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Solid State Structures and Gold−Gold Bonding in Luminescent Halo(dimethylphenylphosphine)gold(I) Complexes

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The structures of the series of two-coordinate gold(I) complexes $\{(Me_2PhP)AuX\}_n$ where X is Cl, Br, or I have been examined by X-ray diffraction. The chloro complex crystallized in two separate polymorphic forms. Colorless hexagonal blocks of $\{(Me_2PhP)AuCl\}_3$ crystallized in the monoclinic space group $P2_1/m$ with $a = 12.141(4)$ Å, $b = 8.433(2)$ Å, $c = 14.834(3)$ Å, and $\beta = 94.15(2)°$ at 130 K with $Z = 2$. Refinement of 2837 reflections and 177 parameters yielded $R = 0.066$ and $R_w = 0.069$. The complex consists of three nearly linear P−Au−Cl units that are connected by Au−Au contacts at 3.091(2) and 3.120(2) Å. Colorless prisms of $\{(Me_2PhP)AuCl\}_2$ form in the orthorhombic space group $P2_12_12_1$ as described earlier (Cookson, P. D.; Tiekink, E. R. T. *Acta Crystallogr.* **1993**, *C49*, 1602). The two nearly linear P−Au−Cl units are staggered and connected through a Au−Au bond (3.230(2) Å). Colorless rectangular prisms of $\{(Me_2PhP)AuBr\}_2$ form in the monoclinic space group $P2_1$ with $a = 9.572(5)$ Å, $b = 8.757(3)$, and $c = 12.915(7)$ at 130 K with $Z = 2$. Refinement of 2469 reflections with 118 parameters yielded $R = 0.080$ and $R_w = 0.084$. $\{(Me_2PhP)AuI\}_2$ is isomorphous with the bromo complex with $a = 9.736(2)$ Å, $b = 8.890(2)$ Å, and $c = 13.160(5)$ Å at 130 K with $Z = 2$. Refinement of 2796 reflections with 119 parameters yielded $R = 0.052$ and $R_w = 0.058$. These complexes are similar to the chloro dimer but with altered orientations of the phenyl substituent. The predicted order of ligand effects (Cl > Br > I) on Au−Au distances from quasi-relativistic calculations is borne out in the experimental values: 3.230 Å (Cl); 3.119 Å (Br); 3.104 Å (I). In dichloromethane, these complexes dissociate into monomeric units but there is some evidence for the presence of dimers in concentrated solutions of the iodide compound.

Introduction

The luminescence of many gold complexes has attracted considerable attention.[1−8] Recent work on the luminescent behavior of monomeric, linear complexes of the type $(Ph_3E)AuX$ (where E is P or As and X is Cl or Br) in the solid state has demonstrated that dual phosphorescences from two excited states occur.[8] The high-energy emission which has its origin at 360 nm has been assigned to an intraligand phosphorescence that results from a phenyl-localized $^3\pi\pi^*$ state. The low-energy emissions, which generally dominate the spectra at room temperature, also appear to be phosphorescence, but a firm explanation was not apparent. One possibility that has been discussed is the presence of a severely perturbed trap or impurity. Another conjecture points to an association or charge transfer between adjacent phenyl moieties of the ligands. This might produce suitable red-shifted $^{1,3}\pi\pi^*$ states. In order to limit interactions between adjacent phenyl moieties, we undertook an examination of the luminescence and other spectroscopic properties of analogous complexes that were formed with dimethylphenylphosphine.[9] In this case, it was expected that the phenyl−phenyl and phenyl−gold interactions would be limited to a few well-defined situations in the solid state. However, the smaller size of this phosphine ligand relative to triphenylphosphine produced another effect. Instead of producing discrete linear complexes, the smaller bulk of this ligand allows the association of individual two-coordinate units to produce dimeric species and in one case a trimeric species that involve weak Au···Au bonds. This structural feature is not surprising. It is well-known that many gold(I) complexes crystallize so that two or more gold(I) ions are in close proximity.[10−14] For an ion as large as Au(I), Au···Au contacts that are less than 3.5 Å have been considered weakly attractive.[12]

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Results

Synthetic Studies. Treatment of a dichloromethane solution of Me_2SAuCl with 1 equiv of dimethylphenylphosphine under an oxygen-free atmosphere gives a colorless solution from which colorless crystals of $(Me_2PhP)AuCl$ are obtained in 80% yield after the addition of diethyl ether. Treatment of **1** with tetra-*n*-butylammonium bromide or tetra-*n*-butylammonium iodide yields $(Me_2PhP)AuBr$ or $(Me_2PhP)AuI$, respectively. Treatment of $(Me_2S)AuBr$ with dimethylphenylphosphine also yields $(Me_2PhP)AuBr$. In deuterated dichloromethane, the $^{31}P\{^1H\}$ NMR spectrum of each of these three gold complexes consists of a singlet at 3.8 ppm for $(Me_2PhP)AuCl$, 7.4 ppm for $(Me_2PhP)AuBr$, and 12.6 ppm for $(Me_2PhP)AuI$. The dependence of the chemical shifts on the halides, I > Br > Cl, follows the periodic trend that is seen for other phosphine gold(I) halo complexes.[15] The appearance of only one resonance for each suggests that the complexes are present in solution as monomeric units. However, for the iodo complex, the chemical shift is concentration dependent. At −70 °C the resonance for a 70 mM solution sample in dichloromethane is found at 11.77 ppm while for a 20 mM solution the resonance is found at 13.17 ppm. This shift probably results from a dynamic equilibrium between monomeric and dimeric forms of the complex (*vide infra*). The chloro and bromo analogs do not show any concentration dependence of the chemical shift.

Absorption Spectra. The room-temperature solution absorption spectra of $(Me_2PhP)AuX$ in CH_2Cl_2 are shown in the top panel of Figure 1. Table 1 summarizes the absorption features and their molar absorptivities. The structured absorption at 260−280 nm, which follows Beer's law, is similar to that seen for other arylphosphine complexes of Au(I).[8] The absorptivities for such arylphosphine gold complexes appear to be roughly proportional to the number of phenyl moieties per formula unit. For example, in the present systems which have only one phenyl moiety per formula unit, the peak absorptivities are $\approx$500 M^{-1} cm^{-1} for the chloro and bromo complexes. In the analogous triphenylphosphine compounds with three phenyl rings per formula unit, the absorptivities are $\approx$2000 M^{-1} cm^{-1}.[8] Gold complexes with non-aryl phosphine ligands absorb only at shorter wavelengths.[2d,e,16]

For $(Me_2PhP)AuCl$, $(Me_2PhP)AuBr$, and $(Me_2PhP)AuI$, the structures in the solution absorption spectra in the 260−280 nm range are similar. As for the systems which contained three phenyl rings per formula unit, these absorptions are assumed to be associated with a ground to singlet $\pi\pi^*$ transition within the phenyl moiety, since they are very close to the lowest singlet state absorption of benzene.[17] This absorption in benzene has an onset at $\approx$265 nm. The lowest energy ground to triplet state absorption of benzene is observed at $\approx$350 nm. A weak absorption in this region was seen in the solution spectra of the $(Ph_3P)AuX$ compounds which have three phenyl rings per formula unit.[8] Therefore, it is not unexpected that this absorption is very weak or absent in the $(Me_2PhP)AuX$.

Additional absorption is evident in the 260−280 nm region for the iodo complex relative to the chloro and bromo complexes. This can be explained in terms of the spectral results of Savas and Mason for $(R_3P)AuX$ (R = methyl or ethyl; X = Cl, Br, or I).[16] The absorption of $(R_3P)AuX$ begins at $\approx$235 nm for the chloro and bromo complexes but at $\approx$253 nm for the iodo system. The additional absorption, and reduced resolution, in the 260−280 nm region for the iodo complex in Figure 1 presumably results from the overlap of this red-shifted transition with the phenyl-localized band. Savas and Mason concluded that this red shift in the iodo complex (relative to the chloro and bromo systems) arises due to the changing composition and energy of the HOMO.[16] They have inferred that, in all $(R_3P)AuX$ compounds, the LUMO is a combination of the phosphorus π and the Au 6p orbitals. The HOMO, however, is predominantly an Au 5d orbital in the chloro and bromo complexes, but in the iodo complex the HOMO involves the filled π orbitals of the iodide. SCF−Xα−SW calculations on $(H_3P)AuX$ and $\{(H_3P)AuX\}_2$ agree with these ideas about the changing composition of the HOMO with changes in the halogen.[9]

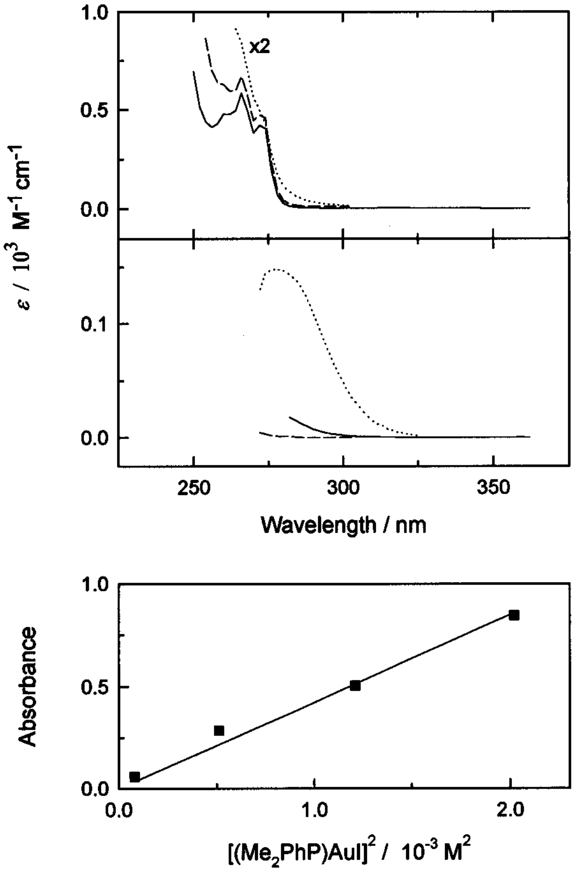

Figure 1. Top panel: Solution absorption spectra of $(Me_2PhP)AuX$ in dichloromethane. Solid line X = Cl; dashed line X = Br; dotted line X = I. The iodo spectrum is divided by 2 to provide a better comparison. Center panel: Subtraction of solution absorptivities of a dilute (4×10^{-3} M) solution from those of a concentrated (4×10^{-2}) solution. Bottom panel: Absorbance dependence on the square of the monomer concentration for the 286 nm band of the iodo complex. The slope is 425 (20) M^{-2} cm^{-1}.

Table 1. Absorption Maxima and Extinction Coefficients for the Major Peaks in the Room-Temperature Absorption Spectra of $(Me_2PhP)AuX$ in Dichloromethane Solution

	ϵ (M^{-1} cm^{-1})		
λ_{max} (nm)	$(Me_2PhP)AuCl$	$(Me_2PhP)AuBr$	$(Me_2PhP)AuI$
260	480	630	
266	585	670	1700
272	425	480	500
286			425[a]

[a] Based on the square of monomer concentration (M^{-2} cm^{-1}).

The solution absorption spectrum of the iodide complex is unique in another way. In dichloromethane a band centered at

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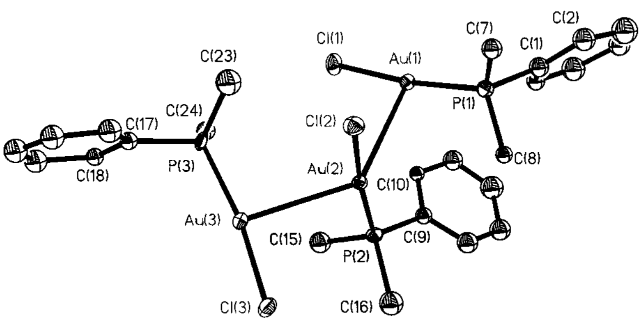


Figure 2. Perspective view of $\{(Me_2PhP)AuCl\}_3$ with 50% thermal contours.

286 nm appears at high concentrations. The middle panel of Figure 1 shows this peak at 286 nm for the iodo complex, whereas none occurs for the chloro and bromo complexes. These spectra are obtained by subtraction of the absorptivities of a dilute solution (4×10^{-3} M) from those of a more concentrated (4×10^{-2} M) solution. The results were also confirmed by inversely varying the concentration and path length for a given complex. The lowest panel of Figure 1 shows that the absorbance of the band at 286 varies quadratically with concentration. This indicates that a dimeric species forms.

Structural Studies. The structures of all of these nominally two-coordinate complexes have been determined by single-crystal X-ray diffraction. During this investigation, it became apparent that the chloro complex crystallized in two different forms. In the initial stages of this project, crystals of the trimeric complex, $\{(Me_2PhP)AuCl\}_3$, formed and were studied spectroscopically. However, we gradually observed anomalies in the spectroscopic features of samples of the chloro complex, and further examination of individual crystals revealed that a second modification was present. The results of a single-crystal X-ray diffraction study showed that these contained the digold compound, $\{(Me_2PhP)AuCl\}_2$. After the presence of this digold form was recognized, the amounts of the corresponding trigold form diminished to the point where eventually only the digold form crystallized. During this time, the bromo and iodo complexes were examined. These formed crystals that were isomorphous with each other but different from either of the crystalline forms of the chloro complex. Despite repeated examination of over 20 different individual crystals of the chloro complex, crystallization of the trigold species or digold complexes which were isomorphous with the bromo or iodo complex was not found.

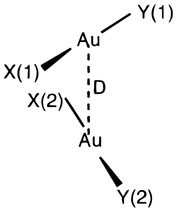
Structure of $\{(Me_2PhP)AuCl\}_3$. This compound crystallizes with one trimeric gold molecule in the asymmetric unit. The structure is shown in Figure 2. Atomic coordinates are given in Table 2, and bond distances and angles are shown in Table 3. The complex consists of three mutually perpendicular (Me_2PhP)AuCl units, which are essentially linear (Cl(1)−Au(1)−P(1), 173.0(3)°; Cl(2)−Au(2)−P(2), 171.8(3)°; Cl(3)−Au(3)−P(3), 171.2(3)°). These linear units are connected by the interactions of pairs of gold atoms at relatively short distances (Au(1)−Au(2), 3.091(2) Å; Au(2)−Au(3), 3.120(2) Å). The P−Au and Cl−Au bond lengths fall within the expected range of metal−ligand distances found in linear univalent phosphine−gold−chloride systems.[18]

The angular geometry about the gold atoms is best viewed by examining the Cl−Au−Au−Cl torsion angles. The angles, Cl(1)−Au(1)−Au(2)−Cl(2) and Cl(2)−Au(2)−Au(3)−Cl(3), are 104.4 and 109.8°, respectively. A survey of a series of compounds which contain the structural entity **A** reveals that the preferred X(1)−Au(1)−Au(2)−X(2) torsion angle is approximately 90° when *D* (the gold−gold separation) falls in the range 3.00−3.25 Å.[13] For larger *D* values ($D > 3.65$ Å), torsion angles of 0 and 180° are more favorable.[13]

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $\{(Me_2PhP)AuCl\}_3$

	x	*y*	*z*	U_{eq}[a]
Au(1)	6440(1)	9224	7709(1)	16(1)
Au(2)	4557(1)	6875(2)	8042(1)	15(1)
Au(3)	2212(1)	6336(2)	7087(1)	17(1)
P(1)	5776(6)	9730(11)	6230(5)	28(2)
P(2)	3915(6)	9049(10)	8860(5)	24(2)
P(3)	1986(6)	4055(10)	7867(5)	24(2)
Cl(1)	7254(6)	9039(10)	9137(4)	18(2)
Cl(2)	5226(6)	4686(9)	7467(5)	18(2)
Cl(3)	2172(6)	8568(10)	6202(5)	19(2)
C(1)	8648(24)	9223(44)	9218(20)	25(7)
C(2)	9207(29)	10010(46)	9929(23)	33(8)
C(3)	10400(32)	9917(56)	9969(28)	46(10)
C(4)	10964(28)	9200(48)	9371(22)	32(7)
C(5)	10367(32)	8491(50)	8625(25)	40(9)
C(6)	9227(26)	8478(40)	8578(21)	24(7)
C(7)	6641(25)	10535(42)	9905(20)	24(7)
C(8)	6929(23)	7267(35)	9663(19)	17(6)
C(9)	6708(24)	4672(39)	7408(18)	20(7)
C(10)	7197(23)	5728(37)	6828(19)	17(6)
C(11)	8361(29)	5714(47)	6770(23)	31(8)
C(12)	8959(34)	4668(53)	7268(24)	42(9)
C(13)	8497(29)	3565(49)	7826(24)	34(8)
C(14)	7402(28)	3628(47)	7906(22)	32(8)
C(15)	4662(27)	4273(48)	6333(21)	32(8)
C(16)	4853(33)	2904(50)	8164(25)	38(9)
C(17)	736(23)	9029(39)	5816(18)	19(6)
C(18)	372(23)	8436(38)	4942(20)	20(6)
C(19)	−823(28)	8703(46)	4693(23)	33(8)
C(20)	−1467(28)	9434(45)	5296(22)	33(8)
C(21)	−1024(28)	9877(46)	6098(23)	33(8)
C(22)	61(28)	9724(45)	6374(23)	32(8)
C(23)	2653(31)	10318(50)	6775(26)	39(9)
C(24)	2955(25)	8356(40)	5209(20)	24(7)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.



A

Structure of $\{Me_2PhP)AuCl\}_2$. After the structure of this molecule had been completed in our laboratory, an independent report on it appeared.[19] However, that report did not recognize that a close Au⋯Au interaction was present. A perspective view of the dimeric molecule is shown in Figure 3. This complex consists of two mutually perpendicular and nearly linear (Me_2PhP)AuCl units (Cl(1)−Au(1)−P(1), 175.3(2)°; Cl(2)−Au(2)−P(2), 177.2(2)°) that are connected by a short Au(1)−Au(2) contact (3.230(2) Å). This distance, while over 0.1 Å longer than the corresponding distance in the trimeric form of this complex, is still in the range where weakly bonding Au−Au interactions occur. The (P−Au−Cl)$_2$ units are found in the expected staggered conformation with a Cl(1)−Au(1)−Au(2)−Cl(2) torsion angle of 115.9°. The P−Au and Cl−Au bond lengths are unexceptional.

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Table 3. Selected Interatomic Distances and Angles for Gold Complexes

	$\{(Me_2PhP)AuCl\}_3$	$\{(Me_2PhP)AuCl\}_2$	$\{(Me_2PhP)AuBr\}_2$	$\{(Me_2PhP)AuI\}_2$
Distances (Å)				
Au(1)−Au(2)	3.091(2)	3.230(2)	3.119(2)	3.104(2)
Au(2)−Au(3)	3.120(2)			
Au(1)−P(1)	2.234(7)	2.236(6)	2.246(9)	2.259(5)
Au(1)−X(1)	2.322(7)	2.316(6)	2.423(4)	2.588(2)
Au(2)−P(2)	2.213(8)	2.232(6)	2.246(10)	2.245(5)
Au(2)−X(2)	2.362(8)	2.311(6)	2.431(4)	2.582(2)
Au(3)−P(3)	2.293(8)			
Au(3)−Cl(3)	2.272(8)			
Angles (deg)				
Au(1)−Au(2)−Au(3)	133.0(1)			
P(1)−Au−X(1)	173.0(3)	175.3(2)	175.0(2)	173.7(1)
P(2)−Au−X(2)	171.8(3)	177.2(2)	176.8(2)	174.7(1)
P(3)−Au−Cl(3)	171.2(3)			

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $\{(Me_2PhP)AuBr\}_2$

	x	*y*	*z*	U_{eq}[a]
Au(1)	7530(1)	6515	9553(1)	26(1)
Au(2)	6724(1)	8737(2)	7593(1)	23(1)
P(1)	6244(10)	4444(10)	8834(6)	28(2)
P(2)	8919(9)	8472(8)	7299(6)	25(2)
Br(1)	9034(3)	8605(4)	10456(2)	29(1)
Br(2)	4313(4)	9124(5)	7828(3)	37(1)
C(1)	6853(63)	2702(40)	9573(39)	65(13)
C(2)	4361(26)	4499(64)	8877(38)	60(12)
C(3)	6291(36)	4092(39)	7404(24)	27(6)
C(4)	7107(35)	2875(36)	7214(23)	25(6)
C(5)	7216(43)	2659(47)	6184(28)	37(8)
C(6)	6308(39)	3530(42)	5359(26)	35(7)
C(7)	5468(34)	4656(37)	5556(23)	26(6)
C(8)	5418(36)	4923(38)	6624(24)	27(6)
C(9)	9819(30)	6682(26)	7803(21)	25(6)
C(10)	10216(34)	9940(34)	7947(26)	35(7)
C(11)	8840(41)	8510(43)	5869(27)	36(8)
C(12)	9867(35)	9244(38)	5508(23)	26(6)
C(13)	9749(55)	9221(65)	4444(36)	58(11)
C(14)	8777(33)	8464(34)	3693(22)	23(6)
C(15)	7698(41)	7656(45)	4048(26)	35(7)
C(16)	7803(41)	7717(45)	5131(27)	35(7)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $\{(Me_2PhP)AuI\}_2$

	x	*y*	*z*	U_{eq}[a]
Au(1)	6871(1)	8402	7588(1)	21(1)
Au(2)	7527(1)	10646(1)	9461(1)	21(1)
P(1)	9015(5)	8591(6)	7234(4)	20(1)
P(2)	6285(5)	12695(6)	8773(4)	19(1)
I(1)	4345(1)	7969(2)	7830(1)	29(1)
I(2)	9036(1)	8429(2)	10412(1)	26(1)
C(1)	8900(15)	8611(20)	5838(11)	14(3)
C(2)	10027(31)	7955(38)	5456(22)	48(6)
C(3)	9824(33)	7977(41)	4368(25)	54(7)
C(4)	8736(28)	8650(35)	3684(25)	45(6)
C(5)	7708(21)	9371(26)	4116(15)	27(4)
C(6)	7746(22)	9251(26)	5164(16)	28(4)
C(7)	10028(26)	10321(3)	7770(19)	38(5)
C(8)	10211(22)	7040(26)	7828(15)	26(4)
C(9)	6339(20)	13118(23)	7423(15)	23(4)
C(10)	5591(24)	12196(30)	6579(17)	32(4)
C(11)	5645(23)	12442(29)	5609(17)	32(4)
C(12)	6296(24)	13695(28)	5373(18)	36(5)
C(13)	7110(29)	14672(41)	6131(22)	49(6)
C(14)	7048(20)	14374(25)	7183(15)	25(4)
C(15)	4353(27)	12671(32)	8721(20)	40(5)
C(16)	6840(22)	14409(28)	9560(17)	31(4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

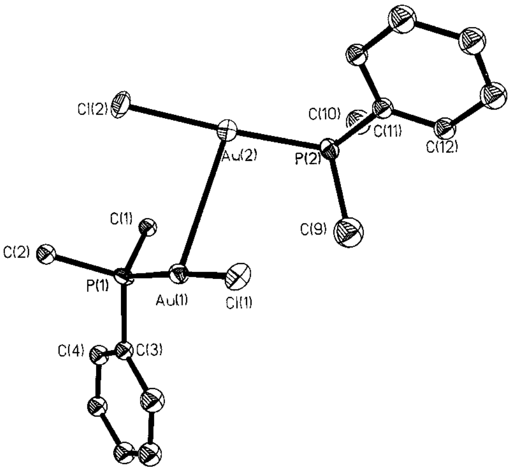

Figure 3. Perspective view of $\{(Me_2PhP)AuCl\}_2$ with 50% thermal contours.

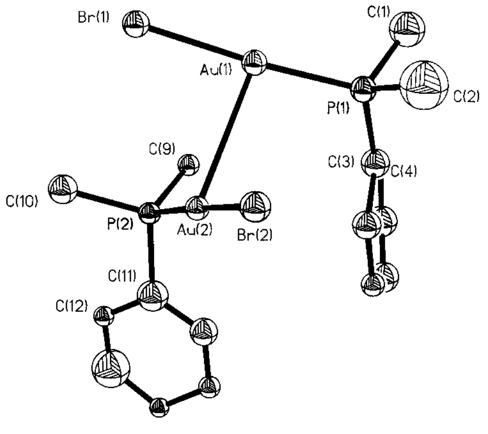

Figure 4. Perspective view of $\{(Me_2PhP)AuBr\}_2$ with 50% thermal contours. $\{(Me_2PhP)AuI\}_2$ has a similar geometry.

Structures of $\{(Me_2PhP)AuBr\}_2$ and $\{Me_2PhP)AuI\}_2$. These compounds form isomorphous crystals with one dimeric gold molecule in the asymmetric unit. Atomic coordinates are given in Tables 4 and 5. Interatomic distances and angles are given in Table 3. A perspective view of the molecular structure of $\{(Me_2PhP)AuBr\}_2$ is shown in Figure 4. The structure of $\{(Me_2PhP)AuI\}_2$ is similar. These complexes consist of two mutually perpendicular and nearly linear $Me_2PhPAuX$ units that are connected through a Au(1)−Au(2) bond of 3.119(2) Å for the bromo complex and 3.104(2) Å for the iodo complex. The $(P-Au-X)_2$ units are found in the expected staggered conformations with X(1)−Au(1)−Au(2)−X torsion angles of 107.6° for the bromo complex and 105.9° for the iodo compound. The P−Au and X−Au bond lengths fall within normal ranges.

Comparison of Figures 3 and 4 shows the marked similarities in the shapes of $\{(Me_2PhP)AuCl\}_2$ and $\{(Me_2PhP)AuBr\}_2$. These drawings, which are presented from similar perspectives, show that the major difference in the two involves the orientation of the phenyl ring that is attached to P(2) in $\{(Me_2PhP)AuCl\}_2$ and P(1) in $\{(Me_2PhP)AuBr\}_2$. In the bromo complex the phenyl ring is oriented so that it is relatively close to Au(2). The center of this ring is 4.553 Å from Au(2). In $\{(Me_2PhP)AuCl\}_2$, however, the corresponding phenyl ring is oriented so that it is much further from Au(1). The corresponding distance from the phenyl ring center to Au(1) is 6.810 Å.

Discussion

This work demonstrates that (phosphine)gold(I) halide complexes are prone to self-association when the phosphine ligand is not large enough to inhibit such association.[20] When the size of the phosphine ligand precludes Au−Au association, other energetically favorable arrangements such as phenyl−phenyl and phenyl−gold interactions become important in determining the solid state structure. The data on the series of binuclear complexes, $\{(Me_2PhP)AuX\}_2$ (X = Cl, Br, I), allow for a comparative assessment of the effect of the halide ligand on the gold−gold interaction. Pyykkö and co-workers have used quasi-relativistic pseudopotentials to examine ligand effects in $\{(H_3P)AuX\}$ and have predicted that the Au−Au separation in such dimers will decrease in the series Cl > Br > I.[21] This agrees well with trends seen in the series of $\{(Me_2PhP)AuX\}_2$ complexes. The calculated Au−Au distances for such dimers with perpendicular orientations of the two linear units are 3.366 Å (Cl), 3.338 Å (Br), and 3.315 Å (I).[22] The experimentally obtained distances in the series of $\{(Me_2PhP)AuX\}_2$ complexes are 3.230 Å (Cl), 3.119 Å (Br), and 3.104 Å (I). The calculations of Pyykkö and co-workers indicate that the attractive Au−Au interaction results from correlation effects that are strongly enhanced by relativistic contributions.[22,23] However, Fackler and co-workers observed the reverse trend in the Au−Au distances in complexes of the type (1,3,5-triaza-7-phosphaadamantane)AuX, where the Au−Au distance is 3.092(1) Å for X = Cl, but it is 3.107(1) Å for X = Br.[2d]

The crystallization of both dimeric and trimeric forms of $\{(Me_2PhP)AuX\}_n$ appears to be limited to the case where X = Cl. It is interesting to note that the Au····Au separations are smaller in the trimeric form. The nature of the crystallization process which can produce these two forms is poorly understood at this stage. Both forms were crystallized from the same solvent system: dichloromethane/diethyl ether. However, once the dimeric form was found and identified, we were no longer able to grow crystals of the trimeric form. Other, equally bizarre, examples of crystallization phenomena have been noted.[24−26]

The spectroscopic data that were obtained from dichloromethane solutions of these complexes indicated that the dimers dissociate when dissolved. However, in the case of the iodo complex, the concentration dependence of the optical absorption spectrum and of the ^{31}P NMR spectra indicate that some degree of dimerization does occur in solution. That it is the iodide complex alone which displays a degree of association is in accord with the theoretical calculations which indicate that the attractive interaction is greatest when an iodide ligand is present. Evidence for attractive Au−Au interactions persisting in solutions of such complexes is limited. However a study of the temperature and concentration effects on the ^{31}P NMR spectra of $ClAuP(Ph_2)CH_2As(Ph)CH_2(Ph_2)PAuCl$ has shown that, in dichloromethane solution, this complex also undergoes self-association that results from two attractive Au−Au interactions.[18]

Experimental Section

Preparation of Compounds. Published methods were used to prepare $(Me_2S)AuCl$ and $(Me_2S)AuBr$.[27] The new gold compounds were prepared under an atmosphere of dioxygen-free dinitrogen. Once isolated, these complexes are stable to moisture and dioxygen.

$\{(Me_2PhP)AuCl\}_2$ and $\{(Me_2PhP)AuCl\}_3$. To 100 mg (0.340 mmol) of $(Me_2S)AuCl$ dissolved in 25 mL dichloromethane was added 48 μL (0.337 mmol) of dimethylphenylphosphine. The mixture was stirred for 2 h. Its volume was reduced by vacuum evaporation, and diethyl ether was added to precipitate a white crystalline powder; yield 100 mg (80%). This compound can be recrystallized from dichloromethane/diethyl ether.

$\{(Me_2PhP)AuBr\}_2$. Method 1. To 110 mg (0.374 mmol) of $(Me_2S)AuBr$ dissolved in 25 mL dichloromethane was added 53 μL (0.374 mmol) of dimethylphenylphosphine. After 2 h of stirring, the volume was reduced and diethyl ether was added to precipitate a white crystalline powder; yield 115 mg (75%). This compound can be recrystallized from dichloromethane/diethyl ether.

Method 2. To 100 mg (0.270 mmol) of $\{(Me_2PhP)AuCl\}_2$ in 25 mL of dichloromethane was added 435 mg (1.35 mmol) of tetra-*n*-butylammonium bromide in 20 mL of methanol. The solution was stirred for 2 h, and then its volume was reduced to 20 mL. Methanol was added to precipitate the product as a white crystalline powder. The complex was recrystallized from dichloromethane/methanol; yield 64 mg (57%).

$\{(Me_2PhP)AuI\}_2$. This was prepared from 100 mg (0.540 mmol) of $\{(Me_2PhP)AuCl\}_2$ and 423 mg (1.35 mmol) of tetra-*n*-butylammonium iodide as described above; yield 62 mg (50%).

Physical Measurements. The compounds $(Me_2PhP)AuX$ were purified by multiple recrystallization, using diffusion of diethyl ether into solutions of CH_2Cl_2.

Optical Spectroscopy. Absorption spectra were collected with a Hewlett-Packard 8450A spectrometer.

^{31}P NMR Spectroscopy. The $^{31}P\{^1H\}$ NMR spectra were recorded with proton decoupling on a General Electric QE-300 NMR spectrometer that operates at 121.7 MHz with an external 85% phosphoric acid standard and the high-field positive convention for reporting chemical shifts.

X-ray Data Collection. $\{(Me_2PhP)AuCl\}_3$. Colorless quasi-hexagonal blocks of the complex were obtained by diffusion of diethyl ether into a dichloromethane solution of the complex. These were coated with a light hydrocarbon oil to minimize exposure to air. The selected crystal was mounted on a glass fiber with silicone grease and placed in the 130 K nitrogen stream of a Siemens Nicolet R3m/V diffractometer that was equipped with a locally modified Enraf Nonius low-temperature apparatus. Unit cell parameters were determined by least-squares refinement of 30 reflections with $30° < 2\theta < 34°$. Two check reflections showed only random (<1%) fluctuation in intensity during data collection. The data were corrected for Lorentz and polarization effects. Crystal data are given in the Supporting Information. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[28]

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{(Me_2PhP)AuBr}$_2$. Colorless rectangular prisms of the complex were obtained by diffusion of diethyl ether into a dichloromethane solution of the complex.

{(Me_2PhP)AuI}$_2$. Colorless rectangular prisms of the complex were obtained by diffusion of diethyl ether into a dichloromethane solution of the complex.

{(Me_2PhP)AuCl}$_2$. Colorless prisms of the complex were obtained by diffusion of diethyl ether into a dichloromethane solution of the complex. Data were gathered as described above.

Structure Solution and Refinement. Calculations were performed using the Siemens SHELXTL PLUS system of programs. The structures were solved from Patterson maps. Hydrogen atoms were included in the refinement model. Their positions were geometrically calculated and refined by the use of a riding model with the C−H distance fixed at 0.96 Å and a common isotropic thermal parameter. Only Au, Cl, and P were allowed to refine anisotropically. An absorption correction was applied.[29] The largest peaks in the final difference maps were as follows: {(Me_2PhP)AuCl}$_3$, 6.31 e Å^{-3}, 1.06 Å from Au(2); {(Me_2PhP)AuBr}$_2$, 8.08 e Å^{-3}, 0.07 Å from Au(2); {(Me_2PhP)AuI}$_2$, 4.15 e Å^{-3}, 0.80 Å from Au(1); {(Me_2PhP)AuCl}$_2$, 1.96 e Å^{-3}, 1.13 Å from Au(2). For the dimeric complexes, the handedness was determined by a SHELXTL PLUS routine.

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Supporting Information Available: Tables of crystal data and structure determination details, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom positions for {(Me_2PhP)AuCl}$_3$, {(Me_2PhP)AuCl}$_2$, {(Me_2PhP)AuBr}$_2$, and {(Me_2PhP)AuI}$_2$ (28 pages). Ordering information is given on any current masthead page.

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