instability arising from this nesting would open a band gap at the Fermi level,[26,28] and the resulting state would become insulating. The fact that $(PT)_3(InI_4)_2$ is a semiconductor at room temperature suggests that the metal–insulator phase transition associated with the nesting has already occurred above room temperature. Then, the crystal structure determined at room temperature is an "average" structure although no extra diffraction peaks arising from a unit cell doubling (associated with the metal–insulator transition) have been observed, even with the more sensitive Weissenberg film method.

Concluding Remarks

Single-crystal X-ray, ESR, and band electronic structure studies show that the $(PT)_3(InI_4)_2$ salt synthesized in the present work consists of PT donor molecules in two different oxidation states (i.e., PT^+ and $PT^{0.5+}$). The semiconducting property of this salt at room temperature and below is explained by electron localization in the stacks of PT^+ cations and by the electronic instability associated with the well-nested Fermi surface of the $(PT)_2{}^+$ dimer layers.

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Supplementary Material Available: Tables of crystal and data collection parameters, calculated hydrogen positions, anisotropic thermal parameters, and least-squares planes (4 pages); tables of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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Two Modes of Chelation for Bis((diphenylphosphino)methyl)phenylarsine. The Structures of $[Au\{(Ph_2PCH_2)_2AsPh\}_2][Au(CN)_2]$ and $Ru\{(Ph_2PCH_2)_2AsPh\}_2Cl_2$

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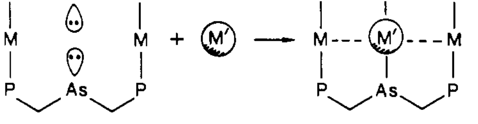
Dpma (bis((diphenylphosphino)methyl)phenylarsine) reacts with gold(I) cyanide to form $[Au(dpma)_2][Au(CN)_2]\cdot CH_2Cl_2\cdot CHCl_3$, which crystallizes in the monoclinic space group $C2/c$ with $Z = 4$, $a = 17.062$ (4) Å, $b = 25.946$ (7) Å, $c = 17.820$ (5) Å, and $\beta = 99.35$ (2)° at 130 K. Least-squares refinement of 389 parameters using 4159 reflections yields $R = 0.073$, $R_w = 0.079$. The structure consists of tetrahedral cations with two six-membered chelate rings and nearly linear $Au(CN)_2$ ions. Dpma reacts with $Ru(dimethyl\ sulfoxide)_4Cl_2$ to give $Ru(dpma)_2Cl_2$. Orange blocks of $Ru(dpma)_2Cl_2$ crystallize in the monoclinic space group $P2_1/n$ with $Z = 4$, $a = 16.357$ (6) Å, $b = 18.416$ (7) Å, $c = 18.502$ (4) Å, and $\beta = 94.77$ (3)° at 130 K. Least-squares refinement of 338 parameters using 7346 data yields $R = 0.051$, $R_w = 0.046$. The ruthenium is six-coordinate with bonds to two trans chloride ligands, to two phosphorus atoms of one chelating dpma, and to an arsenic and a phosphorus atom of a second chelate ring. Steric factors appear responsible for this unusual circumstance where two identical ligands form differently sized chelate rings, and for one of them, arsenic coordination is preferred over phosphorus coordination. ^{31}P NMR spectral data for both complexes are reported.

Introduction

In previous studies we have shown that the tridentate ligand bis((diphenylphosphino)methyl)phenylarsine (dpma) forms metallamacrocycles **1**, which are capable of complexing cations via reaction 1.[1-8] Related binding of anions has also been observed.[9] In this work we have taken advantage of the preferential binding of metal ions to the phosphorus atoms in dpma to create the metallamacrocyclic structures.[10] However, the flexibility of the methylene units within the dpma unit also allows it to adopt chelating structures. In attempts to prepare metallamacrocycles with gold and ruthenium as M in **1**, we have encountered chelate ring formation rather than macrocycle formation. Here we report the preparations, spectroscopic properties, and structures of the first two complexes to contain chelating dpma. While both contain a common $M(dpma)_2$ unit, they differ appreciably since the ruthenium complex contains two differently coordinating dpma ligands.



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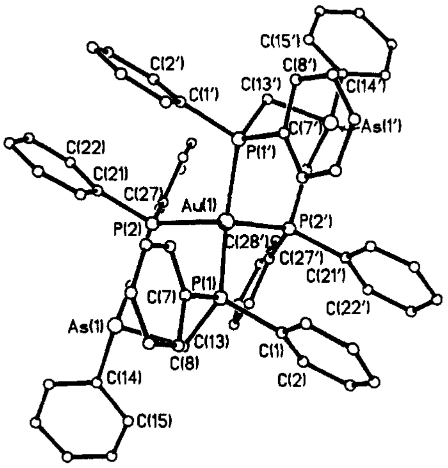

Figure 1. Perspective view of $Au(dpma)_2^+$ in **2**.

Table I. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[Au(dpma)_2][Au(CN)_2]\cdot CH_2Cl_2\cdot CHCl_3$

	x	*y*	*z*	U^a
Au(1)	5000	6277 (1)	7500	32 (1)*
As(1)	3504 (1)	6150 (1)	5496 (1)	37 (1)*
P(1)	3782 (3)	6727 (2)	7084 (3)	37 (2)*
P(2)	5127 (3)	5707 (2)	6449 (3)	34 (1)*
C(1)	3175 (11)	6905 (7)	7827 (10)	43 (6)*
C(2)	2706 (13)	6558 (8)	8096 (12)	58 (8)*
C(3)	2276 (14)	6688 (9)	8682 (15)	69 (10)*
C(4)	2325 (18)	7171 (11)	8926 (17)	101 (13)*
C(5)	2849 (17)	7545 (10)	8651 (16)	99 (13)*
C(6)	3281 (15)	7420 (9)	8104 (13)	70 (9)*
C(7)	3849 (12)	7322 (8)	6524 (12)	57 (8)*
C(8)	3114 (11)	7579 (8)	6238 (14)	65 (9)*
C(9)	3179 (16)	8017 (9)	5821 (17)	99 (12)*
C(10)	3896 (19)	8203 (10)	5727 (22)	126 (17)*
C(11)	4568 (15)	7987 (10)	6091 (18)	104 (13)*
C(12)	4563 (16)	7503 (8)	6455 (13)	75 (9)*
C(13)	3097 (10)	6325 (7)	6425 (9)	37 (6)*
C(14)	2619 (10)	5732 (7)	5017 (8)	34 (6)*
C(15)	1953 (11)	5580 (7)	5362 (10)	44 (7)*
C(16)	1377 (13)	5281 (9)	4982 (11)	59 (8)*
C(17)	1408 (12)	5101 (10)	4284 (12)	65 (9)*
C(18)	2038 (13)	5232 (8)	3921 (11)	61 (8)*
C(19)	2650 (12)	5555 (8)	4278 (11)	55 (8)*
C(20)	4145 (10)	5554 (6)	5899 (9)	33 (6)*
C(21)	5696 (10)	5929 (7)	5723 (10)	37 (6)*
C(22)	6230 (11)	5623 (7)	5419 (10)	41 (6)*
C(23)	6650 (13)	5797 (10)	4867 (12)	59 (9)*
C(24)	6493 (18)	6262 (11)	4565 (12)	81 (11)*
C(25)	5959 (15)	6567 (9)	4890 (13)	63 (9)*
C(26)	5579 (13)	6428 (9)	5433 (13)	62 (9)*
C(27)	5550 (9)	5085 (7)	6758 (10)	35 (6)*
C(28)	5206 (11)	4615 (7)	6487 (10)	43 (6)*
C(29)	5563 (12)	4151 (8)	6767 (12)	54 (8)*
C(30)	6244 (12)	4149 (8)	7292 (12)	54 (8)*
C(31)	6612 (11)	4613 (8)	7514 (10)	48 (7)*
C(32)	6286 (11)	5088 (8)	7256 (9)	44 (7)*
Au(2)	0	4482 (1)	2500	40 (1)*
N(1)	1734 (11)	4521 (7)	2180 (9)	60 (7)*
C(33)	1105 (10)	4515 (7)	2292 (12)	45 (7)*
Cl(1)	3763 (8)	1215 (4)	2565 (8)	79 (5)*
Cl(2)	4801 (5)	663 (4)	3718 (7)	60 (4)*
Cl(3)	3337 (8)	1071 (5)	4031 (8)	86 (6)*
C(34)	3855 (18)	863 (13)	3365 (17)	46 (9)
Cl(4)	4088 (13)	1848 (9)	8281 (12)	80
Cl(5)	4053 (13)	2781 (8)	8953 (12)	80
Cl(6)	3876 (21)	2618 (14)	7720 (19)	80
Cl(7)	4087 (21)	2085 (13)	9062 (19)	80

[a] Asterisk indicates equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table II. Selected Interatomic Distances (Å) and Angles (deg) in $[Au(dpma)_2][Au(CN)_2]\cdot CH_2Cl_2\cdot CHCl_3$[a]

	Distances		
Au(1)–P(1)	2.394 (5)	Au(1)–P(2)	2.425 (5)
As(1)–C(13)	1.950 (18)	As(1)–C(14)	1.940 (16)
As(1)–C(20)	1.962 (16)	P(1)–C(1)	1.866 (20)
P(1)–C(7)	1.852 (21)	P(1)–C(13)	1.839 (17)
P(2)–C(20)	1.841 (16)	P(2)–C(21)	1.832 (19)
P(2)–C(27)	1.817 (18)		
Au(2)–C(33)	1.982 (19)	N(1)–C(33)	1.123 (27)
	Angles		
P(1)–Au(1)–P(2)	103.9 (2)	P(1)–Au(1)–P(1′)	121.7 (2)
P(2)–Au(1)–P(1′)	110.7 (2)	P(1)–Au(1)–P(2′)	110.8 (2)
P(2)–Au(1)–P(2′)	104.8 (2)	C(13)–As(1)–C(14)	98.3 (7)
C(13)–As(1)–C(20)	97.3 (7)	C(14)–As(1)–C(20)	93.9 (7)
Au(1)–P(1)–C(1)	117.1 (6)	Au(1)–P(1)–C(7)	116.5 (7)
C(1)–P(1)–C(7)	105.4 (9)	Au(1)–P(1)–C(13)	110.6 (6)
C(1)–P(1)–C(13)	103.0 (8)	C(7)–P(1)–C(13)	102.5 (8)
Au(1)–P(2)–C(20)	110.7 (6)	Au(1)–P(2)–C(21)	118.5 (6)
C(20)–P(2)–C(21)	103.5 (8)	Au(1)–P(2)–C(27)	112.8 (6)
C(20)–P(2)–C(27)	104.7 (7)	C(21)–P(2)–C(27)	105.4 (8)
C(33)–Au(2)–C(33″)	175.0 (11)	Au(2)–C(33)–N(1)	178.1 (18)

[a] Symmetry codes: prime = $1 - x, y, 1^1/_2 - z$; double prime = $-x, y, {}^1/_2 - z$.

Results

Synthesis and Structure of $[Au(dpma)_2][Au(CN)_2]$ (2). The preferred linear coordination of Au(I)[11] would appear to facilitate the formation of a metallamacrocycle **1** (M = Au). However, a number of attempts to prepare such a species led to the formation of mixtures of products. Thus, the reaction of dpma with the colorless gold(I) salt obtained by reacting $AuCl_4^-$ with ethanol produced a colorless solution with four individual resonances in the ^{31}P NMR spectrum. It was not possible to isolate a pure crystalline material from the mixture. Similarly, reaction of solutions of (OC)AuCl in dichloromethane or a suspension of AuCl in dichloromethane with dpma produced mixtures containing at least four different species (as detected by ^{31}P NMR spectroscopy) from which pure materials could not be isolated. However, the reaction of equimolar amounts of dpma with AuCN in toluene produces a colorless, crystalline solid in good yield. After recrystallization from chloroform/ethyl ether, this material exhibits a single ^{31}P NMR resonance at 1.2 ppm and a CN stretching frequency in the infrared spectrum at 2140 cm^{-1}.

Since the complex was rather soluble in chloroform, we initially expected that it was a molecular species, possibly a metallamacrocycle. Consequently, an X-ray crystallographic study was undertaken. It shows, however, that the complex contains a cation in which a gold ion is bound to the four phosphorus atoms of two dpma ligands in a pseudotetrahedral geometry. One cyanide ligand has been displaced by phosphorus and reacts with a second AuCN molecule to form an $Au(CN)_2^-$ anion. The lack of any reaction between dpma and $K[Au(CN)_2]$ indicates that $Au(CN)_2^-$ is very stable, and its stability may account for some of the driving force in this reaction.

The asymmetric unit of the solid contains half of a cation, half of an $Au(CN)_2^-$ anion, half of a chloroform molecule, and two partially occupied dichloromethane sites. Both Au atoms lie on crystallographic 2-fold axes. There are no unusual contacts between these components. A perspective view and the numbering scheme of the cation are shown in Figure 1. Atomic positional parameters are given in Table I. Table II contains selected interatomic distances and angles.

The geometry about Au(1) is pseudotetrahedral, with a crystallographic C_2 axis bisecting the P(1)–Au(1)–P(1′) and P(2)–Au(1)–P(2′) angles. The P–Au–P angles are distorted from those of an ideal tetrahedron and range from 103.9° for P(1)–Au(1)–P(2) to 121.7° for P(1)–Au(1)–P(1′). The large deviation of the P(1)–Au(1)–P(2) angle from the tetrahedral ideal of 109.7° is probably a consequence of the interaction of the bulky phenyl substituents. Notice that the P(1)–Au(1)–P(2′) angle is affected

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Table III. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $Ru(dpma)_2Cl_2$

	x	*y*	*z*	U^a
Ru	2826 (1)	7197 (1)	5566 (1)	17 (1)*
As(1)	2728 (1)	6878 (1)	7851 (1)	23 (1)*
As(2)	3527 (1)	7972 (1)	4690 (1)	19 (1)*
P(1)	2193 (1)	6311 (1)	6191 (1)	20 (1)*
P(2)	2757 (1)	6605 (1)	4404 (1)	18 (1)*
P(3)	2832 (1)	7993 (1)	6563 (1)	20 (1)*
P(4)	3275 (1)	9350 (1)	3586 (1)	25 (1)*
Cl(1)	1680 (1)	7858 (1)	4984 (1)	23 (1)*
Cl(2)	4121 (1)	6718 (1)	6075 (1)	23 (1)*
C(1)	1780 (4)	6281 (4)	3987 (4)	19 (2)
C(2)	1548 (5)	5561 (4)	4070 (4)	31 (2)
C(3)	793 (5)	5316 (4)	3770 (4)	35 (2)
C(4)	273 (5)	5786 (4)	3381 (4)	34 (2)
C(5)	482 (5)	6495 (4)	3301 (4)	31 (2)
C(6)	1240 (4)	6752 (4)	3603 (4)	26 (2)
C(7)	3478 (4)	5936 (4)	4083 (4)	20 (2)
C(8)	3292 (5)	5568 (4)	3436 (4)	30 (2)
C(9)	3832 (5)	5089 (4)	3178 (4)	34 (2)
C(10)	4577 (5)	4980 (4)	3560 (4)	28 (2)
C(11)	4776 (5)	5362 (4)	4171 (4)	32 (2)
C(12)	4247 (4)	5849 (4)	4442 (4)	26 (2)
C(13)	3010 (4)	7409 (4)	3881 (4)	22 (2)
C(14)	4673 (4)	7948 (4)	4561 (4)	17 (2)
C(15)	4985 (5)	7653 (4)	3952 (4)	38 (2)
C(16)	5833 (5)	7636 (5)	3906 (5)	51 (3)
C(17)	6349 (5)	7905 (4)	4459 (4)	36 (2)
C(18)	6050 (6)	8210 (5)	5043 (5)	54 (3)
C(19)	5195 (6)	8230 (5)	5096 (5)	53 (3)
C(20)	3219 (4)	8990 (4)	4502 (4)	23 (2)
C(21)	2406 (5)	8925 (4)	3059 (4)	30 (2)
C(22)	2532 (5)	8705 (4)	2352 (4)	36 (2)
C(23)	1919 (5)	8394 (4)	1894 (4)	40 (2)
C(24)	1167 (5)	8285 (4)	2142 (4)	39 (2)
C(25)	1017 (5)	8501 (4)	2839 (4)	38 (2)
C(26)	1636 (4)	8824 (4)	3292 (4)	29 (2)
C(27)	2830 (4)	10261 (4)	3684 (4)	26 (2)
C(28)	2275 (5)	10447 (4)	4170 (4)	36 (2)
C(29)	1923 (5)	11140 (5)	4161 (4)	45 (2)
C(30)	2130 (5)	11635 (5)	3652 (4)	42 (2)
C(31)	2683 (5)	11475 (5)	3182 (4)	40 (2)
C(32)	3045 (5)	10781 (4)	3188 (4)	32 (2)
C(33)	3338 (4)	8861 (4)	6448 (4)	21 (2)
C(34)	4179 (4)	8924 (4)	6575 (4)	28 (2)
C(35)	4565 (5)	9591 (4)	6486 (4)	33 (2)
C(36)	4120 (5)	10198 (4)	6266 (4)	33 (2)
C(37)	3292 (5)	10143 (4)	6139 (4)	32 (2)
C(38)	2897 (5)	9481 (4)	6230 (4)	27 (2)
C(39)	1889 (4)	8324 (4)	6916 (4)	22 (2)
C(40)	1132 (4)	8149 (4)	6589 (4)	24 (2)
C(41)	433 (5)	8413 (4)	6862 (4)	29 (2)
C(42)	481 (5)	8843 (4)	7471 (4)	39 (2)
C(43)	1238 (5)	9016 (4)	7802 (4)	36 (2)
C(44)	1934 (5)	8765 (4)	7537 (4)	30 (2)
C(45)	3373 (4)	7627 (4)	7387 (4)	22 (2)
C(46)	3634 (4)	6475 (4)	8471 (4)	26 (2)
C(47)	3864 (5)	5748 (4)	8473 (4)	33 (2)
C(48)	4494 (5)	5486 (4)	8955 (4)	35 (2)
C(49)	4891 (5)	5950 (4)	9453 (4)	34 (2)
C(50)	4676 (5)	6674 (4)	9462 (4)	38 (2)
C(51)	4032 (4)	6929 (4)	8987 (4)	25 (2)
C(52)	2680 (4)	6121 (4)	7101 (4)	23 (2)
C(53)	1110 (4)	6405 (4)	6310 (4)	21 (2)
C(54)	588 (4)	6560 (4)	5697 (4)	26 (2)
C(55)	−217 (5)	6696 (4)	5761 (4)	33 (2)
C(56)	−529 (5)	6660 (4)	6432 (4)	35 (2)
C(57)	−29 (5)	6477 (4)	7039 (4)	39 (2)
C(58)	793 (5)	6359 (4)	6975 (4)	28 (2)
C(59)	2213 (4)	5378 (4)	5841 (4)	22 (2)
C(60)	2908 (4)	5098 (4)	5579 (4)	27 (2)
C(61)	2950 (5)	4400 (4)	5317 (4)	34 (2)
C(62)	2284 (5)	3940 (5)	5348 (4)	37 (2)
C(63)	1588 (5)	4204 (4)	5625 (4)	38 (2)
C(64)	1552 (5)	4906 (4)	5861 (4)	29 (2)

[a] Asterisk indicates equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

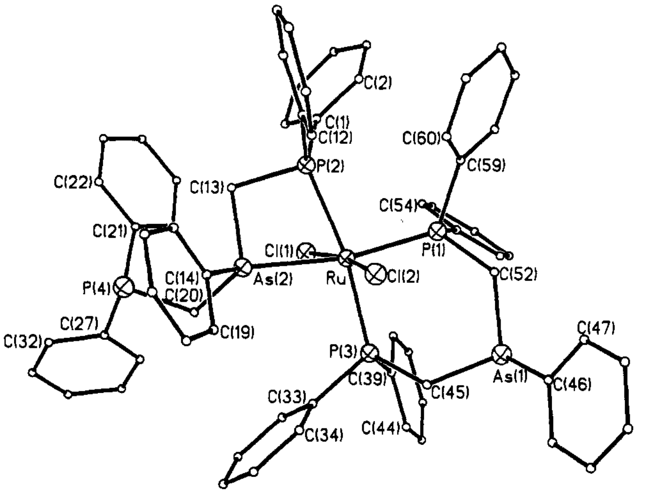

Figure 2. Perspective view of $Ru(dpma)_2Cl_2$ (**3**).

Table IV. Selected Bond Lengths (Å) and Angles (deg) for $Ru(dpma)_2Cl_2$.

Bond Lengths			
Ru–As(2)	2.514 (1)	Ru–P(1)	2.303 (2)
Ru–P(2)	2.404 (2)	Ru–P(3)	2.355 (2)
Ru–Cl(1)	2.430 (2)	Ru–Cl(2)	2.433 (2)
As(1)–C(45)	1.982 (7)	As(1)–C(46)	1.956 (7)
As(1)–C(52)	1.964 (7)	As(2)–C(13)	1.958 (7)
As(2)–C(14)	1.933 (7)	As(2)–C(20)	1.965 (7)
P(1)–C(52)	1.841 (7)	P(1)–C(53)	1.832 (7)
P(1)–C(59)	1.838 (7)	P(2)–C(1)	1.833 (7)
P(2)–C(7)	1.848 (7)	P(2)–C(13)	1.837 (7)
P(3)–C(33)	1.827 (7)	P(3)–C(39)	1.846 (7)
P(3)–C(45)	1.832 (7)	P(4)–C(20)	1.830 (7)
P(4)–C(21)	1.845 (8)	P(4)–C(27)	1.846 (8)
Bond Angles			
As(2)–Ru–P(1)	168.5 (1)	As(2)–Ru–P(2)	70.8 (1)
P(1)–Ru–P(2)	97.9 (1)	As(2)–Ru–P(3)	100.3 (1)
P(1)–Ru–P(3)	91.1 (1)	P(2)–Ru–P(3)	168.3 (1)
As(2)–Ru–Cl(1)	79.4 (1)	P(1)–Ru–Cl(1)	101.9 (1)
P(2)–Ru–Cl(1)	81.6 (1)	P(3)–Ru–Cl(1)	89.3 (1)
As(2)–Ru–Cl(2)	90.9 (1)	P(1)–Ru–Cl(2)	88.4 (1)
P(2)–Ru–Cl(2)	99.0 (1)	P(3)–Ru–Cl(2)	88.7 (1)
Cl(1)–Ru–Cl(2)	169.5 (1)	C(45)–As(1)–C(46)	95.9 (3)
C(45)–As(1)–C(52)	100.4 (3)	C(46)–As(1)–C(52)	97.4 (3)
Ru–As(2)–C(13)	89.8 (2)	Ru–As(2)–C(14)	125.2 (2)
C(13)–As(2)–C(14)	105.3 (3)	Ru–As(2)–C(20)	121.9 (2)
C(13)–As(2)–C(20)	106.2 (3)	C(14)–As(2)–C(20)	104.1 (3)
Ru–P(1)–C(52)	114.3 (2)	Ru–P(1)–C(53)	119.0 (2)
C(52)–P(1)–C(53)	105.4 (3)	Ru–P(1)–C(59)	117.6 (2)
C(52)–P(1)–C(59)	97.2 (3)	C(53)–P(1)–C(59)	100.3 (3)
Ru–P(2)–C(1)	119.9 (2)	Ru–P(2)–C(7)	127.3 (2)
C(1)–P(2)–C(7)	102.6 (3)	Ru–P(2)–C(13)	96.3 (2)
C(1)–P(2)–C(13)	105.8 (3)	C(7)–P(2)–C(13)	100.7 (3)
Ru–P(3)–C(33)	115.2 (2)	Ru–P(3)–C(39)	122.3 (2)
As(2)–C(20)–P(4)	118.5 (4)	Ru–P(3)–C(45)	113.2 (2)
As(1)–C(52)–P(1)	120.0 (4)	As(2)–C(13)–P(2)	97.4 (3)
		As(1)–C(45)–P(3)	111.9 (3)

by the face to face placement of the two phenyl rings containing C(1)–C(6) and C(21′)–C(26′). The separation between the planes of these two rings is 3.59 Å, which is only slightly larger than twice the width of a phenyl ring (1.7 Å). Narrowing of the P(1)–Au(1)–P(2′) angle would force these two rings closer together. The chelating P(1)–Au(1)–P(2′) angle (103.9 (2)°) is nearer the tetrahedral ideal than those found (85.4, 86.1°) in the only other chelated tetrahedral Au(1)) complex, $Au(dppe)_2^+$ where dppe is bis(diphenylphosphino)ethane.[13] The smaller bite of the five-membered chelate ring is presumably responsible for the contraction of that angle. The Au–P bond lengths (2.394 (5), 2.425 (5) Å) are similar and fall into the range found for other gold(I) phosphine complexes.[13]

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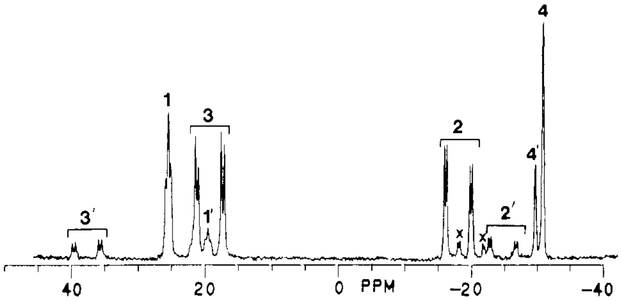


Figure 3. Experimental ^{31}P NMR spectrum of a solution of Ru(dpma)$_2$Cl$_2$ in toluene-d_8 at −60 °C. Resonances of P(1)–P(4) of **3** are indicated by 1–4, while those belonging to **4** are identified as 1′–4′. Resonances indicated by × belong to an unidentified complex.

Both chelate rings in Au(dpma)$_2^+$ have normal chair conformations. These are readily compared to the chelate ring conformation in Pd(dpmp)Cl$_2$ (dpmp is bis((diphenylphosphino)methyl)phenylphosphine).[14] In the latter the PC$_2$P$_2$Pd ring also has the chair conformation, but the Pd center is close to the plane of the C$_2$P$_2$ portion, and the ring has a flattened appearance.

The Au(CN)$_2^-$ anion deviates slightly from the ideal linear geometry, with a C(33)–Au(2)–C(33′) bond angle of 175.0°. The anion also exhibits C_{2v} symmetry, with the C_2 axis bisecting the C(33)–Au(2)–C(33′) angle. This is slightly more bent than has been reported for the C–Au–C angles in Cs$_2$Na[Au(CN)$_2$]$_3$ (178.3°)[15] and Tl[Au(CN)$_2$] (177.1°).[16] The Au–C–N bond angles of 178.1° are also quite normal compared to the 175.8–178.3° reported in the literature; the Au–C and C–N bond lengths are also normal.

Synthesis and Structure of Ru(dpma)$_2$Cl$_2$ (3). As a route to ruthenium complexes that might act as precursors to metallamacrocycle formation, the reaction between dpma and the relatively labile Ru(dmso)$_4$Cl$_2$ (dmso is dimethyl sulfoxide)[17] was examined. In dichloromethane solution, this reaction yields orange Ru(dpma)$_2$Cl$_2$ (**3**). The infrared spectrum confirms the fact that all dmso ligands have been lost; the spectrum obtained resembles those of dpma and its complexes, particularly in the 1200–950-cm^{-1} region where ν(S–O) is expected.

The results of an X-ray crystallographic study show that the complex is molecular with two different chelating dpma ligands. Atomic positional parameters are given in Table III. Figure 2 shows a perspective view of the molecule. Selected bond distances and angles are presented in Table IV.

The ruthenium ion has pseudooctahedral geometry with bonding to two trans chloride ligands, three phosphorus atoms, and one arsenic atom. One of the dpma ligands forms a six-membered chelate ring and binds through two phosphorus atoms, with the internal arsenic atom uncoordinated. The other dpma ligand is bound to form a four-membered chelate ring using a phosphorus atom and an arsenic atom as donors. The remaining phosphorus atom is uncoordinated.

The Ru–Cl distances (2.404 (2), 2.433 (2) Å) are similar to those found in *trans*-Ru(PHMe$_2$)$_4$Cl$_2$ and Ru(PPh$_3$)$_3$Cl$_2$.[19] The Ru–P distances fall in the range 2.3–2.4 Å found for other ruthenium(II) complexes. The Ru–As distance (2.514 Å) is just slightly longer than those found in Ru(As(o-C$_6$H$_4$AsPh$_2$)$_3$)Br$_2$ (range 2.31–2.47 Å).[20]

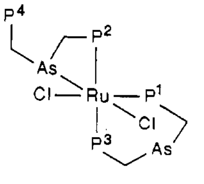
The angular distribution of ligands about ruthenium is distorted from normal octahedral geometry. This is largely due to the presence of the four-membered chelate ring. For example, angles between pairs of cis ligands range from 70.8 to 101.9°. The smallest of these is the P(2)–Ru–As(2) angle, which is within the four-membered chelate ring. Because of this narrow angle, the P(3)–Ru–As(2) and P(1)–Ru–P(2) angles have widened from the ideal 90° to 100.3 (1) and 97.9 (1)°, respectively. In sharp contrast, the P(1)–Ru–P(3) angle in the six-membered chelate ring is 91.1 (1)°. There is also a slight bend to the Cl(1)–Ru–Cl(2) unit; the angle involved is 169.5 (1)°. Because of the constraints of the four-membered chelate ring, the As(2)–C(13)–P(2) angle (97.4 (3)°) is less than the angles at the other, less constricted, methylene groups (range 111.9 (3)–120.0 (4)°).

The six-membered chelate ring in Ru(dpma)$_2$Cl$_2$ has a chair conformation very similar to the conformation in Au(dpma)$_2^+$.

The ^{31}P NMR spectrum obtained from a toluene-d_8 solution of Ru(dpma)$_2$Cl$_2$ at −60 °C is shown in Figure 3. The chemical shift of some of the resonances shows a slight temperature dependence,[21] and this temperature was chosen because it gives the clearest separation of all resonances. A spectral simulation that accounts for all of the major resonances in the spectrum in terms of the structure shown in Figure 2 yields the following parameters: δ(P(1)), 25.2 ppm; δ(P(2)), −18.2 ppm; δ(P(3)), 19.0 ppm; δ(P(4)), −30.9 ppm; J(P(1),P(2)), 29.4 Hz; J((P(1),P(3)), 37.9 Hz; J(P(1),P(4)), 11.5 Hz; J(P(2),P(3)), 311.2 Hz. The most upfield resonance, 4, is due to the uncoordinated phosphorus P(4) (free dpma has a chemical shift of −20.9 ppm), while the resonances labeled 2 and 3 must come from the strongly coupled, trans phosphorus atoms P(2) and P(3), respectively. Resonance 2 is identified with the phosphorus atom P(2) in the four-membered chelate ring, since it is the highest field resonance of all the coordinated phosphorus atoms. Such upfield shifts are common in complexes of the platinum metals with four-membered chelate rings.[22,23] This leaves resonance 1 as due to P(1). Small couplings between P(1) and P(2) and P(3) are observed, and their magnitudes are entirely consistent with the cis orientation of these groups. Interestingly, there is a very small through-space coupling of P(1) with the uncoordinated phosphorus, P(4).

The coupling pattern has been verified by a ^{31}P, ^{31}P COSY experiment. The results are shown in Figure 4. Cross peaks representing coupling between the major peaks in the spectrum are connected above the diagonal. Notice that the long-range coupling of P(1) and P(4) is verified in this experiment through the cross peak labeled a. Additionally, very small couplings are present that do not produce resolvable splitting in the normal spectrum in Figure 3.

The ^{31}P NMR spectrum also contains a set of additional resonances labeled 1′–4′ in Figure 3. These were present in all independently prepared samples of Ru(dpma)$_2$Cl$_2$. Their intensity was unaffected by repeated recrystallization of the complex. Hence, we suspect that they arise from a second isomer of Ru(dpma)$_2$Cl$_2$ that is in equilibrium with the isomer shown in Figure 2. A likely candidate is **4**, an isomer that retains the two types of chelating ligands but has cis chloride ligands. Precedent for this exists in Ru(PPh$_3$)$_2$(PF$_3$)$_2$Cl$_2$, which does have cis chloride ligands.[24] The pattern of these minor resonances resembles that



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[24] A reviewer has suggested that the minor isomer might be one in which the arsenic-bound phenyl groups have an anti orientation rather than the syn orientation shown in Figure 2. Such an isomerization would require either inversion at arsenic, generally a high energy process, or opening of an Ru–As or Ru–P bond.

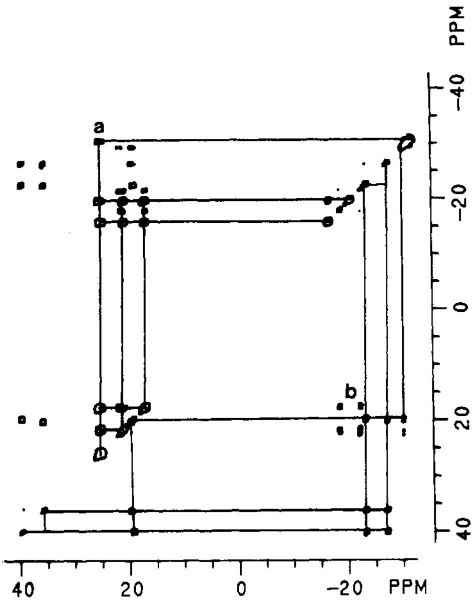

Figure 4. Contour plot of the 81-MHz P,P correlation spectrum (COSY) for $Ru(dpma)_2Cl_2$ in toluene-d_8 at -60 °C. Cross peaks showing coupling between the six resonances of the major isomer are connected above the diagonal. The spectrum below the diagonal has been altered by removing the mirror images of the 11 cross peaks belonging to the major isomer. Connections between the cross peaks that show coupling between the six peaks of the minor isomer are shown. The cross peaks remaining below the diagonal involve resonances of a third substance.

of the major isomer with the following parameters derivable from the spectrum: $\delta(P(1))$, 19.7 ppm; $\delta(P(2))$, -24.9 ppm; $\delta(P(3))$, 37.4 ppm; $\delta(P(4))$, -28.6 ppm; $J(P(1),P(2))$, 30 Hz; $J(P(1),P(3))$, 38 Hz; $J(P(2),P(3))$, 318 Hz. The coupling between these resonances has been confirmed in the COSY experiment. In Figure 4, all of the 11 major cross peaks have been removed below the diagonal so that the cross peaks for the minor isomer, presumably **4**, are more apparent. These have been connected with solid lines. This leaves several cross peaks that belong to yet another species. In particular, the cluster of cross peaks b corresponds to resonances in Figure 3 labeled ×. These are coupled to peaks which must be buried under the resonances of P(3) of the major isomer. Because of this overlapping of resonances, the spectrum contains too little information to derive firm conclusions about the substance responsible for these components.

The continued presence of **3** and **4** and the other unidentified substance in all samples of $Ru(dpma)_2Cl_2$ suggests that a facile equilibration process may interrelate them. Generally, Ru(II) complexes are kinetically inert. In the present case, however, dissociation of the Ru–As bond is facilitated by steric pressures and the strain of the four-membered chelate rings. This would yield a five-coordinate intermediate (analogous to $Ru(PPh_3)_3Cl_2$)[19] that can interconvert **3** into **4**.[25]

Discussion

Despite the fact that both complexes considered here contain a common $M(dpma)_2$ unit, two rather different arrangements of these are found. Clearly, for the tetrahedral gold(I) complex both ligands are able to adopt what must be the generally preferred chelate structure with coordination through the phosphorus atoms. Even with this tetrahedral geometry, it can be seen that there is some problem in accommodating the four PPh_2 units about one metal. There are close phenyl/phenyl contacts that are responsible for widening of two of the P–Au–P angles well beyond the 109.5° tetrahedral ideal. This is almost certainly a steric effect. At one time there was a question whether tetrahedral Au^IP_4 units could exit, since the structures of several forms of $Au(PPh_3)_4^+$ were significantly distorted toward trigonal coordination.[26] However, with the determination of the structure of $Au(PMePh_2)_4^+$ with regular tetrahedral coordination,[27] it is clear that AuP_4 units can assume this regular geometry. It is worthwhile to note that some tetrahedral gold(I) phosphine complexes, most notably $Au(dppe)_2^+$, have antitumor activity.[28]

Table V. Crystallographic Data for **2** and **3**

chem formula	$C_{68}H_{61}Au_2As_2P_4Cl_5N_2$	$C_{64}H_{58}As_2Cl_2P_4Ru$
fw	1751.2	1272.9
space group	$C2/c$	$P2_1/n$
a, Å	17.062 (4)	16.357 (6)
b, Å	25.946 (7)	18.416 (7)
c, Å	17.820 (5)	18.502 (4)
β, deg	99.35 (2)	94.77 (3)
V, $Å^{-3}$	7784 (3)	5630
d_{calcd}(130 K), g/cm^3	1.49	1.50
Z	4	4
radiation (λ, Å)	Mo Kα (0.71069)	Mo Kα (0.71069)
μ(Mo Kα), cm^{-1}	48.7	16.9
transmission factors	0.65–0.72	0.38–0.65
$R(F_o)$	0.073	0.051
$R_w(F_o)$	0.079	0.046

In $Ru(dpma)_2Cl_2$, several unusual circumstances occur. Two identical ligands adopt different structures. A four-membered chelate ring is formed by a ligand that could adopt a less internally strained, six-membered-ring structure. A Ru–As bond is formed when a Ru–P bond could have been made. In general, any metal atom (hard or soft, class A or B) prefers to bind phosphorus rather than arsenic.[10] The cause for these anomalies appears to be steric effects. One can see in $Au(dpma)_2^+$ that the metal environment is crowded. On addition of the two chloride ligands that are present in the ruthenium complex, the coordination sphere becomes even more crowded. That crowding is alleviated by converting one dpma ligand into a four-membered chelate. In this case, the As–Ru–P angle is severely narrowed so that there is more room for the substituents on the arsenic and phosphorus atoms. Moreover, the local environment around the $As(CH_2PPh_2)Ph$ unit must offer less steric hindrance than that which would be provided by a PPh_2 group in its place.

Experimental Section

Preparation of Compounds. Samples of dpma[2] and $Ru(dmso)_4Cl_2$[17] were prepared by standard routes.

$[Au(dpma)_2][Au(CN)_2]$ (2). A solution of 100 mg (0.182 mmol) of dpma in 5 mL of toluene was stirred with 45 mg (0.20 mmol) of solid AuCN. After 24 h the yellow AuCN had nearly disappeared and a white precipitate had formed. The white solid was collected by fitlration and washed with diethyl ether. The product was purified by dissolving it in a minimum quantity of chloroform, filtering the solution, and adding diethyl ether to precipitate colorless needles. The solid was collected by filtration and washed with diethyl ether; yield 110 mg, 76%; ^{31}P NMR singlet at 12 ppm (recorded in $CDCl_3$); IR ν(CN) 2140 cm^{-1}.

$Ru(dpma)_2Cl_2$ (3). A sample (80 mg, 0.18 mmol) of $Ru(dmso)_4Cl_2$ was added in one portion to a stirred solution of 200 mg (0.36 mmol) of dpma in 8 mL of dichloromethane. After the mixture was stirred for 2 h, the orange solution was filtered through Celite to remove unreacted $Ru(dmso)_4Cl_2$. The volume of the filtrate was reduced to 3 mL by vacuum evaporation. Methanol was added to the concentrated solution to give orange crystals of $Ru(dpma)_2Cl_2$. The product was collected by filtration and washed with methanol. Purification was achieved by dissolving the product in a minimum volume of dichloromethane, filtering the solution, and reprecipitating the product by the slow addition of methanol; yield 154 mg, 66%.

X-ray Structure Determination and Refinement for 2. Well-formed crystals of $[Au(dpma)_2][Au(CN)_2]\cdot CH_2Cl_2\cdot CHCl_3$ were obtained by layering a solution of the compound in chloroform/dichloromethane with diethyl ether in a thin tube. A suitable crystal was mounted on a glass fiber by using silicone grease and secured in the cold stream of the diffractometer with the long dimension of the crystal parallel to ϕ. No decay in the intensities of two standard reflections was observed during the course of data collection. Crystal parameters are given in Table V.

The usual corrections for Lorentz and polarization effects were applied to the data. Crystallographic programs used were those of SHELXTL, version 4, installed on a Data General Eclipse computer. Scattering factors and corrections for anomalous dispersion were from ref 29.

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From the observed conditions *hkl*, $h + k = 2n$, and *h*0*l*, $l = 2n$, the two possible space groups are *Cc* (No. 9) and *C*2/*c* (No. 15). Solution of the structure was accomplished by Patterson methods. Both the anion and the cation can be located on crystallographic 2-fold axes. Thus *C*2/*c* is the space group of choice.

An absorption correction was applied.[30] Four low-angle reflections appeared to be affected by extinction and were removed from the set of reflections used in refinement. The lattice molecule of chloroform was disordered and was given an occupancy of 0.5 on the basis of Fourier peak heights. It was refined with inter-chlorine and chlorine–carbon distance constraints by the method of additional observational equations.[4] Another site in the lattice is occupied by two partial molecules of dichloromethane that are rotated approximately 90° with respect to their chlorine–chlorine vectors. They were refined with fixed *U*'s of 0.08 Å^2 and variable occupancies that converged at 0.309 (9) and 0.195 (9), respectively. Hydrogen atoms were included in the structure factor calcualtion at idealized positions by using a model in which the hydrogen atoms ride on the bonded carbon and C–H is 0.96 Å. In the final cycles of refinement all non-hydrogen atoms were assigned anisotropic thermal parameters except the carbon of chloroform and the chlorines of dichloromethane (the latter carbon atom was not located). In the final difference map the largest feature was 2.1 e Å^{-3} in height, in the vicinity of one of the chloroform molecules.

X-ray Structure Determination and Refinement for 3. Orange blocks of Ru(dpma)$_2$Cl$_2$ were obtained by diffusion of methanol into a dichloromethane solution of the complex. Data collection, treatment, and refinement followed by the procedures outlined for **2**. A value of 0.81 e Å^{-3} was found for the largest feature in the final difference map. This was 0.69 Å away from C(19).

Acknowledgment. We thank the National Science Foundation (Grant CHE 8519557) for financial support and Dr. J. de Ropp of the UCD NMR facility for assistance with the NMR experiments.

Supplementary Material Available: Listings of all bond lengths, bond angles, hydrogen atom positions, anisotropic thermal parameters, and data collection parameters (10 pages); listings of observed and calculated structure factors (58 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry, University of Nevada, Reno, Nevada 89557,
and New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801,
and Department of Chemistry and Ames Laboratory, Iowa State University, Ames, Iowa 50011

Kinetic and Thermodynamic Stabilities of the Geometric Isomers of (R$_3$P)$_2$Ru(CO)$_2$Cl$_2$ and (R$_3$P)$_3$Ru(CO)Cl$_2$ Complexes

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and Robert A. Jacobson[1c]

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A series of ruthenium(II) complexes of the type RuCl$_2$(CO)$_2$P$_2$ (P = Bzl$_3$P, Ph$_3$P, Ph$_2$MeP, PhMe$_2$P, Me$_3$P) have been prepared and characterized by elemental analyses, physical properties, infrared spectroscopy, UV–visible spectroscopy, and ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectroscopy. The first-formed complex, with all ligand pairs trans (*ttt*), thermally isomerizes in solution to produce the isomer with all ligand pairs cis (*ccc*). This ccc isomer further isomerizes in solution to produce the thermodynamically preferred isomer with only the phosphine ligands trans (*cct*). The size and basicity of the phosphine affect the isomerization rate, which increases with an increase in size and a decrease in phosphine basicity and proceeds by initial dissociation of carbon monoxide. Activation parameters, ΔS^* and ΔV^*, are both positive for the *ttt*–*ccc* isomerization consistent with a dissociative process. Negative values of ΔS^* for the *ccc* → *cct* isomerization suggest that an associative step may be important. *cis*- and *trans*-RuCl$_2$(CO)P$_3$ complexes with meridionally coordinated phosphines (P = Me$_3$P, PhMe$_2$P, Ph$_2$MeP) were also prepared and characterized by the same methods. The first-formed isomer with trans chlorides thermally isomerizes in solution to the thermodynamically stable isomer with cis chlorides. Positive values of both ΔS^* and ΔV^* are consistent with a dissociative process. Phosphine inhibition of this isomerization indicates initial phosphine dissociation. The crystal structures of *cis*(1)- and *trans*-RuCl$_2$(CO)(Ph$_2$MeP)$_3$ (**1** and **2**, respectively) have been determined by counter methods. Compound **1** crystallizes in space group $P\bar{1}$ with $a = 16.158$ (4) Å, $b = 18.361$ (3) Å, $c = 13.170$ (4) Å, $\alpha = 93.36$ (2)°, $\beta = 108.03$ (3)°, $\gamma = 90.75$ (2)°, and $Z = 4$. Compound **2** crystallizes in space group $P2_1/c$ with $a = 20.373$ (9) Å, $b = 9.831$ (5) Å, $c = 20.689$ (7) Å, $\beta = 117.43$ (3)°, and $Z = 4$. Both structures were refined by least-squares methods with $R = 0.093$ for **1** and $R = 0.069$ for **2** for 4614 and 2974 unique reflections with $I/\sigma(I) \geq 3.0$ for **1** and **2**, respectively. The bond distance of the phosphine trans to carbon monoxide in the trans isomer (d(RuP) = 2.490 (4) Å) is longer than the other two Ru–P distances (2.403 (4) Å). The ^{31}P{^{1}H} NMR data also suggest that this phosphine is relatively weakly bound and so this phosphine likely dissociates as the first step in the geometric isomerization.

Introduction

Following the simultaneous discovery by Wilkinson[2] and Coffey[3] in 1965 of the catalytic homogeneous hydrogenation of terminal alkenes by RhCl(Ph$_3$P)$_3$ under mild conditions, the catalytic reduction of unsaturated organic substrates by transition-metal phosphine complexes has been extensively studied and recently reviewed.[4,5] It is now widely accepted that in order for a metal complex to act as a homogeneous catalyst, there must be a vacant coordination site available on the metal for binding the substrate. For this reason coordinatively unsaturated complexes are especially effective catalysts. Both RhCl(Ph$_3$P)$_3$[6] and RuCl$_2$(Ph$_3$P)$_3$,[7-9] which are among the most active homogeneous hydrogenation catalysts known,[5] are 16-electron species and further dissociate at least one phosphine ligand in solution.

On the other hand, coordinatively saturated complexes must first dissociate a ligand in order to gain entry into a catalytic cycle. As a consequence, catalytic activity may be related to the ease of ligand dissociation. We report here that complexes of the type *trans*-RuCl$_2$(CO)P$_3$ (P = tertiary phosphine) dissociate a phosphine ligand in the course of their geometric isomerization to the thermodynamically preferred cis isomers. Similarly, complexes of the type *ttt*-RuCl$_2$(CO)$_2$P$_2$ have been found to thermally isomerize but by CO dissociation.[10-13] We anticipated that there

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