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Architecture of Crystalline Polymers Formed from the Binuclear Complexes $XAuPh_2P(CH_2)_nPPh_2AuX$ through Weak Au(I)$\cdots$Au(I) Interactions

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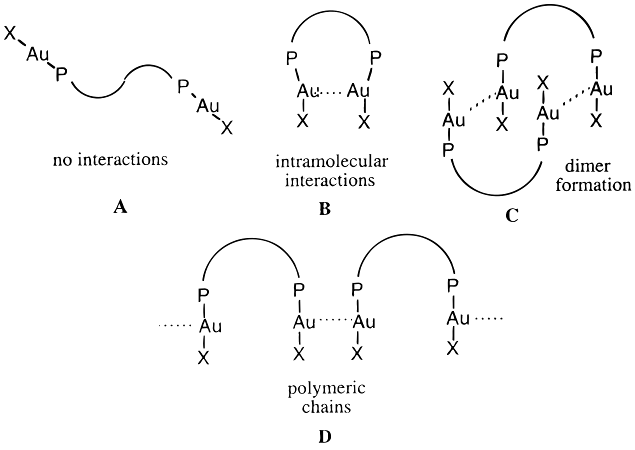
A systematic study is reported of the effects of weak attractive Au$^{I}\cdots$Au^{I} interactions on the solid state structures of six crystalline polymers from molecules of the type XAuP*n*PAuX, where X is iodide or chloride and P*n*P is $Ph_2P(CH_2)_nPPh_2$ with $n = 4-8$. Crystallographic data for the six molecules IAuP4PAuI, IAuP5PAuI, IAuP6PAuI, ClAuP7PAuCl·CH_3OH, IAuP8PAuI·CH_2Cl_2, and ClAuP8PAuCl·CH_2Cl_2 are presented. In each case, the complexes appear to be symmetrical monomeric species in solution, as shown by the simple, single-line ^{31}P NMR spectra. However, they form linear chains in the solid state with individual molecules connected through close Au$\cdots$Au contacts at each end of the molecule. These solids are analyzed in terms of the structures of individual molecules, geometries of Au$\cdots$Au interactions, methods of chain propagation, and relative orientations of individual chains. Only two types of propagation (pure translation and translation along a glide plane) of individual molecules are observed. The chains arrange themselves in three motifs: strands that run parallel, layers of strands that criss-cross, and layers with an interwoven strand structure.

Introduction

Extended solid state structures have the potential for novel mechanical, magnetic, electronic, and optical properties. A challenge facing synthetic chemists is the utilization of molecular self-assembly techniques to build extended structures from small molecular or ionic compounds. Self-assembly occurs as weak intermolecular interactions arrange monomeric complexes into a larger, and often more interesting, supramolecular architecture.[1] Success in this area has been achieved by utilizing hydrogen bonds,[2,3] metal coordination,[4,5] and shaped van der Waals forces.[6]

Contacts between linearly coordinated Au(I) centers that are closer than 3.5 Å are considered attractive auriophilic interactions.[8−10] Theoretical work has revealed that this weakly bonding interaction is the result of correlation effects that are enhanced by relativistic effects.[11] The strength of this attraction has been determined experimentally to be ca. 7−11 kcal/mol.[12,13] Theoretical studies by Pyykkö and co-workers predicted an increase in the strength of this auriophilic interaction for the H_3PAuX system in the series $X = F < CH_3 < H < Cl < CN < Br < I <$ -SCH_3.[11] In this laboratory, this trend has been confirmed for the compounds Me_2PhAuX (X = Cl, Br, I) where the Au(I)$\cdots$(I) contacts decrease in the order Cl > Br > I.[14] A similar trend has been seen for the pair of complexes (1,3,5-triaza-7-phosphaadamantane)AuX (X = Cl, Br).[15]

Chart 1. Structural Motifs for Bridged Digold Complexes



Such Au(I)$\cdots$Au(I) interactions have the potential to self-assemble superstructures through intermolecular interactions. Neutral digold complexes of the type XAu(μ-ditertiary phosphine)AuX, where X is a halide, have the ability to crystallize in one of the four motifs shown in Chart 1. These involve molecules with no intermolecular interactions, **A**,[16] molecules with intramolecular interactions, **B,**[17] molecules that form discrete dimers, **C**,[18,19] and molecules that assemble into polymeric chains, **D**.[16,20] Thus ClAuP1PAuCl[21] has an intramo-

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Table 1. Selected Interatomic Distances (Å) for the Gold Complexes

	IAuP4PAuI	IAuP5PAuI	IAuP6PAuI	ClAuP7PAuCl	ClAuP8PAuCl	IAuP8PAuI
Au···Au	3.148(1)	3.031(1)	3.124(2)	3.264(2)	3.230(1)	3.130(1)
Au−P	2.264(3)	2.252(3)	2.265(8)	2.195(6)	2.246(4)	2.254(4)
			2.254(7)	2.220(5)	2.238(5)	2.256(5)
Au−Cl	2.588(1)	2.572(4)	2.577(2)	2.392(6)	2.300(4)	2.572(2)
			2.560(2)	2.327(5)	2.306(5)	2.575(2)
P−Ca	1.812(12)	1.836(13)	1.863(31)	1.817(20)	1.817(16)	1.814(17)
			1.800(32)	1.847(20)	1.788(16)	1.779(19)
P−Cb	1.819(15)	1.824(11)	1.826(26)	1.864(20)	1.803(17)	1.814(16)
			1.831(26)	1.818(22)	1.825(18)	1.805(16)
P−Cc	1.815(14)	1.823(12)	1.814(29)	1.801(19)	1.802(16)	1.811(16)
			1.803(27)	1.770(23)	1.819(17)	1.817(17)

lecular Au(I)···Au(I) interaction that is facilitated by the small bite of this diphosphine ligand.[17] ClAuP2PAuCl exists in two polymorphic forms: one in which dimers are produced[18] and the other in which polymeric chains are formed.[19] ClAuP3PAuCl and ClAuP5PAuCl also form polymeric chains, while ClAuP4PAuCl crystallizes as a simple molecular entity with no Au(I)···Au(I) interaction. The dimeric form **C** is particularly interesting, since a molecule of this sort was the first to demonstrate that a supramolecular structure connected only by Au(I)···Au(I) interactions could survive in solution as well as in the solid state.[22a] Recently we reported that IAuP6PAuI crystallized to form a novel knitted polymer in which sinusoidal chains of IAuP6PAuI molecules linked through Au(I)···Au(I) interactions were interwoven to form layers.[22b] Here we examine the molecular and supramolecular structures of a series of complexes of the type XAuP*n*PAuX in order to explore the range of crystalline polymer architectures that can be sustained by these Au(I)···Au(I) linkages.

Results

Synthesis. The new diphosphine-bridged gold halide complexes IAuP4PAuI, IAuP5PAuI, IAuP6PAuI, ClAuP7PAuCl, ClAuP8PAuCl, and IAuP8PAuI were synthesized by reaction of (dimethyl sulfide)gold(I) chloride with 0.5 equiv of the diphosphine ligand in dichloromethane. The chloro complexes were isolated from the reaction mixture by partial evaporation and precipitation with diethyl ether. The iodide complexes were formed through a metathesis reaction between the chloride complex in dichloromethane and a 4-fold excess of *n*-propyltris(*n*-butyl)ammonium iodide in methanol. The complexes were soluble in dichloromethane and chloroform and insoluble in diethyl ether and methanol. The ^{31}P NMR spectra of each of the chloride complexes in chloroform-*d* show a singlet *ca.* 30 ppm at 23 °C. The iodide complexes produce solutions that show a single ^{31}P NMR resonance at *ca.* 36 ppm at 23 °C. Thus, in solution at room temperature each of these complexes appears to exist as symmetrical molecular species as is expected from earlier work on ClAu{μ-P(Ph$_2$)CH$_2$As(Ph)CH$_2$(Ph$_2$)P}AuCl which showed that association through Au···Au interactions could only be achieved at low temperatures and high concentrations.[22a] Single crystals suitable for X-ray diffraction were grown by slow diffusion of either diethyl ether or methanol into dichloromethane solutions of the gold compounds.

Crystallographic Studies. Molecular Structures. The molecular structures of the new compounds are compared in Figure 1. For IAuP4PAuI, IAuP5PAuI, IAuP6PAuI, and ClAuP7PAuCl·CH$_3$OH, there is one molecular conformation in each crystal. However for ClAuP8PAuCl·CH$_2$Cl$_2$ and IAuP8PAuI·CH$_2$Cl$_2$, which are isomorphic, there are two distinct molecular conformations present in equal abundances in the crystalline solid. Figure 1 shows the pair of conformations for IAuP8PAuI·CH$_2$Cl$_2$. The structures of the two conformers of ClAuP8PAuCl·CH$_2$Cl$_2$ are similar.

The structures of IAuP4PAuI (a), IAuP8PAuI·CH$_2$Cl$_2$ (e), ClAuP8PAuCl·CH$_2$Cl$_2$ (e), IAuP8PAuI·CH$_2$Cl$_2$ (f), and ClAuP8PAuCl·CH$_2$Cl$_2$ (f) have a crystallographically imposed center of symmetry that is located at the midpoint of the central C−C bond in the hydrocarbon bridge. The structure of IAuP5PAuI (b) has a crystallographic C_2 axis which bisects the central methylene group of the molecule. There is no crystallographic symmetry imposed on the molecules of IAuP6PAuI (c) or ClAuP7PAuCl·CH$_3$OH (d).

The predominant molecular shape adopted by these molecules has the hydrocarbon bridge in a fully elongated form with the gold halide arms resting perpendicular to the line of this bridge. This is seen for the molecules IAuP4PAuI (a), IAuP5PAuI (b), and IAuP8PAuI·CH$_2$Cl$_2$ (e) (and its chloro counterpart), in Figure 1. In these, all of the methylene groups in the hydrocarbon bridge and the phosphorus atoms with their substituents have anti, staggered conformations. The methylene groups and phosphorus atoms in IAuP6PAuI (c) are also in the fully extended, staggered conformations, but one head group is oriented so that the Au−I group is not perpendicular to the direction of the hydrocarbon portion but rather lies nearly parallel to it. In ClAuP7PAuCl·CH$_3$OH (d), one methylene group exhibits gauche, staggered geometry. As a consequence, molecules of ClAuP7PAuCl (d) have a peculiar, twisted shape. In IAuP8PAuI·CH$_2$Cl$_2$ (f), and in its chloro counterpart, the two methylene groups that flank the center of symmetry in the molecule have gauche, staggered conformations. Thus the methylene chain in form f of IAuP8PAuI has a kink at its center.

Selected bond lengths in this series of molecules are given in Table 1. There are only slight differences between the individual molecules, and the bond distances fall within normal limits. There is a small lengthening in the P−Au bond length as well as the expected increase in the Au−X bond length when the halide is changed from chloride to iodide. For the chloride complexes the average P−Au and Au−Cl bond lengths are 2.225 and 2.320 Å, respectively. In comparison, the average P−Au and Au−I bond lengths are 2.258 and 2.574 Å. These bond lengths compare well to the linear (phosphine)gold halide structures found in the Cambridge Crystallographic Data Base.

Selected interatomic bond angles are shown in Table 2. The P−Au−X bond angles range from 165.0(1) in IAuP5PAuI to 176.5(2)° in ClAuP8PAuCl. The apparent dependence of this

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(21) Abbreviations: P1P, bis(diphenylphosphino)methane; P2P, bis(diphenylphosphino)ethane; P3P, bis(diphenylphosphino)propane; P4P, bis(diphenylphosphino)butane; P5P, bis(diphenylphosphino)pentane; P6P, bis(diphenylphosphino)hexane; P7P, bis(diphenylphosphino)heptane; P8P, bis(diphenylphosphino)octane.

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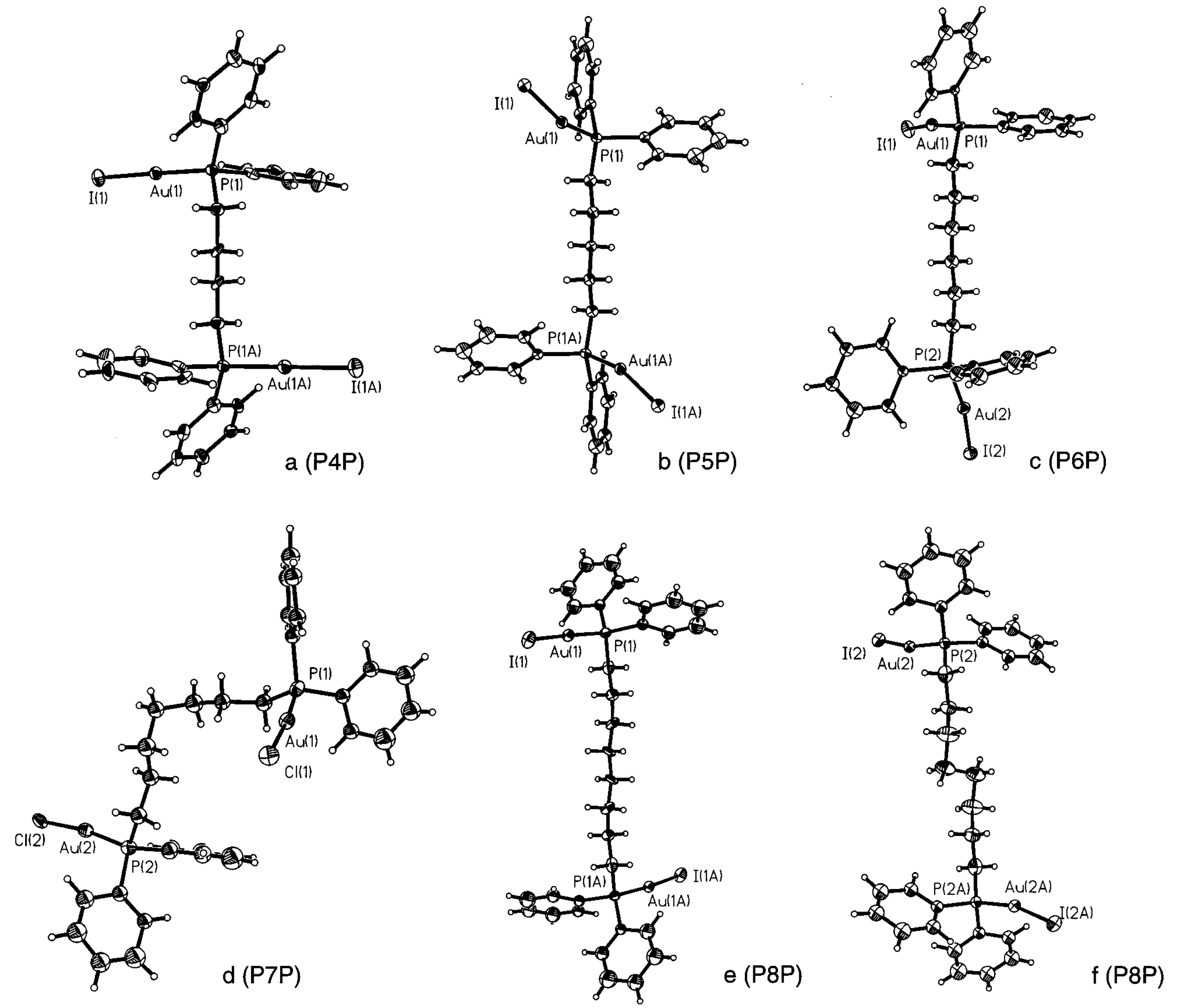

Figure 1. Molecular structures of (a) IAuP4PAuI, (b) IAuP5PAuI, (c) IAuP6PAuI, (d) ClAuP7PAuCl, and (e, f) IAuP8PAuI. IAuP8PAuI and ClAuP8PAuCl are isomorphic, and crystals of both compounds contain equal numbers of molecules in the conformations shown in (e) and (f) for the iodo compound.

Table 2. Selected Interatomic Angles (deg) for the Gold Complexes

	IAuP4PAuI	IAuP5PAuI	IAuP6PAuI	ClAuP7PAuCl	ClAuP8PAuCl	IAuP8PAuI
			Angles			
P−Au−Cl	174.0(1)	165.0(1)	172.0(2)	174.7(2)	176.5(2)	172.9(1)
			170.8(2)	171.9(2)	172.7(2)	166.6(1)
Au···Au−P	105.8(1)	103.1(1)	97.7(2)	100.9(1)	99.4(1)	107.1(1)
			99.9(2)	102.5(1)	103.5(1)	108.0(1)
Au···Au−Cl	80.1(1)	90.3(1)	89.2(1)	82.4(1)	83.2(1)	80.0(1)
			89.4(1)	84.1(1)	83.6(1)	84.7(1)
Au−P−C_a	111.9(4)	120.2(4)	116.6(10)	111.2(8)	110.0(5)	110.6(6)
			111.9(11)	114.7(6)	117.0(6)	117.2(6)
Au−P−C_b	113.3(4)	111.5(4)	117.6(8)	113.2(6)	115.1(5)	114.8(5)
			110.0(9)	112.3(7)	110.9(6)	109.4(5)
Au−P−C_c	116.8(4)	105.8(5)	108.7(10)	115.6(6)	113.0(5)	112.6(5)
			114.0(9)	111.9(7)	111.1(6)	112.5(6)
C_a−P−C_b	106.9(6)	103.9(5)	104.2(13)	105.9(9)	106.7(7)	105.8(7)
			105.0(13)	106.4(9)	107.1(8)	106.6(8)
C_a−P−C_c	100.6(6)	106.4(5)	104.7(13)	104.6(9)	106.5(8)	107.4(8)
			107.4(14)	104.2(10)	103.3(8)	104.2(8)
C_b−P−C_c	106.1(6)	108.2(4)	103.8(12)	105.4(10)	105.0(8)	104.9(7)
			108.0(12)	106.5(10)	106.7(8)	106.1(7)
			Torsion Angles			
P−Au···Au−Cl	83.6	105.2	82.9	69.1	71.0	69.0
			86.5	68.7	74.7	74.6

angle on the nature of the halide is due to the sensitivity of this angle toward Au(I)···Au(I) contacts, which are shorter for the iodide complexes.

Gold(I)−Gold(I) Interactions. Intermolecular gold(I)···gold(I) interactions occur in all of these crystal structures. Distances and angles mentioned in this section are compiled in

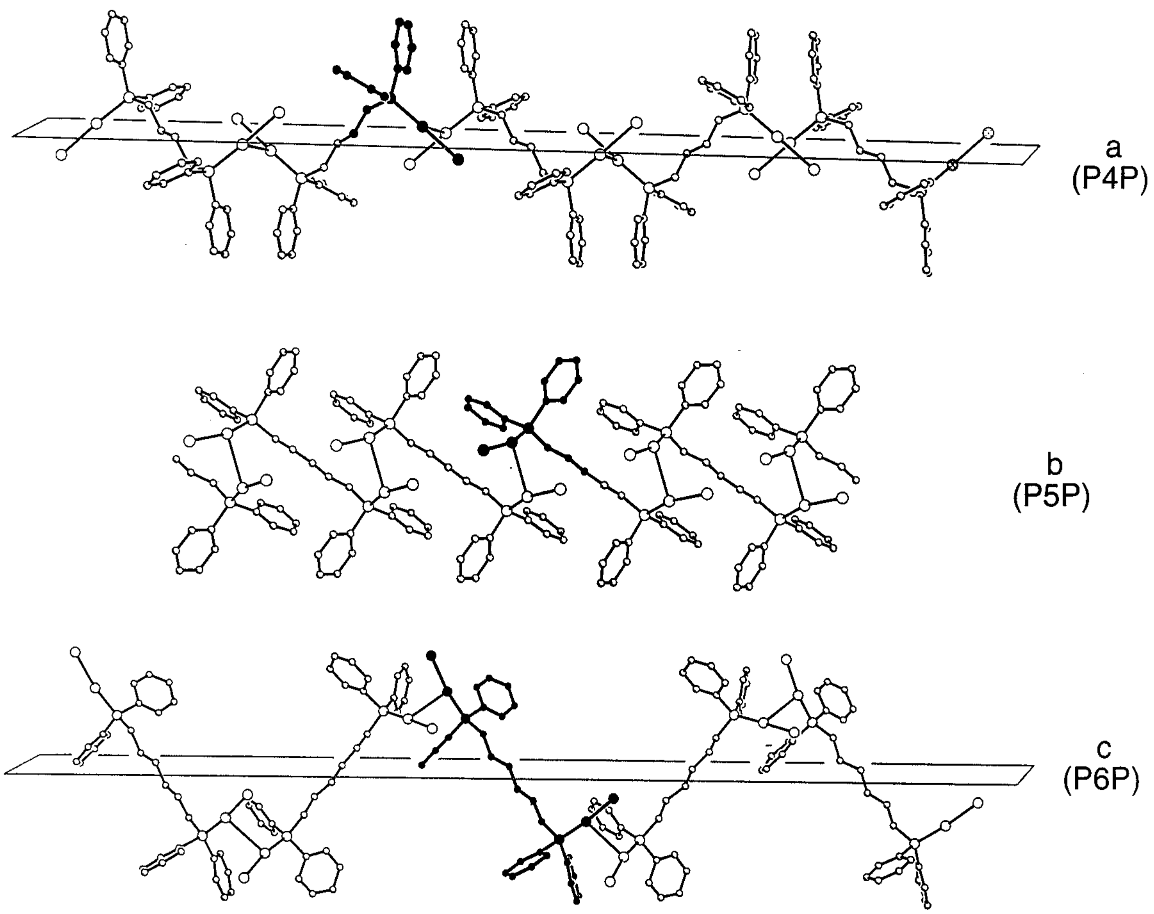

Figure 2. Propagation pathways for chains of (a) IAuP4PAuI, (b) IAuP5PAuI, and (c) IAuP6PAuI. The filled circles indicate the asymmetric unit within the chain. In (a) and (c) the trapezoids indicate the location of the glide planes.

Tables 1 and 2. The separations between the gold centers range from 3.264 Å in ClAuP7PAuCl to 3.031 Å in IAuP5PAuI and are well within the range of 3.0 −3.5 Å, where attractive Au(I)···Au(I) interactions occur. The geometrical description of the attractive Au(I)···Au(I) interaction also includes preferred X−Au···Au−Y torsion angles of 90° and an average value of 90° for the X−Au···Au and Y−Au···Au angles. The structures reported here have a range of P−Au···Au−X torsion angles from 68.7° in ClAuP7PAuCl to 105.2° in IAuP5PAuI. These angles show a slight dependence on the Au···Au separation. The smaller this distance, the larger the torsional angle. In general the P−Au···Au angles are larger than the X−Au···Au angles, but both are *ca.* 90°. This trend is expected, since the phosphorus ligand is larger than the halide anion. The Au···Au separations average 3.247 Å in the chloride structures, but they are significantly shorter, average 3.108 Å, in the iodide structures. The shortening of the Au(I)···Au(I) contact through halide exchange is consistent with both theory and experiment.[11,14,15]

Chain Propagation. All of the six molecules considered here choose polymeric chain formation from the four molecular arrangements given in Chart 1.

Figures 2 and 3 show diagrams of the propagation along individual chains in each of the five different structures reported here. In each drawing, the asymmetric unit is denoted by the section with filled circles. The symmetry transformation needed to convert the asymmetric unit into the molecular unit was discussed in the previous section on molecular structure. In this section, the emphasis is on the organization of molecular units into the chains. If discrete molecules are considered, then two means of propagation are involved: pure translation and translation along a glide plane.

Molecules of IAuP4PAuI and IAuP6PAuI propagate through translation along glide planes which are denoted by the trapezoids in Figure 2. Despite the similar means of propagation, the two chains differ considerably. The chain in IAuP4PAuI is quite compact, as seen in the space-filling model shown in Figure 4. The chain in IAuP6PAuI has a marked sinusoidal shape, and the space-filling model shown in Figure 4 emphasizes the open nature of this chain.

Molecules of IAuP5PAuI propagate via simple translation, as seen in Figure 2. The twisted molecules of ClAuP7PAuCl also propagate to form chains through simple translation, as shown in Figure 3. The chains that result have a helical twist, since individual molecules lack any symmetry, and each molecule within a single chain has the same chirality. Figure 5 shows space-filling models that emphasize the helical nature of the chains that form from the twisted ClAuP7PAuCl molecules. However, ClAuP7PAuCl crystallizes in the noncentrosymmetric space group *Cc*, where mirror planes fall between the individual chains and serve to create equal numbers of chains of opposite chiralities within any individual crystal.

The isomorphic pair ClAuP8PAuCl·CH_2Cl_2 and IAuP8PAuI·CH_2Cl_2 crystallize with two distinct molecular conformations (see (e) and (f) in Figure 1) within each crystal. The chains that form in crystals of these molecules are composed of equal numbers of molecules of the two conformations in a simple pattern, ...(e)(f)(e)(f)(e)(f)..., as seen in Figure 3. The propagation path involves translation of a pair of molecules in conformations e and f.

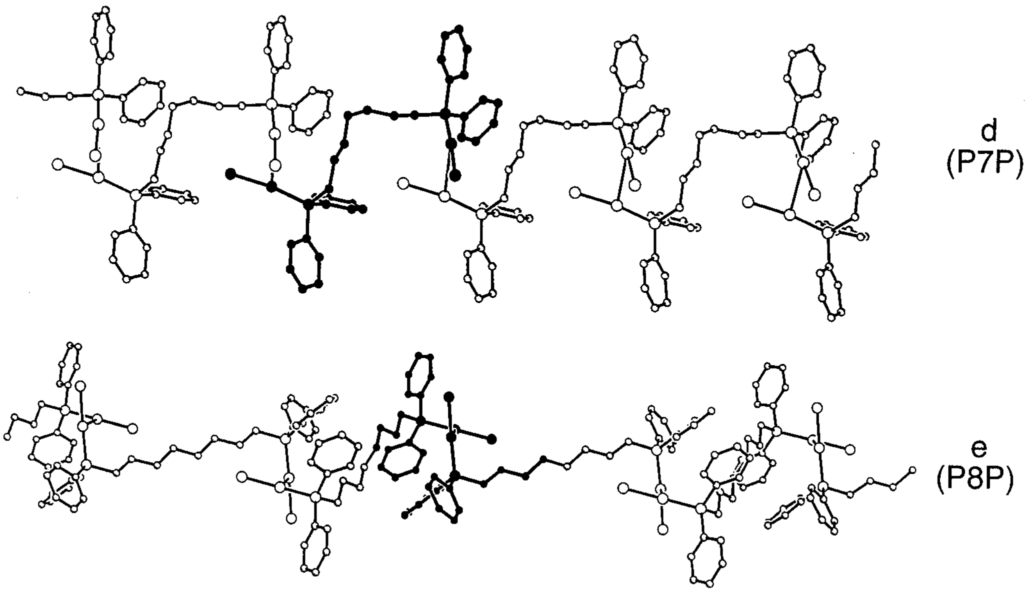

Figure 3. Propagation pathways for chains of (d) $ClAuP7PAuCl\cdot CH_3OH$, (e) $IAuP8PAuI\cdot CH_2Cl_2$ (and $ClAuP8PAuCl\cdot CH_2Cl_2$). The filled circles indicate the asymmetric unit within the chain.

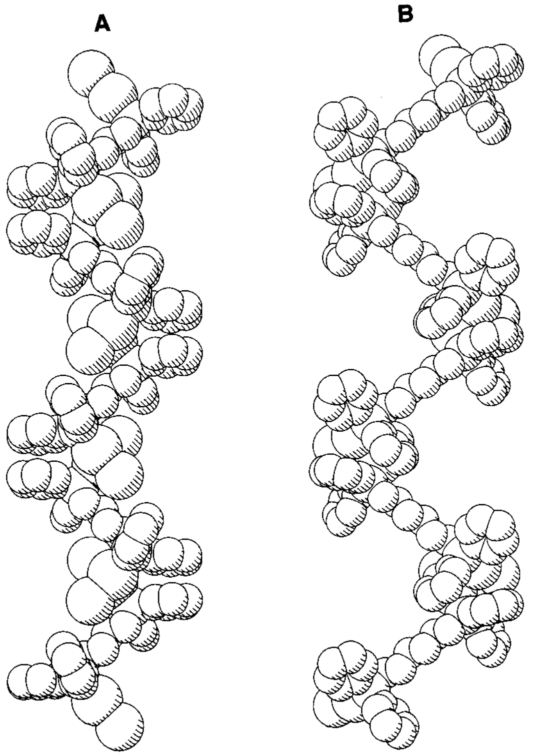

Figure 4. Space-filling diagrams that emphasize (A) the compact nature of the chains of IAuP4PAuI and (B) the more open structure for IAuP6PAuI.

Relative Orientations of Chains. Three basic arrangements of these polymeric chains within the crystals have been found. The most common motif involves chains in which the propagation directions lie parallel to one another. Examples are shown in Figure 6A, which shows the structure of IAuP4PAuI, and Figure 6B, which shows a similar view for IAuP5PAuI.

Molecules of IAuP6PAuI form chains that are interwoven into discrete layers, as previously noted.[22b] Figure 7 shows a view of one layer of this compound. The large voids in the sinusoidal chains, shown in Figure 4, allow one chain to pass over another to produce this complex woven motif. The formation of such a complex, knitted structure is only possible through self-assembly of the molecular pieces through weak intermolecular interactions. Related woven networks have also been prepared by self-assembly means in which hydrogen bonding provides the necessary weak intermolecular connection.[23,24]

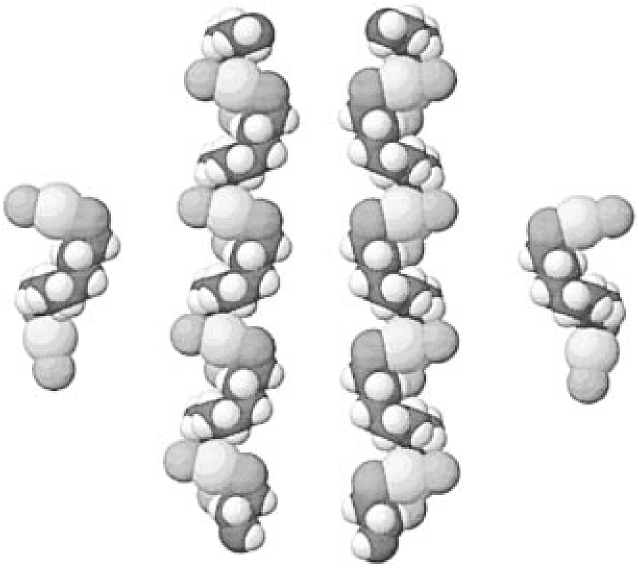

Figure 5. Space-filling diagrams that show (A) individual molecules of ClAuP7PAuCl and (B) helical chains formed from ClAuP7PAuCl molecules.

Chains of molecules of $ClAuP7PAuCl\cdot CH_3OH$ and $IAuP8PAuI\cdot CH_2Cl_2$ (and $ClAuP8PAuCl\cdot CH_2Cl_2$) produce a third structural motif that consists of layers of chains which form criss-crossed patterns. This pattern is shown in Figure 8 for $ClAuP7PAuCl\cdot CH_3OH$ and in Figure 9 for $IAuP8PAuI\cdot CH_2Cl_2$. Within a layer, the molecular chains run roughly parallel to each other. For $ClAuP7PAuCl\cdot CH_3OH$ (Figure 8), each layer of parallel chains consists of only one enantiomer of the helical chains. Looking down the *c* axis reveals an alternation of layers of right and left helical chains. The chains cross one another at an angle of 65°. Although the chains do

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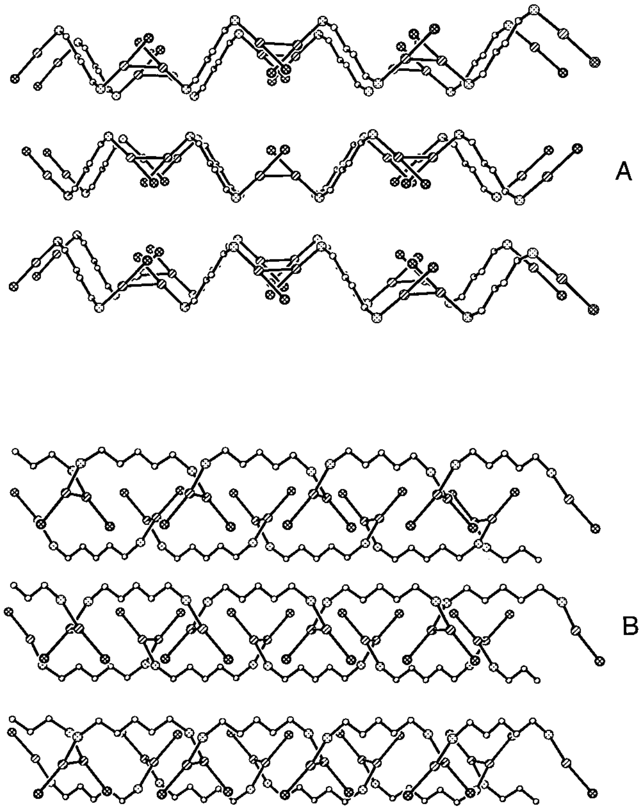

Figure 6. (A) Drawing showing the relationship of the parallel, linear chains in AuP4PAuI. (B) Drawing showing the relationship of the parallel, linear chains in IAuP5PAuI.

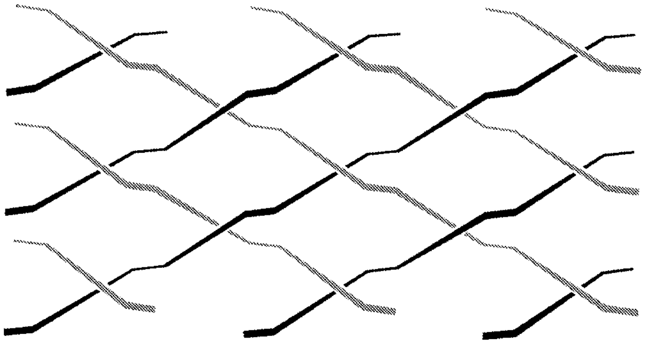

Figure 7. Drawing showing the woven, layered structure found in IAuP6PAuI. The long lines connect the gold atoms within individual molecules of the complexes, while the short lines represent the close intramolecular Au···Au contacts.

not display the complex interwoven structure found for IAuP6PAuI, this is still a highly sophisticated packing motif when one considers that these molecules are not held in a chiral conformation in solution.

Conclusions

This study has shown the prominence of polymeric chains as a structural motif for digold complexes with long bridging phosphine ligands. The large flexible rings which would arise with both intramolecular interactions and dimer formations shown in Chart 1 apparently would not produce the efficient packing that is achieved with the long-chain arrangements that do form. Self-assembly processes can produce some complex structures, such as the woven structure seen in Figure 7 and the helical chains seen in Figures 5 and 8, from rather simple molecular components. The weakness of the Au···Au interaction facilitates this self-assembly process. Related self-assembly of linear chains of complexes of the type RSAu(μ-ditertiary phosphine)AuSR have been reported.[25,26] Recently, Schmidbaur and co-workers have been able to construct novel crystalline polymers that utilize both the auriophilic interactions utilized in this study and hydrogen bonding as the weak interactions that facilitate self-assembly.[27] Further development of this type of intermolecular organization may be expected to develop rapidly.

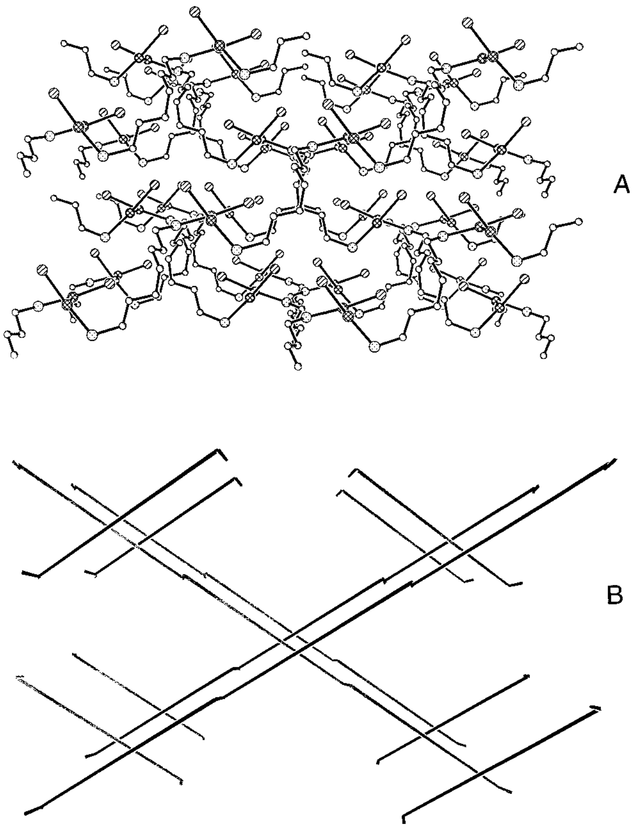

Figure 8. Drawing showing (A) the chains of molecules of ClAuP7PAuCl and (B) the arrangement of layers of these chains into a criss-crossed pattern. In (B) the long lines connect the gold atoms within individual molecules of the complexes, while the short lines represent the close intramolecular Au···Au contacts. The positions of the methanol molecules, which lie in the cavities between the chains, are not shown.

Experimental Section

Synthesis of the Chloride Complexes. ClAuP6PAuCl. (Dimethyl sulfide)gold chloride (31.7 mg, 0.108 mmol) and bis(diphenylphosphino)hexane (24.4 mg, 0.0537 mmol) were placed in a foil-covered Erlenmeyer flask equipped with a magnetic stir bar. After the addition of dichloromethane (15 mL), the reaction mixture was stirred for 2 h. The resulting mixture was filtered through Celite, and the filtrate was concentrated down to 5 mL via rotary evaporation. Gradual addition of diethyl ether produced a white crystalline powder in 84% yield. ^{31}P NMR of a chloroform-*d* solution of this product showed a single peak at 30.0 ppm with reference to an external phosphoric acid standard. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the complex.

ClAuP7PAuCl. This complex was synthesized by following the procedure outlined for ClAuP6PAuCl, but the product did not precipitate

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Table 3. Crystal Data and Data Collection Parameters

	IAuP4PAuI	IAuP5PAuI	IAuP6PAuI	ClAuP7PAuCl·CH_3OH	ClAuP8PAuCl·CH_2Cl_2	IAuP8PAuI·CH_2Cl_2
empirical formula	$C_{14}H_{14}AuIP$	$C_{14.5}H_{15}AuIP$	$C_{15}H_{16}AuIP$	$C_{16}H_{17}AuClO_{0.5}P$	$C_{16.5}H_{19}AuCl_2P$	$C_{16.5}H_{19}AuClIP$
fw	537.1	544.1	551.1	480.7	516.2	607.6
color, habit	colorless, prism	colorless, rods	colorless, plates	colorless, prism	colorless, plate	colorless, plate
crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$Pccn$	$Pbcn$	Cc	$P2_1/n$	$P2_1/n$
a, Å	17.704(4)	22.001(4)	9.707(2)	10.087(4)	9.009(3)	9.619(3)
b, Å	14.167(2)	7.803(2)	19.301(5)	15.678(5)	19.768(6)	19.693(6)
c, Å	11.920(2)	17.334(3)	33.032(7)	21.099(5)	19.956(5)	20.110(6)
β, deg	102.70(2)			100.25(3)	92.26(2)	92.31(3)
V, Å^3	2916.6(9)	2975.7(10)	6189(3)	3283(2)	3551(2)	3806(2)
Z	8	8	16	8	8	8
T, °C	−143	−143	−143	−143	−143	−143
λ (Mo Kα), Å	0.710 73	0.717 03	0.710 73	0.710 73	0.710 73	0.710 73
ρ, g/cm^3	2.446	2.429	2.366	1.945	2.022	2.121
μ, cm^{-1}	122.91	120.48	115.88	92.08	90.8	95.68
R^a (obsd data)	0.0598	0.0480	0.0749	0.0368	0.0820	0.0575
$R_w{}^b$	0.0650	0.0587	0.0800	0.0438	0.0859	0.0583

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o|]^{1/2}$.

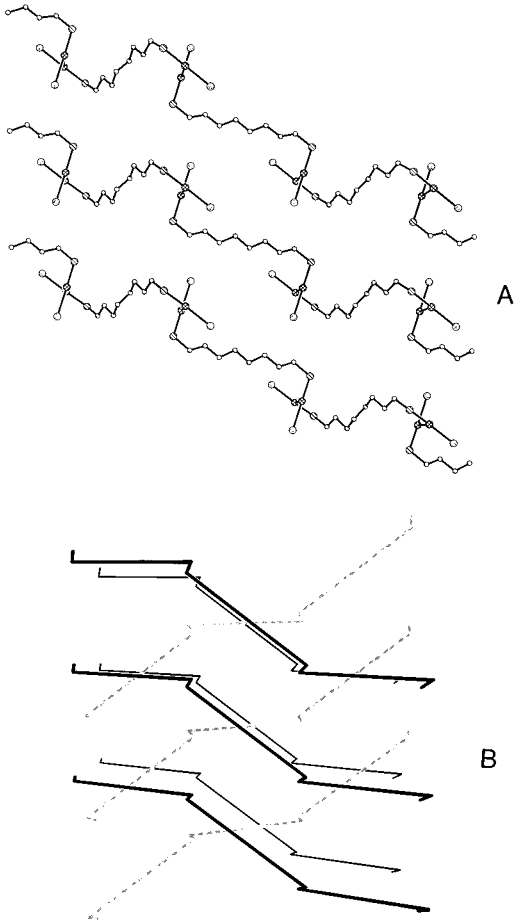

Figure 9. Drawing showing (A) the chains of molecules of IAuP8PAuI (and ClAuP8PAuCl) and (B) the arrangement of these chains into a criss-crossed pattern. In (B) the long lines connect the gold atoms within individual molecules of the complexes, while the short lines represent the close intramolecular Au···Au contacts. The positions of the dichloromethane molecules, which lie in the cavities between the chains, are not shown.

upon addition of either diethyl ether or methanol. Instead, after 2 h the reaction mixture was allowed to stir for 15 min in the light to cause any unreacted (dimethyl sulfide)gold(I) chloride to decompose. The solution was then filtered through Celite, and the solvent was removed via rotary evaporation. ^{31}P NMR: 28.9 ppm, singlet. Single crystals suitable for X-ray diffraction were grown by the diffusion of methanol into a dichloromethane solution of the complex.

ClAuP8PAuCl. This complex was synthesized by following the procedure outlined for ClAuP6PAuCl and crystallized through the addition of diethyl ether to a dichloromethane solution. Yield: 61%. ^{31}P NMR: 30.0 ppm, singlet. Single crystals suitable for X-ray diffraction were grown from a dichloromethane solution of the complex by floating a thin layer of methanol over the dichloromethane solution. Diethyl ether was then added on top of the methanol.

Synthesis of the Iodide Complexes. IAuP4PAuI. A metathesis reaction between ClAuP4PAuCl (23.0 mg, 0.0250 mmol) and a 5-fold excess of tri-*n*-butyl-*n*-proplyammonium iodide (44.7 mg, 0.126 mmol) was carried out. The gold halide complex was dissolved in 15 mL of dichloromethane in a foil-covered beaker that was equipped with a magnetic stir bar. The ammonium iodide salt was dissolved in a minimum amount of methanol, and the solution was added to the dichloromethane solution. The reaction mixture was stirred for 3 h. After the resulting solution was filtered through Celite, additional methanol was added to precipitate the product while the remaining ammonium halide salts were washed away. This white product was dissolved in dichloromethane. The gradual addition of diethyl ether produced a white crystalline powder in 83% yield. ^{31}P NMR of a chloroform-*d* solution of this product showed a single peak at 36.3 ppm. Single crystals suitable for X-ray diffraction were grown by the slow diffusion of diethyl ether into a dichloromethane solution of the complex.

IAuP5PAuI. This complex was synthesized by the use of the procedure outlined for IAuP4PAuI. The white product was crystallized though the addition of methanol to a dichloromethane solution of the complex followed by cooling to 5 °C. Yield: 73%. ^{31}P NMR: 36.2 ppm, singlet. Single crystals suitable for X-ray diffraction were grown by slow diffusion of methanol into a dichloromethane solution of the complex.

IAuP6PAuI. This complex was synthesized by following the procedure outlined for IAuP4PAuI. A white powder formed after the addition of diethyl ether to a dichloromethane solution of the complex. Yield: 66%. ^{31}P NMR: 36.0 ppm, singlet. Single crystals suitable for X-ray diffraction were grown from the slow diffusion of methanol into a dichloromethane solution of this complex.

IAuP8PAuI. This complex was synthesized by following the procedure outlined for IAuP4PAuI. White crystals formed after the addition of methanol to the dichloromethane solution of the complex. Yield: 83%. ^{31}P NMR: 36.2 ppm, singlet. Single crystals suitable for X-ray diffraction were grown from the slow diffusion of methanol into a dichloromethane solution of the complex.

X-ray Data Collection. All crystals were coated with a light hydrocarbon oil and mounted on a glass fiber in a ca. 130 K dinitrogen stream of a Siemens R3m/v diffractometer that was equipped with a locally modified Enraf-Nonius low-temperature apparatus. Cell dimensions were determined by least-squares refinement of ca. 45 reflections in the range of $30° < 2\theta < 40°$. Lorentz and polarization corrections were applied. Data collection parameters are summarized in Table 3.

Solutions and Refinements of the Structures. Solutions and refinements were performed using the SHELXTL PLUS family of programs.[28] Neutral-atom scattering factors, f' and f'', and absorption coefficients were from a standard source.[29] The structure of IAuP8PAuI·CH_2Cl_2 was solved by isomorphic replacement with the atomic positions of ClAuP8PAuCl·CH_2Cl_2. All other structures were solved using Patterson methods. Hydrogen atoms were refined using a riding model and a fixed isotropic thermal parameter. Unless noted below, all other atoms were refined anisotropically. Data were corrected for absorption using the program XABS.[30] Refinement was based on *F* through the use of full-matrix least-squares techniques.

IAuP4PAuI. The largest peak in the final difference map (3.61 e Å^{-3}) was located 0.941 Å from the gold atom.

IAuP5PAuI. This compound shows disorder in the position of the iodine atom. Three sites were found for this atom. Occupancies of 50:25:25 for I(1), I(1*), and I(1′) were assigned from the difference map. Only the gold and the phosphorus atoms were refined anisotropically. The largest peak in the final difference map (2.11 e Å^{-3}) was located between Au(1) and P(1).

ClAuP6PAuCl. Two check reflections for this crystal showed a decrease in intensity of 4% over the course of data collection. The data were corrected for this decay. The largest peak found in the difference map (4.45 e Å^{-3}) was located 0.947 Å from the gold atom.

IAuP6PAuI. Only the gold, iodine, and phosphorus atoms were refined anisotropically. The largest peak in the final difference map (2.23 e Å^{-3}) was located 0.775 Å from Au(1).

ClAuP7PAuCl·CH_3OH. In addition to the complex, a molecule of methanol was found in this structure. For the methanol molecule, the peak of larger electron density was assigned as the oxygen atom. No hydrogen atoms were located for this molecule. Only the gold, chlorine, and phosphorus atoms were refined anisotropically. The largest peak in the difference map (0.91 e Å^{-3}) was located between Au(1) and Cl(1). The handedness was indicated by refinement of the Rogers η parameter to 0.00(7).[28]

ClAuP8PAuCl·CH_2Cl_2. In addition to the complex, a molecule of dichloromethane was located in this structure. The largest peak (4.48 e Å^{-3}) in the final difference map was located 1.47 Å from Au(2) and 0.89 Å from Cl(2).

IAuP8PAuI·CH_2Cl_2. The two check reflections for this crystal showed a decrease in intensity of ca. 2% over the course of the data collection. The data were corrected for this decay. All non-hydrogen atoms except for the phenyl carbons were refined anisotropically. In addition to the complex, a molecule of dichloromethane was found in this structure. The largest peak (2.06 e Å^{-3}) in the final difference map was located 1.046 Å from Au(1).

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Supporting Information Available: Tables giving details of the data collections and structure refinements, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom positions for IAuP4PAuI, IAuP5PAuI, ClAuP7PAuCl·CH_3OH, IAuP8PAuI·CH_2Cl_2, and ClAuP8PAuCl·CH_2Cl_2 (42 pages). Ordering information is given on any current masthead page.

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