Inorg. Chem. **1990**, *29*, 3203-3207

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Preparations and Structures of Two Polynuclear Aggregates Obtained by Using the Metallaligand $\{\mathrm{ClAuPPh_2CH_2}\}_2\mathrm{AsPh}$

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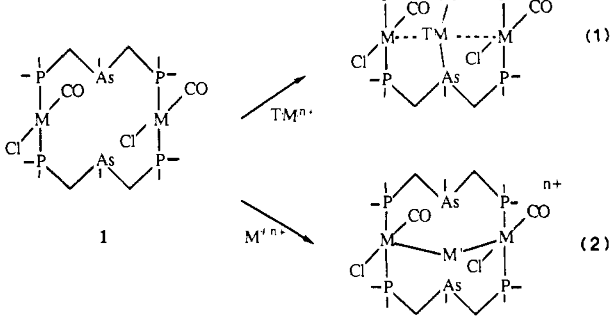
Received January 11, 1990

Treatment of *trans*-Pd(NCPh)$_2$Cl$_2$ with 2 equiv of (ClAuPPh$_2$CH$_2$)$_2$AsPh produces yellow *trans*-PdCl$_2${(ClAuPPh$_2$CH$_2$)$_2$AsPh}$_2$, which crystallizes as a 2.75 dichloromethane solvate in the monoclinic space group $P2_1/n$ with $a = 16.226$ (3) Å, $b = 17.609$ (6) Å, $c = 27.780$ (6) Å, and $\beta = 102.87$ (2)° with $Z = 4$ at 130 K. Refinement of 3612 reflections with $I > 2\sigma(I)$ and 334 parameters yields $R = 0.110$ and $R_w = 0.097$. The structure consists of a planar *trans*-PdCl$_2$As$_2$ unit irregularly surrounded by four linear ClAuP units. The Pd···Au separations range from 3.358 (6) to 6.389 (6) Å. The electronic absorption spectrum of the complex is similar to that of PdCl$_2$(AsPh$_3$)$_2$; this indicates that the palladium center is electronically unaffected by the presence of its gold neighbors. Reaction of (ClAuPPh$_2$CH$_2$)$_2$AsPh, (Ph$_2$PCH$_2$)$_2$AsPh, and Rh$_2$(CO)$_4$(μ-Cl)$_2$ in dichloromethane followed by the addition of ammonium hexafluorophosphate yields orange [Au$_2$Rh(CO)Cl{μ-(Ph$_2$PCH$_2$)$_2$AsPh}$_2$][PF$_6$]$_2$. This crystallizes as a 0.5 dichloromethane solvate in the triclinic space group $P\bar{1}$ with $a = 12.217$ (3) Å, $b = 24.882$ (8) Å, $c = 26.677$ (10) Å, $\alpha = 112.83$ (3)°, $\beta = 91.19$ (3)°, $\gamma = 95.52$ (2)°, and $Z = 4$ at 130 K. Refinement of 8480 reflections with $I > 2\sigma(I)$ and 738 parameters yielded $R = 0.098$ and $R_w = 0.094$. The structure of the cation consists of a planar Rh(CO)ClAs unit surrounded by two, nearly linear P$_2$Au groups with Rh–Au distances of 3.006 (2) and 3.028 (2) Å in one of the two independent cations and 3.034 (2) and 3.074 (2) Å in the other. The electronic absorption spectrum (λ_{max} 464 nm; ϵ 3.8 × 10^4 M^{-1} cm^{-1}) indicates that a significant interaction exists between the central rhodium ion and its two gold neighbors. This complex also shows photoluminescence (λ_{max} 620 nm) in dichloromethane solution at 25 °C.

Introduction

The availability of the metallamacrocycles **1a** (M = Ir) and **1b** (M = Rh), M$_2$(CO)$_2$Cl$_2$(μ-dpma)$_2$, where dpma is bis(diphenylphosphinomethyl)phenylarsine, allows the rational construction of nearly linear trinuclear aggregates[1] (see eqs 1 and 2; for clarity phenyl groups are indicated by a dash in all structural formulae). With transition metals (TM^{n+}), complexation (eq 1) invariably involves coordination of the two arsenic atoms along with possible bonding interactions with the metal ions (M), the chloride ligands, and the carbon monoxide ligands.[2] With main-group ions possessing an s^2 electronic configurations (Tl$^+$, Sn^{2+}, Pb^{2+}, Sb^{3+}), bonding occurs exclusively through the metal centers (eq 2) without the involvement of the arsenic atoms.[3] A continuing focus of our research is the development of new metallamacrocycles or their synthetic equivalents. Extensive efforts to obtain the hypothetical gold metallamacrocycle **2** have not produced this substance.[4-6] However, a number of other gold complexes of dpma have been obtained, and among these the digold complex **3** represents a convenient building block for the synthesis of new polynuclear aggregates. Complex **3**, which has been fully characterized including an X-ray crystal structure, contains two, widely separated P–Au–Cl units and an uncoordinated arsenic atom, which should make it capable of forming complexes similar to those of triphenylarsine.[6] Moreover, under appropriate conditions it acts as a synthon for **2**.



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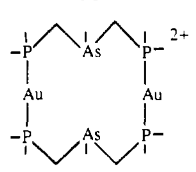
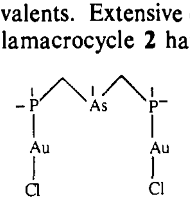
(1)

(2)



2 (hypothetical)



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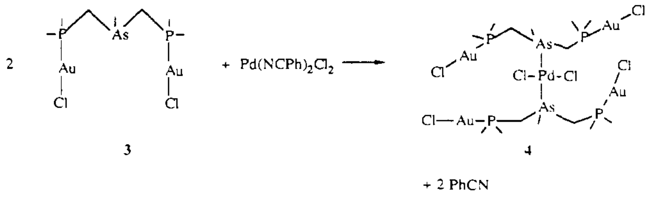
Results

Preparation and Structure of *trans*-PdCl$_2$(dpmaAu$_2$Cl$_2$)$_2$ (4). Addition of a brown dichloromethane solution of Pd(NCPh)$_2$Cl$_2$ to 2 equiv of colorless **3** results in the formation of a yellow solution from which yellow crystals of *trans*-PdCl$_2$(dpmaAu$_2$Cl$_2$)$_2$ (**4**) can be isolated in 56% yield (eq 3). At 23 °C the ^{31}P NMR spectrum consists of a single resonance at 21.2 ppm (versus 23.9 ppm for the free ligand **3**). Thus, all P–Au–Cl units are equivalent in solution. The spectrum is unchanged on cooling to −60 °C. The electronic spectrum of **4** (trace A) is compared to that of Pd(AsPh$_3$)$_2$Cl$_2$ (trace B) in Figure 1. The two spectra are similar with the predominant electronic transition of the PdAs$_2$Cl$_2$ units at 355 nm in **4** and at 365 nm in Pd(AsPh$_3$)$_2$Cl$_2$. (The gold complex **3** is transparent in this region with significant absorption only at wavelengths less than 300 nm.) The small shift in absorption maximum is in the reverse direction of that seen for interacting metal centers.[7,8] There is some difference in extinction coefficients for the two complexes. The data suggest that the



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4

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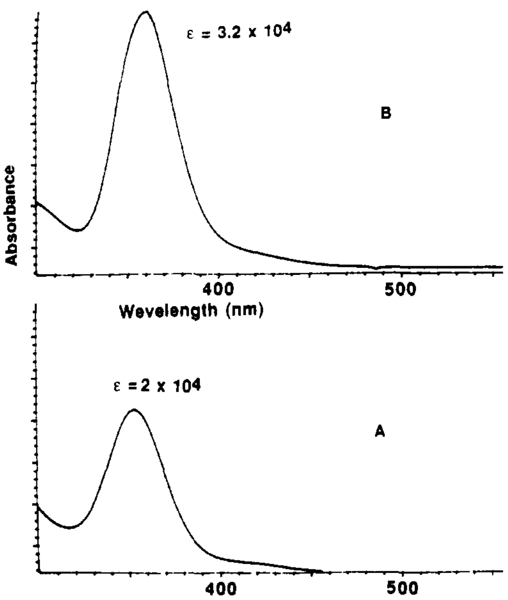

Figure 1. Electronic absorption spectra of dichloromethane solutions of (A) *trans*-$PdCl_2(dpmaAu_2Cl_2)_2$ (**4**) and (B) $PdCl_2(AsPh_3)_2$.

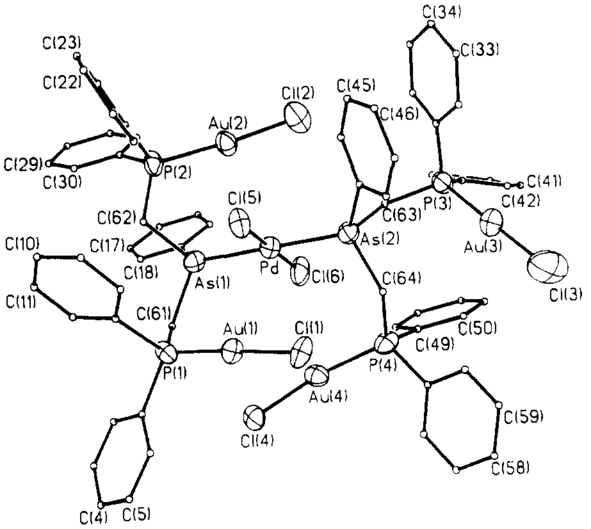

Figure 2. Perspective view of *trans*-$PdCl_2(dpmaAu_2Cl_2)_2$ (**4**), showing 50% thermal contours for heavy atoms and uniform, arbitrarily sized circles for carbon atoms.

palladium chromophore is not strongly influenced by the presence of the four P–Au–Cl moieties.

The results of a crystallographic study of **4** as its 2.75 dichloromethane solvate are shown in Figure 2. Selected interatomic distances and angles are given in Table I. An abbreviated list of atomic coordinates (excluding the 10 phenyl rings) is given in Table II. As seen in Figure 2, the molecule consists of a *trans*-$PdAs_2Cl_2$ core. The trans geometry is almost certainly sterically enforced by the bulky nature of the two arsine ligands. The two trans bond angles at palladium (Cl(5)–Pd–Cl(6) = 177.2 (6)°; As(1)–Pd–As(2) = 179.0 (3)°) are nearly linear, and the range of cis bond angles (88.9 (5)–92.0 (5)°) is near 90°. Thus, the palladium ion has its usual planar geometry. Similarly, the P–Au–Cl units are nearly linear with the P–Au–Cl angles ranging from 171.6 (6) to 177.0 (9)°. None of the metal–ligand distances are exceptional; all fall within normal ranges.

Within **4**, the palladium ion is surrounded by three PAuCl units involving Au(1), Au(2), and Au(4). The other PAuCl unit involving Au(3) is quite remote from this core. Nevertheless, the Pd⋯Au distances are all longer than 3.35 Å and beyond the distance where significant bonding is expected. While short Au⋯Au contacts (as short as 2.77 Å) are prevalent in gold(I) complexes,[9,10] the Au⋯Au contacts in **4** are all also greater than 3.35 Å. These nonbonded contacts are listed in Table I. The lack of significant metal–metal interaction within this complex may result from the crowded environment that must accommodate ten phenyl rings and five metal ions. Additionally, there are no close Au⋯Au contacts between molecules. The shortest intermolecular distance is 8.88 Å.

Table I. Bond Lengths (Å) and Angles (deg) for *trans*-$PdCl_2(dpmaAu_2Cl_2)_2$ (**4**)

	Bond Distances		
Au(1)–Cl(1)	2.308 (16)	Au(1)–P(1)	2.206 (20)
Au(2)–Cl(2)	2.287 (21)	Au(2)–P(2)	2.258 (21)
Au(3)–Cl(3)	2.298 (22)	Au(3)–P(3)	2.247 (17)
Au(4)–Cl(4)	2.259 (19)	Au(4)–P(4)	2.255 (21)
Pd–As(1)	2.405 (9)	Pd–As(2)	2.404 (9)
Pd–Cl(5)	2.275 (18)	Pd–Cl(6)	2.262 (20)
	Nonbonded Separations		
Pd⋯Au(1)	3.683 (6)	Au(1)⋯Au(2)	6.515 (6)
Pd⋯Au(2)	3.358 (6)	Au(1)⋯Au(3)	8.068 (6)
Pd⋯Au(3)	6.389 (6)	Au(1)⋯Au(4)	3.362 (6)
Pd⋯Au(4)	3.872 (6)	Au(2)⋯Au(3)	8.131 (6)
		Au(2)⋯Au(4)	7.170 (6)
		Au(3)⋯Au(4)	6.636 (6)
	Bond Angles		
P(1)–Au(1)–Cl(1)	173.9 (7)	As(1)–Pd–As(2)	179.0 (3)
P(2)–Au(2)–Cl(2)	175.8 (7)	Cl(5)–Pd–Cl(6)	177.2 (6)
P(3)–Au(3)–Cl(3)	177.0 (9)	As(1)–Pd–Cl(5)	92.0 (5)
P(4)–Au(4)–Cl(4)	171.6 (6)	As(1)–Pd–Cl(6)	90.2 (5)
		As(2)–Pd–Cl(5)	89.0 (5)
		As(2)–Pd–Cl(6)	88.9 (5)

Table II. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for *trans*-$PdCl_2(dpmaAu_2Cl_2)_2$ (**4**)

	x	*y*	*z*	U^a
Au(1)	5610 (2)	4243 (2)	1927 (1)	39 (1)*
Au(2)	7032 (2)	3450 (2)	4257 (1)	48 (1)*
Au(3)	1918 (2)	3179 (2)	3330 (1)	56 (1)*
Au(4)	4535 (2)	2598 (2)	1843 (1)	45 (1)*
Pd	5761 (3)	3298 (3)	3127 (2)	41 (2)*
As(1)	7178 (4)	3112 (4)	3023 (2)	40 (3)*
As(2)	4337 (4)	3462 (4)	3224 (2)	40 (3)*
Cl(1)	4254 (10)	4702 (9)	1850 (7)	47 (7)*
Cl(2)	5991 (12)	2986 (13)	4610 (7)	77 (10)*
Cl(3)	712 (16)	3589 (15)	2790 (8)	110 (13)*
Cl(4)	5557 (11)	2396 (10)	1424 (6)	48 (8)*
Cl(5)	5934 (11)	4580 (10)	3179 (7)	50 (8)*
Cl(6)	5523 (11)	2033 (11)	3053 (7)	60 (9)*
Cl(7)	5488 (14)	5513 (13)	−359 (8)	88 (8)
Cl(8)	6860 (17)	6601 (16)	−230 (10)	119 (9)
Cl(9)	4001 (13)	268 (12)	1383 (7)	74 (7)
Cl(10)	3385 (15)	1190 (13)	531 (8)	92 (8)
Cl(11)	8845 (24)	5971 (22)	605 (14)	68 (12)
Cl(12)	9640 (33)	4762 (27)	1179 (18)	119 (19)
Cl(13)	9023 (24)	1547 (25)	2093 (14)	76 (13)
Cl(14)	10248 (29)	2089 (29)	1587 (17)	109 (18)
P(1)	6930 (12)	3910 (10)	1955 (6)	39 (8)*
P(2)	8103 (12)	3949 (11)	3962 (7)	46 (8)*
P(3)	3062 (11)	2720 (12)	3863 (6)	44 (8)*
P(4)	3385 (12)	2725 (11)	2165 (7)	43 (8)*

[a] Asterisk indicates equivalent isotropic *U* defined as one-third of the tarce of the orthogonalized U_{ij} tensor. Carbon atom positions are omitted; see supplementary material.

Preparation and Structure of $[Au_2Rh(CO)Cl(\mu\text{-dpma})_2][PF_6]_2$. The combination of $Au_2Cl_2(\mu\text{-dpma})$ with another 1 equiv of dpma provides a useful synthon for the hypothetical **2**. Although **2** has not as yet been isolated from this mixture, the mixture does react to give a product in which a metal ion is bound to the center of **2**. Thus, addition of $Rh_2(CO)_4(\mu\text{-Cl})_2$ to a mixture of **3** and dpma followed by precipitation with ammonium hexafluorophosphate

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(9) Jones, P. G. *Gold Bull.* **1981**, *14*, 102; **1981**, *14*, 159; **1983**, *16*, 114; **1986**, *19*, 46.

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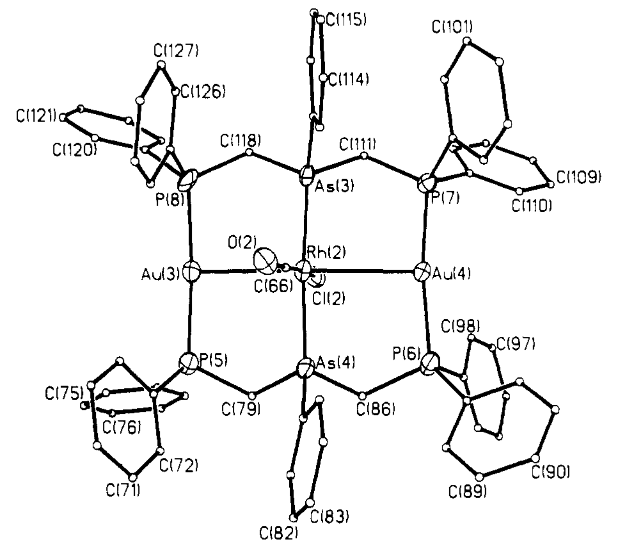
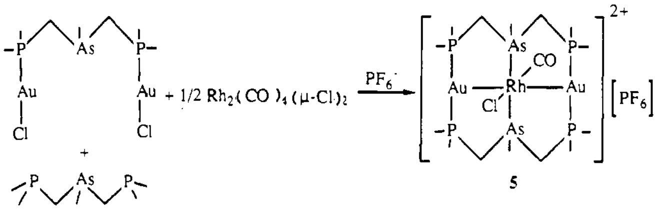


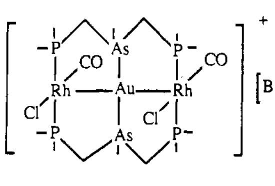
Figure 3. Perspective view of $[Au_2Rh(CO)Cl(\mu\text{-dpma})_2]^{2+}$, showing 50% thermal contours for heavy atoms and uniform, arbitrarily sized circles for carbon atoms.

gives orange crystals of $[Au_2Rh(CO)Cl(\mu\text{-dpma})_2][PF_6]_2$ (**5**) in 72% yield (eq 4). In dichloromethane solution **5** exhibits a singlet



(4)

at 35.8 ppm for the cation as well as a septet at −143.5 ppm due to the anion. The lack of Rh/P coupling indicates that the rhodium ion is not directly bonded to the phosphorus atoms. The infrared spectrum of the complex as a Nujol mull shows two carbon monoxide stretching bands at 1999 and 1996 cm^{-1}. The occurrence of two bands results from the presence of two independent molecules in the lattice (vide infra). In dichloromethane solution, however, only one band is observed (at 1993 cm^{-1}). The carbonyl stretching frequency occurs at higher energy than seen for $Rh(CO)Cl(AsPh_3)_2$ (1973 cm^{-1})[7] or for the inside-out analogue of **5**, $[Rh_2Au(CO)_2Cl_2(\mu\text{-dpma})_2][BPh_4]$ (**6**) (ν(CO) 1974, 1964



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cm^{-1}).[11] The increase in ν(CO) for **5** may reflect the effect of the increasing positive charge in the complex and restriction of the degree of Rh to carbon monoxide back-bonding.

The structure of $[Au_2Rh(CO)Cl(\mu\text{-dpma})_2][PF_6]_2\cdot0.5CH_2Cl_2$ has been determined by X-ray crystallography. The asymmetric unit consists of two independent cations, four hexafluorophosphate ions, and a dichloromethane molecule. There are no unusual contacts between these units. Both cations have similar structures. Figure 3 shows a view of one of these. Selected interatomic distances and angles are given in Table III, while Table IV presents the atomic coordinates of the two cations with the omission of the coordinates of the 20 phenyl rings (and of the hexafluorophosphate ions and the dichloromethane molecule). Table III is arranged to allow for facile comparison of the structural parameters for the two cations.

Table III. Selected Interatomic Distances (Å) and Angles (deg) for $[Au_2Rh(CO)Cl(\mu\text{-dpma})_2]^{2+}$

cation 1		cation 2	
	Distances		
Rh(1)–Au(1)	3.028 (2)	Rh(2)–Au(3)	3.034 (2)
Rh(1)–Au(2)	3.006 (2)	Rh(2)–Au(4)	3.074 (2)
Rh(1)–As(1)	2.406 (5)	Rh(2)–As(3)	2.418 (5)
Rh(1)–As(2)	2.418 (5)	Rh(2)–As(4)	2.414 (5)
Rh(1)–C(1)	1.64 (41)	Rh(2)–C(66)	1.69 (42)
Rh(1)–Cl(1)	2.382 (12)	Rh(2)–Cl(2)	2.384 (12)
Au(1)–P(1)	2.324 (11)	Au(3)–P(5)	2.330 (12)
Au(1)–P(4)	2.326 (11)	Au(3)–P(8)	2.299 (12)
Au(2)–P(2)	2.299 (11)	Au(4)–P(6)	2.311 (12)
Au(2)–P(3)	2.320 (10)	Au(4)–P(7)	2.285 (10)
	Angles		
Au(1)–Rh(2)–Au(2)	156.8 (1)	Au(3)–Rh(2)–Au(4)	151.4 (1)
Cl(1)–Rh(1)–C(1)	175.7 (9)	Cl(2)–Rh(2)–C(66)	173.4 (12)
As(1)–Rh(1)–As(2)	171.0 (2)	As(3)–Rh(2)–As(4)	170.6 (2)
As(1)–Rh(1)–Cl(1)	85.1 (3)	As(3)–Rh(2)–Cl(2)	85.4 (3)
As(1)–Rh(1)–C(1)	97.8 (12)	As(3)–Rh(2)–C(66)	96.9 (12)
As(2)–Rh(1)–Cl(1)	86.0 (3)	As(4)–Rh(2)–Cl(2)	85.6 (3)
As(2)–Rh(1)–C(1)	91.1 (12)	As(4)–Rh(2)–C(66)	92.3 (12)
P(1)–Au(1)–P(4)	172.2 (4)	P(5)–Au(3)–P(8)	175.9 (4)
P(2)–Au(2)–P(3)	168.6 (5)	P(6)–Au(4)–P(7)	164.5 (4)

Table IV. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[Au_2Rh(CO)Cl(\mu\text{-dpma})_2](PF_6)_2$

	x	*y*	*z*	U^a
Rh(1)	1728 (2)	4780 (1)	7168 (1)	25 (1)*
Au(1)	3554 (1)	5789 (1)	7593 (1)	32 (1)*
Au(2)	592 (1)	3575 (1)	6937 (1)	38 (1)*
As(1)	2564 (3)	4354 (2)	6314 (2)	26 (2)*
As(2)	1081 (3)	5128 (2)	8078 (2)	29 (2)*
P(1)	3081 (9)	6108 (5)	8494 (4)	34 (5)*
P(2)	−175 (9)	3877 (5)	7768 (4)	36 (5)*
P(3)	1449 (9)	3112 (5)	6138 (4)	34 (5)*
P(4)	4272 (8)	5481 (5)	6739 (4)	28 (5)*
Cl(1)	3097 (8)	4371 (4)	7514 (4)	36 (5)*
O(1)	167 (22)	5333 (14)	6735 (11)	60 (15)*
C(14)	2335 (28)	5508 (16)	8614 (14)	23 (9)
C(21)	722 (38)	4484 (22)	8304 (20)	62 (14)
C(46)	2766 (29)	3541 (16)	6126 (15)	29 (10)
C(53)	4139 (28)	4701 (16)	6434 (14)	24 (9)
Rh(2)	3025 (2)	9879 (1)	2197 (1)	26 (1)*
Au(3)	1087 (1)	10541 (1)	2678 (1)	32 (1)*
Au(4)	4204 (1)	8764 (1)	1826 (1)	33 (1)*
As(3)	2042 (3)	9454 (2)	1311 (2)	28 (2)*
As(4)	3894 (3)	10155 (2)	3096 (2)	31 (2)*
P(5)	1832 (9)	10839 (5)	3568 (4)	38 (5)*
P(6)	5032 (9)	8946 (5)	2672 (5)	35 (5)*
P(7)	3297 (9)	8335 (5)	985 (4)	31 (5)*
P(8)	280 (8)	10303 (5)	1822 (5)	37 (5)*
Cl(2)	1889 (8)	9164 (4)	2399 (4)	34 (4)*
O(2)	4106 (19)	10877 (12)	2029 (10)	40 (12)*
C(66)	3751 (29)	10445 (16)	2105 (15)	27 (10)
C(79)	2790 (32)	10359 (18)	3662 (16)	37 (11)
C(86)	4355 (29)	9525 (17)	3227 (15)	30 (10)
C(111)	1914 (31)	8583 (18)	994 (16)	36 (11)
C(118)	431 (33)	9554 (19)	1369 (17)	43 (12)

[a] Asterisk indicates equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. Phenyl carbon atoms are omitted; see supplementary material.

The cation consists of a planar $Rh(CO)ClAs_2$ core bracketed by two nearly linear P_2Au units. Thus, it can be considered the Rh(CO)Cl adduct of the hypothetical metallamacrocycle **2**. (The iridium analogue of **5**, which has been synthesized by an entirely different route, is isostructural with **5**.[12]) Although each cation

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Table V. Crystal Data, Data Collection, and Structure Solution Parameters for **5** and **4**

	$[Au_2Rh(CO)Cl(\mu\text{-dpma})_2]$-$[PF_6]_2 \cdot 0.5CH_2Cl_2$ (**5**)	*trans*-$PdCl_2$-$(dpmaAu_2Cl_2)_2 \cdot 2.75CH_2Cl_2$ (**4**)
formula	$C_{65.5}H_{59}As_2Au_2Cl_2F_{12}OP_6Rh$	$C_{67}H_{64}As_2Au_4Cl_{12}P_4Pd$
fw	1993.60	2462.87
color and habit	orange blocks	yellow blocks
cryst system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a, Å	12.217 (3)	16.226 (3)
b, Å	24.882 (8)	17.609 (6)
c, Å	26.677 (10)	27.780 (6)
α, deg	112.83 (3)	
β, deg	91.19 (3)	102.87 (2)
γ, deg	95.52 (2)	
V, Å^3	7424 (4)	7738 (3)
T, K	130	130
Z	4	4
cryst dimens, mm	0.10 × 0.10 × 0.23	0.13 × 0.15 × 0.18
d_{calcd}, g cm^{-3}	1.78	2.11
radiation (λ, Å)	Mo Kα (0.71069)	
μ(Mo Kα), cm^{-1}	52.96	91.58
range of transm factors	0.49–0.54	0.23–0.37
R^a	0.098	0.110
$R_w{}^a$	0.094 [$w = 1/\sigma^2(F_o)$]	0.097 [$w = 1/\sigma^2(F_o)$]

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

has no crystallographically imposed symmetry, each has a virtual mirror plane containing the $Au_2Rh(CO)Cl$ units as well as a virtual 2-fold axis down the OCRhCl unit. Thus, it is not surprising that the four phosphorus atoms are equivalent in solution. The P-Au-P angles range from 175.9 (4) to 164.5 (4)°, and in each case the slight bend is such that the gold ions are displaced toward the rhodium ion. The rhodium ion is symmetrically positioned between the gold ions with the Rh–Au distances of 3.028 (2) and 3.006 (2) Å in cation 1 and 3.034 (2) and 3.074 (2) Å in cation 2. The Au–Rh–Au angles are 156.8 (1) and 151.4 (1)° so that the chain of three metal ions is somewhat bent. The bond lengths within the coordination environments of the three metal ions all fall within normal ranges. For example, the bond lengths at rhodium are similar to those seen in $[Rh_2Ir(\mu\text{-Cl})Cl(CO)_3(\mu\text{-dpma})_2]^+$,[2b] and the bonding parameters at gold are similar to those in $[(Ph_2MeP)_2Au]^+$ [13] and $[\{(cyclohexyl)_3P\}_2Au]^+$ [14] except for the inward bend toward rhodium.

The orange color of $[Au_2Rh(CO)Cl(\mu\text{-dpma})_2]^{2+}$ results from an intense absorption at 464 nm (ϵ 28 800 M^{-1} cm^{-1}) that is seen in its electronic spectrum (Figure 4). In comparison $Rh(CO)Cl(AsPh_3)_2$ shows no significant absorption in this region but rather an intense band at 357 nm (ϵ 3700 M^{-1} cm^{-1}).[7] The shift of this absorption feature to low energy is consistent with work on the effect of proximity of metal ions upon one another.[7,8,11] Interaction of the three filled d_{z^2} orbitals approximately directed along the Au–Rh–Au axis and the corresponding three empty p_z orbitals leads to an interaction along this $d^{10}d^8d^{10}$ chain which is similar to that described previously for $d^8d^8d^8$ and $d^8d^{10}d^8$ chains.[2b,11] Thus, the bonding interactions within this Au_2Rh chain can be related to the qualitative molecular orbital diagram presented earlier for the $d^8d^{10}d^8$ Ir_2Au chain in the iridium analogue of **6** (Figure 6 of ref 11). Moreover, the absorption spectra of both **5** and its inside-out analogue **6** show similar transitions (at 464 nm for **5** and 472 nm for **6**).[11]

As with a number of other nearly linear chain complexes with related electronic structures,[3,10] **5** is luminescent in solution. Trace B of Figure 4 shows the luminescence that results from excitation of a dichloromethane solution of **5** at 23 °C at 474 nm. A broad emission (maximum at 620 nm) is observed with a shoulder at high energies. The excitation spectrum for emission at 620 nm parallels to the absorption spectrum.

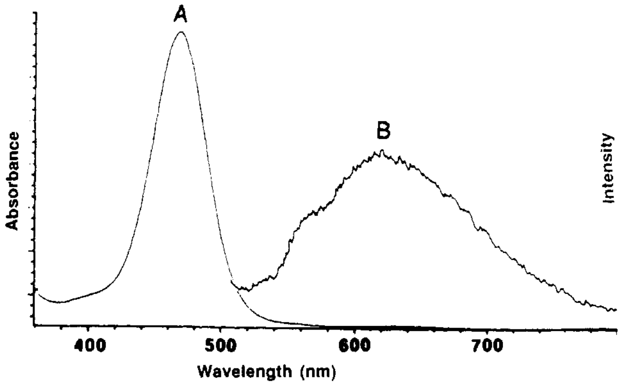

Figure 4. Electronic absorption (A, left) and emission (B, right) from dichloromethane solutions of $[Au_2Rh(CO)Cl(\mu\text{-dpma})_2][PF_6]_2$.

The difference in metal–metal interactions in **4** and **5** requires comment. In **5** significant interactions occur between the d_{z^2} and p_z orbitals along the Au–Rh–Au axis. No counterparts are seen in **4**. This may arise in part because of a different electronic structure for the $PdAs_2Cl_2$ and $Rh(CO)As_2Cl$ cores. For the latter it is fairly clear that the d_{z^2} orbital is the HOMO, while much less is known about the electronic structure of the $PdAs_2Cl_2$ complex. Its structure may have the d_{xy} orbital as the HOMO as proposed for some planar d^8 complexes.[15] Additionally the surrounding ligand structure in **5** favors metal–metal bonding by positioning two bridging ligands along the Au–Rh–Au chain. In contrast, in **4** the array of four bulky Ph_2PAuCl substituents may create an environment that is too crowded to facilitate electronic interactions among the constituents.

Experimental Section

Preparation of Compounds. The compounds $Au_2Cl_2(\mu\text{-dpma})$ (from dpma and $(Me_2S)AuCl)^6$ and dpma[2] were prepared as previously described. All the compounds were synthesized in air, and the pure complexes are both air-stable as solids and in solution.

***trans*-$PdCl_2(dpmaAu_2Cl_2)_2$ (4).** A solution of 2.9 mg (0.0076 mmol) of *trans*-$Pd(NCPh)_2Cl_2$ in a minimum volume of dichloromethane was added to a solution of 15.4 mg (0.0152 mmol) of $Au_2Cl_2(\mu\text{-dpma})$ in minimum volume of dichloromethane. The solution immediately turned yellow in color and was stirred for 2 h. Yellow crystals of **4** were formed by adding ethyl ether. The product was recrystallized by dissolution in

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(13) Guy, J. J.; Jones, P. G.; Sheldrick, G. N. *Acta Crystallogr., Sect. B* **1976**, *B32*, 1937.

(14) Muir, J. A.; Muir, J. J.; Lorca, E. *Acta Crystallogr., Sect. B* **1980**, *B36*, 931.

(15) Martin, D. S., Jr. In *Extended Linear Chain Compound*; Miller, J. S., Ed.; Plenum Press: New York, 1982; Vol. 1, p 409.

dichloromethane and precipitation by the addition of ethyl ether; yield 9.4 mg (56%).

$[Au_2Rh(CO)Cl(\mu\text{-dpma})_2][PF_6]_2$ (5). A solution of 29 mg (0.053 mmol) of dpma was added to a solution of 54 mg (0.053 mmol) of $Au_2Cl_2(\mu\text{-dpma})$ in dichloromethane. After the mixture was stirred for several minutes, 17 mg (0.10 mmol) of ammonium hexafluorophosphate in a 1:1 mixture of dichloromethane and methanol was added. A 10-mg (0.027-mmol) amount of $Rh_2(CO)_4(\mu\text{-Cl})_2$ was added to react with the solution mixture, and it turned to an orange solution with a trace amount of white impurities. The solution was filtered, and orange crystals were formed by the addition of ethyl ether. The final product was recrystallized by dissolution in dichloromethane and precipitation by the addition of ethyl ether; yield 75 mg (72%).

X-ray Data Collection. $[Au_2Rh(CO)Cl(\mu\text{-dpma})_2][PF_6]_2\cdot0.5CH_2Cl_2$ (5). Orange blocks were formed by slow diffusion of ethyl ether into a dichloromethane solution of the complex. The crystals were removed from the diffusion tube and rapidly coated with light hydrocarbon oil to reduce loss of solvent from the crystal. The crystal was mounted in the cold stream of a Syntex $P2_1$ diffractometer equipped with a modified LT-1 low-temperature apparatus. Unit cell dimensions were obtained from a least-square fit of 21 reflections with $15° \leq 2\theta \leq 38°$. No decay in intensities during data collection of two standard reflections occurred. Data collection parameters are summarized in Table V.

***trans*-$PdCl_2(dpmaAu_2Cl_2)_2$ (4).** Yellow blocks were formed by slow diffusion ethyl ether into a dichloromethane solution of the compound. The space group $P2_1/n$ was uniquely determined by the observed conditions $h0l$, $h + l = 2n$ and $0k0$, $k = 2n$. No decay in the intensities of two standard reflections occurred during data collection. Data collection parameters are summarized in Table V. All other data collection procedures were identical with those of the rhodium complex.

Solution and Refinement of Structures. $[Au_2Rh(CO)Cl(\mu\text{-dpma})_2][PF_6]_2\cdot0.5CH_2Cl_2$. All structure determination calculations were done on a Data General Eclipse MV/10000 computer using the SHELXTL version 5.1 software package. The positions of the two gold atoms and the rhodium atom were generated from FMAP8, the Patterson-solving routine of SHELXTL. This compound is isostructural with its iridium analogue and all initial atom positions were obtained from that structure. Anisotropic thermal parameters were assigned to the elements gold, rhodium, phosphorus, arsenic, and the oxygen atom on the carbonyl group. Anisotropic thermal parameters were also assigned to the phosphorus and fluorine on the two anions and the chloride bonded to the rhodium atom. Isotropic thermal parameters were used for all other atoms. Scattering factors and corrections for anomalous dispersions were taken from a standard source.[15] The final stages of refinement included an absorption correction.[16] Due to the dominance of the scattering by heavy atoms, hydrogen atoms were not included. The final R value of 0.099 was computed with a data to parameter ratio of 11.73. This yielded a goodness-of-fit of 1.513 and a maximum shift/esd of 0.18 for U_{11} at C(58) in the last cycle of refinement. A value of 2.92 e/Å^3 was found as the largest feature on the final difference Fourier map. This peak was located 1.11 Å from Au(4). The phenyl rings were all refined as rigid hexagons with the C–C distance fixed at 1.39 Å. Two disordered dichloromethane solvent molecules were also found to be half-occupied, and the two chlorine atoms were reset during refinement at a separation of 2.9 Å. The weighting scheme used was $w = [\sigma^2(F_o)^{-1}]$. Corrections for anomalous dispersions were applied to all atoms.

***trans*-$PdCl_2(dpmaAu_2Cl_2)_2\cdot2.75CH_2Cl_2$.** The positions of the four gold atoms and the palladium atom were generated by direct methods. Other atom positions were located from successive difference Fourier maps. Anisotropic thermal parameters were assigned to the elements gold, palladium, phosphorus, arsenic, and the chlorine atoms bonded to gold and palladium. The final R value of 0.110 was computed with a data to parameter ratio of 10.8. This yielded a goodness-of-fit of 1.504 and a maximum shift/esd of −0.015 for z of C(18) in the last cycle of refinement. A value of 2.67 e/Å^3 was found as the largest feature on the final difference Fourier map. This peak was located 1.47 Å from Cl(11). The treatment of phenyl rings and dichloromethane solvent molecules was the same as that for $[Au_2Rh(CO)Cl(\mu\text{-dpma})_2][PF_6]_2$. As stated above, hydrogens were not included. The weighting scheme used was $w = [\sigma^2(F_o)^{-1}]$.

Acknowledgment. We thank the National Science Foundation (Grant CHE 894209) for support and Johnson Matthey, Inc., for a loan of rhodium salts.

Supplementary Material Available: Tables of atomic coordinates and thermal parameters, bond distances, bond angles, anisotropic thermal parameters, and crystal refinement data for **4** and **5** (14 pages); listings of observed and calculated structure factors (72 pages). Ordering information is given on any current masthead page.

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(16) *International Tables of X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(17) The method obtains an empirical absorption tensor from an expression relating F_o and F_c: Moezzi, B. Ph.D. Thesis, University of California, Davis, CA, 1987.