Four-Coordinate Gold(I), Silver(I), and Copper(I) Complexes with a Large-Span Chiral Ditertiary Phosphine Ligand

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The ligand L = $Ph_2PCH_2CHEtOPPh_2$ (*R*,*S*) with two chemically different donor sites and a center of chirality in the middle of the loop connecting the phosphorus atoms has been chosen for the preparation of a series of gold(I), silver(I), and copper(I) complexes. The ligand-to-metal ratio was allowed to vary between 2:1, 1:1, and 1:2. The 1:1 complexes $[LAuX]_2$ with X = Cl, Br, I, and SCN have been found to be components of solution equilibria (in di- or trichloromethane) of various cyclic dinuclear isomers involving also several complexes generated in ligand redistribution processes. However, single crystals (X = Cl, Br) obtained from these solutions are composed solely of centrosymmetrical dimers where the two metal atoms are part of 12-membered rings and are bridged transannularly by two halogen atoms. By symmetry, the metal bridging by the two ligands L follows a head-to-tail pattern and involves a pair of enantiomers of L. The silver compound $[LAgClO_4]_2$ has an analogous structure with the silver atoms attaining coordination number 4 by perchlorate bridging. The copper complex $[LCuCl]_2$ is a tricyclic binuclear compound where each copper atom is chelated by an individual ligand L and doubly halogen bridged with the second metal atom. The 2:1 complex $[L_2Au]Cl$ is assigned a bis-chelated structure with the tetracoordinated metal atom as a spiro center of two six-membered rings. The solution ^{31}P NMR spectra show the presence of various stereoisomers which are readily identified via the strong couplings mediated by the metal center. Only small *J*(P, P′) values would be expected for P−P′ coupling along the ligand PCCOP′ loops. The spectrum of the dinuclear 1:2 complex $L(AuCl)_2$ features only two singlet ^{31}P resonances.

Introduction

The coordination chemistry of gold(I) is dominated by complexes with coordination number two (CN 2) in a linear geometry. The number of examples with higher coordination numbers is growing only slowly, as illustrated by recent reviews.[1]

The majority of these complexes is based on mono- or polydentate tertiary phosphine ligands that are known to be the most powerful ligands for gold(I).[2] There is a limit to the coordination of phosphines at gold(I) caused simply by steric congestion in cations of the formula $[Au(PR_3)_4]^+$ with its rather small metal Au^+ cation,[3] and therefore this type of complex can only be obtained with small phosphines PR_3.[4] The literature still has no fully confirmed example, e.g., of a salt containing the cation $[Au(PPh_3)_4]^+$ with simple triphenylphosphine ligands,[5] and it is only with bidentate tetraphenyldiphosphines, like $Ph_2PCH_2CH_2PPh_2$ (dppe), that clear-cut tetracoordination is reached as in $[Au(dppe)_2]^+$.[6] These compounds have attracted considerable interest because some of the salts show chemotherapeutic potential for the treatment of arthritis, and also antitumor activity.[7]

Bis(diphenylphosphino)methane (dppm), with its smaller bite, does not form a mononuclear, tetracoordinate complex with gold(I), and binuclear species are formed instead.[8] Ditertiary phosphines with a larger ligand span have been investigated repeatedly regarding their chelating or bridging properties for gold(I),[9] but very little is known about ligands where the donor centers are bridged by loops other than simple polymethylene chains $-(CH_2)_n-$.

The present report is a summary of the results of our recent study of gold(I) complexes with a large-span, chiral diphosphine. This work was initiated because the coordination chemistry of gold(I) with chiral ligands is poorly developed even for compounds with the standard CN 2.[10] Stereoisomerism for

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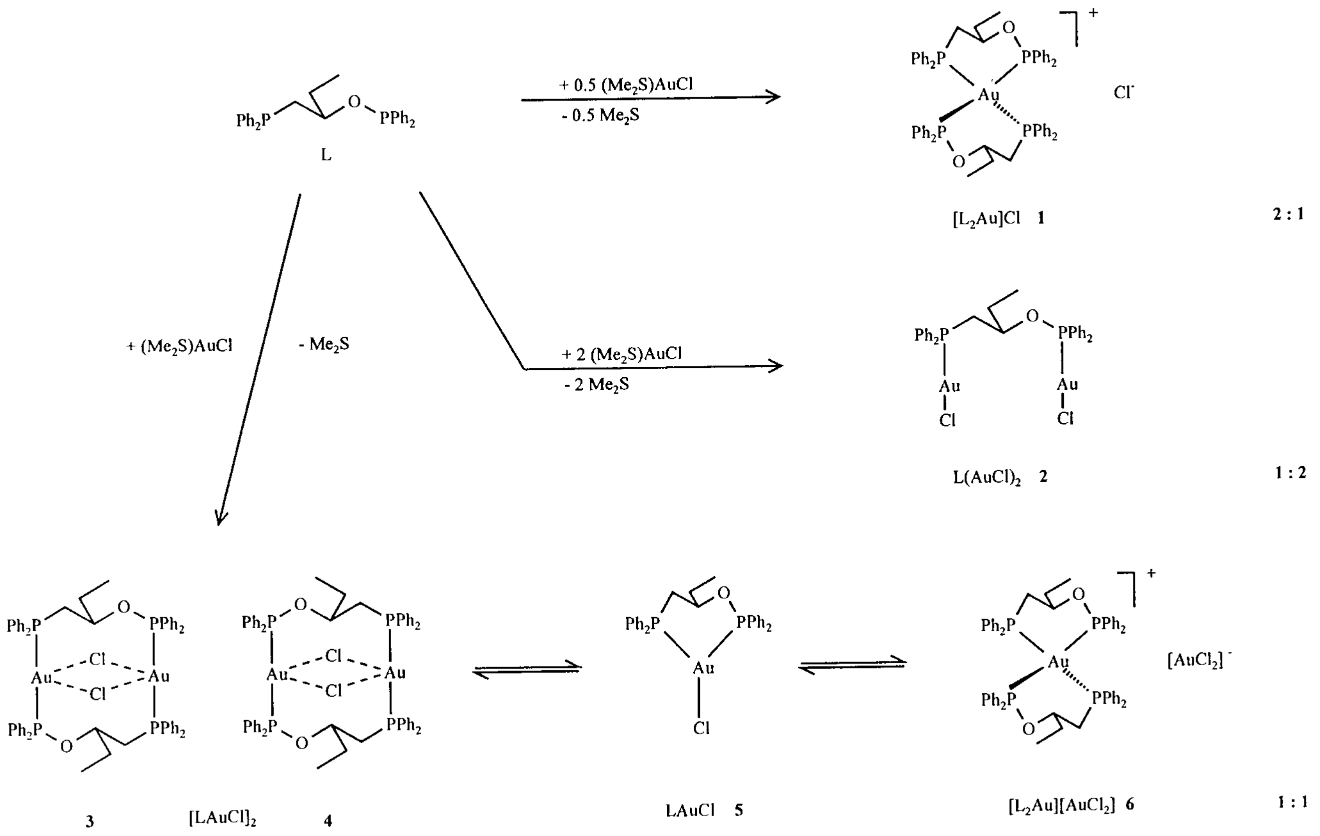
Scheme 1



tetracoordinate (tetrahedral) gold(I) was investigated for only very few isolated cases in the past.[11]

Preparation and Properties of the Complexes

The bidentate ligand L (Scheme 1) chosen for the present investigation was selected as an example where (a) the two phosphorus donor centers are chemically inequivalent (one is a tertiary phosphine, the other is a phosphinite) and (b) the loop connecting these donor centers features a carbon-based center of chirality.

Unsymmetrical bisphosphorus ligands with chemically different phosphorus atoms are of considerable interest because they allow a detailed investigation of coordination compounds of these ligands by ^{31}P NMR spectroscopy.[12]

The racemic ligand L is prepared (in 78% yield) from the reaction of potassium diphenylphosphide and 1,2-epoxybutane, followed by treatment with equivalent quantities of chlorodiphenylphosphine in tetrahydrofuran starting at −78 °C and reaching ambient temperature toward the end of the synthesis. The racemic mixture is obtained as a colorless liquid which can be used without further purification. Its identity and purity were confirmed by NMR spectra.

The 1:1, 2:1, and 1:2 complexes of L with gold(I) chloride are readily prepared by the reaction of appropriate amounts of the ligand and chloro(dimethyl sulfide)gold(I) in tetrahydrofuran at ambient temperature. High yields of crystalline products were obtained for all three stoichiometries (Scheme 1).

The 1:1 complexes of gold(I) bromide, iodide, and thiocyanate were synthesized from bromo(tetrahydrothiophene)gold(I) and equimolar quantities of the ligand L or by anion metathesis using KI or KSCN, respectively, in a two-phase system (H_2O/CH_2Cl_2).

The analogous 1:1 complexes with AgCl, AgBr, $AgClO_4$, and CuCl can be synthesized by treating slurries of these salts in dichloromethane (AgCl, AgBr), tetrahydrofuran ($AgClO_4$), or dichloromethane/acetonitrile (CuCl) with the ligand L.

NMR Spectra and Solution Structures. The 1:2 complex $L(AuCl)_2$ (**2**) is a colorless solid which dissolves readily in chloroform. The ^{31}P NMR spectrum of the solution shows two singlet resonances for the two different ends of the ligand, but only one of these is shifted strongly to lower field (by $\Delta\delta$ 44.2 ppm) as compared to the parent ligand, while the other is displaced by only 2.3 ppm. There is no NMR evidence for the presence of isomers and a simple structure with both phosphorus atoms coordinated to an AuCl unit is proposed, analogous to the findings for 1:2 complexes of dppm, dppe, and their homologues.[9]

By contrast, the solution of the 1:1 complex with AuCl (“LAuCl”) in chloroform shows a very complex $^{31}P\{^1H\}$ NMR spectrum which is indicative of the existence of various isomers (Scheme 1) and ligand redistribution products. The signals are all broad at room temperature, and upon cooling there is extensive splitting into various sets of multiplets, suggesting ligand exchange equilibria.

These equilibria include the products of ligand redistribution such as $[L_2Au]Cl$ and $L(AuCl)_2$ etc., and in fact the resonances of $L(AuCl)_2$ and $[L_2Au]Cl$ (above and below) have been detected in the low-temperature spectrum of “LAuCl”.

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(10) (a) Bayler, A.; Bowmaker, G. A.; Schmidbaur, H. *Inorg. Chem.* **1996**, *35*, 5959. (b) Bayler, A.; Bauer, A.; Schmidbaur, H. *Z. Naturforsch.* **1997**, *52B*, 1477. (c) Papathanasious, P.; Salem, G.; Waring, P.; Willis, A. C. *J. Chem. Soc., Dalton Trans.* **1997**, 3435.

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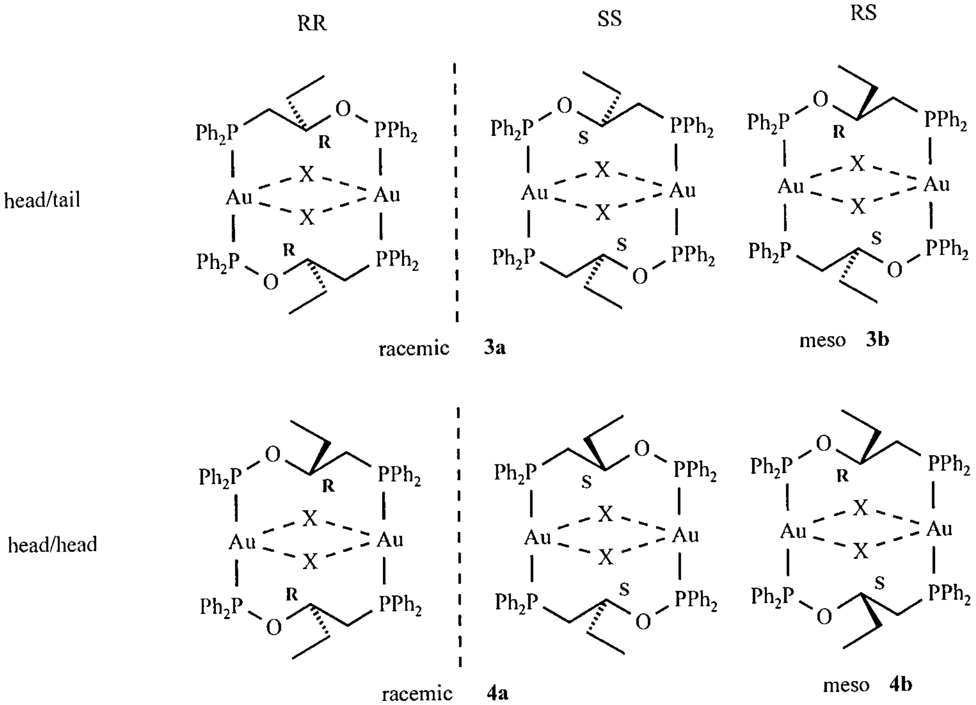
Chart 1. Stereoisomerism in the Annular Dinuclear 1:1 Complexes $[LAuX]_2$ (X = Cl, Br, I, SCN)



Single crystals of “LAuCl” could be grown, and their structure has been determined in a X-ray diffraction study (below). From this study it follows that the compound is a centrosymmetrical dimer in the solid state containing the two L enantiomers bridging the gold atoms in a head-to-tail fashion (**3**). This unit, if persistent in solution, should therefore show only two ^{31}P NMR signals. Since many more resonances are actually observed (also after dissolving the single crystals in chloroform), one has to conclude that this form is undergoing fast ligand scrambling in solution. For a 12-membered ring as present in the crystal, four diastereomers can be drawn, which should exhibit four sets of ^{31}P NMR signals (Chart 1). As already mentioned many more resonances are actually observed owing to ligand redistribution, which has not been followed in detail.

The 1:1 complexes with AuBr, AuI, and AuSCN show similar spectral properties, but fewer species are present in solution, indicating less extensive ligand redistribution.

In the low-temperature spectra of “LAuBr” and “LAuI” in chloroform the resonances of the undissociated annular binuclear complexes $[LAuX]_2$ can be readily identified besides the minor resonances for the ligand redistribution products $[L_2Au]X$ and $L(AuX)_2$. Head-to-tail coordination of the two ligands (**3a**, **3b**) gives rise to a pair of doublets for the phosphino and phosphinito phosphorus atoms, respectively. The coupling constants $^2J_{P,PO}$ = 346 Hz (X = Br) and $^2J_{P,PO}$ = 338 Hz (X = I) are rather large, as expected for linear two-coordinate gold(I) compounds.[13] For the corresponding head-to-head isomers (**4a**, **4b**), two singlets appear in the $^{31}P\{^1H\}$ NMR spectrum and no coupling between the phosphorus atoms through the ligand backbone can be observed.

No further signal splitting indicating the existence of distinct racemic and meso diastereomers could be observed down to −60 °C.

Owing to the presence of two spin $^1/_2$ nuclei $^{107/109}Ag$, the NMR spectra of the 1:1 silver complexes show additional splittings of the phosphorus signals at low temperature, which disappear at room temperature due to ligand scrambling. The systems with X = Cl, Br are complicated by ligand exchange processes to give signal patterns similar to the gold(I) analogues.

In the case of the weakly coordinating anion ClO_4^- this ligand redistribution is a slow process on the NMR time scale and the low-temperature spectrum can be assigned solely to the cyclic dinuclear complexes $[LAgClO_4]_2$ in head-to-tail ($^2J_{P,PO}$ = 168 Hz, $^1J_{^{107}Ag,P}$ = 490 Hz, $^1J_{^{107}Ag,PO}$ = 543 Hz) and head-to-head ($^1J_{^{107}Ag,P}$ = 512, $^1J_{^{107}Ag,PO}$ = 547 Hz) constitution. The coupling constants $^1J_{^{109}Ag,P}$ and $^1J_{^{107}Ag,P}$ are in the ratio of the gyromagnetic factors (1.15) of the two metal isotopes. The $^1J_{^{107}Ag,P}$ values are also in good agreement with literature data reported for other silver(I) derivatives with two tertiary phosphines coordinated to the metal center.[14] Signal splitting due to racemic and meso diastereomers could not be observed for the $AgClO_4$ complex.

The $^{31}P\{^1H\}$ NMR spectrum of the 1:1 complex with CuCl, recorded immediately after dissolving single crystals in chloroform, shows a reduced multiplet complexity. Only a pair of broad doublets for the chemically inequivalent phosphorus atoms appears in the room-temperature spectrum, consistent with a structure as present in the crystal (below), with L chelating the metal center. The observed splitting can be explained by P−P coupling transmitted through the metal center ($^2J_{P,PO}$ = 153 Hz). Broadening of the signals is caused presumably by $^{63/65}Cu-^{31}P$ quadrupole relaxation, as generally observed for phosphine complexes of copper(I) with low symmetry.[15]

After several days additional peaks appear in the spectrum of the solution owing to ligand redistribution processes. The copper complex therefore appears to have a higher kinetic stability compared to the corresponding gold and silver complexes.

The 2:1 Complex $[L_2Au]Cl$. The reaction of two equivalents of L with Me_2SAuCl is proposed to give the bis-chelated

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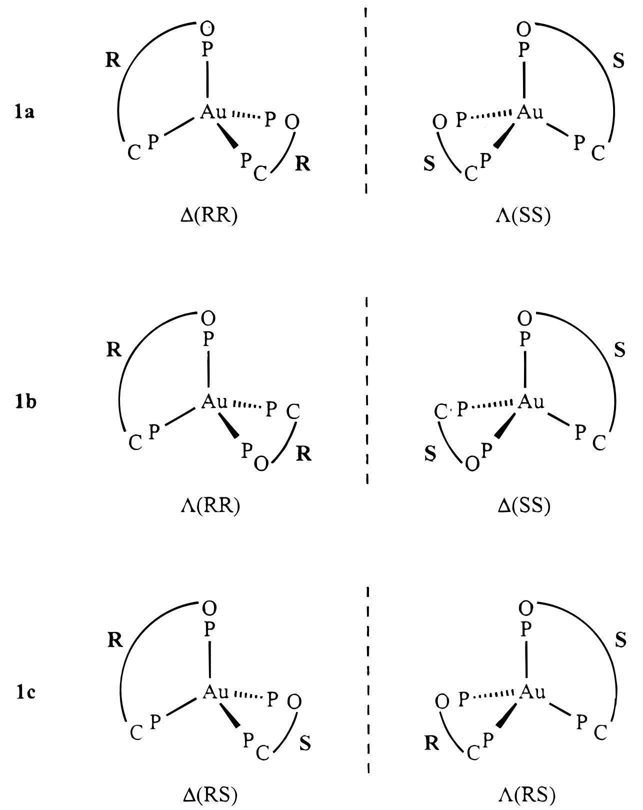
Chart 2. Stereoisomerism in the Tetrahedral Cation of $[L_2Au]Cl$



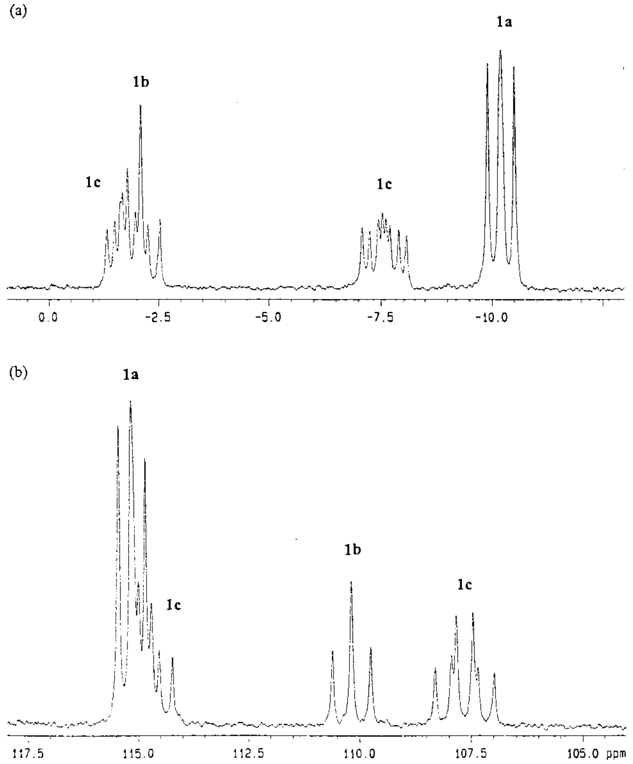


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of $[L_2Au]Cl$ in $CDCl_3$ at −60 °C. (a) Phosphine region; (b) phosphinite region. The spectrum was analyzed as overlapping spin systems for the distinct diastereomers **1a** (AA′XX′), **1b** (BB′YY′), and **1c** (ABXY).

tetracoordinated gold(I) species $[L_2Au]Cl$ (Scheme 1, **1**), based on the observation that the bis(phosphines) dppe and dppp also form stable spiro complexes with gold(I) contained in two five- or six-membered chelate rings.[9a]

Tetrahedral, bis-chelated complexes with unsymmetrical bidentate ligands (with two chemically inequivalent phosphorus atoms in the case of L) can exist as enantiomers with absolute configurations Δ and Λ.[16] For the 2:1 complex of AuCl with the chiral ligand L three pairs of enantiomers have to be considered (Δ(RR), Λ(SS); Λ(RR), Δ(SS); Δ(RS), Λ(RS)) (Chart 2). The spectra at the low-temperature limit indeed show the expected three multiplets, the pattern of which could be analyzed by computing the corresponding AA′XX′ (**1a**), BB′YY′ (**1b**), and ABXY (**1c**) spin systems (Figure 1). Upon warming, coalescence is observed owing to increasingly rapid exchange processes.

As e.g. shown for compounds **2**−**4** (above), P−P′ coupling through the ligand backbone is very small and cannot be resolved for the 1:2 and 1:1 complexes with L bridging two metal centers. The observation of spin systems with large J(P, P′) coupling constants, which lead to complex multiplet patterns for the 2:1 compounds (Figure 1), can thus be taken as indicative of the chelating nature of L, which gives rise to strong P−P′ coupling mediated by the metal center.

Solid State Structures. Single crystals of a quality acceptable for X-ray diffraction studies could only be obtained for the 1:1 complexes of the ligand with AuCl, AuBr, $AgClO_4$, and CuCl.

The two gold(I) halide complexes are isomorphous with only minor differences in the individual molecular structures, and therefore only the bromide $[LAuBr]_2$ is discussed here in detail as a representative example. Crystal data and other details are summarized in Table 1. The molecular structure and the atomic numbering are shown in Figure 2 with selected bond lengths and angles in the figure caption.

The two compounds, $[LAuCl]_2$ and $[LAuBr]_2$, crystallize in the monoclinic space group $P2_1/n$ with two formula units in the unit cell. The lattices contain centrosymmetrical binuclear molecules which feature a 12-membered ring with a transannular double-bridging of the metal atoms by the halogen atoms. The triatomic units P−Au−P are strongly bent [158.96(5)°] owing to the coordination of the two halogen atoms. The two bromo bridges are not symmetrical with distances at Au−Br 3.106(1) and Au−Br′ 3.128(1) Å and the Au−Br−Au′ angles close to rectangular [88.40(5)°].

As governed by the symmetry element of point group C_i the two ligands in the molecule are a pair of enantiomers (R, S), and each gold atom is coordinated to two different ends of the ligands, i.e., Ph_2PCH_2 and Ph_2PO. The sequence of the ligands is thus head-to-tail. The crystallographical refinement of the bridges as CH_2 or O is not entirely conclusive because of the minute differences in the R factors, and some minor disorder has to be admitted, but these are not affecting the basic principle of the structure. (As shown by NMR spectroscopy (above) some isomerization through ligand redistribution also takes place in solution.)

The silver complex $[LAgClO_4]_2$ crystallizes in the triclinic space group $P\bar{1}$ with two formula units in the unit cell. The asymmetric unit contains two halves of crystallographically independent dimers, with the two other halves generated by centers of inversion. One of the two molecules is shown in Figure 3. The two molecules have very similar dimensions and conformations as shown by the superposition presented in Figure 4.

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[16] Ernst, R. E.; O'Connor, M. J.; Holm, R. H. *J. Am. Chem. Soc.* **1967**, *89*, 6104.

Table 1. Crystal Data, Data Collection, and Structure Refinement

	$[LAuCl]_2$	$[LAuBr]_2$	$[LAuClO_4]_2\cdot{}^1/_2CH_2Cl_2$	$[LCuCl]_2$
crystal data				
empirical formula	$C_{56}H_{56}Au_2Cl_2O_2P_4$	$C_{56}H_{56}Au_2Br_2O_2P_4$	$C_{56.5}H_{57}Ag_2Cl_3O_{10}P_4$	$C_{56}H_{56}Cu_2Cl_2O_2P_4$
M_r	1295.72	1438.64	1341.99	1082.87
crystal system	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.496(1)	11.503(1)	11.335(2)	9.315(1)
b (Å)	17.818(1)	17.962(2)	12.881(1)	11.793(1)
c (Å)	12.659(1)	12.727(1)	21.766(2)	13.010(1)
α (deg)	90	90	94.89(1)	102.37(1)
β (deg)	98.20(1)	97.88(1)	91.85(1)	103.51(1)
γ (deg)	90	90	113.33(1)	104.89(1)
V (Å^3)	2566.5(5)	2604.8(4)	2899.9(6)	1284.5(2)
ρ_{calc} (g cm^{-3})	1.747	1.834	1.537	1.400
Z	2	2	2	1
F(000)	1320	1392	1362	560
μ(Mo Kα) (cm^{-1})	59.80	73.24	9.80	10.98
data collection				
T (°C)	−74	−74	−91	−78
scan mode	ω	$\omega-\theta$	ω	$\omega-\theta$
hkl range	−14→14, 0→21, 0→15	0→14, 0→22, −16→16	−13→13, −15→15, 0→26	−11→11, −15→13, −16→16
$\sin(\theta/\lambda)_{max}$ (Å^{-1})	0.62	0.64	0.62	0.64
no. of measd reflcns	5269	5919	11323	11311
no. of unique reflcns	5037 [$R_{int} = 0.0189$]	5648 [$R_{int} = 0.0289$]	11323	5598 [$R_{int} = 0.0207$]
no. of reflcns used for refinement	4993	5605	9692	5274
abs corrn	ψ scans	ψ scans	none	none
T_{min}/T_{max}	0.66/0.99	0.45/0.99	−	−
refinement				
no. of refined parameters	298	298	694	300
final R values [$I > 2\sigma(I)$]				
$R1^a$	0.0317	0.0395	0.0436	0.0437
$wR2^b$	0.0642	0.0920	0.1035	0.1178
(shift/error)$_{max}$	<0.001	<0.001	<0.001	<0.001
ρ_{fin}(max/min) (e Å^{-3})	1.303/−0.769	2.256/−1.161	0.763/−0743	0.834/−0.776

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0238$ ($[LAuCl]_2$), 0.0464 ($[LAuBr]_2$), 0.0631 ($[LAuClO_4]_2\cdot{}^1/_2CH_2Cl_2$), 0.0801 ($[LCuCl]_2$); $b = 5.89$ ($[LAuCl]_2$), 9.50 ($[LAuBr]_2$), 0.31 ($[LAuClO_4]_2\cdot{}^1/_2CH_2Cl_2$), 0.59 ($[LCuCl]_2$).

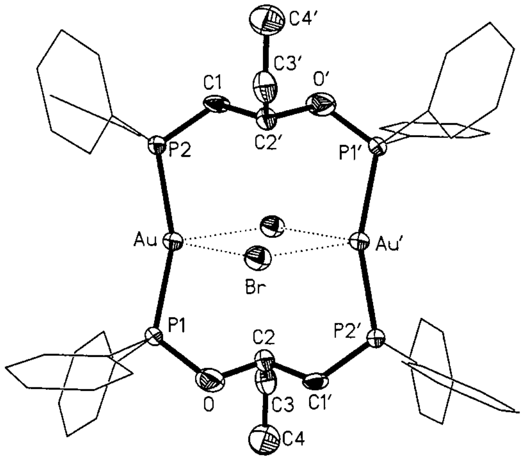

Figure 2. Molecular structure of compound $[LAuBr]_2$ (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Au−P1, 2.294(1); Au−P2, 2.304(1); Au−Br, 3.106(1); Au−Br′, 3.128(1); P1−Au−P2, 158.96(5); Au−Br−Au′, 88.40(5).

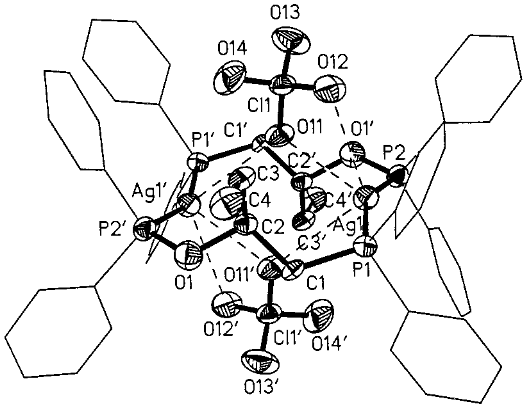

Figure 3. Molecular structure of compound $[LAuClO_4]_2$ (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Ag1−P1, 2.401(1); Ag1−P2, 2.408(1); Ag1−O11, 2.626(1); Ag1−O11′, 2.905(1); P1−Ag1−P2, 157.13(4); Ag1−O11−Ag1′, 107.30(5).

Pairs of ligand enantiomers L (*R*, *S*) are bridging the two metal atoms (head-to-tail) to give 12-membered rings with the silver atoms connected transannularly and unsymmetrically by perchlorate anions above and below the ring. Each perchlorate anion is chelating one of the silver atoms and bridging the two symmetry-related silver atoms via one oxygen atom, e.g. O11 bridging Ag1 and Ag1′. The 12-membered rings are more heavily puckered than the gold heterocycles (above), but the angles P−Ag−P at the silver atoms [P1−Ag1−P2, 157.13(4)°; P3−Ag2−P4, 157.63(5)°] are about the same as in the gold compounds. There is again some crystallographic disorder (ring folding and CH_2/O substitution) in the ligand bridges, reminiscent of the ligand scrambling observed for solutions of the compound by NMR spectroscopy.

Crystals of the copper(I) complex $[LCuCl]_2$ (triclinic, space group $P\bar{1}$, $Z = 1$) also contain dinuclear complex molecules, but the ligands L are chelating rather than bridging the metal centers (Figure 5). The two ligands are related by a crystallographic center of inversion and are thus enantiomers (*R*, *S*). The copper atoms are bridged unsymmetrically by two chloride

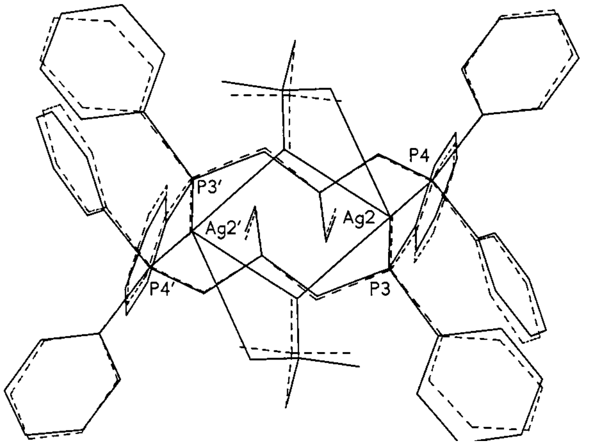

Figure 4. Superposition of the two independent molecules of $[LAuClO_4]_2$.

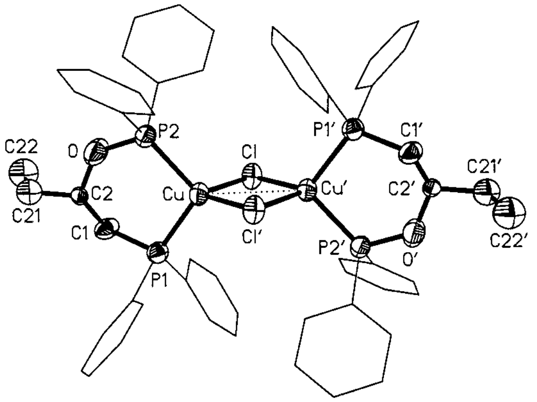

Figure 5. Molecular structure of compound $[LCuCl]_2$ (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Cu−P1, 2.2455(7); Cu−P2, 2.2186(8); Cu−Cl, 2.3055(8); Cu−Cl′, 2.4218(7); P1−Cu−P2, 103.10(3); Cu−Cl−Cu′, 79.54(2); Cl−Cu−Cl′, 100.46(2).

anions [Cu−Cl, 2.3055(8) Å; Cu−Cl′, 2.4218(7) Å] with large angles at Cu/Cu′ [100.46(2)°] and small angles at Cl/Cl′ [79.54(2)°]. Each copper atom is thus a spiro center for a six- and a four-membered ring.[17]

This structure (Figure 5) reflects the preference of copper(I) for fully tetrahedral coordination as opposed to silver(I) and in particular to gold(I) where linear two-coordination is more common. Because of the small covalent radius of copper(I), the transannular Cu---Cu′ contact [3.0255(6) Å] is not expected to contribute significantly to the bonding in the four-membered ring, while Ag---Ag and Au---Au contacts of this order of magnitude would have to be taken as sub-van der Waals distances.[18] However, the distances in $[LAgClO_4]_2$ and $[LAuCl]_2$ above are well beyond this critical range.

Experimental Section

All experiments were carried out under dry, purified nitrogen. Solvents were dried, distilled and stored over molecular sieves in a nitrogen atmosphere. Glassware was oven-dried, evacuated, and filled with nitrogen. Chloro(dimethyl sulfide)gold(I)[19] and bromo(tetrahydrothiophene)gold(I) [(tht)AuBr][20] were prepared according to established literature procedures.

NMR: JEOL JNM-GX 400 and JEOL JNM-LA 400 instruments; $CDCl_3$ as solvent and internal standard, converted to TMS for ^1H and $^{13}C\{^1H\}$; H_3PO_4 (85%) as external standard for $^{31}P\{^1H\}$; spectra were measured at room temperature or as otherwise noted. MS: Finnigan MAT 90 (fast atom bombardment).

***R*/*S*-(1-Diphenylphosphinobut-2-yl)diphenylphosphinite (L).** A solution of potassium diphenylphosphide (5.0 mmol) in 30 mL of THF is cooled to −78 °C and 1,2-epoxybutane (7.5 mmol, 650 μL) is added. Upon warming to room temperature within 3 h the color of the reaction mixture changes from intense orange to pale yellow. Chlorodiphenylphosphine (5.0 mmol, 674 μL) is then added dropwise, and the resulting turbid solution is stirred for 2 h at ambient temperature. The solvent is removed under reduced pressure, and the residue is extracted with diethyl ether (2 × 20 mL). The resulting colorless solution of L in diethyl ether is stable at −30 °C and can be used for the following reactions without further purification; yield 1.73 g (78%).

^1H NMR: δ 0.80 (t, $^3J_{H,H} = 7.3$ Hz, 3H) CH_3; 1.62−1.83 (m, 2H) $CH_2{-}CH_3$; 2.27 (dd, $^2J_{H,H} = 13.8$ Hz, $^2J_{H,P} = 7.5$ Hz, 1H), 2.53 (dd, $^2J_{H,H} = 13.8$ Hz, $^2J_{H,P} = 5.9$ Hz, 1H) $CH_2{-}P$; 3.89 (m, 1H) CH; 7.15−7.70 (m, 20 H) arene H. $^{13}C\{^1H\}$ NMR: δ 9.7 (s) CH_3; 30.1 (dd, $^3J_{C,P} = 4.6$ Hz, $^3J_{C,P'} = 7.7$ Hz) $CH_2{-}CH_3$; 35.8 (dd, $^1J_{C,P} = 15.3$ Hz, $^3J_{C,P'} = 5.4$ Hz) $CH_2{-}P$; 80.6 (dd, $^2J_{C,P} = 20.0$ Hz, $^2J_{C,P'} = 17.7$ Hz) CH; 128.7−133.4 (m) $C_{2/3/4/5/6}$; 139.1 (d, $^1J_{C,P} = 13.8$ Hz), 139.4 (d, $^1J_{C,P} = 13.0$ Hz) $C_1{-}P$; 143.4 (d, $^1J_{C,P'} = 16.9$ Hz), 143.5 (d, $^1J_{C,P'} = 17.7$ Hz) $C_1{-}PO$. $^{31}P\{^1H\}$ NMR: δ −23.2 (d, $^4J_{P,PO} = 7.0$ Hz) $Ph_2P{-}R$; 107.4 (d, $^4J_{P,PO} = 7.0$ Hz) $Ph_2P{-}OR$.

$L(AuCl)_2$. The phosphine L (93 mg, 0.21 mmol) and Me_2SAuCl (124 mg, 0.42 mmol) are dissolved in 10 mL of THF to give a colorless solution, which is stirred for 1 h at ambient temperature. Addition of pentane leads to precipitation of the white product, which is filtered off, washed with pentane, and dried in a vacuum to yield 173 mg (90%).

^1H NMR: δ 0.77 (t, $^3J_{H,H} = 7.3$ Hz, 3H) CH_3; 1.75−1.87 (m, 2H) $CH_2{-}CH_3$; 2.78 (ddd, $^2J_{H,H} = 13.8$ Hz, $^2J_{H,P} = 11.0$ Hz, $^3J_{H,H} = 6.3$ Hz, 1H), 3.17 (ddd, $^2J_{H,H} = 13.8$ Hz, $^2J_{H,P} = 11.3$ Hz, $^3J_{H,H} = 5.5$ Hz, 1H) $CH_2{-}P$; 4.51 (m, 1H) CH; 7.30−7.82 (m, 20 H) arene H. $^{13}C\{^1H\}$ NMR: δ 9.1 (s) CH_3; 29.4 (dd, $^3J_{C,P} = 6.6$ Hz, $^3J_{C,P'} = 4.5$ Hz) $CH_2{-}CH_3$; 33.8 (dd, $^1J_{C,P} = 36.4$ Hz, $^3J_{C,P'} = 5.4$ Hz) $CH_2{-}P$; 80.2 (s) CH; 128.0−128.9 (m) C_1; 129.0−129.8 (m) $C_{3/5}$; 131.9−133.5 (m) $C_{2/4/6}$. $^{31}P\{^1H\}$ NMR: δ 21.0 (s) $Ph_2P{-}R$; 109.7 (s) $Ph_2P{-}OR$.

L_2AuCl. To a solution of L (413 mg, 0.94 mmol) in 20 mL of THF is added Me_2SAuCl (138 mg, 0.47 mmol) at room temperature, and the resulting clear solution is stirred for 1 h. Upon addition of pentane a pale yellow precipitate is obtained, which is filtered off and dried in a vacuum; yield 430 mg (82%). ^1H NMR: δ 0.75 (t, b, 3H) CH_3; 1.6−1.8 (m, b, 2H) $CH_2{-}CH_3$; 2.4 (m, b, 1H), 2.8 (m, b, 1H) $CH_2{-}P$; 3.5 (m, b, 1H) CH; 6.8−7.8 (m, 20 H) arene H. $^{31}P\{^1H\}$ NMR: δ −5 (m, b) $Ph_2P{-}R$; 113 (m, b) $Ph_2P{-}OR$. MS (FAB), *m*/*z*: 1081.9 (100) $[L_2Au]^+$, 639.5 (57) $[LAu]^+$.

$[LAuCl]_2$. L (648 mg, 1.46 mmol) is dissolved in 20 mL of THF and Me_2SAuCl (431 mg, 1.46 mmol) is added. After stirring for 1 h at room temperature the solution is evaporated to dryness. Recrystallization of the residue from dichloromethane/pentane affords the product as colorless crystals suitable for X-ray diffraction; yield 620 mg (63%). $^{31}P\{^1H\}$ NMR, $[L_2AuCl]$: δ −5 (m, b) $Ph_2P{-}R$; 113 (m, b) $Ph_2P{-}OR$. $[L(AuCl)_2]$: δ 21.0 (s, b) $Ph_2P{-}R$; 109.7 (s, b) $Ph_2P{-}OR$. MS (FAB), *m*/*z*: 1313.7 (28) $[L_2Au_2{}^{37}Cl]^+$, 1311.7 (52) $[L_2Au_2{}^{35}Cl]^+$, 1080.9 (22) $[L_2Au]^+$, 871.9 (30) $[LAu_2{}^{37}Cl]^+$, 869.9 (77) $[LAu_2{}^{35}Cl]^+$, 638.2 (100) $[LAu]^+$.

$[LAuBr]_2$. L (110 mg, 0.25 mmol) and (tht)AuBr (91 mg, 0.25 mmol) are dissolved in 10 mL of CH_2Cl_2 to give a colorless solution, which is stirred for 1 h at ambient temperature. Careful layering of the solution with hexane induces precipitation of the product as colorless crystals suitable for X-ray diffraction; yield 142 mg (79%). $^{31}P\{^1H\}$ NMR (−60 °C): $[LAuBr]_2$: δ 31.9 (d, $^2J_{P,PO} = 346$ Hz) $Ph_2P{-}R$; 128.9

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(d, $^2J_{P,PO}$ = 346 Hz) $Ph_2P{-}OR$. 32.0 (s) $Ph_2P{-}R$; 126.5 (s) $Ph_2P{-}OR$. $[L(AuBr)_2]$: δ 23.3 (s) $Ph_2P{-}R$; 112.2 (s) $Ph_2P{-}OR$. $[L_2AuBr]$ data are very similiar to those of $[L_2AuCl]$. MS (FAB), *m*/*z*: 1358.3 (27) $[L_2Au_2Br]^+$, 1080.3 (26) $[L_2Au]^+$, 916.4 (31) $[LAu_2{}^{81}Br]^+$, 914.4 (31) $[LAu_2{}^{79}Br]^+$, 638.6 (48) $[LAu]^+$. Anal. Calcd for $C_{56}H_{56}P_4O_2Au_2Br_2$ (1438.77): C, 46.75; H, 3.92; Au, 27.4. Found: C, 46.46; H, 3.89; Au, 28.1.

$[LAuI]_2$. A 10 mL amount of an aqueous solution of KI (1.0 g, excess) is added to a solution of $[LAuCl]_2$ (135 mg, 0.2 mmol) in 10 mL of CH_2Cl_2. The resulting two-phase system is stirred vigorously for 5 h. The aqueous layer is separated and washed with 10 mL of CH_2Cl_2. The dichloromethane extracts are combined and dried with $MgSO_4$, and the solvent is evaporated in a vacuum to leave a white crystalline product. Crystals obtained from dichloromethane/pentane were not suitable for X-ray diffraction; yield 254 mg (83%). $^{31}P\{^1H\}$ NMR, $[LAuI]_2$: δ 29.2 (d, $^2J_{P,PO}$ = 338 Hz) $Ph_2P{-}R$; 126.5 (d, $^2J_{P,PO}$ = 338 Hz) $Ph_2P{-}OR$. 28.5 (s) $Ph_2P{-}R$; 111.4 (s) $Ph_2P{-}OR$. $[L(AuI)_2]$: δ 24.9 (s) $Ph_2P{-}R$; 113.9 (s) $Ph_2P{-}OR$. MS (FAB), *m*/*z*: 1404.3 (3) $[L_2Au_2I]^+$, 1080.3 (2) $[L_2Au]^+$, 962.2 (5) $[LAu_2I]^+$, 638.6 (4) $[LAu]^+$. Anal. Calcd for $C_{56}H_{56}P_4O_2Au_2I_2$ (1532.77): C, 43.88; H, 3.68; Au, 25.7. Found: C, 43.64; H, 3.53; Au, 26.3.

$[LAuSCN]_2$. The procedure given above for $[LAuI]_2$ was followed, using 1.0 g of KSCN and 135 mg (0.2 mmol) of $[LAuCl]_2$. The product is obtained as a yellow crystalline solid; yield 240 mg (86%). $^{31}P\{^1H\}$ NMR, $[L_2AuSCN]$: data similar to $[L_2AuCl]$. $[L(AuSCN)_2]$: δ 27.6 (s, b) $Ph_2P{-}R$; 117.4 (s, b) $Ph_2P{-}OR$. MS (FAB), *m*/*z*: 1337.4 (40) $[L_2Au_2SCN]^+$, 1081.9 (52) $[L_2Au]^+$, 894.5 (74) $[LAu_2SCN]^+$, 639.4 (100) $[LAu]^+$. Anal. Calcd for $C_{56}H_{56}P_4O_2Au_2S_2N_2$ (1395.13): C, 49.93; H, 4.05; S, 4.6; N, 2.01. Found: C, 48.26; H, 4.16; S, 5.2; N, 2.05.

$[LAgCl]_2$. AgCl (67 mg, 0.47 mmol) is suspended in a solution of L (207 mg, 0.47 mmol) in 15 mL of CH_2Cl_2, and the mixture is stirred for 18 h with protection against incandescent light at room temperature. The resulting clear solution is concentrated under vacuum and layered with pentane to precipitate the product as colorless crystals, which are filtered off, washed with pentane, and dried in a vacuum; yield 195 mg (71%). $^{31}P\{^1H\}$ NMR: δ −3 (b) $Ph_2P{-}R$; 114 (b) $Ph_2P{-}OR$. MS (FAB), *m*/*z*: 1423.7 (4) $[L_2Ag_4Cl_3]^+$, 1279.6 (7) $[L_2Ag_3Cl_2]^+$, 1135.6 (4) $[L_2Ag_2Cl]^+$, 993.7 (27) $[L_2{}^{109}Ag]^+$, 991.7 (25) $[L_2{}^{107}Ag]^+$, 693.1 (50) $[LAg_2Cl]^+$, 551.1 (92) $[L^{109}Ag]^+$, 549.1 (100) $[L^{107}Ag]^+$. Anal. Calcd for $C_{56}H_{56}P_4O_2Ag_2Cl_2$ (1171.60): C, 57.41; H, 4.82; Ag, 18.41. Found: C, 57.07; H, 4.81; Ag, 17.7.

$[LAgBr]_2$. The procedure given above was followed using 66 mg (0.35 mmol) of AgBr and 149 mg (0.35 mmol) of L; yield 150 mg (68%). $^{31}P\{^1H\}$ NMR: δ −5 (b) $Ph_2P{-}R$; 112 (b) $Ph_2P{-}OR$. MS (FAB), *m*/*z*: 1369.7 (3) $[L_2Ag_3Br_2]^+$, 1181.7 (8) $[L_2Ag_2Br]^+$, 993.7 (16) $[L_2{}^{109}Ag]^+$, 991.7 (16) $[L_2{}^{107}Ag]^+$, 737.2 (60) $[LAg_2Br]^+$, 551.2 (91) $[L^{109}Ag]^+$, 549.1 (100) $[L^{107}Ag]^+$. Anal. Calcd for $C_{56}H_{56}P_4O_2Ag_2Br_2$ (1260.50): C, 53.36; H, 4.48. Found: C, 52.61; H, 4.46.

$[LAgClO_4]_2$. A solution of $AgClO_4$ (106 mg, 0.51 mmol) in 5 mL of THF and a solution of L (227 mg, 0.51 mmol) in 10 mL of THF are mixed and stirred for 1 h at ambient temperature. After a few minutes, precipitation of a pale yellow product begins, which is completed by the addition of 20 mL of hexane. The product is filtered off, washed with hexane, and dried in a vacuum. Colorless crystals suitable for X-ray diffraction were obtained by layering a dichloromethane solution with pentane; yield 203 mg (61%). $^{31}P\{^1H\}$ NMR: δ 3.4 (2dd, $^2J_{P,PO}$ = 168 Hz, $^1J_{^{107}Ag,P}$ = 490 Hz, $^1J_{^{109}Ag,P}$ = 563 Hz) $Ph_2P{-}R$; 115.8 (2dd, $^2J_{P,PO}$ = 168 Hz, $^1J_{^{107}Ag,PO}$ = 543 Hz, $^1J_{^{109}Ag,PO}$ = 622 Hz) $Ph_2P{-}OR$. 5.4 (2d, $^1J_{^{107}Ag,P}$ = 512 Hz, $^1J_{^{109}Ag,P}$ = 587 Hz) $Ph_2P{-}R$; 116.0 (2d, $^1J_{^{107}Ag,PO}$ = 547 Hz, $^1J_{^{109}Ag,PO}$ = 628 Hz) $Ph_2P{-}OR$. MS (FAB), *m*/*z*: 1197.6 (16) $[L_2Ag_2ClO_4]^+$, 993.0 (9) $[L_2{}^{109}Ag]^+$, 991.0 (10) $[L_2{}^{107}Ag]^+$, 550.3 (95) $[L^{109}Ag]^+$, 548.3 (100) $[L^{107}Ag]$. Anal. Calcd for $C_{56}H_{56}P_4O_{10}Cl_2Ag_2$ (1299.60): C, 51.76; H, 4.34; Ag, 16.6. Found: C, 51 65; H, 4.09; Ag, 16.4.

$[LCuCl]_2$. CuCl (43 mg, 0.43 mmol) is added to a solution of L (183 mg, 0.43 mmol) in 20 mL of dichloromethane/acetonitrile (1:1) and the resulting suspension is stirred for 22 h at room temperature. The turbid solution is filtered and the volatiles are removed from the filtrate in a vacuum. Recrystallization of the residue from dichloromethane/diethyl ether affords the product as colorless crystals suitable for X-ray diffraction; yield 151 mg (65%). $^{31}P\{^1H\}$ NMR: δ −23.0 (d, b, $^2J_{P,P}$ = 153 Hz) $Ph_2P{-}R$; 92.0 (d, b, $^2J_{P,P}$ = 153 Hz) $Ph_2P{-}OR$. MS (FAB), *m*/*z*: 1047.7 (6) $[L_2Cu_2Cl]^+$, 947.7 (31) $[L_2Cu]^+$, 605.2 (42) $[LCu_2Cl]^+$, 540.2 (34) $[LCuCl]^+$, 505.3 (100) $[LCu]^+$. Anal. Calcd for $C_{56}H_{56}P_4O_2Cu_2Cl_2$ (1082.96): C, 62.11; H, 5.21. Found: C, 61.45; H, 5.50.

Crystal Structure Determinations. Specimens of suitable quality and size were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection on an Enraf Nonius CAD4 diffractometer (Mo Kα radiation, λ(Mo Kα) = 0.710 73 Å). During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. Lp correction was applied. The structures were solved by Patterson and direct methods ($[LCuCl]_2$), respectively (SHELXS-86), and completed by full-matrix least-squares techniques against F^2 (SHELXL-93). The thermal motion of all nonhydrogen atoms was treated anisotropically, except for those of the CH_3CH_2 unit of $[LCuCl]_2$, which was disordered and refined isotropically in split positions (50:50). Due to very large thermal parameters of the solvent CH_2Cl_2 in the lattice of $[LAgClO_4]_2$, its occupancy was lowered to 50%. All structures suffered from a disorder in the bridging atoms, were the assignment of CH_2 and O was not entirely conclusive. Attempts to resolve this disorder were not successful. All hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{iso(fix)} = 1.5U_{eq}$ of the attached C atom). Further information on crystal data, data collection, and structure refinement are summarized in Table 1. Important interatomic distances and angles are shown in the corresponding figure captions.

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Supporting Information Available: Tables of data collection and refinement parameters, atomic coordinates, and thermal parameters including hydrogens, complete bond distances and angles, and anisotropic displacement parameters (20 pages). Ordering information is given on any current masthead page.

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