hz, PF$_6$$^-$).

(*M*,*M*)-[Au$_2$\{(*R*,*R*)-tetraphos\}$_2$](PF$_6$)$_2$/(*P*,*P*)-[Au$_2$\{(*S*,*S*)-tetraphos\}$_2$](PF$_6$)$_2$. This compound was prepared as described in ref 4, but with use of (*R**,*R**)-(±)-tetraphos. Yield: 53%. Mp: >230 °C. Anal. Calcd for C$_{84}$H$_{84}$Au$_2$F$_{12}$P$_{10}$: C, 49.8; H, 4.2. Found: C, 49.2; H, 4.2. ^{31}P NMR (CD$_2$Cl$_2$): δ 24.9−26.5 (m, 4P, inner-P), 18.8−20.5 (m, 4P, outer-P), −143.8 (sept, 2P, $^1J_{PF}$ = 715.7 Hz, PF$_6$$^-$).

[Au(dppe)$_2$]PF$_6$·CH$_2$Cl$_2$. A solution of dppe (0.69 g, 1.7 mmol) and [AuCl(SMe$_2$)] (0.24 g, 0.8 mmol) in dichloromethane (20 mL) was treated with a solution of ammonium hexafluorophosphate (0.87 g, 5.2 mmol) in water (10 mL), and the mixture was vigorously stirred for 30 min. The organic phase was separated, dried (MgSO$_4$), and evaporated to dryness. Recrystallization of the residue from dichloromethane by the addition of diethyl ether gave the pure product as colorless prisms of the *1-dichloromethane solvate*. Yield: 0.55 g (60%). Mp: >230 °C. Anal. Calcd for C$_{52}$H$_{48}$-AuF$_6$P$_5$·CH$_2$Cl$_2$: C, 52.0; H, 4.3. Found: C, 52.4; H, 4.3. ^{31}P NMR (CD$_2$Cl$_2$): δ 21.6 (s, 4P), −143.9 (sept, 1P, $^1J_{PF}$ = 709.1 Hz, PF$_6$$^-$).

Molecular Recognition. A solution of (*R**,*S**)-tetraphos (0.1347 g, 2 mmol), (*R**,*R**)-(±)-tetraphos (0.1343 g, 2 mmol), (*S*,*S*)-(+)-tetraphos (0.1345 g, 2 mmol), dppe (0.0798 g, 2 mmol), and [AuCl(SMe$_2$)] (0.2069 g, 7 mmol) in dichloromethane (30 mL) was treated with a solution of ammonium hexafluorophosphate (1.41 g, 8.7 mmol) in water (20 mL), and the mixture was vigorously stirred for 1 h. The organic phase was separated, dried (MgSO$_4$), and evaporated to dryness. The residue was dissolved in CD$_2$Cl$_2$, and the ^{31}P NMR spectrum (2D *J*-resolved) was recorded. The spectrum showed the presence of an equimolar mixture of (*H*,*H*)-(*M*,*P*)-[Au$_2$\{(*R**,*S**)-tetraphos\}$_2$](PF$_6$)$_2$ (δ 23.3−25.0, 17.5−19.2), (*M*,*M*)-[Au$_2$\{(*R*,*R*)-tetraphos\}$_2$](PF$_6$)$_2$/(*P*,*P*)-[Au$_2$\{(*S*,*S*)-tetraphos\}$_2$]-(PF$_6$)$_2$ (δ 24.9−26.5, 18.8−20.5), (*M*,*M*)-[Au$_2$\{(*R*,*R*)-tetraphos\}$_2$]-(PF$_6$)$_2$ (δ 24.9−26.5, 18.8−20.5), and [Au(dppe)$_2$]PF$_6$ (δ 21.6).

Crystal Structures. X-ray diffraction data were collected on single crystals selected from samples of (*H*,*H*)-(*M*,*P*)-[Ag$_2$\{(*R**,*S**)-tetraphos\}$_2$](PF$_6$)$_2$ and (*H*,*H*)-(*M*,*P*)-[Au$_2$\{(*R**,*S**)-tetraphos\}$_2$]-(PF$_6$)$_2$. Crystal data and experimental parameters are given in Table 1. Intensity data were corrected for absorption in each case.[21,22]

The structure of the silver complex was solved by heavy-atom methods[23] and refined using standard techniques.[24] Full-matrix least-squares refinement was performed on *F*; non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were included at calculated positions.

Refinement of the gold complex was not straightforward. Initial solution was obtained using direct methods[25] in the space group *Pnam*, but poor agreement factors and nonsensical interatomic distances and angles in some parts of the molecule indicated that the space group was incorrect. There are eight formula units in the unit cell of the crystal, which is metrically orthorhombic. The structure is best described in the monoclinic space group *P*..2$_1$ as a displacive modulation of a parent *Pnam* structure with the same unit cell parameters. The asymmetric unit contains one cation and one anion in general positions and half of each of the two anions situated on the mirror plane. This modulation may be approximated as the antisymmetric displacement of two *P*.2$_1$/*a*. substructures that interleave perpendicular to **c**, so as to avoid difficulties associated with the packing of the cations across the mirror planes at *z* = ±^{1}/$_4$ of *Pnam*. An antisymmetric displacement of the substructures

(20) Dash, K. C.; Schmidbaur, H. *Chem. Ber.* **1973**, *106*, 1221−1225.

(21) Coppens, P. In *Crystallographic Computing*; Ahmed, F. R., Hall, S. R., Huber, C. P., Eds.; Munksgaard: Copenhagen, 1970; pp 255−270.

(22) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *24*, 351−359.

(23) *PATTY*: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF Program System*; Technical Report of the Crystallographic Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1992.

(24) *teXsan: Single-Crystal Structure Analysis Software*, version 1.8; Molecular Software Corporation: The Woodlands, TX, 1992−1997.

(25) *SIR92*: Altomare, A.; Cascarano, G.; Giacovazza, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

parallel to **a** would lower the symmetry to *Pna*2_1; the corresponding displacement parallel to **b** would lower the symmetry to *P*$2_1 2_1 2_1$. If both displacements occur, the symmetry is lowered to *P*..2_1. This concept was sufficient to guide a hierarchical evaluation of the structure starting from a rather poor structure determination and refinement ($R(F) = 0.35$) in *Pnam*. The overall sign of the antisymmetric displacements parallel to **a** selects the handedness for the crystal, and the overall sign of the antisymmetric displacements parallel to **b** selects between different orientations of the same structure. The correct description required a partial disorder/partial twinning model, as described in the CIF. Refinement with the program RAELS allowed extensive use of constraints and restraints and inclusion of stacking faults and twinning in the model.[26] Final refinement was performed on *F*, and hydrogen atoms were included at calculated positions.

Supporting Information Available: Additional crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

(26) *RAELS:* Rae, A. D. *A Comprehensive Constrained Least-Squares Refinement Program*; Australian National University: Canberra, A.C.T., Australia 0200.