

Geometric Changes Occurring on Silver Chloride Binding by the Metallamacrocyclic

 $\text{Rh}_2(\text{CO})_2\text{Cl}_2\{\mu\text{-(Ph}_2\text{PCH}_2)_2\text{AsPh}\}_2$

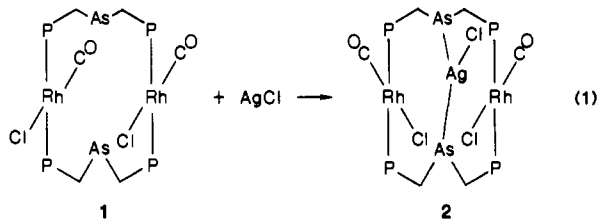
Alan L. Balch,* Mauro Ghedini,† Douglas E. Oram, and Philip E. Reedy, Jr.

Received August 19, 1986

Solid silver chloride dissolves in dichloromethane solutions of the metallamacrocyclic $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2$ (dpma is bis((diphenylphosphino)methyl)phenylarsine) to form $\text{Rh}_2\text{Ag}(\text{CO})_2\text{Cl}_3(\mu\text{-dpma})_2$, which has been isolated as yellow crystals. Yellow-orange crystals of $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2\cdot\text{CH}_2\text{Cl}_2$ were grown by diffusion of ether into a dichloromethane solution of the complex. They belong to the triclinic space group system, $P\bar{1}$ (No. 2), with $a = 12.731(2)$ Å, $b = 12.849(2)$ Å, $c = 20.024(2)$ Å, $\alpha = 86.11(1)^\circ$, $\beta = 83.01(1)^\circ$, $\gamma = 75.00(1)^\circ$, at 130 K, $Z = 2$, and $R = 0.036$ for 8144 reflections with $I > 3\sigma(I)$ and 385 parameters. The open macrocycle exists with Rh(CO) and As-Ph groups on opposite sides of the ring so that the two Rh(CO) groups are cis to one another and the two AsPh groups are also cis to each other. The arsenic lone pairs point out, away from the center of the macrocycle. Yellow-orange crystals of $\text{Rh}_2\text{Ag}(\text{CO})_2\text{Cl}_3(\mu\text{-dpma})_2\cdot 2\text{CH}_2\text{Cl}_2$ were grown similarly. They belong to the triclinic space group system $P\bar{1}$ (No. 2), with $a = 10.960(4)$ Å, $b = 15.091(5)$ Å, $c = 21.696(6)$ Å, $\alpha = 95.27(3)^\circ$, $\beta = 101.60(3)^\circ$, $\gamma = 94.08(3)^\circ$, at 130 K, $Z = 2$, and $R = 0.061$ for 8685 reflections with $I > 3\sigma(I)$ and 419 parameters. The silver chloride is bound at the center of the macrocycle by the two arsenic atoms in a distorted-trigonal-planar fashion. The arsenic atoms have turned inward in comparison to the parent metallamacrocyclic so that they can bind the silver. The Ag...Rh distances (3.354(1), 3.399(1) Å) are long and do not indicate any bonding between them.

Introduction

The metallamacrocyclic $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2$ (**1**) (dpma is bis((diphenylphosphino)methyl)phenylarsine) and its iridium analogue bind a variety of metal ions through the initially uncoordinated arsenic atoms.¹⁻⁶ Metal-metal bond formation accompanies the binding of the d^8 metals rhodium(I),¹ iridium(I),¹ and palladium(II)^{2,6} to **1**. Here we describe the binding of a d^{10} ion, Ag(I), as depicted in eq 1, and compare the structures of the free and silver chloride bound metallamacrocyclics.



Results

One equivalent of solid silver chloride dissolves in a dichloromethane solution of **1** to give a yellow solution from which yellow crystals of $\text{Rh}_2\text{Ag}(\text{CO})_2\text{Cl}_3(\mu\text{-dpma})_2$, **2**, can be obtained by the addition of ethyl ether. Alternately, silver nitrate and tetraphenylarsonium chloride can be successively added to a cold solution of **1** to give **2** in higher yield. The infrared spectrum of the product has a strong carbon monoxide stretching vibration at 1970 cm^{-1} , which is only slightly different in energy than that of **1** (1978 cm^{-1}). The ^{31}P NMR spectrum of **2** in dichloromethane is a simple doublet at 28.1 ppm with $^1J(\text{P,Rh}) = 124\text{ Hz}$. This indicates that the phosphines remained bound to rhodium after silver chloride binding.

Crystal and Molecular Structure of $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2$ (1**).** The asymmetric unit contains one molecule of **1** and one of dichloromethane with no unusual intermolecular contacts. A drawing of **1** is shown in Figure 1. Figure 2 shows stereoscopic views of the molecule. Atomic positional parameters are given in Table I. Tables II and III present selected interatomic distances and angles that are organized to allow comparison between **1** and **2**.

The complex consists of two $\text{Rh}(\text{CO})\text{ClP}_2$ units bridged through the two dpma ligands. While these two $\text{Rh}(\text{CO})\text{ClP}_2$ units are crystallography distinct, their structural features are quite similar and similar to other rhodium complexes containing the same set of ligands.⁷⁻¹⁰ The $\text{Rh}(\text{CO})\text{Cl}$ units have adopted a cis orientation

with respect to one another. Each $\text{Rh}(\text{CO})\text{ClP}_2$ unit is nearly planar. The largest out-of-plane distances are 0.069 Å for P(3) and P(4), which are both displaced to the same side of the plane around Rh(2). For comparison P(1) and P(2) on Rh(1) are also displaced on the same side of the coordination plane but by only 0.035 Å. The two $\text{Rh}(\text{CO})\text{ClP}_2$ planes are nearly parallel; the dihedral angle between them is only 2° .

The two dpma ligands stretch between the rhodium ions in such a way that the arsenic lone pairs point away from the relatively open center of the macrocycle. The nonbonded As...As separation is 5.258(1) Å. The phenyl groups on each arsenic atom are oriented cis to one another and trans to the carbon monoxide ligands on rhodium.

Although the two $\text{Rh}(\text{CO})\text{ClP}_2$ units in **1** are different in the solid state, normal molecular motion in solution renders them equivalent. Thus only single ^{31}P and ^{13}C (from ^{13}CO -enriched material) NMR resonances are observed in solutions of **1**.¹ Conformational flexibility also allows the arsenic atoms to fold inward so that they can coordinate metal atoms at the center of the macrocycle.

Crystal and Molecular Structure of $\text{Rh}_2\text{Ag}(\text{CO})_2\text{Cl}_3(\mu\text{-dpma})_2$ (2**).** The solid contains one molecule of **2** and two of dichloromethane in the asymmetric unit. There are no unusual intermolecular contacts. A drawing of **2** with its numbering scheme is presented in Figure 3. Figure 4 shows stereoscopic views of the adduct. Atomic positional parameters are collected in Table IV, while selected interatomic distances and angles are compiled in Tables II and III, respectively.

The adduct consists of the basic skeleton of **1**, which has a silver chloride unit bound to the two arsenic atoms. Compound **2** has no crystallographically imposed symmetry. However it approximates C_{2v} symmetry with the idealized C_2 axis aligned with the Ag-Cl bond. The coordination environment of the silver is trigonal planar. The atomic displacements (Å) from the least-squares plane through the AgAs_2Cl unit are quite small: Ag, 0.0043; As(1);

† Permanent address: Dipartimento di Chimica, Università Della Calabria, I 87030 Arcavacata (CS), Italy.

- Balch, A. L.; Fossett, L. A.; Olmstead, M. M.; Reedy, P. E., Jr. *Organometallics* **1986**, *5*, 1929.
- Balch, A. L.; Fossett, L. A.; Olmstead, M. M.; Oram, D. E.; Reedy, P. E., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 5272.
- Balch, A. L.; Fossett, L. A.; Guimerans, R. R.; Olmstead, M. M.; Reedy, P. E., Jr. *Inorg. Chem.* **1986**, *25*, 1397.
- Balch, A. L.; Fossett, L. A.; Guimerans, R. R.; Olmstead, M. M.; Reedy, P. E., Jr.; Wood, F. E. *Inorg. Chem.* **1986**, *25*, 1248.
- Reedy, P. E., Jr. Ph.D. Thesis, University of California, Davis, 1987.
- Bailey, D. A.; Balch, A. L.; Fossett, L. A.; Olmstead, M. M.; Reedy, P. E., Jr., submitted for publication.
- Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1979**, *18*, 2700.
- Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2500.
- Guimerans, R. R.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 1677.
- Balch, A. L.; Fossett, L. A.; Guimerans, R. R.; Olmstead, M. M. *Organometallics* **1985**, *4*, 781.

Table I. Atom Coordinates ($\times 10^4$) and Temperature Factors ($\text{\AA}^2 \times 10^3$) for $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2\cdot\text{CH}_2\text{Cl}_2$ (1)

atom	x	y	z	U^a	atom	x	y	z	U^a
Rh(1)	3649 (1)	7137 (1)	3815 (1)	12 (1)*	C(28)	-821 (4)	4394 (4)	1427 (3)	27 (1)
Rh(2)	2724 (1)	6797 (1)	1275 (1)	12 (1)*	C(29)	59 (4)	4395 (4)	947 (3)	29 (1)
P(1)	1858 (1)	7151 (1)	3710 (1)	14 (1)*	C(30)	541 (4)	5248 (4)	886 (3)	23 (1)
P(2)	5432 (1)	7300 (1)	3844 (1)	13 (1)*	C(31)	486 (4)	7786 (4)	370 (2)	16 (1)
P(3)	4549 (1)	6505 (1)	1439 (1)	13 (1)*	C(32)	-591 (4)	8328 (4)	274 (3)	24 (1)
P(4)	853 (1)	7208 (1)	1194 (1)	14 (1)*	C(33)	-842 (4)	8765 (4)	-358 (3)	31 (1)
As(1)	-65 (1)	7995 (1)	2748 (1)	14 (1)*	C(34)	-33 (4)	8641 (4)	-896 (3)	28 (1)
As(2)	6160 (1)	7444 (1)	2246 (1)	13 (1)*	C(35)	1018 (4)	8075 (4)	-810 (3)	24 (1)
Cl(1)	3133 (1)	9044 (1)	3673 (1)	20 (1)*	C(36)	1288 (4)	7656 (4)	-182 (2)	20 (1)
Cl(2)	2613 (1)	8673 (1)	1105 (1)	22 (1)*	C(37)	5493 (4)	6713 (4)	710 (2)	16 (1)
Cl(3)	4296 (1)	1361 (2)	2274 (1)	51 (1)*	C(38)	5095 (4)	7279 (4)	131 (2)	17 (1)
Cl(4)	2008 (1)	1641 (1)	2098 (1)	56 (1)*	C(39)	5835 (4)	7510 (4)	-394 (3)	26 (1)
O(1)	4122 (3)	4764 (3)	3967 (2)	30 (1)	C(40)	6954 (4)	7195 (4)	-347 (3)	26 (1)
O(2)	2900 (3)	4455 (3)	1467 (2)	28 (1)	C(41)	7342 (4)	6622 (4)	221 (3)	26 (1)
C(1)	3954 (4)	5696 (4)	3914 (2)	17 (1)	C(42)	6619 (4)	6366 (4)	742 (2)	19 (1)
C(2)	2829 (4)	5367 (4)	1386 (2)	16 (1)	C(43)	5234 (4)	5155 (4)	1737 (2)	16 (1)
C(3)	5822 (4)	8143 (4)	3134 (2)	16 (1)	C(44)	5504 (4)	4330 (4)	1287 (3)	24 (1)
C(4)	4671 (3)	7420 (3)	2071 (2)	14 (1)	C(45)	5981 (4)	3280 (4)	1496 (3)	26 (1)
C(5)	86 (4)	8280 (4)	1760 (2)	15 (1)	C(46)	6207 (4)	3044 (4)	2154 (3)	30 (1)
C(6)	1455 (4)	7874 (4)	2929 (2)	15 (1)	C(47)	5947 (4)	3866 (4)	2605 (3)	31 (1)
C(7)	846 (4)	7775 (4)	4388 (2)	17 (1)	C(48)	5462 (4)	4914 (4)	2399 (3)	23 (1)
C(8)	1130 (4)	8358 (4)	4866 (2)	21 (1)	C(49)	6335 (4)	8743 (4)	1715 (2)	14 (1)
C(9)	344 (4)	8853 (4)	5375 (3)	26 (1)	C(50)	7084 (4)	9261 (4)	1898 (2)	18 (1)
C(10)	-714 (4)	8752 (4)	5413 (3)	28 (1)	C(51)	7365 (4)	10088 (4)	1494 (2)	23 (1)
C(11)	-1002 (4)	8166 (4)	4944 (3)	28 (1)	C(52)	6911 (4)	10395 (4)	893 (3)	24 (1)
C(12)	-229 (4)	7666 (4)	4439 (2)	21 (1)	C(53)	6155 (4)	9902 (4)	710 (3)	25 (1)
C(13)	1598 (4)	5830 (4)	3662 (2)	17 (1)	C(54)	5849 (4)	9086 (4)	1122 (2)	21 (1)
C(14)	1354 (4)	5257 (4)	4250 (3)	26 (1)	C(55)	6608 (4)	6118 (3)	3866 (2)	14 (1)
C(15)	1292 (4)	4208 (4)	4221 (3)	33 (1)	C(56)	7654 (4)	6154 (4)	3584 (2)	21 (1)
C(16)	1470 (4)	3705 (5)	3614 (3)	35 (1)	C(57)	8540 (4)	5266 (4)	3638 (3)	28 (1)
C(17)	1688 (4)	4275 (4)	3027 (3)	37 (1)	C(58)	8389 (4)	4332 (4)	3977 (3)	26 (1)
C(18)	1760 (4)	5328 (4)	3053 (3)	28 (1)	C(59)	7356 (4)	4286 (4)	4277 (3)	25 (1)
C(19)	-710 (4)	9512 (4)	2968 (2)	18 (1)	C(60)	6480 (4)	5174 (4)	4220 (2)	21 (1)
C(20)	-241 (4)	10345 (4)	2725 (3)	25 (1)	C(61)	5567 (4)	7959 (4)	4599 (2)	17 (1)
C(21)	-783 (4)	11408 (4)	2855 (3)	33 (1)	C(62)	6023 (4)	8841 (4)	4578 (2)	20 (1)
C(22)	-1790 (5)	11636 (5)	3232 (5)	39 (1)	C(63)	6187 (4)	9243 (4)	5181 (2)	24 (1)
C(23)	-2258 (5)	10821 (4)	3484 (3)	36 (1)	C(64)	5917 (4)	8765 (4)	5789 (3)	27 (1)
C(24)	-1716 (4)	9761 (4)	3352 (3)	28 (1)	C(65)	5450 (4)	7907 (4)	5811 (3)	34 (1)
C(25)	153 (4)	6122 (4)	1307 (2)	15 (1)	C(66)	5262 (4)	7511 (4)	5219 (3)	28 (1)
C(26)	-738 (4)	6121 (4)	1778 (2)	20 (1)	C(68)	3287 (5)	728 (5)	2123 (3)	42 (2)
C(27)	-1225 (4)	5256 (4)	1846 (2)	23 (1)					

^aAn asterisk denotes the equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table II. Selected Interatomic Distances (\AA)

	$\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2$ (1)	$\text{Rh}_2\text{Ag}(\text{CO})_2\text{Cl}_3(\mu\text{-dpma})_2$ (2)
Rh(1)–P(1)	2.310 (1)	2.316 (3)
Rh(1)–P(2)	2.341 (1)	2.316 (3)
Rh(1)–Cl(1)	2.373 (1)	2.346 (3)
Rh(1)–C(1)	1.794 (5)	1.793 (9)
Rh(2)–P(3)	2.316 (1)	2.316 (3)
Rh(2)–P(4)	2.326 (1)	2.310 (3)
Rh(2)–Cl(2)	2.381 (1)	2.348 (3)
Rh(2)–C(2)	1.808 (5)	1.782 (10)
Rh(1)···Rh(2)	5.428 (1)	6.131 (1)
As(1)···As(2)	5.258 (1)	4.829 (2)
Ag–Cl(3)		2.548 (3)
Ag–As(1)		2.585 (2)
Ag–As(2)		2.561 (2)
Ag···Rh(1)		3.354 (1)
Ag···Rh(2)		3.399 (1)

0.0015; As(2), -0.0016; Cl(3), -0.0011. However, the angles at Ag deviate considerably from the ideal of 120° with the As–Ag–As angle being opened to $139.5 (1)^\circ$. The two As–Ag–Cl angles are rather different: $104.9 (1)$ and $115.6 (1)^\circ$. The Ag–Cl distance is shorter than the Ag–Cl distances (ca. 2.65\AA) in phosphine complexes where the chloride is a bridging ligand.^{11,12} Complexes with terminal Ag–Cl units appear to be rare. The Ag–As distances

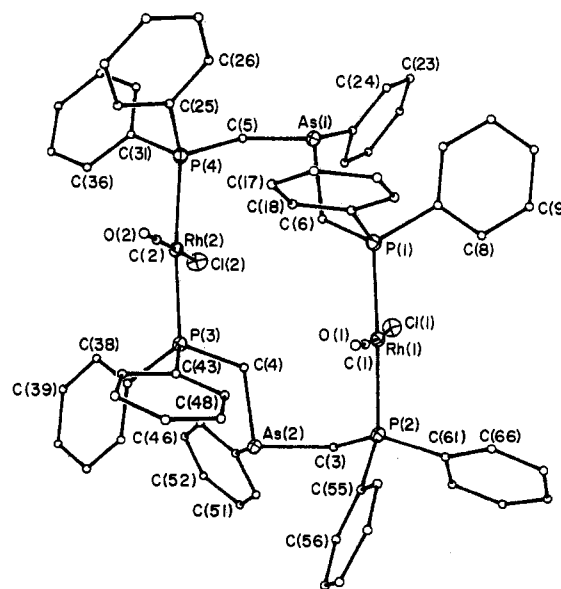


Figure 1. Perspective view of $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2$ (1) showing 50% thermal ellipsoids for non-carbon atoms and uniform, arbitrarily sized circles for carbon atoms.

fall within the range $2.47\text{--}2.72 \text{\AA}$ observed for such distances in other Ag(I) complexes.^{13–15} The two rhodium atoms are so far

(11) Teo, B. K.; Calabrese, J. C. *Inorg. Chem.* **1976**, *15*, 2467.

(12) Churchill, M. R.; Donahue, J.; Rotella, F. J. *Inorg. Chem.* **1976**, *15*, 2752.

(13) Blundell, T. L.; Powell, H. M. *J. Chem. Soc. A* **1971**, 1685.

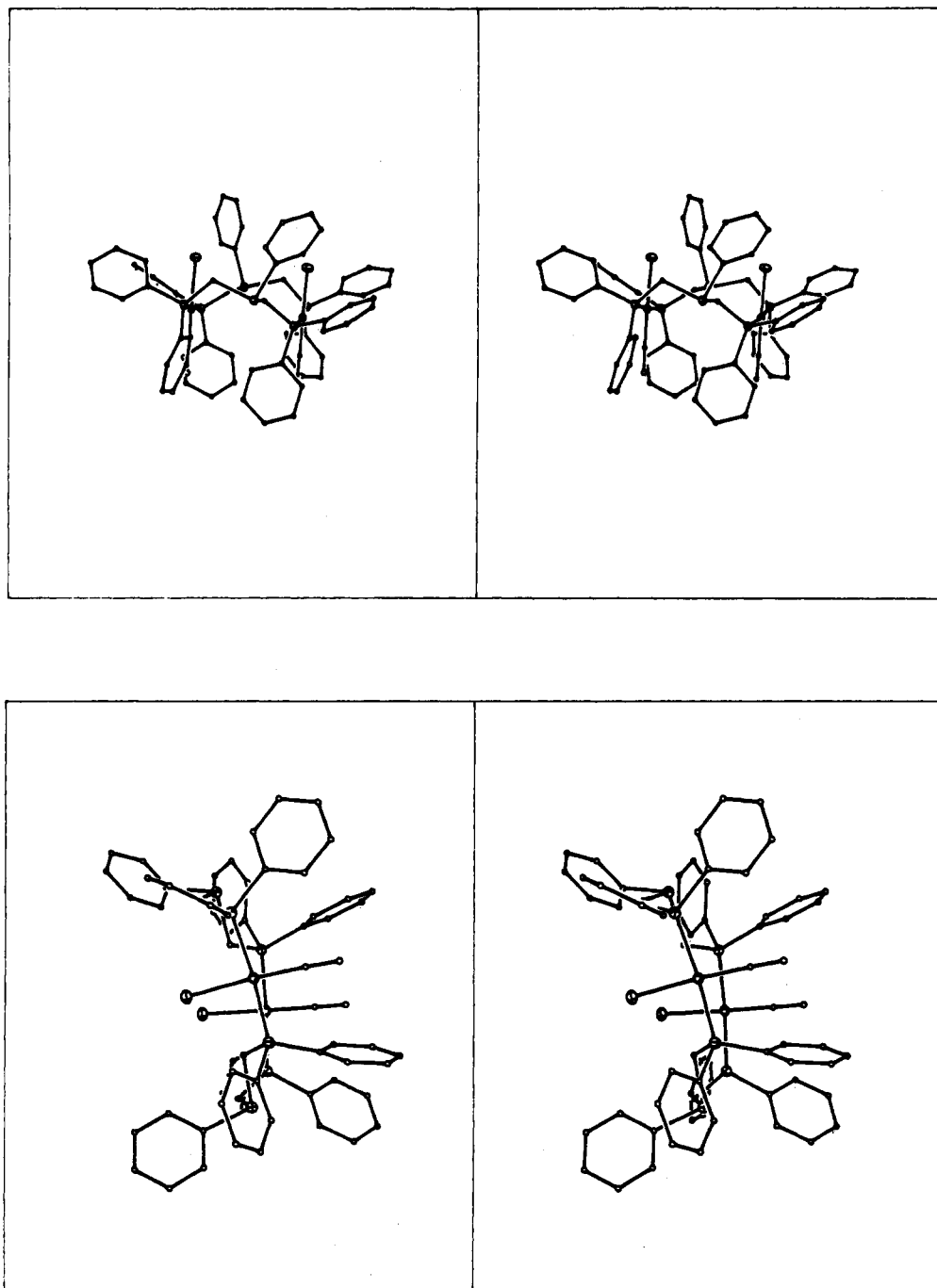


Figure 2. Two stereoscopic drawings of $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2$ (1).

Table III. Selected Interatomic Angles (deg)

	$\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2$ (1)	$\text{Rh}_2\text{Ag}(\text{CO})_2\text{Cl}_3(\mu\text{-dpma})_2$ (2)
P(1)-Rh(1)-P(2)	173.6 (1)	169.1 (1)
Cl(1)-Rh(1)-C(1)	176.4 (2)	174.3 (3)
P(1)-Rh(1)-Cl(1)	87.8 (1)	87.2 (1)
P(1)-Rh(1)-C(1)	88.7 (2)	92.2 (3)
P(2)-Rh(1)-Cl(1)	86.6 (1)	84.2 (1)
P(2)-Rh(1)-C(1)	97.0 (2)	95.8 (3)
P(3)-Rh(2)-P(4)	174.5 (1)	172.9 (1)
Cl(2)-Rh(2)-C(2)	178.7 (1)	175.4 (3)
P(3)-Rh(2)-C(2)	89.2 (1)	84.6 (1)
P(3)-Rh(2)-C(2)	90.3 (2)	95.5 (3)
P(4)-Rh(2)-Cl(2)	87.7 (1)	88.5 (1)
P(4)-Rh(2)-C(2)	92.9 (1)	91.3 (3)
As(1)-Ag-As(2)		139.5 (1)
As(1)-Ag-Cl(3)		104.9 (1)
As(2)-Ag-Cl(3)		115.6 (1)
Rh(1)...Ag...Rh(2)		130.4 (1)

from the silver (3.354 (1), 3.399 (1) Å) that no direct bonding is present. The AgCl unit enters the macrocycle so that it is trans to the two Rh-Cl units. Thus the local dipole orientations in this region are favorable, a feature that we have suggested in one another case as directing the relative ligand orientation in a binuclear complex.¹⁶

The two rhodium ions have retained their nearly planar coordination environments. The atomic displacements (Å) from their respective least-squares planes are as follows: Rh(1), 0.109; P(1), -0.033; P(2), -0.033; Cl(1), -0.031; C(1), 0.040; Rh(2), 0.060; P(3), 0.019; P(4), 0.020; Cl(2), -0.058; C(2), 0.006. These two planes, however, are no longer nearly parallel as they are in 1.

(14) Cooper, M. K.; Nyholm, R. S.; Curreck, P. W.; McPartlin, M. *J. Chem. Soc. Chem. Commun.* 1974, 343.

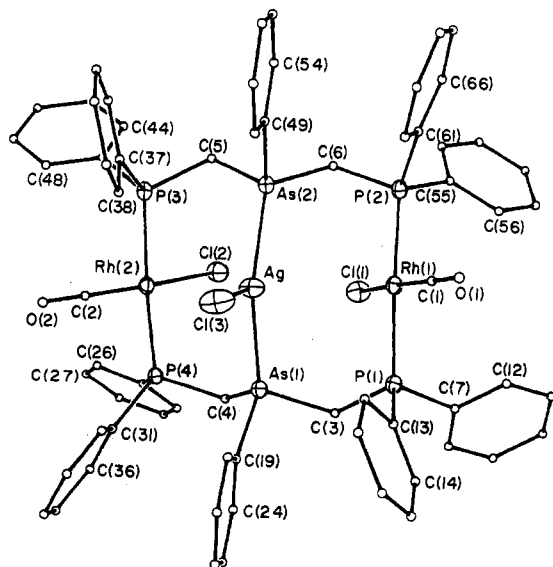
(15) Nardelli, M.; Pelizzi, C.; Pelizzi, G.; Tarasconi, P. *J. Chem. Soc., Dalton Trans.* 1985, 321.

(16) Balch, A. L.; Guimerans, R. R.; Linehan, J.; Wood, F. E. *Inorg. Chem.* 1985, 24, 2021.

Table IV. Atom Coordinates ($\times 10^4$) and Temperature Factors ($\text{\AA}^2 \times 10^3$) for $\text{Rh}_2\text{Ag}(\text{CO})_2\text{Cl}_3(\mu\text{-dpma})_2\cdot 2\text{CH}_2\text{Cl}_2$ (**2**)

atom	x	y	z	U^a	atom	x	y	z	U^a
Rh(1)	978 (1)	1262 (1)	3629 (1)	17 (1)*	C(25)	-1308 (8)	3980 (6)	813 (4)	21 (2)
Rh(2)	1419 (1)	2950 (1)	1211 (1)	17 (1)*	C(26)	-1132 (9)	4060 (7)	202 (4)	29 (2)
Ag	2397 (1)	2510 (1)	2731 (1)	27 (1)*	C(27)	-2155 (10)	4119 (7)	-286 (5)	41 (3)
As(1)	728 (1)	3592 (1)	2882 (1)	18 (1)*	C(28)	-3346 (10)	4078 (7)	-167 (5)	38 (3)
As(2)	2537 (1)	939 (1)	2209 (1)	16 (1)*	C(29)	-3524 (10)	3976 (7)	430 (5)	37 (2)
P(1)	186 (2)	2536 (2)	4009 (1)	19 (1)*	C(30)	-2511 (10)	3926 (7)	921 (5)	35 (2)
P(2)	1375 (2)	-108 (2)	3176 (1)	16 (1)*	C(31)	637 (8)	5174 (6)	1594 (4)	20 (2)
P(3)	74 (2)	3992 (2)	1439 (1)	18 (1)*	C(32)	1810 (9)	5431 (6)	1965 (4)	26 (2)
P(4)	2542 (2)	1785 (2)	950 (1)	17 (1)*	C(33)	2264 (10)	6320 (7)	2099 (5)	39 (3)
Cl(1)	-658 (2)	1183 (2)	2736 (1)	28 (1)*	C(34)	1517 (10)	6967 (8)	1851 (5)	42 (3)
Cl(2)	-265 (2)	1897 (2)	1207 (1)	27 (1)*	C(35)	363 (10)	6732 (7)	1489 (5)	38 (2)
Cl(3)	4475 (2)	3360 (2)	3289 (1)	37 (1)*	C(36)	-99 (9)	5830 (6)	1363 (4)	28 (2)
Cl(4)	1343 (3)	8450 (2)	589 (1)	50 (1)*	C(37)	4235 (8)	1888 (6)	1200 (4)	19 (2)
Cl(5)	3987 (3)	8630 (3)	561 (2)	73 (1)*	C(38)	4838 (9)	2522 (6)	1707 (4)	26 (2)
Cl(6a)	5356 (8)	5998 (6)	3120 (4)	60	C(39)	6096 (9)	2515 (7)	1956 (5)	32 (2)
Cl(6b)	6768 (8)	5374 (6)	2190 (4)	60	C(40)	6769 (10)	1892 (7)	1701 (5)	36 (2)
Cl(7a)	5564 (8)	5998 (6)	1952 (4)	60	C(41)	6177 (10)	1260 (7)	1203 (5)	35 (2)
Cl(7b)	7090 (8)	4958 (6)	2838 (4)	60	C(42)	4922 (9)	1277 (7)	953 (5)	31 (2)
O(1)	2826 (7)	1251 (5)	4819 (4)	47 (2)	C(43)	2295 (8)	1471 (6)	102 (4)	21 (2)
O(2)	3452 (8)	4267 (6)	1094 (4)	52 (2)	C(44)	1668 (8)	668 (6)	-199 (4)	22 (2)
C(1)	2120 (9)	1268 (6)	4349 (4)	26 (2)	C(45)	1551 (9)	443 (7)	-849 (4)	31 (2)
C(2)	2650 (9)	3750 (6)	1146 (4)	27 (2)	C(46)	2059 (10)	1043 (7)	-1195 (5)	35 (2)
C(3)	-480 (8)	3214 (6)	3393 (4)	18 (2)	C(47)	2675 (11)	1855 (8)	-910 (5)	47 (3)
C(4)	-539 (8)	3744 (6)	2131 (4)	18 (2)	C(48)	2777 (9)	2074 (7)	-262 (4)	32 (2)
C(5)	2159 (8)	761 (6)	1277 (4)	21 (2)	C(49)	4154 (8)	465 (6)	2404 (4)	17 (2)
C(6)	1431 (8)	-64 (5)	2342 (4)	17 (2)	C(50)	5132 (8)	985 (6)	2796 (4)	21 (2)
C(7)	-1154 (8)	2221 (6)	4352 (4)	21 (2)	C(51)	6317 (9)	660 (7)	2948 (4)	28 (2)
C(8)	-2276 (9)	2598 (7)	4205 (4)	30 (2)	C(52)	6489 (9)	-173 (7)	2704 (4)	30 (2)
C(9)	-3306 (10)	2276 (7)	4429 (5)	33 (2)	C(53)	5497 (9)	-709 (7)	2310 (4)	29 (2)
C(10)	-3208 (9)	1583 (7)	4804 (4)	31 (2)	C(54)	4337 (9)	-395 (6)	2164 (4)	24 (2)
C(11)	-2073 (10)	1209 (7)	4963 (5)	35 (2)	C(55)	88 (8)	-928 (6)	3184 (4)	17 (2)
C(12)	-1053 (9)	1534 (7)	4732 (4)	31 (2)	C(56)	-459 (9)	-902 (7)	3717 (4)	28 (2)
C(13)	1240 (8)	3318 (6)	4593 (4)	24 (2)	C(57)	-1430 (10)	-1513 (7)	3749 (5)	39 (3)
C(14)	803 (11)	3894 (7)	5022 (5)	42 (3)	C(58)	-1873 (10)	-2172 (7)	3254 (5)	38 (2)
C(15)	1630 (11)	4524 (8)	5434 (6)	50 (3)	C(59)	-1386 (10)	-2212 (7)	2712 (5)	35 (2)
C(16)	2904 (12)	4596 (8)	5423 (6)	50 (3)	C(60)	-404 (8)	-1594 (6)	2679 (4)	25 (2)
C(17)	3323 (11)	4032 (8)	4987 (5)	42 (3)	C(61)	2772 (8)	-661 (5)	3483 (4)	16 (2)
C(18)	2514 (9)	3398 (7)	4582 (4)	30 (2)	C(62)	3867 (8)	-155 (6)	3787 (4)	22 (2)
C(19)	1190 (8)	4816 (6)	3291 (4)	24 (2)	C(63)	4949 (8)	-570 (6)	3982 (4)	23 (2)
C(20)	2404 (10)	5027 (7)	3628 (4)	32 (2)	C(64)	4935 (9)	-1478 (6)	3856 (4)	27 (2)
C(21)	2696 (11)	5860 (8)	3984 (5)	44 (3)	C(65)	3861 (8)	-1983 (6)	3560 (4)	25 (2)
C(22)	1825 (10)	6463 (8)	3995 (5)	39 (3)	C(66)	2763 (8)	-1587 (6)	3367 (4)	22 (2)
C(23)	636 (10)	6262 (7)	3649 (5)	39 (3)	C(67)	2487 (12)	8254 (9)	149 (6)	57 (3)
C(24)	321 (10)	5428 (7)	3296 (5)	33 (2)	C(68)	5508 (16)	5142 (12)	2572 (8)	60

^a An asterisk denotes the equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

**Figure 3.** Perspective view of $\text{Rh}_2\text{Ag}(\text{CO})_2\text{Cl}_3(\mu\text{-dpma})_2$ (**2**).

In order to accommodate the binding of the AgCl unit, the two RhP_2CCl planes are turned away from the AgAs_2Cl moiety so that the dihedral angle between the two RhP_2CCl planes is 69.2° . As a result, the nonbonded $\text{Cl}(1)\cdots\text{Cl}(2)$ separation in has de-

creased from $5.333(3) \text{ \AA}$ in **1** to $3.678(3) \text{ \AA}$ in **2**. This brings the $\text{Cl}\cdots\text{Cl}$ contacts close to the sum of the van der Waals radii for two chlorine atoms (3.60 \AA).¹⁷ Within the $\text{Rh}(\text{CO})\text{CIP}_2$ units the bond angles and distances have undergone only minor changes upon binding of silver chloride as can be seen from Table II.

In order to chelate the silver ion, the macrocycle has had to fold the two arsenic atoms inward. As a result the nonbonded $\text{As}\cdots\text{As}$ separation has decreased from $5.258(1) \text{ \AA}$ in **1** to $4.829(2) \text{ \AA}$ in **2**. The arsenic lone pairs no longer point away from the center of the macrocycle in **2** but rather are directed to coordinate the silver. This change pulls the arsenic-bound phenyl groups in between the phenyl groups bound to phosphorus and creates two stacks of three phenyl groups that are aligned nearly parallel to one another and are separated by ca. 3.2 \AA . The central contraction caused by binding within the As_2Ag group is not mirrored by the behavior of the rhodium ions. These have moved away from the center of the macrocycle. The nonbonded $\text{Rh}\cdots\text{Rh}$ separation in **1** is $5.428(1) \text{ \AA}$ while in **2** it is opened to $6.131(1) \text{ \AA}$. We interpret this as evidence for repulsive interactions between the metal ions in the $\text{Rh}\cdots\text{Ag}\cdots\text{Rh}$ chain. These changes are dictated by the specific metal-metal interactions, not by the nature of the macrocycle and the bridging dpma ligands. Much shorter metal-metal separations (down to 2.7 \AA) have already been observed in dpma-bridged complexes.¹⁻⁶

(17) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.

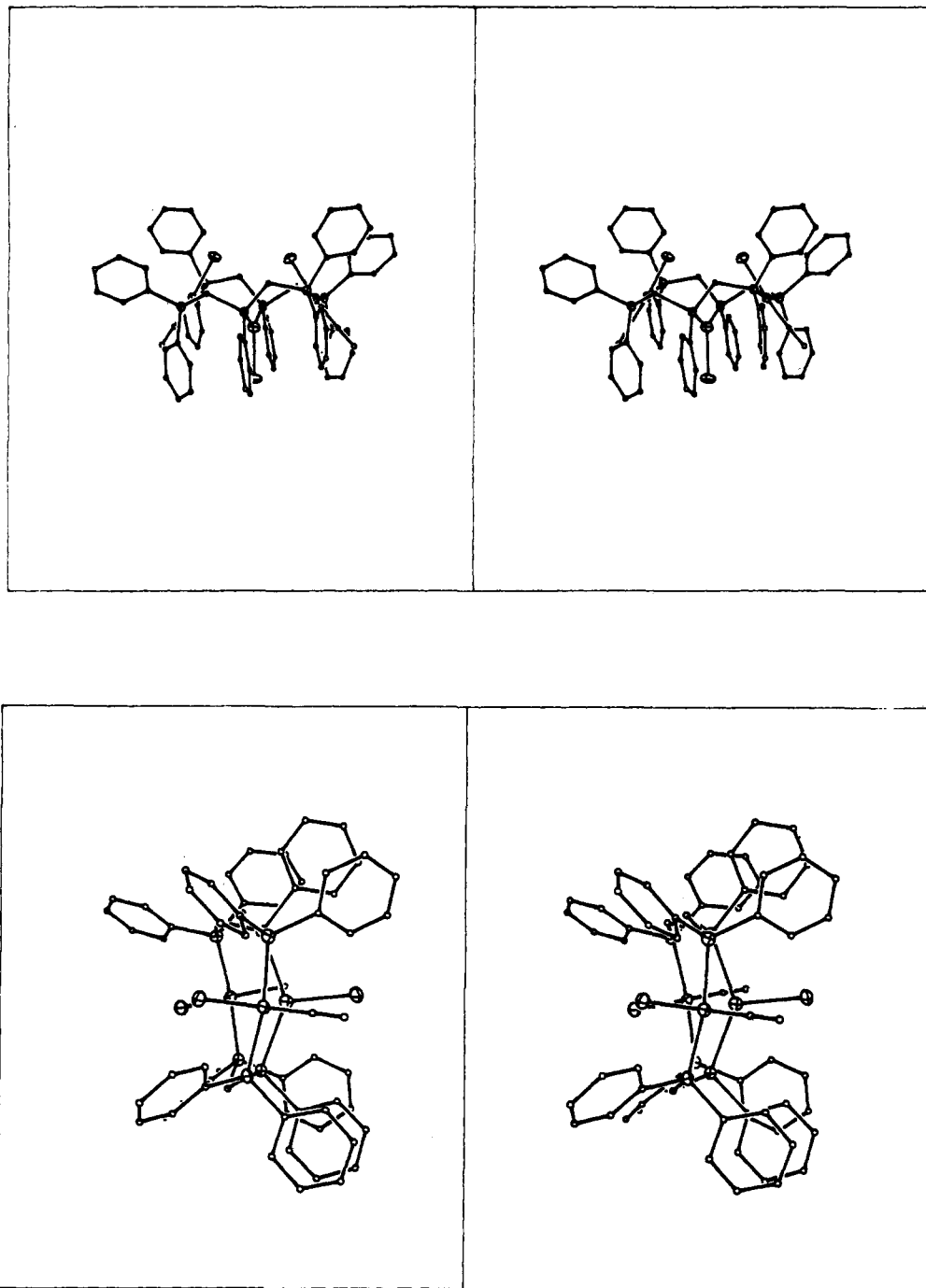


Figure 4. Two stereoscopic drawings of $\text{Rh}_2\text{Ag}(\text{CO})_2\text{Cl}_3(\mu\text{-dpma})_2$ (2).

Discussion

The macrocycle in **1** could exist as five stereoisomers. There are shown in Chart I. The material examined in our structural study is isomer A. In this isomer the locations of the carbon monoxide ligands and arsenic-bound phenyl groups alternate from side to side as one proceeds around the ring. Interconversions between these isomers are not expected to be facile processes. The size of the center of the macrocycle is too small to allow a simple rotation of the Cl-Rh-CO group about the P-Rh-P axis to interconvert cis and trans orientations of the Cl-Rh-CO units. Likewise barriers to inversion at (dialkylphenyl)arsines are ca. 43 kcal/mol,¹⁸ so direct thermal interconversions of cis and trans As-phenyl orientations are not likely at room temperature.

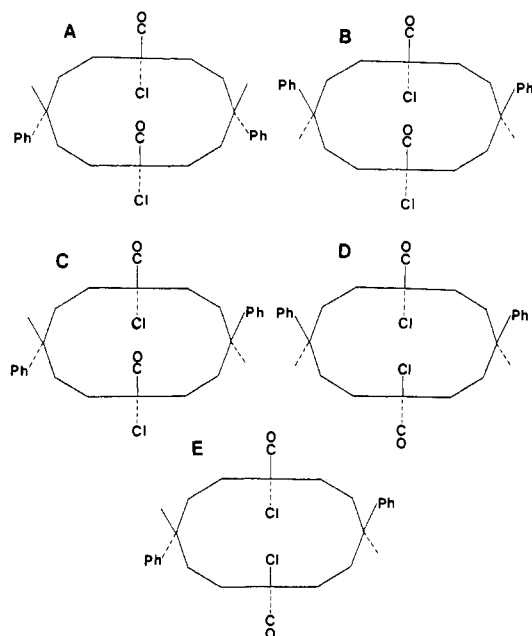
We have looked for, but not found, evidence for the presence of other isomers of **1** after preparation (in 77% yield) by our

standard route.¹ The ³¹P, ¹H, and ¹³C NMR spectra (reported in ref 1) for samples of **1** dissolved in dichloromethane or toluene show no additional resonances that could be assigned to different isomers. Solutions of **1** in toluene are stable for hours with no sign of isomerization. In dichloromethane, **1** is less stable; some $[\text{Rh}_3(\mu\text{-dpma})_2(\mu\text{-Cl})\text{Cl}(\text{CO})_3]^+$ gradually forms.⁴

We suspect that isomer A of **1** is the thermodynamically favored isomer. A major factor in stabilizing this isomer may be the disposition of polar groups around the ring. The negative ends of the polar Rh-Cl groups and the arsenic lone pairs are situated in alternate fashion on opposite sides of the ring. Thus local dipole-dipole interactions are uniquely favorable in this isomer. We further suspect that Rh-ligand bond making and breaking occur relatively readily during the preparation of **1** through associative processes. As a result of the ease of ring opening at rhodium when added nucleophiles are present, the thermodynamically favored isomer is eventually produced, and that is what is isolated.

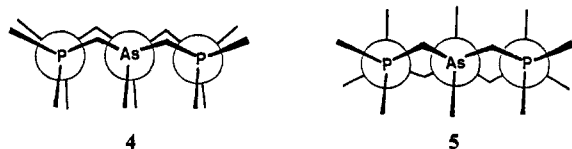
(18) Senkler, G. H.; Mislow, K. *J. Am. Chem. Soc.* **1972**, *94*, 291.

Chart I



The structure of **1** can be compared to other related macrocycles. Dimeric $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2$ consists of a smaller, eight-membered ring with *trans*-Cl-Rh-CO units.⁸ The two rhodium ions are separated by only 3.2386 (5) Å. Binuclear $\text{Ir}_2(\text{CO})_2\text{Cl}_2\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}_2$ (**3**) has methylene groups replacing the AsPh groups in **1** and iridium replacing rhodium. Like **1**, **3** has the Cl-Ir-CO groups widely separated (5.620 (1) Å) and *cis* to one another.¹⁹ However the two $\text{Ir}(\text{CO})\text{ClP}_2$ planes are far from parallel in **3**. The layouts of the bridging ligands in the two complexes differ also. In **3** the methylene chain is in a fully elongated form with the PC_3P unit stretched out into a planar unit. In **1**, however the PCAsCP unit is not stretched into such a planar array, rather it is kinked at arsenic. This kink appears to be formed in order to separate the two arsenic lone pairs so that they do not point toward one another. Complex **1** can also be compared to the macrocycles formed from 2,6-bis(diphenylphosphino)pyridine ($(\text{Ph}_2\text{P})_2\text{py}$).²⁰ Here $\text{Rh}_2(\text{CO})_2\text{Cl}_2\{\mu\text{-}(\text{Ph}_2\text{P})_2\text{py}\}_2$ forms two isomers in solution, presumably with *cis*- and *trans*-Cl-Rh-CO groups, along with chloro-bridged A-frame $[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})\{\mu\text{-}(\text{Ph}_2\text{P})_2\text{py}\}_2]\text{Cl}$.²⁰ Crystallographic characterization of these, however, is not available.

Complexation of silver chloride by **1** retains the macrocycle unit intact with the orientation of groups on rhodium and arsenic preserved. In fact, in most examples encountered to date where a metal ion is added to **1** (or its iridium analogue), we find the core stereochemistry of **1** is retained.^{1,2,5,6} Notice that of the five stereoisomers in Chart I, only three, A, B, and D, have the arsenic lone pairs oriented mutually *cis*. These forms can bind a metal to give the flexible chain structure that is shown in **4** as a Newman



projection down the P-M-P and As-M-As axes.¹⁰ Isomers C and E however, would produce a fundamentally different arrangement upon complexation of an added metal. These would lead to the more rigid isomer **5**, which is also shown as a Newman projection. All trinuclear complexes involving either dpma or

dpmp (bis((diphenylphosphino)methyl)phenylphosphine) examined so far^{1-6,9,10} have these *trans* ligands arranged as shown in **4**, or a kinked variant (see structures **7** and **8** of ref 10) obtained by simultaneous rotation of a pair of opposed methylene groups.

The long Ag...Rh separations and the increase in the Rh...Rh separation in **2** relative to **1** argue against a bonding interaction between these metal ions. Compounds that unquestionably have Rh-Ag bonds have much shorter separations. The Ag-Rh distance in $(\eta^5\text{-C}_5\text{H}_5)_2(\mu\text{-CO})\text{Rh}(\mu\text{-dpmp})(\mu\text{-AgOPF}_2\text{O})$ is 2.689 (2) Å,²¹ and in $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})(\text{PPh}_3)_2\text{Ag}][\text{PF}_6]$ they are 2.651 (1) and 2.636 (1) Å.²² It is informative to realize that shorter separations between two d^8 or two d^{10} metal ions are also found in polyphosphine-bridged complexes. The Rh...Rh separations in $\text{Rh}_2(\mu\text{-dpmp})_2(\text{CO})_3(\mu\text{-Cl})\text{Cl}$ are 3.180 (1) and 3.164 (1) Å.⁹ Ag...Ag separations ranging from 3.0 to 3.3 Å have been seen in a diphosphine-bridged species.²³⁻²⁶ While attractive metal-metal interactions are seen in d^8 - d^8 dimers^{27,28} and in d^{10} - d^{10} dimers as well,^{29,30} the geometry of **2** strongly suggests repulsive interactions along this $d^8d^{10}d^8$ chain.

Experimental Section

Preparation of Compounds. The ligand, dpma,² and complex **1** were prepared as described previously.

$\text{Rh}_2\text{Ag}(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2$, Method 1. Solid silver chloride (60 mg, 0.42 mmol) was suspended in a yellow solution of 65 mg (0.045 mmol) of **1** in 7 mL of dichloromethane. The mixture was stirred at 25 °C for 12 h and then filtered to remove the excess silver chloride. Addition of ethyl ether to the orange filtrate followed by cooling to -20 °C caused the product to precipitate as yellow microcrystals. These were collected by filtration and washed with ethyl ether; yield 30%.

Method 2. A solution of 7.0 mg (0.041 mmol) of silver nitrate in 0.25 mL of methanol was added with stirring to a cold (-20 °C) solution of 50 mg (0.035 mmol) of $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2$ in 2 mL of dichloromethane. The reaction mixture changed rapidly from yellow to light orange. After the mixture was stirred for several minutes, a solution of 17 mg (0.041 mmol) of tetraphenylarsonium chloride in 1 mL of dichloromethane was added, and the color turned to golden yellow. After the solution was warmed to room temperature, a small amount of grayish white precipitate formed and was removed by filtration. The filtered solution was evaporated to a volume of 1 mL under a stream of nitrogen, and diethyl ether was added to precipitate the yellow crystalline product. The product was collected by filtration and washed with diethyl ether; yield 44 mg (80%).

X-ray Data Collection, Solution, and Refinement. Yellow orange parallelepipeds of $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2\text{CH}_2\text{Cl}_2$ (**1**) and yellow-orange, dichroic crystals of $\text{Rh}_2\text{Ag}(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2\text{2CH}_2\text{Cl}_2$ (**2**) were grown by slow diffusion of ether into dichloromethane solutions of **1** and **2**, respectively. The crystals were removed from the diffusion tube and rapidly coated with a light hydrocarbon oil to reduce loss of solvent from the crystal. The crystals were mounted in the cold stream of a Syntex P2₁ diffractometer equipped with a modified LT-1 low-temperature apparatus. Accurate unit cell parameters were obtained from a least-squares refinement of 17 reflections with $30^\circ \leq 2\theta \leq 35^\circ$. The crystal lattices for both **1** and **2** were found to be triclinic *P* by the automatic indexing routine of the software available on the Syntex P2₁ diffractometer; no symmetry was observed in any of the axial photographs. Data collection parameters are summarized in Table V. The data were corrected for Lorentz and polarization effects.

All calculations were done on a Data General Eclipse computer using the SHELXTL Version 4 software package. The reflection list showed no

- (21) Bruno, G.; Schiavo, S. L.; Piraino, P.; Faraone, F. *Organometallics* **1985**, *4*, 1098.
- (22) Connelly, N. G.; Lucy, A. R.; Payne, J. D.; Galas, A. M. R.; Geiger, W. E. *J. Chem. Soc., Dalton Trans.* **1983**, 1879.
- (23) Aly, A. A. M.; Neugebauer, D.; Orama, O.; Schubert, U.; Schmidbaur, U.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 125.
- (24) Schmidbaur, H.; Aly, A. A. M.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 846.
- (25) Schubert, U.; Neugebauer, D.; Aly, A. A. M. *Z. Anorg. Allg. Chem.* **1980**, *464*, 217.
- (26) Ho, D. M.; Bau, R. *Inorg. Chem.*, **1983**, *22*, 4073.
- (27) Mann, K. R.; Gordon, J. G., II; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 3553.
- (28) Mann, K. R.; Lewis, N. S.; Williams, R. M.; Gray, H. B.; Gordon, J. G., II. *Inorg. Chem.* **1978**, *17*, 828.
- (29) Dedieu, A.; Hoffman, J. *Am. Chem. Soc.* **1978**, *100*, 2074.
- (30) Mehrotra, P. K.; Hoffman, R. *Inorg. Chem.* **1978**, *17*, 2187.

(19) Wang, H. H.; Pignolet, L. H.; Reedy, P. E., Jr.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1987**, *26*, 377.

(20) Balch, A. L.; Hope, H.; Wood, F. E. *J. Am. Chem. Soc.* **1985**, *107*, 6936.

Table V. Crystal Data for **1** and **2**

	$\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2$ CH_2Cl_2 (1)	$\text{Rh}_2\text{Ag}(\text{CO})_2\text{Cl}_3(\mu\text{-dpma})_2$ $2\text{CH}_2\text{Cl}_2$ (2)
formula	$\text{C}_{67}\text{H}_{60}\text{As}_2\text{Cl}_4\text{O}_2\text{P}_4\text{Rh}_2$	$\text{C}_{68}\text{H}_{62}\text{As}_2\text{Cl}_7\text{O}_2\text{P}_4\text{Rh}_2$
fw incl solvent	1486.58	1638.86
cryst syst	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
cryst dimens, mm	$0.35 \times 0.17 \times 0.17$	$0.30 \times 0.13 \times 1.00$
color and habit	yellow-orange parallelepipeds	yellow-orange needles
unit cell dimens ^a		
<i>a</i> , Å	12.731 (2)	10.960 (4)
<i>b</i> , Å	12.849 (2)	15.091 (5)
<i>c</i> , Å	20.024 (2)	21.696 (6)
<i>α</i> , deg	86.11 (1)	95.27 (3)
<i>β</i> , deg	83.01 (1)	101.60 (3)
<i>γ</i> , deg	75.00 (1)	94.08 (3)
<i>V</i> , Å ³	3138 (2)	3485 (2)
ρ_{calcd} , ^b g cm ⁻³	1.50	1.56
<i>Z</i>	2	2
radiatn: ^c λ , Å	Mo K α ; 0.071 069	Mo K α ; 0.071 069
μ (Mo K α), cm ⁻¹	17.80	19.06
range of abs cor factors	1.73–2.03	1.52–2.53
scan type; $2\theta_{\text{max}}$, deg	ω ; 45	ω ; 50
scan range, deg	1.0	1.6
octants	$+h, \pm k, \pm l$	$+h, \pm k, \pm l$
scan speed, deg min ⁻¹	15	15
check reflns interval no.	2 measured every 198 reflections	2 measured every 198 reflections
no. of unique data	11 047	12 256
no. of data with $I > 3\sigma(I)$	8144	8685
<i>R</i>	0.036	0.061
<i>R_w</i>	0.034	0.067
no. of params	385	419

^a At 130 K. ^b At 140 K. ^c Graphite monochromator.

systematic absences, which implied that the space group was either $P1$ or $P\bar{1}$. On the basis of the Patterson map and the distribution of $|E^2 - 1|$, the centrosymmetric space group $P\bar{1}$ was selected for both **1** and **2**. The structure of **1** was solved by locating both rhodium atom positions using the Patterson map. Other atom positions were located from successive difference Fourier maps. Anisotropic thermal parameters were assigned to the rhodium, arsenic, phosphorus, and chlorine atoms while isotropic thermal parameters were used for the remaining non-hydrogen

atoms. Refinement of these atoms converged at 0.056. The final stages of refinement included an absorption correction.³¹ All hydrogen atoms were fixed at calculated positions by using a riding model in which the C–H vector is fixed at 0.96 Å and the isotropic thermal parameter for each hydrogen atom is set to 1.2 times the value for the carbon atom to which it is bonded. The final *R* value of 0.036 was computed from 385 least-squares parameters and 8144 reflections. This yielded a goodness of fit of 1.30 and a mean shift/esd of 0.023 for U_{11} of C(12) on the last cycle of refinement. A value of 0.68 e/Å³ was found as the largest feature on the final difference Fourier map. This peak was found 0.58 Å away from a chlorine in a crystallized dichloromethane molecule. The weighting scheme used was $w = [\sigma^2(F_o) + 0.001F_o^2]^{-1}$. Corrections for anomalous dispersion were applied to all atoms. Neutral-atom scattering factors were those of Cromer and Waber.³²

For **2** the position of the two arsenic, the two rhodium, and the silver atoms were generated from FMAP 8, the Patterson-solving routine of SHELXTL Version 4. Other atom positions were located from successive difference Fourier maps. From a later difference map it appeared that one of the dichloromethane molecules was disordered into two approximately equal pairs of chlorines. It was refined by fixing all the thermal parameters at 0.06 and tying the occupancies together as a free variable, *K*, which converged at 0.816 (7) (carbon occupancy was *K* and all chlorines had occupancy *K*/2). Anisotropic thermal parameters were assigned to all rhodium, silver, arsenic, and phosphorus atoms and the nondisordered chlorine atoms. The final stages of refinement included an absorption correction and the treatment of all hydrogen atoms as described for **1**. The final *R* value of 0.061 was computed from 419 least-squares parameters and 8685 reflections. This yielded a goodness of fit of 1.52 and a mean shift/eds of 0.037, for the *x* coordinate of a disordered chlorine atom, in the last cycle of refinement. The largest feature on the final difference Fourier map (4.4 e/Å³) was 0.100 Å away from a disordered chlorine atom.

Acknowledgment. We thank the National Science Foundation (Grants CHE 8217954 and CHE 8519557) for financial support, Dow Corning Corp. for a fellowship for P.E.R., and the Università Degli Studi Delia Calabria for a study leave for M.G.

Supplementary Material Available: Tables of complete bond distances and angles, anisotropic thermal parameters, hydrogen atom coordinates, isotropic thermal parameters, and least-squares planes for **1** and **2** (17 pages); tables of structure factors for **1** and **2** (90 pages). Ordering information is given on any current masthead page.

- (31) XABS, an absorption correction program, produces an absorption tensor from an expression relating F_o and F_c : Hope, H.; Moezzi, B. Department of Chemistry, University of California, Davis, CA, unpublished results.
- (32) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV: (a) pp 149–150; (b) pp 99–101.