above, but by use of [[*S*-(*R**,*S**)],(*R*)]-**7b**, this complex was produced in 96% yield as pale yellow plates: mp >300 °C dec; $[\alpha]_D$ −10.7° (*c* 0.51, CH_2Cl_2).

[*S*-(*R,*S**)]-1-(Methylphenylarsino)-2-(methylphenylphosphino)benzene, [*S*-(*R**,*S**)]-1.** Decomposition of [*R*-(*R**,*S**)]-**8** by the usual method liberated this enantiomer in 90% yield as white plates: mp 67–68 °C (after recrystallization from methanol); $[\alpha]_D$ +15.5° (*c* 0.42, CH_2Cl_2); ^1H NMR ($CDCl_3$) identical with that of the corresponding racemic material.

[*R*-(*R,*S**)]-1-(Methylphenylarsino)-2-(methylphenylphosphino)benzene, [*R*-(*R**,*S**)]-1.** This enantiomer was displaced from [*R*-(*R**,*S**)]-**8** by cyanide in 90% yield. It crystallized as white needles: mp 67–68 °C; $[\alpha]_D$ −15.5° (*c* 0.48, CH_2Cl_2); ^1H NMR ($CDCl_3$) identical with that of the racemic material.

[*SP*-4-4-1-[*R*-(*R,*R**)],2-(*R*)]-[1-[1-(Dimethylamino)ethyl]naphthyl-*C*,*N*][1-(methylphenylarsino)-2-(methylphenylphosphino)benzene-*As*,*P*]palladium(II) Hexafluorophosphate, [[*R*-(*R**,*R**)],-(*R*)]-7b.** Bridge splitting of (*R*)-**6** by [*R*-(*R**,*R**)]-**1** in methanol, followed by the addition of NH_4PF_6, produced this compound in 90% yield as colorless prisms (from acetone–diethyl ether): mp 251 °C dec; $[\alpha]_D$ −402° (*c* 0.69, Me_2CO); ^1H NMR (Me_2SO-d_6) δ 1.83 (d, 3, *J* = 6 Hz, CMe), 2.36 (s, 3, AsMe), 2.44 (d, 3, *J* = 10 Hz, PMe), 2.68 (br s, 3, NMe), 3.16 (br d, 3, *J* = 3 Hz, NMe), 4.68 (m, 1, CH), 7.1–8.1 (br m, 20, aromatics); conductivity Λ_M = 43.0 Ω^{-1} cm^2 mol^{-1} (10^{-3} M in CH_2Cl_2 at 20 °C).

[*SP*-4-4-1-[*S*-(*R,*R**)],2-(*R*)]-[1-[1-(Dimethylamino)ethyl]naphthyl-*C*,*N*][1-(methylphenylarsino)-2-(methylphenylphosphino)benzene-*As*,*P*]palladium(II) Hexafluorophosphate, [[*S*-(*R**,*R**)],-(*R*)]-7b.** As above, but by use of [*S*-(*R**,*R**)]-**1**, this compound was isolated in 92% yield: mp 252–53 °C dec; $[\alpha]_D$ +246° (*c* 0.67, acetone); ^1H NMR (Me_2SO-d_6) δ 1.69 (d, 3, *J* = 6 Hz, CMe), 2.36 (s, 3, AsMe), 2.41 (d, 3, *J* = 10 Hz, PMe), 2.86 (br s, 6, NMe_2), 4.63 (m, 1, CH), 6.85 (d of d, 1, J_{HH} = 9 Hz, J_{PH} = 6 Hz, C(7)H), 7.3–8.4 (br m, 19, aromatics); conductivity Λ_M = 38.8 Ω^{-1} cm^2 mol^{-1} (10^{-3} M in CH_2Cl_2 at 20 °C).

Epimerization Studies. Enantiomer [*R*-(*R**,*R**)]-**1** was heated at 140 °C for 2 h. ^1H NMR spectroscopy indicated a 1:1 mixture of [*R*-(*R**,*R**)]- and [*R*-(*R**,*S**)]-**1**. Recrystallization from hot methanol gave a sample of [*R*-(*R**,*R**)]-**1**, mp 93–94 °C. Enantiomer [*R*-(*R**,*S**)]-**1** was isolated via its (thiocyanato)nickel(II) complex, mp 233–4 °C.

Enantiomer [*S*-(*R**,*S**)]-**1** was similarly converted into a 1:1 mixture of itself and [*S*-(*R**,*R**)]-**1** as evidenced by ^1H NMR spectroscopy and isolation of the components.

Protonation Reactions. [*R*-(*R,*R**)]-Methyl[2-(methylphenylarsino)phenyl]phenylphosphonium Tetrafluoroborate, [*R*-(*R**,*R**)]-9.** A solution of [*R*-(*R**,*R**)]-**1** (0.5 g) in dichloromethane (50 mL) was treated with aqueous HBF_4 (40% w/w, 5 mL). The mixture was shaken for 5 min and the organic layer separated, washed with water, and dried ($MgSO_4$). The product was isolated from the organic phase. Recrystallization from a dichloromethane–diethyl ether mixture gave white needles: mp 163–164 °C; 0.54 g (87%); $[\alpha]_D$ +99.8° (*c* 0.46, CH_2Cl_2); ^1H NMR at −90 °C (CD_2Cl_2) δ 1.03 (s, 3, AsMe), 2.62 (br d, 3, PMe), 7.10–8.20 (br m, 14, aromatics), 8.45 (br d, 1, *J* = 530 Hz, PH) (PH not observed at 34 °C).

[*R*-(*R,*S**)]-Methyl[2-(methylphenylarsino)phenyl]phenylphosphonium Tetrafluoroborate, [*R*-(*R**,*S**)]-9.** This salt was prepared from [*R*-(*R**,*S**)]-**1** in 90% yield by the method described above. It was isolated as white needles: mp 132–133 °C; $[\alpha]_D$ +37.9° (*c* 0.42, CH_2Cl_2); ^1H NMR at −90 °C (CD_2Cl_2) δ 1.42 (s, 3, AsMe), 2.59 (br d, 3, PMe), 6.85–8.36 (br m, 14, aromatics), 8.62 (br d, 1, *J* = 527 Hz, PH)(PH not observed at 34 °C).

No evidence of epimerization of the tertiary arsenic centers in either of the phosphonium salts was found upon heating to 80 °C in 1,2-dichlorobenzene in the presence of HBr.

Registry No. (*R**,*R**)-(±)-**1**, 87711-52-2; (*R**,*S**)-(±)-**1**, 87711-53-3; [*S*-(*R**,*R**)]-**1**, 87760-08-5; [*R*-(*R**,*R**)]-**1**, 87760-09-6; [*S*-(*R**,*S**)]-**1**, 87760-10-9; [*R*-(*R**,*S**)]-**1**, 87760-11-0; (*R**,*R**)-(±)-**2**, 87711-57-7; (*R**,*S**)-(±)-**2**, 87760-14-3; (*R*)-**3**, 73089-54-0; [[*R*-(*R**,*R**)],(*R*)]-**4a**, 87728-20-9; [[*S*-(*R**,*R**)],(*R*)]-**4a**, 87760-27-8; [[*R*-(*R**,*R**)],(*R*)]-**4b**, 87711-59-9; [[*S*-(*R**,*R**)],(*R*)]-**4b**, 87760-16-5; [*R*-(*R**,*R**)]-**5**, 87711-60-2; [*S*-(*R**,*R**)]-**5**, 87760-17-6; (*R*)-**6**, 80145-77-3; [[*R*-(*R**,*S**)],(*R*)]-**7a**, 87760-28-9; [[*S*-(*R**,*S**)],(*R*)]-**7a**, 87760-75-6; [[*R*-(*R**,*S**)],(*R*)]-**7b**, 87711-62-4; [[*S*-(*R**,*S**)],(*R*)]-**7b**, 87760-19-8; [[*R*-(*R**,*R**)],(*R*)]-**7b**, 87760-23-4; [[*S*-(*R**,*R**)],(*R*)]-**7b**, 87760-25-6; [*R*-(*R**,*S**)]-**8**, 87760-20-1; [*S*-(*R**,*S**)]-**8**, 87760-21-2; [*R*-(*R**,*R**)]-**9**, 87760-12-1; [*R*-(*R**,*S**)]-**9**, 87760-13-2; [NiSCN-[(*R**,*S**)-**1**]$_2$]SCN, 87711-56-6; (*R**,*R**)-(±)-[Ni(CO)$_2$(diph)], 87760-26-7; (*R**,*S**)-(±)-[Ni(CO)$_2$(diph)], 77029-28-8; (*R**,*R**)-(±)-dias, 55289-90-2; (*R**,*S**)-diph, 72091-02-2; (*R**,*S**)-dias, 55289-91-3; PHMePh, 6372-48-1; AsHMePh, 53979-86-5; (±)-1-chloro-2-(acetylphenylphosphino)benzene, 87711-54-4; 1,2-dichlorobenzene, 95-50-1.

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Stereochemistry and Dynamic Properties of Tetrahedral Gold(I) Complexes Containing Chiral Phosphorus and Arsenic Bidentates

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Bis(bidentate)gold(I) complexes containing the diastereoisomers and enantiomers of the ligands 1,2-phenylenebis(methylphenylphosphine) and its arsenic analogue and of 1-(methylphenylarsino)-2-(methylphenylphosphino)benzene have been prepared and their stereochemistry and dynamic properties investigated by ^1H NMR spectroscopy. Rapid redistribution of the bidentates occurs in the complexes of the bis(tertiary arsine) and in those of the mixed-donor ligand, but in complexes of the bis(tertiary phosphine) redistribution is slow enough to allow separation of racemic and meso complexes by fractional crystallization. Furthermore, variable-temperature ^1H NMR studies of complexes of the type (±)-[Au((*R**,*S**)-bidentate)$_2$]PF_6 indicate facile epimerization of the tetrahedral gold center.

Introduction

Whereas a considerable expansion in the study of gold chemistry has taken place in recent years, notably concerning aspects of organometallic and of cluster compounds,[1] very little additional work on classical bis(bidentate)gold(I) systems has been reported since the pioneering studies of Nyholm[2] and of Mann.[3,4] This earlier work did not concern itself with the dynamics of the tetrahedral cations in solution, although the

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0020-1669/83/1322-4054$01.50/0

failure of Mann and co-workers[3,4] to resolve certain asymmetric compounds of this type may be taken as tacit evidence of rearrangement.

In previous work we have been concerned with the stereochemistry and stability of square-planar and square-pyramidal complexes of bivalent nickel,[5] palladium, and platinum,[6] containing the diastereoisomers and enantiomers of 1,2-phenylenebis(methylphenylphosphine)[7] and its arsenic analogue.[8] The propensity of complexes of this type to undergo internal isomerization and redistribution of the bidentate ligands was noteworthy. In this article, the stability of tetrahedral cations of the type $[Au(bidentate)_2]^+$ has been examined in considerable detail for an isostructural series of complexes containing symmetrical bidentate bis(tertiary phosphines) and bis(tertiary arsines), as well as the racemic and optically active forms of the new unsymmetrical bidentate (R^*,R^*)-(±)- and (R^*,S^*)-(±)-1-(methylphenylarsino)-2-(methylphenylphosphino)benzene.[9]

Results and Discussion

The stereoisomeric forms of the ligands 1,2-phenylenebis(methylphenylphosphine) (diph) and its arsenic analogue (dias) and of 1-(methylphenylarsino)-2-(methylphenylphosphino)benzene (phas) are depicted in Figure 1. For each ligand the R^*,R^* diastereoisomer[10] was separated from the R^*,S^* diastereoisomer by fractional crystallization from methanol; the latter was purified via its (thiocyanato)nickel(II) complex. Resolutions of the R^*,R^* forms of the three ligands, as well as the R^*,S^* form of phas, were accomplished by the method of metal complexation.[7-9]

The complexes were prepared from $Et_4N[AuBr_2]$[12] by treatment with 2 equiv of the appropriate form of the ligand. This gave the complex bromides, which were converted to the corresponding hexafluorophosphates by the addition of NH_4PF_6. The complexes vary in color from pale yellow to white and are air-stable crystalline solids. Selected physical and spectroscopic data for the hexafluorophosphate salts are assembled in Table I: the corresponding bromides are more labile and were not investigated in depth.

Symmetrical Bidentates. The stereochemistries of tetrahedral cations[13] arising from the various forms of the symmetrical bidentates are shown in Figure 2. In the solid state, the bis[1,2-phenylenebis(dimethylarsine)]gold(I) cation is known to be tetrahedral.[15] The optically active forms of the ligand, R-(R^*,R^*) or S-(R^*,R^*), produce discrete optically active complexes, but the corresponding racemic material may lead to a mixture of internally diastereoisomer products: an achiral meso complex containing bidentates of opposite chirality and a racemic complex in which both bidentates possess the same chirality. The latter can be unequivocally identified if the ^1H NMR spectrum of the corresponding optically active species is available for comparison, since the spectra are identical. The meso and racemic complexes are not internally related: interconversion between the two is definitive of intermolecular ligand redistribution. Moreover, because the shielding pattern of the methyl groups is quite different in the two diastereoisomers, ^1H NMR spectroscopy can be used to monitor the redistribution process. A study of meso ⇌ racemic interconversion in bis(bidentate) complexes is, therefore, a powerful probe into the lability of coordinated ligands. The achiral R^*,S^* diastereoisomers of the symmetrical bidentates produce racemic mixtures of discrete chiral products of C_2 symmetry (Figure 2).

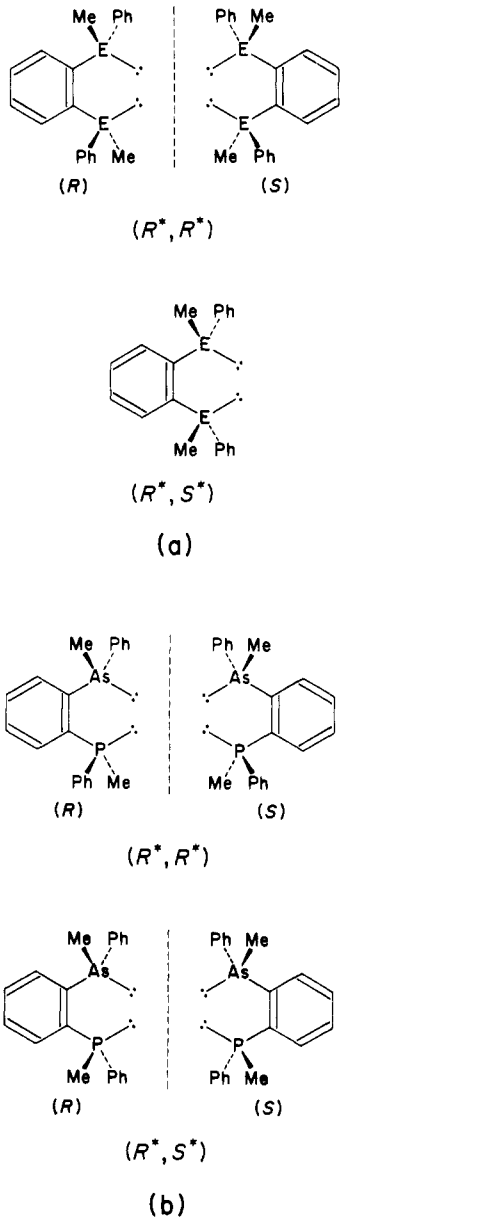

Figure 1. Stereoisomerism in the compounds 1,2-phenylenebis(methylphenylphosphine) (E = P) and its arsenic analogue (E = As) (a) and in 1-(methylphenylarsino)-2-(methylphenylphosphino)benzene (b).

Bis(tertiary phosphine) Complexes. The reaction of [S-(R^*,R^*)]-diph with the dibromoaurate(I) led to the expected optically active product, viz., (−)-$[Au([R$-(R^*,R^*)]-diph)$_2]Br$. The ^1H NMR spectrum of the salt contains a slightly broadened singlet (unresolved coupling to ^{31}P nuclei) at δ 2.20 in CD_2Cl_2, due to the equivalent PMe groups.[16] The optically active hexafluorophosphate was prepared from a solution of the bromide by adding aqueous NH_4PF_6. Use of the racemic

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(10) The nomenclature used throughout this paper is consistent with that used by the Chemical Abstracts Service.[11] In the present situation [R-(R^*,S^*)]-phas denotes R-As,S-P.
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(16) Unless stated differently, ^1H NMR spectra were recorded at 304 K.
(17) The full formula of the meso complex is given in order to avoid confusion with the racemic complex.

Table I. Selected Physical and Spectroscopic Data for the Complexes [Au(bidentate)$_2$]PF$_6$

	mp, °C	$[\alpha]_D$,[a] g/100 mL	δ(EMe)[b] E = P	δ(EMe)[b] E = As
(−)-[Au([*R*-(*R**,*R**)]-diph)$_2$]PF$_6$[c]	217-219	−374 (0.960)	2.18 s	
(±)-[Au((*R**,*R**)-diph)$_2$]PF$_6$	253-255		2.18 s	
[Au([*R*-(*R**,*R**)]-diph)([*S*-(*R**,*R**)]-diph)]PF$_6$	208-210		1.65 s	
(±)-[Au((*R**,*S**)-diph)$_2$]PF$_6$	258-260		1.52 s, 2.26 s	
(−)-[Au([*R*-(*R**,*R**)]-dias)$_2$]PF$_6$[c]	228-230	−186 (0.479)		2.02 s
(±)-[Au((*R**,*R**)-dias)$_2$]PF$_6$[d]	222-224			1.72 s, 2.02 s
(±)-[Au((*R**,*S**)-dias)$_2$]PF$_6$	193-195			1.88 s (1.75 s, 2.13 s)[f]
(−)-[Au([*R*-(*R**,*R**)]-phas)$_2$]PF$_6$[c]	230-232	−229 (0.342)	2.22 t[e] (2.30 t)	1.98 s (2.08 s)
(±)-[Au((*R**,*R**)-phas)$_2$]PF$_6$[d]	210 dec		1.86 t, 2.22 t	1.54 s, 1.98 s
(−)-[Au([*R*-(*R**,*S**)]-phas)$_2$]PF$_6$[c]	215 dec	−36 (0.382)	2.08 t (1.91 t, 2.29 t)	1.68 s (1.38 s, 2.12 s)
(±)-[Au((*R**,*S**)-phas)$_2$]PF$_6$[d]	224 dec		2.02 t, 2.08 t (1.80 t, 1.91 t, 2.29 t)	1.68 s, 1.78 s (1.38 s, 1.61 s, 2.12 s)

[a] Determined in CH_2Cl_2 at 20 °C at concentrations (g mL^{-1}) quoted in parentheses. [b] Chemical shifts quoted relative to Me_4Si as internal reference in solutions in CD_2Cl_2 at 304 K; values in parentheses at 183 K. All compounds have aromatic absorptions in the region δ 7.1-7.8. [c] Enantiomers of opposite configuration have equal and opposite values of $[\alpha]_D$ but otherwise have identical physical properties. [d] These compounds exist in solution as inseparable mixtures of racemic and meso complexes. [e] Virtual triplets were observed for PMe resonances in phas complexes with $J_{PH} = {}^1/_2|{}^2J_{PH} + {}^4J_{PH}| = 3$ Hz indicating a large value of $^2J_{PP}$.[19] [f] $T_c = 244$ K.

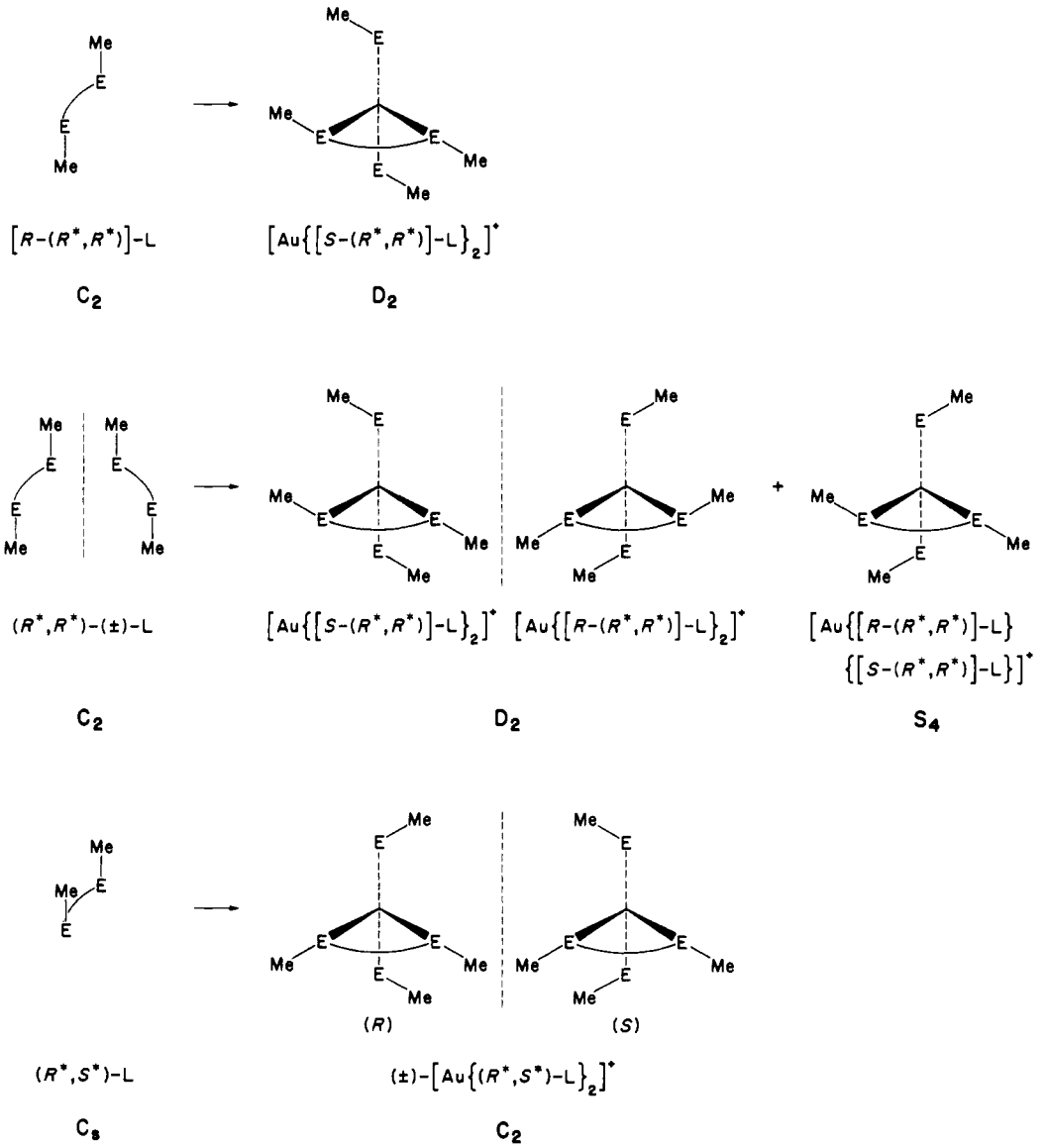

Figure 2. Stereoisomeric cations arising from the diastereoisomers and enantiomers of 1,2-phenylenebis(methylphenylphosphine) (E = P) and its arsenic analogue (E = As) (phenyl groups omitted for clarity).

ligand (*R**,*R**)-(±)-diph led to a single diastereoisomer in 88% yield that exhibited a PMe resonance at δ 2.20 in CD_2Cl_2, and was accordingly identified as the racemic complex (±)-[Au((*R**,*R**)-diph)$_2$]Br. In the presence of a trace of (*R**,*R**)-(±)-diph in ethanol, the kinetically favored racemic product undergoes a redistribution of ligands with formation of an equilibrium mixture involving the corresponding meso diastereoisomer:

$$(\pm)\text{-}[Au((R^*,R^*)\text{-diph})_2]X \rightleftharpoons [Au([R\text{-}(R^*,R^*)]\text{-diph})([S\text{-}(R^*,R^*)]\text{-diph})]X$$

Redistribution of ligands also occurs slowly under ambient conditions in the absence of added ligand. An equilibrium racemic:meso = 1:1.7 mixture of complexes in dichloromethane was established within 8 days for the bromide, but the hexafluorophosphate took months to reach a similar position. The pure racemic complex crystallized from the equilibrium mixture in dichloromethane when diethyl ether was slowly added, although the meso complex was the one to crystallize (ca. 90% pure) from an ethanol solution under similar conditions. The latter was brought to purity in a single recrystallization from ethanol. The corresponding hexafluorophosphates were prepared by metathesis with NH_4PF_6. The behavior of these complexes is reminiscent of that observed for similar bis(tertiary arsine) complexes of bivalent nickel[5] and palladium.[6]

The chiral meso diastereoisomer of the ligand (R^*,S^*)-diph gave the expected complex upon reaction with $Et_4N[AuBr_2]$, which was subsequently converted to the hexafluorophosphate salt. The ^1H NMR spectrum of the latter contains a pair of resonances for the nonequivalent PMe groups, consistent with a tetrahedral structure (Table I). The peaks present at 305 K coalesce into a singlet at 393 K (nitrobenzene solution). Since ligand redistribution in complexes of this type is slow at this temperature, as evidenced by the failure to observe interconversion between the corresponding racemic and meso complexes under the same conditions, the averaging of the resonances found in the complex of the R^*,S^* ligand is attributed to racemization of the tetrahedral gold(I) center. No attempt was made to resolve the complex.

Bis(tertiary arsine) Complexes. These are much more labile than the corresponding bis(tertiary phosphine) complexes. Again, because of their greater stability toward redistribution of ligands, the hexafluorophosphate salts were chosen for detailed study: they were prepared from the corresponding bromides by metathesis with NH_4PF_6 (Table I). The ^1H NMR spectrum of the optically active compound in CD_2Cl_2 exhibits a sharp AsMe singlet at δ 2.02. Use of the racemic ligand (R^*,R^*)-(±)-dias, however, gave a product showing two AsMe resonances of equal intensity, one of which is identical in position with that observed for the optically active compound (Table I). The racemic and meso complexes could not be separated by fractional crystallization. The equilibrium concentration of diastereoisomeric complexes formed within the time of mixing of solutions of the corresponding enantiomers of opposite configuration, as determined by ^1H NMR spectroscopy.

The ^1H NMR spectrum of $(\pm)\text{-}[Au((R^*,S^*)\text{dias})_2]PF_6$ contains a single sharp AsMe singlet at δ 1.88 in CD_2Cl_2 at 304 K, but the expected pair of singlets for the static structure are observed at 183 K. The lower barrier to racemization of the tetrahedral gold(I) center when surrounded by arsenic rather than phosphorus atoms is noteworthy.

The Unsymmetrical Bidentate. Complexes of (R^*,R^*)- and (R^*,S^*)-phas. The stereochemistries of the tetrahedral cations formed by 1-(methylphenylarsino)-2-(methylphenylphosphino)benzene are illustrated in Figures 3 and 4. Both diastereoisomers of the ligand are chiral. Each form has been resolved and the enantiomers assigned absolute configurations on the basis of ^1H NMR data collected from internally diastereoisomeric palladium(II) complexes containing the bis(tertiary) ligand and (*R*)-dimethyl[1-(1-ethyl)naphthyl]amine.[9] The enantiomers of the R^*,R^* and R^*,S^* forms of the ligand give rise to pairs of racemic complexes, which are epimeric at the metal center. In a kinetically stable system with respect to ligand redistribution, interconversion between the epimers corresponds to racemization of the tetrahedral cation:

$$(R)\text{-}[Au([R\text{-}(R^*,R^*)]\text{-phas})_2]X \rightleftharpoons (S)\text{-}[Au([R\text{-}(R^*,R^*)]\text{-phas})_2]X \quad (1)$$

$$(R)\text{-}[Au([R\text{-}(R^*,S^*)]\text{-phas})_2]X \rightleftharpoons (S)\text{-}[Au([R\text{-}(R^*,S^*)]\text{-phas})_2]X \quad (2)$$

The epimerizations represented by eq 1 and 2 are, in principle, observable by ^1H NMR spectroscopy. Inspection of the structures in Figures 3 and 4 reveals that the PMe groups are syn to one another in one of the epimers of each pair and anti in the other. When an optically active ligand is employed, meso complex formation is eliminated and eq 1 and 2 correspond to the only interconversions possible. The situation represented by eq 1 may be difficult to detect by ^1H NMR spectroscopy, however, because of the virtually identical environment of the methyl groups in the two epimers. On the other hand, substantially different shielding of the methyl groups is present in the two species involved in eq 2.

The ^1H NMR spectrum of the complex $[Au([R\text{-}(R^*,R^*)]\text{-phas})_2]PF_6$ in CD_2Cl_2 contains a triplet at δ 2.22 for the PMe groups and a sharp singlet at δ 1.98 for the AsMe groups. Cooling of the solution to 183 K caused a slight broadening of the signals. Unless complex formation is stereospecific, and this is unlikely on steric grounds (vide supra), the NMR data are consistent with rapid epimerization of the complex (compared to the NMR time scale) or lack of resolution in the spectrum at this temperature. The methyl resonances were not resolved at 200 MHz and 183 K. Use of the racemic ligand (R^*,R^*)-(±)-phas led to a hexafluorophosphate salt showing a pair of PMe triplets and a pair of AsMe singlets (Table I). The four absorptions are of equal intensity. Since the positions of the resonances due to the racemic complex can be assigned from data on the optically active complex, the peaks at δ 1.86 and 1.54 are due to the meso complex (±)-$[Au([R\text{-}(R^*,R^*)]\text{-phas})([S\text{-}(R^*,R^*)]\text{-phas})]PF_6$. An NMR experiment indicated that the racemic ⇌ meso equilibrium was established within the time of mixing of CD_2Cl_2 solutions of the enantiomerically pure hexafluorophosphate salts of opposite chirality.

The spectra were more revealing for the (R^*,S^*)-phas derivatives. The optically active hexafluorophosphate salt again displayed an averaged spectrum at 304 K corresponding to rapid epimerization of the central gold atom as represented by eq 2. When cooled to 183 K, however, the sample exhibits two sets of resonances of equal intensity for the two epimers (Table I). The following assignment of methyl resonances was made after consideration of relative shielding patterns: $(R)\text{-}[Au([R\text{-}(R^*,S^*)]\text{-phas})_2]PF_6$ δ 2.29 (br s, PMe), 1.38 (s, AsMe); $(S)\text{-}[Au([R\text{-}(R^*,S^*)]\text{-phas})_2]PF_6$ δ 2.12 (s, AsMe), 1.91 (br s, PMe).

Reaction of (R^*,S^*)-(±)-phas with $Et_4N[AuBr_2]$ produced a salt of the expected composition. The ^1H NMR spectrum of the hexafluorophosphate in the methyl region consists of a pair of overlapping triplets (J = 3 Hz) at δ 2.08 and 2.20 due to PMe groups and a pair of sharp singlets at δ 1.78 and 1.68 for the AsMe groups. The resonances at δ 2.08 and 1.68 are due to the racemic epimers $(\pm)\text{-}[Au((R^*,S^*)\text{-phas})_2]PF_6$ (Table I) and the other two to the meso complex (±)-$[Au([R\text{-}(R^*,S^*)]\text{-phas})([S\text{-}(R^*,S^*)]\text{-phas})]PF_6$. A static asymmetric meso complex should give rise to four methyl resonances (Figure 4), and these were observed at 183 K superimposed upon the identifiable pairs of resonances due to the epimeric racemic complexes (Table I). Coincidental overlap of two of the absorptions at the slow-exchange limit resulted in a six-line spectrum, although ^{31}P decoupling identified the PMe resonances and made a complete assignment possible. The ^1H NMR spectrum of the meso complex in the methyl region at 183 K is δ 2.29 (PMe), 2.12 (AsMe), 1.80 (PMe), and 1.61 (AsMe).

Inversion of Tetrahedral Metal Center. The variable-tem-

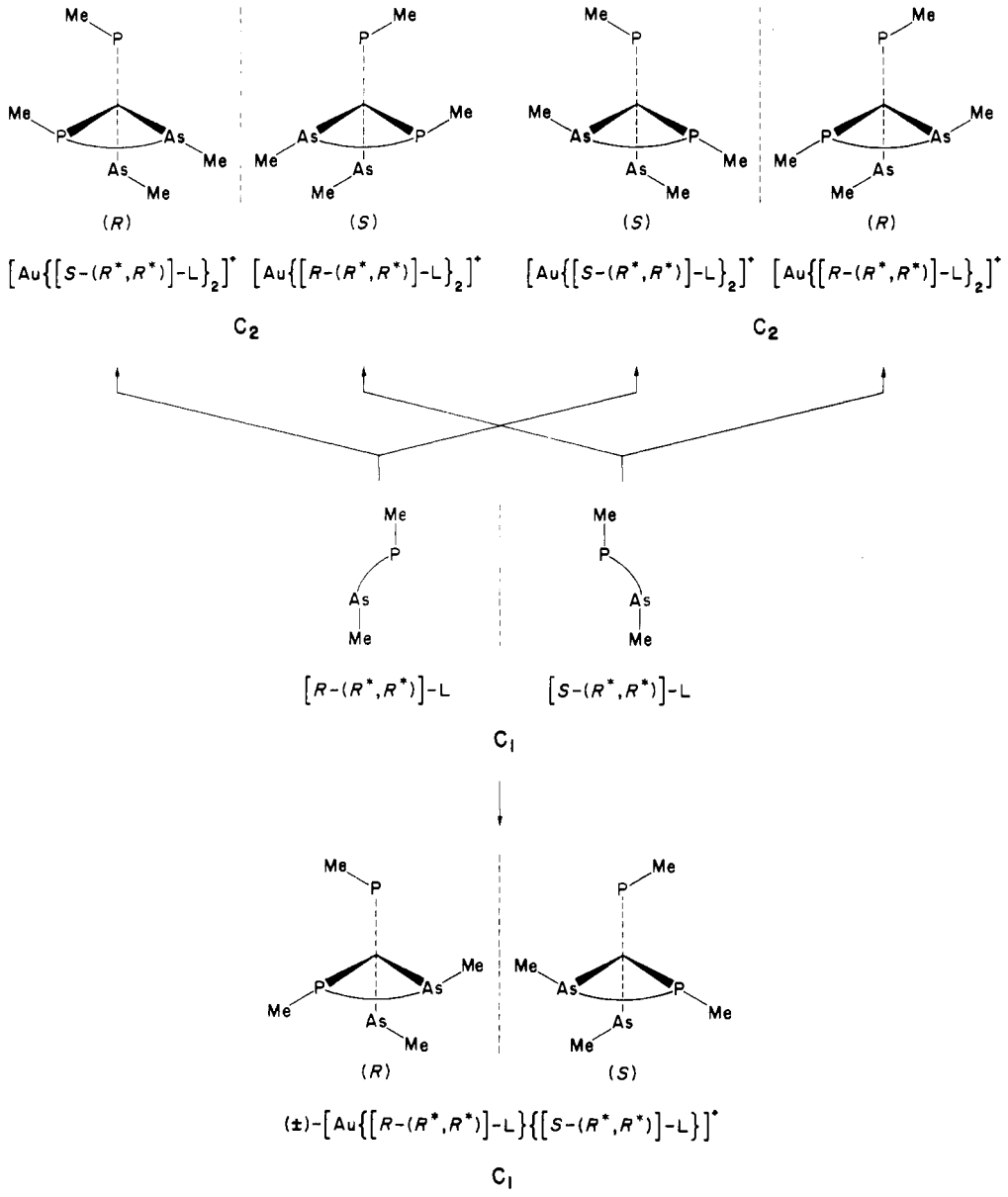

Figure 3. Stereoisomeric cations arising from the enantiomers of (*R**,*R**)-(±)-1-(methylphenylarsino)-2-(methylphenylphosphino)benzene.

perature ^{1}H NMR spectra of (±)-[Au((*R**,*S**)-diph)$_2$]PF_6 are consistent with a low barrier to inversion of the tetrahedral gold(I) atom. At 298 K the half-life for the racemization is 0.8 s as determined from a plot of ln k vs. T^{-1} for the series of rate constants arising from the simulation of the experimentally obtained spectra by use of DNMR3[18] (E_a = 97 ± 14 kJ mol^{-1}). Since bis(tertiary phosphine) complexes of this type are kinetically stable with respect to redistribution of ligands under these conditions (vide supra), this unexpectedly low value of the barrier to racemization of the metal centers accounts for the failure of earlier resolution attempts on similar compounds.[3,4]

The barrier to racemization for the tetrahedral gold(I) atom is lower in complexes of dias and phas. This was determined by analysis of the variable-temperature ^{1}H NMR spectra of the complexes (±)-[Au((*R**,*S**)-bidentate)$_2$]PF_6 for both ligands. Although ligand redistribution is slow enough at 304 K for racemic and meso complexes of the *R**,*R** forms of the ligands to be observed by ^{1}H NMR spectroscopy, racemization of the metal center in the corresponding complexes of the *R**,*S** ligand is too rapid for the nonequivalent methyl groups to be seen under the same conditions. The nonequivalence is evident at 183 K for both complexes, however. Present data are insufficient for detailed comment upon the mechanism of the racemization process, but the trend in rates suggests dissociation of at least one tertiary donor group from the metal may be involved.

Experimental Section

^{1}H NMR spectra were recorded on a Varian HA 100 spectrometer. Optical rotations were measured at 20 °C in a 1-dm cell by use of a Perkin-Elmer Model 241 polarimeter. Elemental analyses were performed by staff within the school.

The ligands were prepared and the diastereoisomers separated and resolved as previously described: 1,2-phenylenebis(methylphenylphosphine),[7] 1,2-phenylenebis(methylphenylarsine),[8] 1-(methylphenylarsino)-2-(methylphenylphosphino)benzene.[9] Tetraethylammonium dibromoaurate(I) was prepared by the method of Braunstein and Clark.[12]

[*T*-4-[*R*-(*R,*R**)]]-Bis[1,2-phenylenebis(methylphenylphosphine)]gold(I) Bromide, (−)-[Au([*R*-(*R**,*R**)]-diph)$_2$]Br.** Solid [*S*-(*R**,*R**)]-diph (2.0 g) was added in portions to a stirred suspension of $Et_4N[AuBr_2]$ (1.5 g) in ethanol (25 mL). A solid derivative formed initially, but this dissolved after stirring for 30 min to give a pale yellow solution. The solvent was evaporated off, and the residue was dissolved in dichloromethane (15 mL); the solution was washed with water and then dried over $MgSO_4$. Dilution of the dried solution with diethyl

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(19) Crocker, C.; Goodfellow, R. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1687.

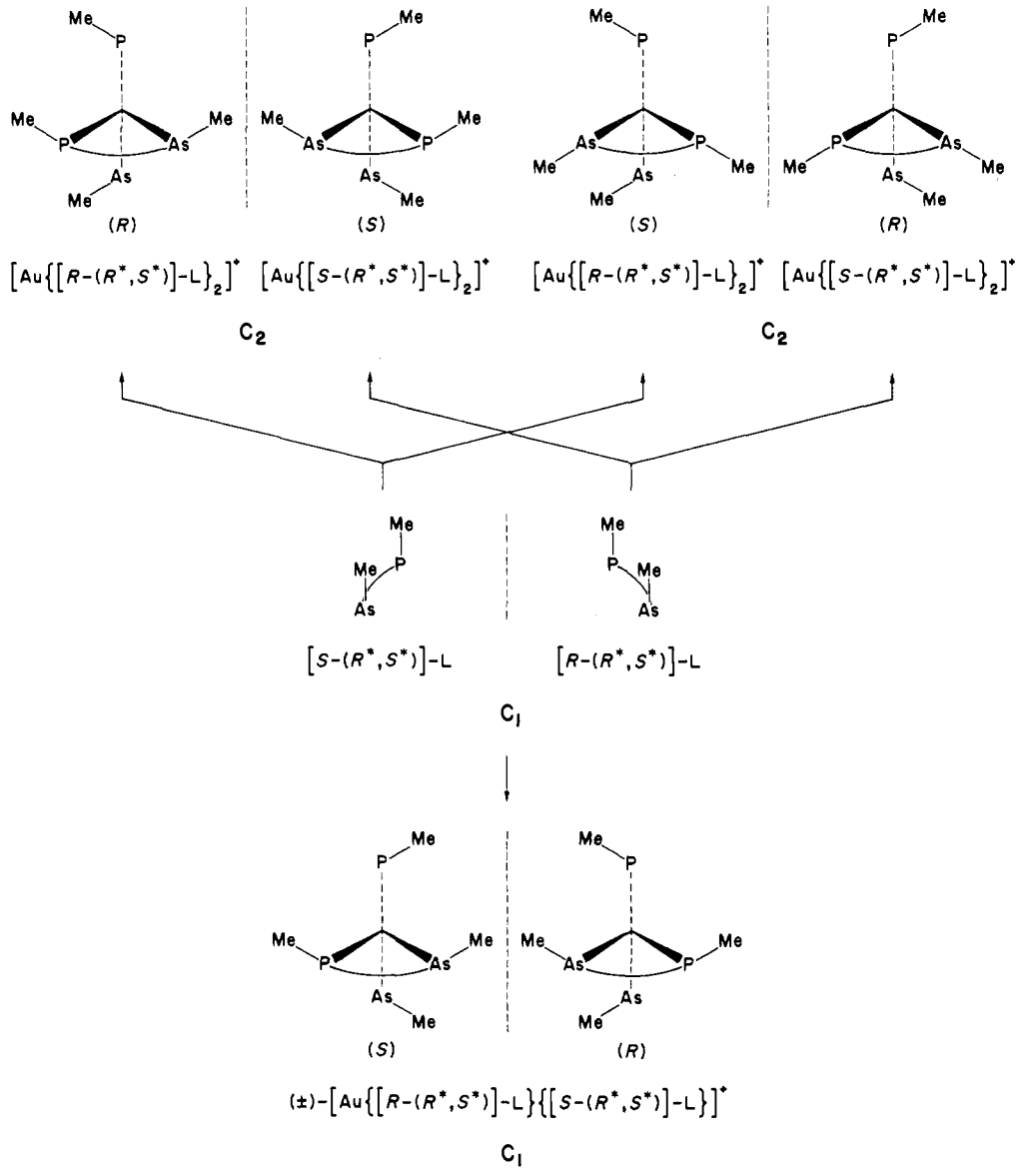

Figure 4. Stereoisomeric cations arising from the enantiomers of (*R**,*S**)-(±)-1-(methylphenylarsino)-2-(methylphenylphosphino)benzene.

ether precipitated the crystalline product, which was recrystallized from the same solvent mixture as colorless needles: mp 230–232 °C; 2.5 g (88%); $[\alpha]_D$ −393° (*c* 0.165, CH_2Cl_2). Anal. Calcd for $C_{40}H_{40}AuBrP_4$: C, 52.1; H, 4.4. Found: C, 52.3; H, 4.4. ^1H NMR data are given in Table I.

[*T*-4-[*R*-(*R,*R**)]]-Bis[1,2-phenylenebis(methylphenylphosphine)]gold(I) Hexafluorophosphate, [Au([*R*-(*R**,*R**)]-diph)$_2$]PF$_6$.** A solution of [Au([*R*-(*R**,*R**)]-diph)$_2$]Br (0.3 g) in methanol (2 mL) was treated with NH_4PF_6 (0.15 g) in water (2 mL). The white precipitate was filtered off and washed with water. After recrystallization from acetone by the addition of diethyl ether, the pure product ws isolated as colorless crystals: mp 217–219 °C; 0.26 g (83%); $[\alpha]_D$ −374° (*c* 0.96, CH_2Cl_2). Anal. Calcd for $C_{40}H_{40}AuF_6P_5$: C, 48.7; H, 4.1. Found: C, 48.9; H, 4.3.

[*T*-4-(*R,*R**)]-(±)-Bis[1,2-phenylenebis(methylphenylphosphine)]gold(I) Bromide, [Au((*R**,*R**)-diph)$_2$]Br.** By use of the above method the racemic complex was obtained from (*R**,*R**)-(±)-diph in 88% yield as colorless needles, mp 163–165 °C. ^1H NMR data (CD_2Cl_2) are identical with those of pure enantiomer (Table I).

[*T*-4-(*R,*R**)]-Bis[1,2-phenylenebis(methylphenylphosphine)]gold(I) Bromide, [Au([*R*-(*R**,*R**)]-diph)([*S*-(*R**,*R**)]-diph)]Br.** A small quantity of (*R**,*R**)-(±)-diph was added to a solution of (±)-[Au((*R**,*R**)-diph)$_2$]Br (3.0 g) in ethanol (15 mL). After ca. 4 h, the solution was filtered and carefully diluted with diethyl ether. The product that crystallized was shown by ^1H NMR to consist of 90% of the desired meso complex and 10% of the hitherto described racemic complex. Recrystallization of the mixture from ethanol–diethyl ether gave pale yellow crystals of the pure meso complex: mp 259–260 °C; 2.3 g (77%). Anal. Calcd for $C_{40}H_{40}AuBrP_4$: C, 52.1; H, 4.4. ^1H NMR data (CD_2Cl_2) are detailed in Table I.

The hexafluorophosphate salts of the racemic and meso complexes containing (*R**,*R**)-(±)-diph were prepared in high yield and purified as described for the corresponding optically active material. Selected properties of the two complexes are given in Table I. The bis(bidentate)gold(I) salts listed in Table I were prepared from the appropriate forms of dias and phas by use of the method detailed for the diph complexes. Elemental analyses were satisfactory for all compounds.

Registry No. (−)-[Au([*R*-(*R**,*R**)]-diph)$_2$]PF$_6$, 87696-79-5; (±)-[Au((*R**,*R**)-diph)$_2$]PF$_6$, 87760-02-9; [Au([*R*-(*R**,*R**)]-diph)([*S*-(*R**,*R**)]-diph)]PF$_6$, 87758-37-0; (±)-[Au((*R**,*S**)-diph)$_2$]PF$_6$, 87758-39-2; (−)-[Au([*R*-(*R**,*R**)]-dias)$_2$]PF$_6$, 87696-81-9; (±)-[Au((*R**,*R**)-dias)$_2$]PF$_6$, 87758-41-6; (±)-[Au(*R**,*S**)-dias)$_2$]PF$_6$, 87758-43-8; (−)-[Au([*R*-(*R**,*R**)]-phas)$_2$]PF$_6$, 87696-83-1; (±)-[Au((*R**,*R**)-phas)$_2$]PF$_6$, 87758-45-0; (−)-[Au([*R*-(*R**,*S**)]-phas)$_2$]PF$_6$, 87758-47-2; (±)-[Au((*R**,*S**)-phas)$_2$]PF$_6$, 87758-49-4; (−)-[Au([*R*-(*R**,*R**)]-diph)$_2$]Br, 87696-84-2; [*S*-(*R**,*R**)]-diph, 72150-63-1; $Et_4N(AuBr_2)$, 50481-00-0; [Au((*R**,*R**)-diph)$_2$]Br, 87758-50-7; (*R**,*R**)-(±)-diph, 72091-01-1; [Au([*R*-(*R**,*R**)]-diph)([*S*-(*R**,*R**)]-diph)]Br, 87758-51-8.