Homochiral Self Recognition in Gold-Phosphane-Helicates

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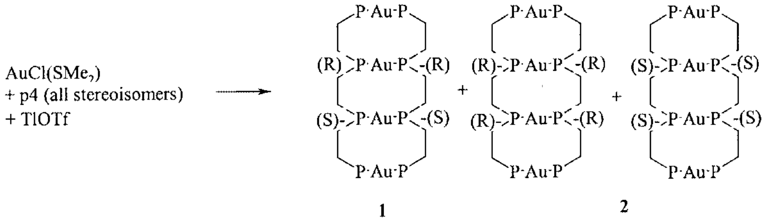
Treatment of Au(SMe$_2$)Cl with a mixture of (R^*,S*)- and (R^*,R*)-(±)-p4 (p4 = 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane) and TlOTf produces [Au$_4$(R,S-p4)$_2$](OTf)$_4$ (**1**) and a racemic compound of [Au$_4$(R,R-p4)$_2$](OTf)$_4$ and [Au$_4$(S,S-p4)$_2$](OTf)$_4$ (**2**). Compounds **1** and **2** were isolated as colorless crystals and characterized by single crystal X-ray diffraction. In both **1** and **2**, four gold atoms are bridged by two p4 ligands. The structure of **1** is a *meso*-helicate composed of a P, an M and a central achiral domain. The ligands exhibit a head-to-head arrangement. The structures of **2** consist of a non-palindromic double helix. In both **1** and **2** the R centers induce a left-handed (M) and the S centers a right-handed (P) helicity. The helical elements of both **1** and **2** are unsaturated and show Au···Au interactions.

Introduction

Most of the activity in the area of helical complexes has been concentrated on achiral ligands.[1,2] More recently, however, chiral ligands have been used and interest has become focused towards stereoselective helical induction by enantiopure ligands.[3] One report deals with the stereospecific assembly of a racemic compound of homochiral dinuclear helicates from a racemic tetradentate nitrogen donor ligand.[4]

The object of this paper is the investigation of chiral self-recognition during the assembly of double stranded helicates in the presence of all stereoisomers of a ligand containing two chiral centers. The linear tetraphosphane ligand p4 (1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane, $Ph_2P-CH_2-CH_2-PPh-CH_2-CH_2-PPh-CH_2-CH_2-PPh_2$) exists as ($R^*$,S*) and ($R^*$,R*)-(±) stereoisomers. In this ligand, the chiral phosphorus centers act as donor atoms, whilst most other chiral ligands used in helicate architecture contain achiral donor atoms and some non-coordinating chiral centers attached to the ligand. We report here on the reaction of Au(SMe$_2$)Cl with p4 in a stoichiometry that provides two phosphorus donor atoms per gold center. A complex with the ratio Au:P = 2:8, [Au$_2${(R,R)-p4}$_2$](PF$_6$)$_2$ has been synthesized previously using enantiopure p4.[5] The structure consists of a *parallel helix*,[6] in which the two ligands form two helices whose helical axes are not defined by the metal ions but run parallel to the Au−Au vector. The Au centers are coordinated by four phosphorus atoms. As far as we know this, and the related silver complex,[5] are the sole published complexes containing more than one p4 ligand. A complex of the composition [(AuCl)$_4$(p4)], whose stereochemistry was not specified, has been patented as an antitumor agent.[7]



1 2

(charges and anions omitted)

Scheme 1

Results and Discussion

The reaction of Au(SMe$_2$)Cl with a mixture of all stereoisomers of p4 and TlOTf in the molar ratio of 4:2:4 in MeOH produces two compounds of the composition [Au$_4$-

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$(p4)_2](OTf)_4$ which were separated by fractional crystallization from MeOH and isolated as colorless crystals. The less soluble isomer contains exclusively (*R*,*S*)-p4 ligands (**1**) and the other contains p4 with the configurations (*R*,*R*)- or (*S*,*S*)-(**2**) (Scheme 1).

Crystals of **1**·2MeOH or **1**·2EtOH were grown by slow evaporation of solutions of **1** in MeOH or EtOH. The EtOH solvate shows a more compact packing, whilst the structures of the cations are almost identical for both solvates. The cation of **1**·2EtOH (shown in Figure 1, selected distances and angles are presented in Table 1 and the data for **1**·2MeOH are provided as supporting information) contains four gold atoms bridged by two p4 ligands. The assembly is stereoselective in view of the coordination of two (*R*,*S*)-p4 ligands and the head-to-head arrangement of the ligands, i.e. one gold center is coordinated by two *R* phosphorus atoms and another by two *S* phosphorus atoms. The stereoselective coordination of four gold atoms is reflected by a center of symmetry in the cation $[Au_4(\mu^4\text{-}R,S\text{-}p4)_2]^{4+}$ in the crystal lattice.

The structure of the cation of **1**·2EtOH shown in Figure 1 is a *meso*-helicate: The two terminal $(Au-P-CC-P)_2$ rings form double helices whose axes pass through the gold atoms. In keeping with the center of symmetry, these domains exhibit opposite helicities: The *R* centers induce an M handedness and the S centers a P sense. The central $(Au-P-CC-P)_2$ element is achiral and adopts a centrosymmetric chair-like geometry. The Au−Au distance of the helical domains [2.9802(4) Å] indicates a 1,6-transannular Au−Au d^{10}-d^{10} interaction in the 10-membered $(Au-P-CC-P)_2$ rings while there is no contact between the inner gold atoms 2 and 2A [4.1062(5) Å]. The axes of the two helical domains are not co-linear.

Crystals of **2**·2MeOH were grown by slow evaporation of a solution of **2** in MeOH. There are two crystallographically

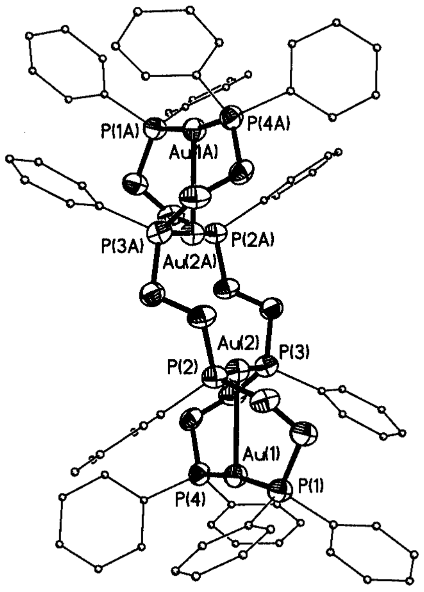

Figure 1. Structure of the cation of **1**

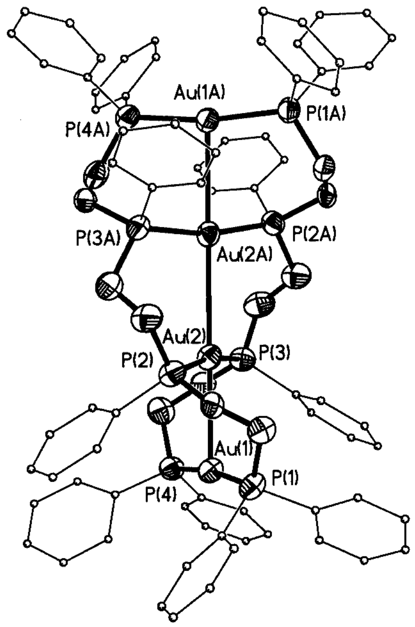

Figure 2. Structure of the M-$[Au_4(\mu\text{-}(R,R)\text{-}p4)_2](OTf)_4$ isomer of the first of two crystallographically independent helicates of **2**

Table 1. Selected distances (Å) and angles (°) of **1** and the two crystallographically independent complexes of **2**

1		**2**		**2**	
Au1−Au2	2.9802(4)	Au1−Au2	3.0898(9)	Au11−Au22	3.0955(14)
Au2−Au2A	4.1062(5)	Au2−Au2A	3.3292(13)	Au22−Au33	3.3404(14)
Au1−P1	2.324(2)	Au1−P1	2.317(5)	Au33−Au44	3.071(2)
Au1−P4	2.319(2)	Au1−P4	2.317(5)	Au11−P11	2.313(4)
Au2−P2	2.310(2)	Au2−P2	2.313(4)	Au22−P22	2.322(4)
Au2−P3	2.309(2)	Au2−P3	2.323(5)	Au33−P33	2.321(5)
P1−Au1−P4	170.14(6)	P1−Au1−P4	171.0(2)	Au44−P44	2.323(5)
P2−Au2−P3	173.76(6)	P2−Au2−P3	168.0(2)	P11−Au11−P11A	170.9(2)
Au1−Au2−Au2A	160.676(13)	Au1−Au2−Au2A	179.62(3)	P22−Au22−P22A	168.4(2)
P1−Au1−Au2−P2	47.64(7)	P1−Au1−Au2−P2	53.71(17)	P33−Au33−P33A	168.0(2)
P4−Au1−Au2−P3	49.28(6)	P4−Au1−Au2−P3	53.08(17)	P44−Au44−P44A	170.0(3)
		P2−Au2−Au2A−P3A	28.66(17)	P11−Au11−Au22−P22	52.52(17)
				P22−Au22−Au33−P33	28.61(17)
				P33−Au33−Au44−P44	53.43(17)

independent complexes with very similar structures which are shown in different perspectives in Figure 2 and 3. The structures consist of two ligand strands wrapped as a double helix around a linear Au_4 rod. The helices stereoselectively contain either two *R*,*R*- or two *S*,*S*-p4 ligands.

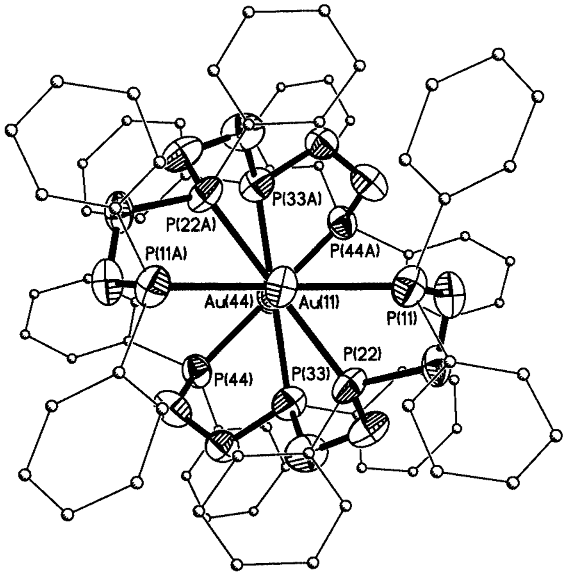

Figure 3. View of the P-[Au_4(μ-(*S*,*S*)-p4$)_2$](OTf$)_4$ isomer of the second of two crystallographically independent helicates of **2** along the Au_4 chain

The configuration of the helices is dictated by that of the ligands analogously to **1**: the *R* centers are related to an M helix and the S centers to P. In keeping with the centrosymmetric space group, crystals of **2** are a racemic compound of equal amounts of P and M helices. The helices are nonpalindromic (see Figure 3): the pitch angle of the outer (Au−P−CC−P$)_2$ segments of **2** amounts to 53.2° (mean value), and the inner (Au−P−CC−P$)_2$ segments display a significantly smaller helical twist of 28.6° (mean value). The helical twist in the trinuclear helicate [Au_3(μ^3-pp2$)_2$](OTf$)_3$ (pp2 = PhP($CH_2CH_2PPh_2$$)_2$] is between 50.66(7)° and 54.57(6)°.[8]

The helicates are unsaturated in view of the gold-gold distances, which all are within the range of Au−Au d^{10}-d^{10} interactions.[9] The separation of the inner Au centers (3.33 Å, mean value) is significantly larger than the contact between inner and outer gold atoms (3.09 Å, mean value).

The stereoselective coordination of the four gold atoms by two ligand strands in **2** is reflected in the symmetry of the complexes in the crystal lattice: The different [Au_4(μ^4-*R**,R*-p4$)_2$$]^{4+}$ cations in **2** both show internal C_2 symmetry: The twofold axis in one complex is essentially perpendicular to the helical axis bisecting it between the two inner gold atoms; in the other complex it coincides with the Au_4 chain forming the helical axis. Both crystallographically independent cations display idealized D_2 point symmetry. The symmetry of [Au_4(μ^4-*R**,R*-p4$)_2$$]^{4+}$ in the solid state is remarkable because the existence of different crystallographic symmetry elements in the same helicate seems to be uncommon and because there are no precedents for a twofold symmetry parallel to the helical axis in the space group *C*2/*c*, which is the most frequently occurring space group for helicates.[2]

The crystal packing of **2** is unusual. Because of their cylindrical shape, helicates tend to align themselves along to the helical axis.[2] In contrast, the crystal packing of **2** (Figure 4) produces a sheet of alternatingly parallel and perpendicular helices. Two of the four OTf anions of **2** are located between the terminal gold atoms of one helicate and the two central Au atoms of the neighboring helicates within this sheet; the nearest Au···O and Au···F distances are 3.1 and 3.3 Å, respectively. The sequence of the sheets along *c* is an AB arrangement: In one sheet (A) all helices parallel to the twofold crystallographic axis are built from ligands with an *R*,*R* configuration and the helices perpendicular to the twofold crystallographic axis contain *S*,*S* ligands; the reverse is true for the next sheet (B). The remaining two OTf anions are between the sheets without any contacts to gold atoms.

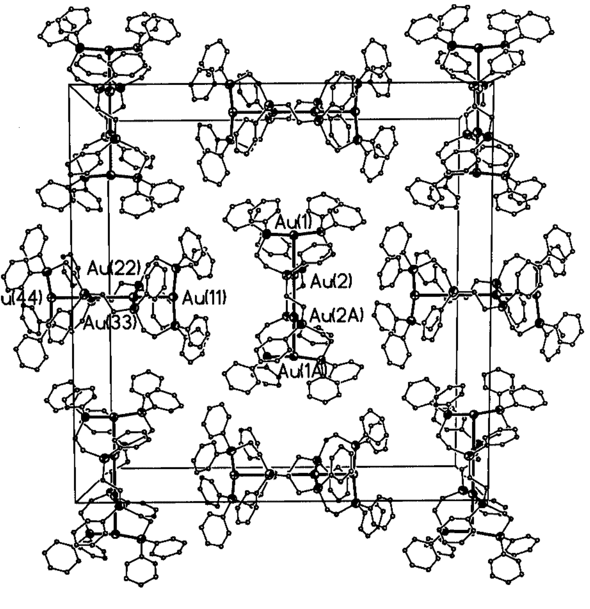

Figure 4. Structure **2** packed along *c*; the anions and solvate molecules have been omitted for clarity

Although the structures of **1** and **2** are essentially different, they display some similarities. The conformation of the substituents of the diagonal phosphorus donor atoms at each gold atom is eclipsed in the view along the P−Au−P axis, the outer phosphorus atoms display a torsion angle C(phenyl)−P−Au−P−C(phenyl) of ca. 0° whereas the inner phosphorus atoms show corresponding angles of approximately 120°. The mean dihedral P−C−C−P angles of the ligand backbone in the different (Au−P−CC−P$)_2$ segments increase in the order 67.9° (**1**, outer segment) < 69.5° (**2**, outer segment) < 104.6° (**2**, inner segment) < 127.14° (**1**, inner segment) and roughly correlate with the Au−Au distances.

Steric reasons may control the formation of helicates or *meso*-helicates: A geometrical extrapolation of [$Au_3(\mu^3$-pp2$)_2$](OTf)$_3$ [8] does not exclude the formation of a helical structure from (*R,S*)-p4 ligands. In fact, a *meso*-helicate is observed for **1**. Possible factors of strain are different steric requirements concerning the coordination geometry of gold and the conformation of the p4 ligands. A possible indicator of such a strain is that all Au atoms are shifted slightly towards the center of the complex cations (P−Au−P = 173.76−168.0°). This shift is particularly pronounced for the inner gold atoms in compound **2**. Related effects are present in [$Au_3(\mu^3$-pp2$)_2$](OTf)$_3$.[8] More data is available on the control of the formation of triple-stranded helicates or *meso*-helicates from achiral ligands. This is related to the rigidity and the form (S or C type) of the ligands, the nature of the spacer (even or odd number of alkylene chains and the chirality of the spacers) and the presence of suitable templates.[10]

Chiral self-recognition has been attributed firstly to the conformational rigidity of the ligand and secondly to the tendency of a more compact structure resulting in maximal intramolecular van der Waals interactions.[4] The first aspect does not apply to the present system in view of the flexibility of the p4 ligand used, whereas the second is thought to control the chiral self-recognition described in this paper.

Experimental Section

The ligand p4 was obtained commercially [(*R**,S*)/(*R**,R*)-(±) ratio ca. 5:1]. Chemical analyses were performed by the Institut für physikalische Chemie, Universität Wien.

Synthesis of 1·2EtOH and 2·2MeOH: A mixture of Au(SMe$_2$)Cl (58.9 mg, 0.200 mmol), p4 (67.1 mg, 0.100 mmol) and TlOTf (70.7 mg, 0.200 mmol) in MeOH (1 mL) was stirred for 2 h. The TlCl precipitate was removed and the solvent evaporated to a volume of ca. 0.2 mL resulting in a colorless precipitate, which was collected, dried and dissolved in EtOH. Crystals of X-ray quality of **1**·2EtOH were obtained from the first fraction by slow evaporation of this solution. Yield 30 mg (21%, not optimized). $C_{88}H_{84}Au_4F_{12}O_{12}P_8S_4$·2EtOH: calcd. C 39.22, H 3.43; found C 39.1, H 3.3.

The mother liquor mentioned above (MeOH solution) was reduced to a volume of ca. 0.1 mL. Further evaporation of the mother liquor gave X-ray quality crystals of **2**·2MeOH. Yield 6 mg, (4%, not optimized). $C_{88}H_{84}Au_4F_{12}O_{12}P_8S_4$·2MeOH: calcd. C 38.75, H 3.32; found C 38.8, H 3.2.

X-ray Crystallography: The data collection was performed on a Nonius Kappa CCD equipped with graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å) and a nominal crystal-to-area-detector distance of 36 mm. Intensities were integrated using DENZO and scaled with SCALEPACK.[11] Several scans in the φ and ω direction were made to increase the number of redundant reflections, which were averaged over the refinement cycles. This procedure replaces an empirical absorption correction. The structures were solved with direct methods and refined against F^2 using the SHELX program suite.[12,13] Hydrogen atoms were added geometrically and refined using a riding model. All non-hydrogen atoms of compound **1** were refined with anisotropic displacement parameters. In compound **2** nearly all OTf anions and the solvent molecules MeOH are highly disordered and were refined isotropically. Five OTf anions are found in the asymmetric unit, three in a general position and two with occupancy of 0.5 near a crystallographic twofold rotation axis, which passes in a sloping manner through the C−S axis of the OTf anions. Only one OTf anion in a general position is well ordered and could be refined anisotropically. The two others, which are placed between the layers, are 1:1 disordered by a small movement of the complete anion with two common oxygen atoms for both positions. The disorder of these anions leads partly to overlying positions and bond restraints must be used to minimize correlation effects.

CCDC-179094 (**1**·EtOH), -179095 (**1**·2MeOH) and -179096 (**2**·2MeOH) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystallographic data for new complexes

	1·2EtOH	**2**·2MeOH
Empirical formula	$C_{92}H_{96}Au_4F_{12}O_{14}P_8S_4$	$C_{90}H_{92}Au_4F_{12}O_{14}P_8S_4$
Formula mass (g mol^{-1})	2817.55	2789.50
Temperature (K)	223(2)	223(2)
Wavelength (Å)	0.71073	0.71073
Space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
a (Å)	11.1975(2)	28.4795(7)
b (Å)	26.9696(7)	28.5089(7)
c (Å)	17.1861(5)	25.0645(6)
β (deg)	100.900(2)	97.390(1)
V (Å^3)	5096.4(2)	20181.3(9)
Z	2	8
D (g cm^{-3})	1.836	1.836
μ (mm^{-1})	6.028	6.088
Final $R1$[a] [$I > 2\sigma(I)$]	0.0330	0.0545
$wR2$[a] (all data)	0.0781	0.1288

[a] $R1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, $wR2 = \{\Sigma[w(F_0{}^2 - F_c{}^2)^2]/\Sigma[w(F_0{}^2)^2]\}^{1/2}$.

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