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Heterodinuclear Bis(diphenylphosphino)methane-Bridged Molybdenum (d^6)–Gold (d^{10}) Complexes: Metal–Metal Interactions and Ligand Oxidation

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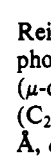
Reinvestigation of the reaction between Ph_3PAuCl and *mer*-Mo(dpm-*P,P'*)(dpm-*P*)$(CO)_3$ (dpm = bis(diphenylphosphino)methane) has shown it to be solvent dependent. The reaction in benzene yields orange $\{(OC)_3ClMo(\mu\text{-dpm})_2Au\}$ as reported before. Crystallization from benzene/diethyl ether gives $\{(OC)_3ClMo(\mu\text{-dpm})_2Au\}\cdot 2(C_2H_5)_2O$, which forms in the triclinic space group $P\bar{1}$ with a = 13.699 (3) Å, b = 14.159 (4) Å, c = 16.187 (3) Å, α = 90.84 (2)°, β = 112.11 (2)°, and γ = 103.34 (2)° at 130 K with Z = 2. Refinement of 9985 reflections and 658 parameters yielded R = 0.051 and R_w = 0.049. The structure consists of *trans*-$P_2Mo(CO)Cl$ and *trans*-P_2Au units with a long, nonbonded Mo···Au separation of 3.302 (1) Å. In dichloromethane solution the same reaction produces yellow $[(dpm\text{-}O)_2Mo(CO)_2AuPPh_3](PF_6)$ after the addition of ammonium hexafluorophosphate. Some gold metal precipitates and the dpm ligand is oxidized to $Ph_2P(O)CH_2PPh_2$ (dpm-*O*). $[(dpm\text{-}O)_2Mo(CO)_2AuPPh_3](PF_6)\cdot CH_2Cl_2\cdot 0.25CH_3OH\cdot 0.25H_2O$ crystallizes in the monoclinic space group $P2_1/c$ with a = 27.489 (8) Å, b = 24.472 (5) Å, c = 22.085 (11) Å, and β = 102.07 (3)° at 130 K with Z = 8. Refinement of 9202 reflections and 576 parameters yielded R = 0.092 and R_w = 0.091. The structure consists of a seven-coordinate molybdenum that is coordinated by two chelating dpm-O ligands, two terminal carbon monoxide ligands, and the $AuPPh_3$ unit. The Mo–Au distances (2.691 (3), 2.709 (3) Å) in the two independent cations found in the asymmetric unit are consistent with the presence of a single bond between these atoms.

Introduction

Recently we have prepared and structurally characterized a number of polynuclear complexes, **1–3**, containing gold(I) (d^{10}) and iridium(I) (d^8) centers.[1-3] An interesting array of chemical bonding between these two metal centers has been uncovered. Many compounds with Au–Ir separations of ca. 3.0 Å are intensely colored and intensely luminescent due to electronic transitions that are localized within the Au/Ir chromophore. Bonding models have been developed to account for the structural and spectroscopic properties.



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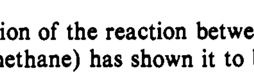

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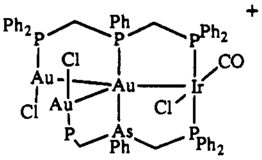

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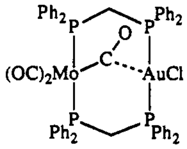
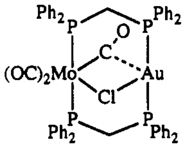
We sought to extend this work to examine the interaction of gold(I) with d^6 metal centers in similar ligating environments. This presents an immediate challenge, since d^6 metal centers are largely six-coordinate and allow limited access for the formation of metal–metal bonds. However, an interesting group of heterodinuclear species has been reported.[4] Among these was the Au/Mo complex $\{(OC)_3MoCl(\mu\text{-dpm})_2Au\}$ (dpm = bis(diphenylphosphino)methane), for which two structures, A and B, had been proposed. These structural proposals were developed because of the spectroscopic similarities between this complex and those of $\{(OC)_2W(\mu\text{-CO})(\mu\text{-dpm})_2(\mu\text{-Cl})Cu\}$, for which structure **4** was established through an X-ray diffraction study.[4]



A



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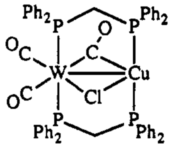

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In **4**, a significant bonding interaction between tungsten and copper was indicated by the relatively short W–Cu distance (2.759 (4) Å). In examining $\{(OC)_3MoCl(\mu\text{-dpm})_2Au\}$, we discovered that it possessed a strucure different from **4** or the proposed structures A and B. Moreover, minor modification of its synthesis led to the preparation of another compound in which dpm was oxidized. These results are described here.

Results

The reactions observed when *mer*-Mo(dpm-*P,P'*)(dpm-*P*)$(CO)_3$ is treated with Ph_3PAuCl are summarized in Scheme I. As reported by Shaw and co-workers,[4] the reaction in benzene yields $\{(OC)_3MoCl(\mu\text{-dpm})_2Au\}$ (**5**). This compound is also formed from the reaction of *mer*-Mo(dpm-*P,P'*)(dpm-*P*)$(CO)_3$ and $(Me_2S)AuCl$. The orange compound **5** crystallizes readily from benzene. It has good solubility in dichloromethane but is

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(1) Balch, A. L.; Catalano, V. J. *Inorg. Chem.* **1991**, *30*, 1302.
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(3) Balch, A. L.; Catalano, V. J.; Noll, B. C.; Olmstead, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 7558.
(4) Blagg, A.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1987**, 769.

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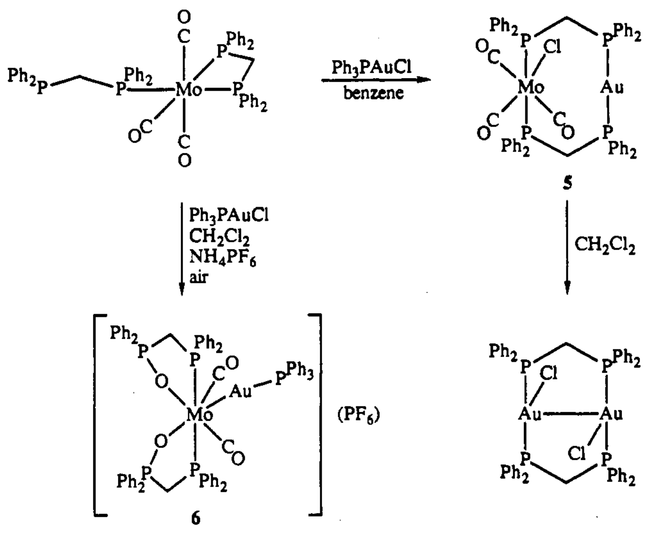
Scheme I



not stable in solution. When dissolved in dichloromethane, it initially produces a ^{31}P NMR spectrum that consists of a pair of triplets at 40.5 and 30.2 ppm as previously reported.[4] However, a singlet at 33.2 ppm grows in intensity as the sample ages. During the process, an unattractive, green-brown powder precipitates from solution. The identity of this amorphous material was not pursued, but the species remaining in solution was identified as $Au_2(\mu\text{-dpm})_2Cl_2$[5,6] on the basis of its ^{31}P NMR chemical shift.

When *mer*-Mo(dpm-*P*,*P*′)(dpm-*P*)$(CO)_3$ is treated with Ph_3PAuCl in dichloromethane in air, the mixture turns cloudy and a precipitate of gold metal forms. Addition of ammonium hexafluorphosphate produces the bright yellow salt [(dpm-*O*)$_2$Mo$(CO)_2AuPPh_3](PF_6)$ (**6**). When a 3:1 gold to molybdenum ratio of reagents is used, the yield of **6** is remarkably high (83% based on *mer*-Mo(dpm-*P*,*P*′)(dpm-*P*)$(CO)_3$), but the same product is also obtained, albeit in lower yield (32%), when a 1:1 Au:Mo ratio is employed. When this reaction is run in dioxygen-free solvents at a 3:1 Au:Mo ratio, **6** is formed in only 5% yield. The infrared spectrum of **6** in Nujol mull reveals the presence of two carbon monoxide stretching vibrations at 1815 and 1747 cm^{-1} and a P–O stretch at 1134 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum of this product is shown in Figure 1. Three resonances labeled A–C with relative intensities of 2:1:2 are observed. Resonance B with its lower intensity is assigned to the triphenylphosphine phosphorus atom. Resonance A is assigned to the phosphorus atoms (P(2) and P(4) of Figure 4 (vide infra)) of the phosphine oxide moiety on the basis of the chemical shift. Resonance C is assigned to the phosphorus atoms (P(1) and P(3) of Figure 4) that are coordinated to molybdenum. Resonance A is coupled to resonance C and appears as a triplet. Resonance C is also coupled to resonance B, so it appears as a triplet of doublets while resonance B appears as a simple triplet.

The detailed structures of both **5** and **6** have been established by X-ray diffraction studies.

Structure of $\{(OC)_3MoCl(\mu\text{-dpm})_2Au\}\cdot 2(C_2H_5)O$. The compound crystallizes with one molecule of the complex and two molecules of diethyl ether in the asymmetric unit. There are no unusual contacts between them. The diethyl ether molecules are not acting as ligands. Atomic positional parameters are given in Table I. Table II contains selected interatomic distances and angles.

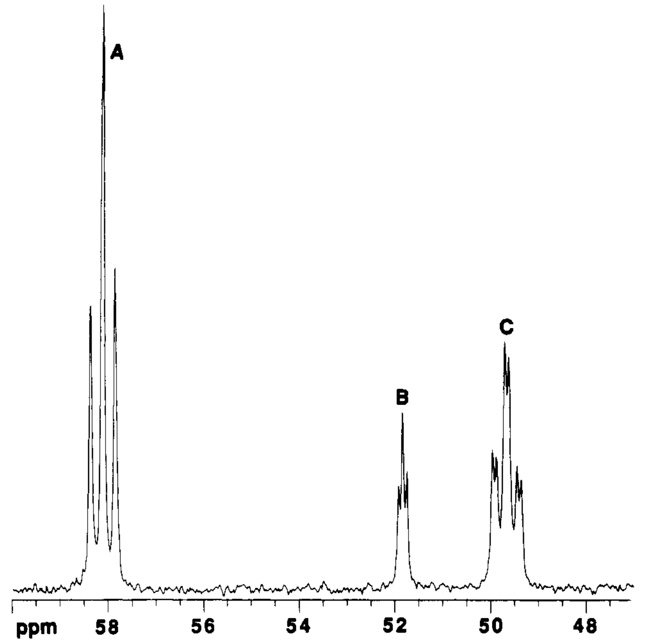


Figure 1. Portion of the 81-MHz $^{31}P\{^1H\}$ NMR spectrum of [(dpm-*O*)$_2$Mo$(CO)_2AuPPh_3](PF_6)$ in dichloromethane-d_2 at 23 °C showing the resonances of the cation. Spectral parameters: δ_a, 57.8 ppm; δ_b, 51.6 ppm; δ_c, 49.4 ppm; $J(P_a,P_c)$, 32.0 Hz, $J(P_b,P_c)$, 10.6 Hz.

Table I. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $\{(OC)_3MoCl(\mu\text{-dpm})_2Au\}\cdot 2Et_2O$[a]

	x	*y*	*z*	*U*(eq)
Au	829 (1)	272 (1)	2800 (1)	19 (1)
Mo	2803 (1)	1797 (1)	2429 (1)	17 (1)
Cl	743 (1)	1332 (1)	1267 (1)	22 (1)
P(1)	2887 (1)	305 (1)	1680 (1)	19 (1)
P(2)	1116 (1)	−1074 (1)	2191 (1)	19 (1)
P(3)	514 (1)	1548 (1)	3482 (1)	20 (1)
P(4)	2207 (1)	3119 (1)	2952 (1)	18 (1)
O(1)	3391 (4)	1068 (3)	4339 (3)	32 (2)
O(2)	3715 (4)	3050 (4)	1134 (4)	39 (2)
O(3)	5291 (4)	2558 (4)	3513 (3)	32 (2)
C(1)	3024 (5)	1245 (5)	3600 (5)	22 (3)
C(2)	3256 (6)	2583 (5)	1518 (5)	25 (3)
C(3)	4341 (6)	2273 (5)	3104 (4)	22 (3)
C(16)	1648 (5)	−716 (4)	1325 (4)	20 (2)

[a] Phenyl carbons omitted: see supplementary material.

The structure of the binuclear complex, which has no crystallographically imposed symmetry, is shown in Figure 2. The Mo···Au distance (3.302 (1) Å) is too long for there to be a direct Mo–Au bond. In contrast, the Mo–Au distances in $\{(\eta\text{-}C_5H_4\text{-}CHO)Mo(CO)_3AuPPh_3\}$[7] and $\{(Ph_3PAu)_7Mo(CO)_3\}$,[8] where Mo–Au bonds exist, fall in the 2.71–2.86-Å range. The Mo···Au separation in **5** is also longer than the nonbonded P···P separations (3.124 (4), 3.199 (4) Å) within the dpm ligands. This is another indication that there is no bond between molybdenum and gold in this complex.

The complex is best viewed as a zwitterionic assembly of a *trans*-P_2Au^+ unit and a *trans*-$P_2Mo(CO)_3Cl^-$ unit. These are connected by the two bridging dpm ligands. The geometry of each of these portions is relatively undisturbed by the presence of the other. Thus the P–Au–P portion shows nearly linear geometry, as expected for two-coordinate gold. Likewise, the coordination about molybdenum is pseudooctahedral. The distortions from regular octahedral coordination appear to result from the need to accommodate the two metal centers with essentially repulsive interactions between them. The P(1)–Mo–P(4) unit is bent to allow for the relatively long Mo···Au distance. The relationship of the gold center to the $Mo(CO)_3Cl$ unit is best

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Table II. Selected Interatomic Distances and Angles in $\{(OC)_3MoCl(\mu\text{-dpm})_2Au\}\cdot 2(C_2H_5)_2O$

	Distances (Å)		
Au–P(2)	2.311 (2)	Au–P(3)	2.308 (2)
Au···Mo	3.302 (1)		
Mo–P(1)	2.468 (2)	Mo–P(4)	2.462 (2)
Mo–C(1)	2.004 (7)	Mo–C(2)	2.053 (8)
Mo–C(3)	1.918 (6)	Mo–Cl	2.654 (2)
C(1)–O(1)	1.167 (8)	C(2)–O(2)	1.15 (1)
C(3)–O(3)	1.181 (8)	P(1)···P(2)	3.124 (4)
P(3)···P(4)	3.199 (4)		
	Angles (deg)		
P(2)–Au–P(3)	175.9 (1)	P(1)–Mo–P(4)	165.1 (1)
P(1)–Mo–C(1)	94.0 (2)	P(1)–Mo–C(2)	88.8 (2)
P(1)–Mo–C(3)	96.5 (2)	P(1)–Mo–Cl	83.8 (1)
P(4)–Mo–C(1)	89.3 (2)	P(4)–Mo–C(2)	94.1 (2)
P(4)–Mo–C(3)	98.4 (2)	P(4)–Mo–Cl	81.6 (1)
Cl–Mo–C(1)	113.7 (2)	Cl–Mo–C(2)	90.0 (2)
Cl–Mo–C(3)	169.5 (2)	C(1)–Mo–C(2)	156.2 (2)
C(2)–Mo–C(3)	79.5 (3)	C(1)–Mo–C(3)	76.7 (3)
Mo–C(1)–O(1)	164.2 (5)	Mo–C(2)–O(2)	166.5 (5)
Mo–C(3)–O(3)	179.1 (6)	P(1)–C(16)–P(2)	116.0 (3)
P(3)–C(41)–P(4)	120.6 (4)		

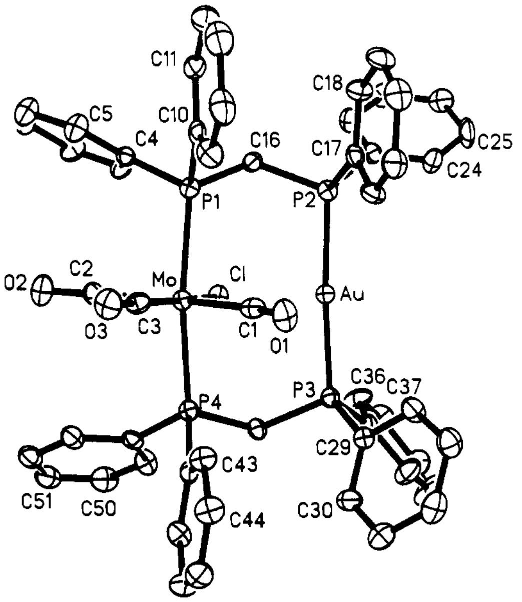

Figure 2. Perspective view of $\{(OC)_3MoCl(\mu\text{-dpm})_2Au\}$ showing 50% thermal contours for all atoms.

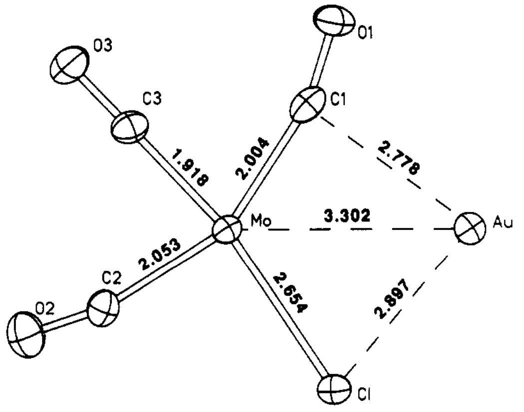

Figure 3. View of the $(OC)_3MoClAu$ core of $\{(OC)_3MoCl(\mu\text{-dpm})_2Au\}$ showing some of the interatomic distances (Å). The C(1)–Mo–Cl angle is 113.7 (2)°.

seen by examining Figure 3, which shows a view of the nearly planar $AuMo(CO)_3Cl$ unit. The Cl–Mo–C(1) angle has opened to accommodate the presence of the gold center. This angle (113.7°) is the widest of all of the angles between cis ligands on molybdenum.

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $[(dpm\text{-}O)_2(OC)_2MoAuPPh_3](PF_6)\cdot CH_2\cdot 0.25MeOH\cdot 0.25H_2O$

	x	*y*	*z*	*U*(eq)
Au(1)	2209 (1)	2586 (1)	5056 (1)	27 (1)^a
Mo(1)	1797 (1)	3505 (1)	5391 (1)	21 (1)^a
P(1)	1161 (2)	2784 (3)	5474 (3)	25 (2)^a
P(2)	1209 (2)	3525 (3)	6539 (3)	28 (2)
P(3)	2199 (2)	4368 (3)	5318 (3)	22 (2)^a
P(4)	1153 (2)	4488 (3)	4574 (3)	27 (2)^a
P(5)	2591 (3)	1799 (3)	4913 (3)	31 (3)
O(1)	2797 (6)	3200 (7)	6262 (8)	41 (5)
O(2)	1970 (6)	3499 (7)	4042 (8)	39 (5)
O(3)	1575 (5)	3814 (6)	6229 (7)	27 (4)
O(4)	1124 (6)	3996 (6)	4991 (7)	21 (4)
C(1)	2408 (9)	3275 (10)	5908 (11)	27 (6)
C(2)	1929 (8)	3450 (9)	4554 (11)	16 (5)
C(15)	800 (8)	3114 (9)	5980 (10)	21 (6)
C(40)	1787 (7)	4719 (8)	4652 (10)	14 (5)
C(85)	4049 (8)	5150 (9)	2566 (11)	22 (6)
C(110)	4463 (8)	7399 (9)	2049 (10)	20 (6)
Au(2)	2754 (1)	6592 (1)	1266 (1)	43 (1)^a
Mo(2)	3592 (1)	6398 (1)	2129 (1)	20 (1)^a
P(6)	3640 (2)	5622 (3)	2846 (3)	21 (2)^a
P(7)	4499 (2)	5501 (3)	2250 (3)	23 (2)^a
P(8)	3864 (2)	7163 (3)	1521 (3)	23 (2)^a
P(9)	4348 (3)	7374 (3)	2815 (3)	27 (2)^a
P(10)	2074 (3)	6855 (4)	565 (4)	57 (4)^a
O(5)	2689 (6)	6797 (7)	2639 (8)	37 (5)
O(6)	3270 (7)	5500 (8)	1143 (9)	51 (5)
O(7)	4361 (6)	6100 (6)	2124 (7)	29 (4)
O(8)	4049 (5)	6881 (6)	2901 (7)	25 (4)
C(71)	3022 (9)	6637 (10)	2385 (12)	33 (7)
C(72)	3348 (9)	5861 (10)	1515 (12)	33 (7)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. Parameters for phenyl carbons, hexafluorophosphate anions, and solvent are omitted: see supplementary material.

The Mo–Cl distance is also very long, 2.654 (2) Å. This distance lies outside the range (2.335–2.618 Å, mean 2.446 Å) of 242 Mo–Cl distances contained in the Cambridge Crystallographic Data Base[9] for compounds containing the MoP_2Cl structural unit. The low formal oxidation state of molybdenum (Mo(0)) may contribute to the exceptionally long Mo–Cl distance in $\{(OC)_3ClMo(\mu\text{-dpm})_2Au\}$.

It is informative to compare the structure of $\{(OC)_3ClMo(\mu\text{-dpm})_2Au\}$ with that of the W/Cu compound $\{(OC)_2W(\mu\text{-}CO)(\mu\text{-dpm})_2(\mu\text{-}Cl)Cu\}$ (**4**).[4] In the latter, the Cu–W distance (2.759 (4) Å) is considerably shorter than the Mo–Au distance (3.302 (1) Å). In the W/Cu compound, this shorter metal–metal distance is consistent with the presence of a direct bond between the metals. Additionally, the Cu–Cl and Cu–C distances (2.553 (5) and 2.267 (8) Å, respectively) have been interpreted to indicate that the chloride is nearly symmetrically bound to tungsten and copper in **4** and that one of the carbonyl ligands is semibridging. In **5** however, the Au···Cl and Au···C distances (2.897 (2) and 2.778 (6) Å, respectively) are too long for either of these units to participate in significant bridging interactions.

Structure of $[(dpm\text{-}O)_2Mo(CO)_2AuPPh_3](PF_6)\cdot CH_2Cl_2\cdot 0.25CH_3OH\cdot 0.25H_2O$. This crystallizes with two independent cations, two hexafluorophosphate ions, and the occluded solvent in the asymmetric unit. Selected atomic positional parameters for the two cations are given in Table III. Table IV contains selected interatomic distances and angles for the two cations. As can be seen from the table, these two are similar in their dimensions.

The structure of one of the cations is shown in Figure 4. The molybdenum is seven-coordinate. There are two chelating dpm-*O* ligands, two terminal carbon monoxide ligands, and the $AuPPh_3^+$ group coordinated to molybdenum. The Mo–Au distance (2.691 (3) Å) is indicative of the existence of a single bond between these entities. It is 0.61 Å shorter than the Mo···Au separation

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[9] Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146.

Table IV. Selected Interatomic Distances and Angles for $[(dpm\text{-}O)_2Mo(CO)_2AuPPh_3](PF_6)\cdot CH_2Cl_2\cdot 0.25CH_3OH\cdot 0.25H_2O$

	cation I	cation II
	Distances (Å)	
Mo–Au	2.691 (3)	2.708 (3)
Mo–P(1)	2.516 (7)	2.508 (7)
Mo–P(3)	2.406 (7)	2.438 (7)
Mo–O(3)	2.20 (2)	2.24 (2)
Mo–O(4)	2.23 (2)	2.23 (2)
Mo–C(1)	1.91 (2)	1.91 (3)
Mo–C(2)	1.96 (2)	1.87 (3)
Au–P(5)	2.246 (7)	2.256 (8)
Au–C(1)	2.50 (2)	2.41 (3)
Au–C(2)	2.44 (2)	2.43 (3)
P(2)–O(3)	1.51 (2)	1.52 (2)
P(4)–O(4)	1.53 (2)	1.49 (2)
C(1)–O(1)	1.20 (3)	1.20 (3)
C(2)–O(2)	1.17 (3)	1.23 (3)
	Angles (deg)	
P(1)–Mo–P(3)	163.0 (2)	160.0 (2)
C(2)–Mo–O(3)	162.7 (7)	163.0 (8)
C(1)–Mo–O(4)	161.9 (8)	165.0 (8)
Au–Mo–O(3)	136.5 (4)	136.0 (4)
Au–Mo–O(4)	134.8 (4)	134.8 (4)
P(3)–Mo–Au	119.3 (2)	121.0 (2)
P(1)–Mo–C(2)	106.8 (6)	107.0 (8)
P(1)–Mo–C(1)	106.7 (8)	103.5 (8)
C(1)–Mo–C(2)	103.3 (10)	103.8 (11)
P(3)–Mo–O(3)	88.1 (4)	80.2 (4)
C(2)–Mo–O(4)	88.0 (7)	88.7 (8)
C(1)–Mo–O(3)	87.9 (9)	88.0 (9)
P(3)–Mo–C(1)	86.5 (7)	84.1 (8)
P(1)–Mo–O(4)	82.8 (4)	80.2 (4)
P(1)–Mo–O(3)	82.0 (4)	81.6 (4)
P(3)–Mo–O(4)	81.6 (4)	88.0 (4)
P(3)–Mo–C(2)	79.5 (7)	88.8 (8)
O(3)–Mo–O(4)	78.2 (6)	78.2 (6)
P(1)–Mo–Au	76.9 (2)	78.3 (2)
C(2)–Mo–Au	60.8 (6)	60.9 (7)
C(1)–Mo–Au	63.2 (7)	59.9 (7)
Mo–Au–P(5)	172.3 (2)	173.6 (3)

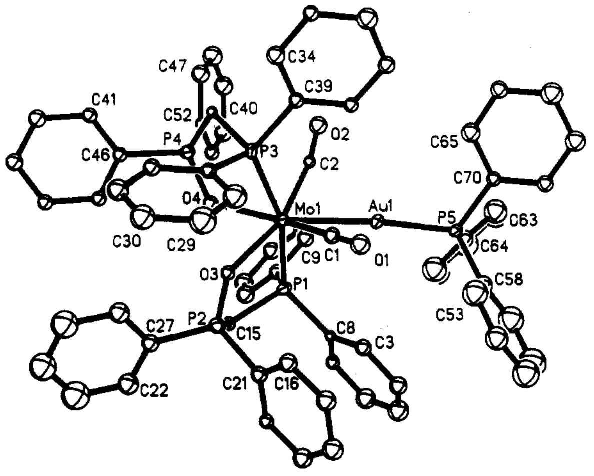

Figure 4. Perspective view of $[(dpm\text{-}O)_2Mo(CO)_2AuPPh_3]^+$ showing 30% thermal contours for all atoms.

in **5** and is also shorter than the Mo–Au bond length (2.7121 (5) Å) in $(\eta^5\text{-}C_5H_4CHO)Mo(CO)_3AuPPh_3$.[7]

The coordination geometry about molybdenum is best described as approximating a capped octahedron with the $AuPPh_3$ portion as the capping group and the remaining six ligands representing a distorted octahedron. The idealized internal ligand angles within a capped octahedron involve the following: three at 160°, three at 130°, three at 108.8°, three at 83.1°, six at 82.0°, and three at 70°.[10] For comparison in **6**, we find three in the range 163–160°, three in the range 140–119°, three in the range 103–107°, three in the range 88–86°, seven in the range 86–76°, and two in the range 63–59° for each cation. Comparison of the ideal angles for a pentagonal bipyramid, a capped trigonal prism, or a 4:3 piano stool structure (see ref 10) shows poorer correlation between the ideal and observed angles. The principal distortion present in **6** is a displacement of the capping $AuPPh_3$ group toward the two carbon monoxide ligands. This may result from any attractive interaction between these units, or it may be dictated by the bulk of the $AuPPh_3$ portion. The exterior of the molecule is formed by the 11 phenyl rings that protrude from the dpm-*O* and PPh_3 ligands. The need to accommodate these substituents certainly plays a major role in determining the geometry of this crowded species.

As expected, the Mo–Au–P angles (172.3, 173.6°) in **6** are nearly linear.

Discussion

This work demonstrates that the reaction between *mer*-Mo(dpm-*P,P'*)(dpm-*P*)$(CO)_3$ and Ph_3PAuCl can lead to two very different products and that the choice of solvent for the reaction is critical. The two products, **5** and **6**, both are binuclear complexes that contain molybdenum and gold, but only the latter contains a Mo–Au bond. Both **5** and **6** can be viewed as containing six-coordinate Mo(0) centers, but in **6** one pair of the molybdenum d_π electrons is used to form a dative Mo–Au bond. However, in **5** no Mo–Au bond is present. In this context, the $AuPR_3^+$ unit in **6** is a better acceptor of molybdenum electrons than is the $Au(PR_3)_2^+$ unit in **5**. In both **5** and **6** the gold achieves the common two-coordinate, linear structure.

Despite similarities in the spectroscopic features of $\{(OC)_2W(\mu\text{-}CO)(\mu\text{-}dpm)_2(\mu\text{-}Cl)Cu\}$ (**4**) and $\{(OC)_3MoCl(\mu\text{-}dpm)_2Au\}$ (**5**), these two complexes have different structures. Most significantly, **5** lacks a Mo–Au bond and its chloro and carbon monoxide ligands do not fill a bridging role. It is particularly striking to note the similarity in the C–O stretching vibrations for these two complexes. **4**: 1952, 1838, 1784 cm^{-1}. **5**: 1952, 1830, 1780 cm^{-1}. Certainly, the low-energy absorption in the case of **5** is not diagnostic of the presence of a bridging carbon monoxide ligand.

The conversion of dpm into the monoxide, dpm-*O*, that is involved in the synthesis of **6** is remarkable. Despite the wide use of dpm as a ligand for constructing mono, di-, and trinuclear complexes, reactions of dpm-containing metal complexes usually proceed without alteration of this diphosphine.[11-14] Shaw and co-workers[4] did notice that the reaction of *fac*- or *mer*-M(dpm-*P,P'*)(dpm-*P*)$(CO)_3$ (M = Cr, Mo, W) with silver(I) compounds yielded silver metal and an oxidized complex of Cr, Mo, or W, but these complexes were not identified. The fact that the oxidation of the dpm ligand stops at the monooxide stage is particularly interesting. This may reflect the stability of the five-membered chelate rings that occur in **6**. The reaction leading to the formation of dpm-*O* in **6** is a complex one that appears to involve both Au(I) and dioxygen as oxidants, since both of these are necessary for preparation of **6** in good yield.

The unsymmetrical oxide dpm-*O*, which is present in **6**, has been prepared previously through the reaction of ((diphenylphosphoryl)methyl)lithium with diphenylchlorophosphine.[15,16] The resulting ligand has been used to form complexes with cadmium-

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(II) and mercury(II) halides.[15] Related complexes with chromium, molybdenum, and tungsten tetracarbonyls have also been reported.[15]

Experimental Section

Preparation of Compounds. *mer*-Mo(dpm-*P,P'*)(dpm-*P*)$(CO)_3$ was prepared as previously described.[17]

$\{(OC)_3ClMo(\mu\text{-dpm})_2Au\}$. This was obtained from the reaction of *mer*-Mo(dpm-*P,P'*)(dpm-*P*)$(CO)_3$ and Ph_3PAuCl in benzene as reported by Blagg et al.[4] Me_2SAuCl may be substituted for Ph_3PAuCl in this procedure. In solution, the product is very sensitive to warming above 30 °C. Infrared: ν(CO) 1952, 1830, 1780 cm^{-1} (Nujol mull). The ^{31}P NMR spectrum of a freshly prepared solution of the complex in dichloromethane consists of two triplets at 40.5 and 30.2 ppm with $J(P,P)$ = 30.2 Hz. However, a singlet also appears at 33.2 ppm shortly after preparation, and this resonance grows in intensity with time. This feature is found in samples prepared from either Ph_3PAuCl or Me_2SAuCl and hence is not due to Ph_3PAuCl, which does also produce a ^{31}P NMR resonance at 33.2 ppm. On the basis of its chemical shift, the material cannot be any of the following: (^{31}P NMR, chemical shift (ppm)): dpm (−23.0, singlet), dpm-*O*[15,16] (27.7, −28.4, two singlets), $Ph_2P(O)CH_2P(O)Ph_2$[15,16] (24.2, singlet), (μ-dpm)Au_2Cl_2[18] (26.1, singlet), (dpm)$Mo(CO)_4$[19] (1.5 singlet), $(dpm)_2MoCl_2(CO)_2$[20] (32, −25, sextet and doublet). However, we have verified that $Au_2(\mu\text{-dpm})_2Cl_2$[5,6] does produce a singlet at 33.2 ppm in dichloromethane.

$[(Ph_2PCH_2P(O)Ph_2)_2Mo(CO)_2AuPPh_3](PF_6)$. Solid Ph_3PAuCl (220 mg, 0.443 mmol) was added to a solution of 140 mg (0.148 mmol) of *mer*-Mo(dpm-*P,P'*)(dpm-*P*)$(CO)_3$ in 40 mL of dichloromethane. The solution immediately turned orange. After being stirred for 30 min, the solution lightened in color to a pale yellow and appeared cloudy due to the formation of a solid (metallic gold). After an additional hour of stirring, 17 mg (1.060 mmol) of ammonium hexafluorophosphate in 30 mL of methanol was added. The solution was stirred for 1 h and filtered through a bed of Celite. The volume of the filtrate was reduced to 10 mL, and diethyl ether was slowly added until yellow crystals of the product formed. These were collected by filtration and washed with diethyl ether. The product was recrystallized from dichloromethane/diethyl ether and vacuum-dried; yield 174 mg (83%). Infrared: ν(CO) 1815, 1747 cm^{-1} (Nujol mull). ^1H NMR: CH_2 protons, 3.53, 3.23 ppm in CD_2Cl_2. The ^{31}P NMR spectrum is given in Figure 1.

$\{(OC)_3MoCl(\mu\text{-dpm})_2Au\}\cdot 2(C_2H_5)_2O$ (5). X-ray Data Collection. Orange parallelepipeds of the complex were obtained by diffusion of diethyl ether into a dichloromethane solution of the complex under a purified dinitrogen atmosphere. Crystal growth was accompanied by considerable sample decomposition, which produced a green-brown powder as well as the desired crystals. (An infrared spectrum of these orange crystals verified that they were representative of the sample described above.) These were coated with a light hydrocarbon oil, mounted on a glass fiber with silicone grease, and placed in the 130 K nitrogen stream of a Syntex $P2_1$ diffractometer that was equipped with a locally modified LT-1 low-temperature apparatus. Unit cell parameters were determined by least-squares refinement of 13 reflections with 12° < 2θ < 24°. Two check reflections showed only random (<3%) fluctuation in intensity during data collection. The data were corrected for Lorentz and polarization effects. Crystal data are given in Table V. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[21]

Solution and Structure Refinement. Calculations were performed using the Siemens SHELXTL PLUS system of programs. The structure was solved by Patterson methods. Hydrogen atoms were included in the refinement model. Their positions were calculated by the use of a riding model with C–H distances fixed at 0.96 Å and a thermal parameter of U = 0.05 $Å^2$. An absorption correction was applied.[22] All non-hydrogen atoms were refined anisotropically. The largest peak in the final difference map had a density of 1.38 e/$Å^3$ and was 1.13 Å from the gold atom.

Table V. Crystallographic Data

$\{(OC)_3MoCl(\mu\text{-dpm})_2Au\}\cdot 2(C_2H_5)_2O$ (**5**)	
$C_{61}H_{63}AuClMoO_5P_4$	fw = 1328.3
a = 13.699 (3) Å	$P\bar{1}$, triclinic
b = 14.159 (4) Å	T = 130 K
c = 16.187 (3) Å	λ(Mo Kα) = 0.710 73 Å
α = 90.84 (2)°	μ(Mo Kα) = 3.038 mm^{-1}
β = 112.11 (2)°	d_{calc} = 1.569 $Mg{\cdot}m^{-3}$
γ = 103.34 (2)	transm factors = 0.24–0.56
V = 2812.4 (11) $Å^3$	$R(F_o)^a$ = 0.051
Z = 2	$R_w(F_o)^a$ = 0.048
$[(dpm\text{-}O)_2Mo(CO)_2AuPPh_3](PF_6)\cdot CH_2Cl_2\cdot 0.25CH_3OH\cdot 0.25H_2O$ (**6**)	
$C_{70}H_{62.5}AuCl_2F_6MoO_{4.5}P_6$	fw = 1639
a = 27.489 (8) Å	$P2_1/c$, monoclinic
b = 24.472 (5) Å	T = 130 K
c = 22.085 (11) Å	λ(Mo Kα) = 0.710 73 Å
β = 102.07 (3)°	μ(Mo Kα) = 2.47 mm^{-1}
V = 14528 (9) $Å^3$	d_{calcd} = 1.509 $Mg{\cdot}m^3$
Z = 8	transm factors = 0.53–0.85
$R(F_o)^1$ = 0.092	$R_w(F_o)^a$ = 0.091

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

$[(dpm\text{-}O)_2Mo(CO)_2AuPPh_3](PF_6)\cdot CH_2Cl_2\cdot 0.25CH_3OH\cdot 0.25H_2O$ (6). X-ray Data Collection. Yellow plates of the complex were formed by slow diffusion of diethyl ether into a dichloromethane solution of the complex. These were coated with a light hydrocarbon oil, mounted on a glass fiber with silicone grease, and placed in the 130 K nitrogen stream of a Siemens R3m/V diffractometer that was equipped with a locally modified Enraf-Nonius low-temperature apparatus. Unit cell parameters were determined by least-squares refinement of 13 reflections with 15° < 2θ < 26°. The unique space group $P2_1/c$ (No. 14) was determined by the following conditions: $0k0$, $k = 2n$; $h0l$, $l = 2n$. Two check reflections showed only random (<5%) fluctuations in intensity during data collection. The data were corrected for Lorentz and polarization effects. Crystal data are given in Table V.

Solution and Structure Refinement. The structure was solved by Patterson methods. The asymmetric unit contains two crystallographically independent molecules. Superposition of these molecules shows that they are similar except for orientation of the phenyl rings. All phenyl carbons were refined as members of rigid bodies. One of the hexafluorophosphate anions showed disorder; both were refined with constrained geometry. Two molecules of dichloromethane occupy four sites in the symmetric unit. Two of these sites are badly disordered, and the best model was chosen after refining site occupancy factors. Anisotropic thermal parameters were refined for molybdenum, gold, and phosphorus in the cations. Other atoms were refined isotropically. Hydrogen atoms were included in refinement model. Their positions were calculated by the use of a riding model with C–H distances fixed at 0.96 Å and a thermal parameter of U = 0.048 $Å^2$. An absorption correction was applied.[22] The maximum residual electron density in the final difference map was 1.98 e/$Å^3$, 0.73 Å from Cl(2). The crystal used for data collection was poorly diffracting and showed broad peak scans. This and the severe disorder in the solvent positions contribute to the somewhat high residuals.

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Supplementary Material Available: Tables of crystal data, atomic positional parameters, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom positions for **5** and **6** (26 pages). Ordering information is given on any current masthead page.

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