Notes

Solid-State Tetramer vs Solution-State Dimer. Reinvestigation of $[Ag_2(OAc)_2(dppm)]_2$ and Its dppm Addition Product $[Ag(OAc)(dppm)]_2$ (dppm = $Ph_2PCH_2PPh_2$)

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Introduction

We have shown recently that an array of structural possibilities can occur when silver(I) is bonded to a bidentate phosphine such as 1,1′-bis(diphenylphosphino)ferrocene (dppf) and a mobile ligand such as nitrate and carboxylate.[1] The interplay of three parameters—(i) the geometrical flexibility of Ag(I), (ii) cone and bite angle changes of the phosphine, and (iii) coordination mode fluxionality of the phosphine and supporting ligands—make structural prediction virtually impossible. Spectroscopic characterizations of these structures are further hampered by the ligand lability on Ag(I) which forces structural reorganization upon dissolution. During our work on the dppf complexes, an interesting paper by van Koten *et al.*[2] especially caught our attention. It reports a dinuclear structure for $Ag_2(OAc)_2(dppm)$ (dppm = bis(diphenylphosphino)methane) and that this complex is *"isolated even under conditions of excess phosphine"*.[2] This work was later substantiated in a elaborate spectroscopic report.[3] Our observation on the analogous dppf complex suggests otherwise—it is tetranuclear in the solid state and rapidly reacts with excess dppf. This apparent contradiction did not appear reasonable and prompted us to reinvestigate this dppm complex.

Results and Discussion

Dppm reacts with 2 equiv of AgOAc to give a stoichiometric complex $[Ag_2(\mu\text{-}O_2CCH_3\text{-}O,O')(\mu\text{-}O_2CCH_3\text{-}O)(\mu\text{-dppm})]_2$, **1**. Single-crystal X-ray diffraction study of the dihydrate reveals a centrosymmetric tetranuclear aggregate which is different from the dinuclear structure reported in solution. (Figure 1). It consists of two disilver fragments linked by two acetate molecules in a monoatomic mode. The Ag(I) atoms in each fragment are bridged by dppm and acetate in an *anti*−*syn* fashion. The molecule as a whole comprises a 12-membered central ring fused between two 8-membered rings. An oxygen atom from each acetate bridge is H-bonded further to a lattice water molecule. For each acetate bridge, there are strong (2.265(11) Å for Ag(1)−O(1) and 2.232(11) Å for Ag(2)−O(3)) and weak (2.397(11) Å for Ag(2)−O(2) and 2.485(10) Å for Ag(1a)−O(3)) Ag−O bonds.

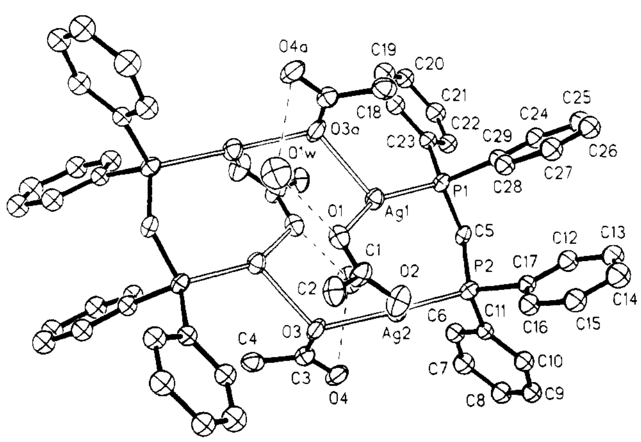

Figure 1. ORTEP plot (30% thermal ellipsoids) of the molecular structure of $[Ag_2(\mu\text{-}O_2CCH_3\text{-}O,O')(\mu\text{-}O_2CCH_3\text{-}O)(\mu\text{-dppm})]_2\cdot 2H_2O$, **1**.

Complex **1** reacts rapidly with 2 molar equiv of dppm to give $[Ag(\eta^2\text{-OAc})(\mu\text{-dppm})]_2$, **2**. Although this phosphine addition was apparently not observed by van Koten,[4] formation of $[Ag_2X_2(P\text{-}P)_2]_m$ (P-P = diphosphine) complexes[5] is known to be facile. There are also more examples of the 2:2 (Ag:P-P) complexes than 2:1 complexes as in $[Ag_2X_2(P\text{-}P)]_n$.[1a,6] X-ray analysis of **2** (as a 1:2 $CHCl_3$ solvate) yielded a "face-to-face" dinuclear structure with the Ag(I) atoms doubly-bridged by dppm to give an 8-membered ring (Figure 2). Each Ag(I) is stabilized by a chelating acetato group to give an 18-electron configuration. The bond angles on the distorted tetrahedral Ag(I) range between 50.4(2) and 146.1(1)°. An oxygen on each acetate is H-bonded to a chloroform solvate. The *anti* conformation of the acetate attachment contrasts the *syn* form in the related nitrato complex $[Ag(NO_3)(dppm)]_2$.[7] Conversion of **1** to **2** can be visualized in five consecutive steps (Figure 3), namely, (i) breaking of the two weakest Ag−O bonds (*viz.* Ag(1)−O(3a) and Ag(1a)−O(3)), (ii) end approach of dppm to compensate for electron loss, (iii) cleavage of the next weakest Ag−O links (*viz.* Ag(2)−O(2) and Ag(2a)−O(2a)), (iv) closing the metallocycle by attaching the dangling phosphine, and (v) chelation of the dangling acetate to give a saturated complex. A similar conversion from $Ag_4X_4L_2$ to dimeric $Ag_2X_2L_2$ has been observed.[8] Higher steric demand and electronic saturation in **2** probably account for the significantly weaker Ag−P (2.455(3) Å (mean)) and Ag−O (2.579(5) Å (mean)) bonds compared to those of **1** (2.377(4) Å (mean) and 2.345(11) Å (mean), respectively). Unlike $[Ag(NO_3)(dppf)]_2$, **2** does not react further with excess dppm. Coordinative saturation of the metals and the strong chelating property of acetate are obviously responsible.

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(4) Reasons for this apparent contradiction are presently unclear as experimental details of this phosphine addition are not reported.

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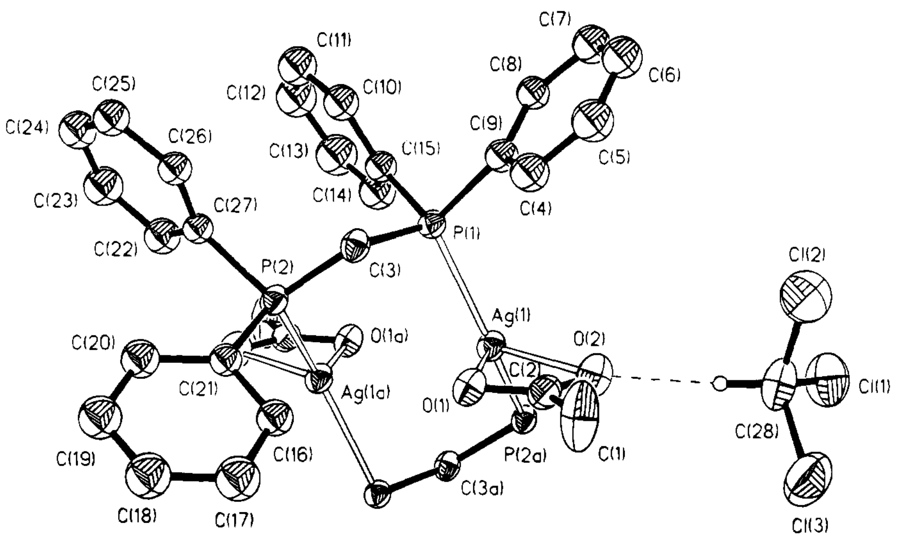

Figure 2. ORTEP plot (30% thermal ellipsoids) of the molecular structure of [Ag(η^2-O$_2$CCH$_3$)(μ-dppm)]$_2$·2CHCl$_3$, **2**.

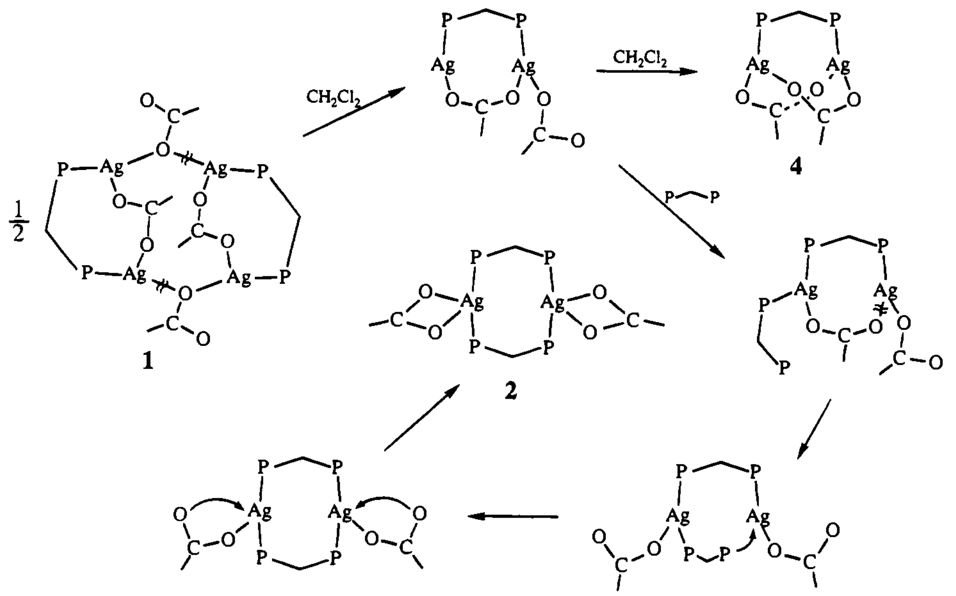

Figure 3. Possible mechanistic pathway for converting **1** to **2** and Ag$_2$(μ-O$_2$CCH$_3$-*O,O'*)$_2$(μ-dppm), **4**.

The different skeletal characteristics of dppm[9] and dppf[10] can in principle stabilize different structures for complexes with the same stoichiometric formula. But, to date there are very few models which could permit such direct comparison. Between **1** and **2**, the dppf analogue (**3**)[1a] (Figure 4) is only known for **1**. Structures of **1** and **3** share three main features—(i) tetrameric, (ii) bridging diphosphine, and (iii) two [Ag$_2$(μ-OAc)-(μ-P-P)] fragments linked together by two acetate bridges. The main differences between **1** and **3** are as follows: (i) Ag(I) in **1** is trigonal planar but tetrahedral in **3**; (ii) the acetates linking the Ag$_2$ fragments are one-atom bridges in **1**, but in **3** they cap three metal centers. As a result, the heavy atoms in **1** constitute an open and near-planar network, whereas **3** is folded to give a "chaired" configuration. These differences are ascribed to the different coordination modes of acetates in **1** and **3**, which in turn are traced to the differences in stereogeometries of dppm and dppf. These structures illustrate the very adaptable characteristics of carboxylates in supporting polynuclear aggregates.[11] Dppm is naturally suited to support two metal centers in close proximity[12] (e.g. the Ag(I) atoms in **2** are locked to close proximity (Ag(1)–Ag(1a) = 3.194(2) Å)). Despite its larger bite size, dppf can coordinate likewise; this is helped by the facile twisting mechanism about the –C$_5$H$_4$–Fe–C$_5$H$_4$– centroid. Such twist however disrupts the planarity of the {Ag$_2$P$_2$} entity and pulls out two Ag(I) atoms from an otherwise rhombuslike arrangement of the four Ag atoms.

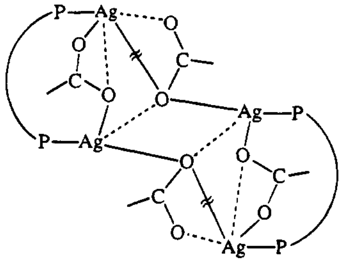

Figure 4. Structural relationship between **1** and its dppf analogue, **3**. (P-P = dppm or dppf; solid lines represent the structure of **1**, and two of these are replaced by broken lines in the structural formula of **3**.)

Molecular weight (MW) determination suggested that **1** dissociates significantly in solution. Its ^{31}P NMR spectrum, which is temperature-dependent, shows that its dinuclear silver

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Table 1. Crystallographic Data for $[Ag_2(\mu\text{-}O_2CCH_3\text{-}\mathit{O,O'})(\mu\text{-}O_2CCH_3\text{-}\mathit{O})(dppm)]_2\cdot 2H_2O$, **1**, and $[Ag(\eta^2\text{-}O_2CCH_3)(\mu\text{-}dppm)]_2\cdot 2CHCl_3$, **2**

chemical formula	$[Ag(O_2CCH_3)_3\text{-}(Ph_2PCH_2PPh_2)]\cdot H_2O$	$[Ag(O_2CCH_3)\text{-}(Ph_2PCH_2PPh_2)]_2\cdot CHCl_3$
fw	932.71	1341.2
space group	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)
a, Å	16.336(3)	11.080(3)
b, Å	18.298(4)	11.374(7)
c, Å	19.105(5)	12.367(5)
α, deg	95.27(4)	
β, deg	101.09(3)	
γ, deg	99.72(4)	
V, Å^3	5711(2)	1495(1)
Z	8	1
T, K	291	291
λ(Mo Kα), Å	0.710 73	0.710 73
ϱ_{calc}, g cm^{-3}	1.708	1.490
μ, mm^{-1}	1.52	1.07
no. of obsd rfclns	2401 ($\lvert F_o\rvert \ge 6.0\sigma(\lvert F_o\rvert)$)	3803 ($\lvert F_o\rvert \ge 6.0\sigma(\lvert F_o\rvert)$)
$R(F_o)^a$	0.073	0.069
$R_w(F_o)^b$	0.089	0.095

[a] $R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$. [b] $R_w = [\sum w^2(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w^2\lvert F_o\rvert^2]^{1/2}$.

Table 2. Atomic Coordinates ($\times 10^5$ for Ag; $\times 10^4$ for Other Atoms) and Equivalent Isotropic Displacement Coefficients[a] (Å^2 × 10^4 for Ag; $\times 10^3$ for Other Atoms) of Selected Non-Hydrogen Atoms

atom	*x*	*y*	*z*	U_{eq}
(a) $[Ag_2(\mu\text{-}O_2CCH_3\text{-}\mathit{O,O'})(\mu\text{-}O_2CCH_3\text{-}\mathit{O})(dppm)]_2\cdot 2H_2O$, **1**				
Ag(1)	39621(8)	1455(6)	47132(6)	493(4)
Ag(2)	50415(8)	2675(7)	33986(6)	544(5)
O(1)	5005(7)	908(6)	4991(5)	54(4)
O(2)	5166(8)	1442(6)	3944(6)	74(5)
C(1)	5293(11)	1391(8)	4581(9)	56(6)
C(2)	5868(11)	1948(8)	4903(8)	65(7)
O(3)	6137(7)	−122(6)	3989(5)	59(4)
O(4)	6350(7)	−782(6)	3029(5)	67(5)
C(3)	6508(10)	−629(9)	3655(8)	48(6)
C(4)	7141(10)	−1065(8)	4040(8)	63(7)
O(1W)	5129(8)	1527(7)	6412(6)	89(6)
P(1)	2830(2)	−199(2)	3992(2)	40(1)
P(2)	3880(3)	104(2)	2679(2)	42(1)
C(5)	3113(9)	−490(7)	3081(7)	42(5)
(b) $[Ag(\eta^2\text{-}O_2CCH_3)(\mu\text{-}dppm)]_2$, **2**				
Ag(1)	6266(5)	13353(5)	5752(5)	475(2)
C(1)	−286(13)	2324(13)	3823(10)	112(6)
C(2)	7(8)	1949(8)	2721(7)	57(3)
O(1)	−650(7)	1045(6)	2130(5)	75(3)
O(2)	879(6)	2619(6)	2433(5)	70(3)
P(1)	−1394(2)	1674(2)	−476(2)	45(1)
P(2)	−2687(2)	−909(2)	−471(2)	44(1)
C(3)	−2650(7)	687(6)	−27(7)	47(3)
C(28)	2198(11)	4867(11)	4076(10)	91(5)
Cl(1)	3575(3)	5491(3)	3667(3)	110(2)
Cl(2)	1179(4)	5873(3)	3982(3)	114(2)
Cl(3)	2581(4)	4515(4)	5431(3)	135(2)

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

isomer, **4**, is the sole dissociation product (Figure 3). The spectrum at −50 °C is identical to that reported.[2] The structure of **4** in solution has been correctly proposed by van Koten *et al.*[2] This dissociation of **1** to give $[Ag_2(OAc)_2(dppm)]$, **4**, is easily perceived by cleaving the weakest Ag−O links (Ag(1)−O(3a) and Ag(1a)−O(3)) and subsequent attachment of free oxygen (O(4) and O(4a) of the dangling acetate to the unsaturated Ag(1) and Ag(1a) (Figures 1 and 3). MW measurement of **2** is in agreement with its dimeric structure in the solid state. Its variable temperature ^{31}P NMR spectra however reveal an equilibrium between **2**, a major species, and two unidentified minor species.

To conclude, all our data on **4** agree with those reported by van Koten[2,3] in pointing to a dinuclear structure. However, this complex is isolated as a tetranuclear complex in its solid state. This result demonstrates a polymerization isomerism between solid and solution states for carboxylato diphosphine complexes. It also cautions the use of solution data in the elucidation of solid-state structures in these labile complexes.

Experimental Section

All preparations were routinely carried out under dry argon atmosphere and in dry oxygen-free solvents. All ^{1}H and ^{31}P NMR spectra were recorded on a Bruker ACF 300 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory at the Chemistry Department in NUS. Molecular weight measurements were carried out at Galbraith Laboratories, Inc., Knoxville, TN, using vapor pressure osmometry.

$[Ag_2(\mu\text{-}O_2CCH_3\text{-}\mathit{O,O'})(\mu\text{-}O_2CCH_3\text{-}\mathit{O})(\mu\text{-}dppm)]_2\cdot 2H_2O$ (1). To an CH_2Cl_2 solution (16 mL) of dppm (0.157 g, 0.41 mmol) was added solid $AgCO_2CH_3$ (0.136 g, 0.82 mmol). The mixture was stirred for 1 h to give a clear solution. Filtration, concentration, and cooling gave rise to a white precipitate. Isolation and recrystallization of this solid from CH_2Cl_2/hexane yielded colorless crystals of **1**. Yield: 0.243 g (83%). Anal. Calcd: C, 47.31; H, 4.10; Ag, 29.30; P, 8.41. Found: C, 47.29; H, 3.97; Ag, 28.00; P, 7.54. MW: 1128 (CH_2Cl_2). Calcd MW: **1**, 1436; $[Ag_2(OAc)_2(dppm)]$, 718. IR (cm^{-1}): ν(OAc) 1656 m, 1552 s (br), 1375 m, 1329 m (KBr). ^{1}H NMR (CD_2Cl_2): δ 3.29 (t, $-PCH_2P-$, *J*(H−P) 10.2), 2.33 (s, H_2O), 1.86 (s, CH_3CO_2-) (25 °C); δ 4.38 (s (br), H_2O), 3.01 (s (br), $-PCH_2P-$), 1.86 (s, CH_3CO_2-) (−50 °C). ^{31}P NMR (CD_2Cl_2): δ 7.54 (s (br)) (25 °C); δ 6.03 [$J(^{109}Ag-P) = 729$, $J(^{107}Ag-P) = 633$, $^3J(^{109}Ag-P) = -7.4$, $^3J(^{107}Ag-P) = -6.0$, $^2J(P-P) = 175$ Hz] (−50 °C).

$[Ag(\eta^2\text{-}O_2CCH_3)(\mu\text{-}dppm)]_2$ (2). As solid dppm (0.056 g, 0.14 mmol) was added to a MeOH solution (30 mL) of 1 (0.104 g, 0.072 mmol), it dissolved readily and the mixture was stirred at room temperature for 1 h to give a clear solution. 2 was isolated and purified similarly to 1. Yield: 0.110 g (71%). Anal. Calcd: C, 58.87; H, 4.57; Ag, 19.57; P, 11.24. Found: C, 58.47; H, 4.38; Ag, 19.47; P, 10.48. MW: 1146 (CH_2Cl_2). Calcd MW: 1103. IR (cm^{-1}): ν(OAc) 1560 s, 1398 m (KBr). ^{1}H NMR (−50 °C, CD_2Cl_2): δ 3.55 (s (br), $-PCH_2P-$), 1.61 (s, CH_3CO_2-) (+ minor species at 3.34 ($-PCH_2P-$) and 1.90 (CH_3CO_2-)). ^{31}P NMR (−50 °C, CD_2Cl_2): δ 4.44 (+ unknown species at −3.86 and −2.15).

X-ray Crystal Structure Determination. Colorless polyhedral crystals of **1** and prismatic crystals of **2** suitable for single-crystal X-ray diffractometry were grown by slow diffusion of hexane into the sample solutions in $CHCl_3$. The crystals used for analysis are of approximate dimension 0.24 × 0.28 × 0.50 for **1** and 0.28 × 0.40 × 0.40 mm for **2**. The data crystal for **2** was sealed under N_2 in a Lindemann glass capillary. Totals of 5048 and 4957 independent reflections ($2\theta_{max}$ 50°) for **1** and **2** were measured on a Nicolet R3m/V diffractometer using graphite-monochromated Mo Kα radiation. Agreement between equivalent reflections is 0.022 for **1** and 0.035 for **2**. Determination

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Table 3. Selected Bond Distances (Å) and Angles (deg)[a]

(a) $[Ag_2(\mu\text{-}O_2CCH_3\text{-}O,O')(\mu\text{-}O_2CCH_3\text{-}O)(dppm)]_2\cdot 2H_2O$, **1**

Distances

Ag(1)−P(1)	2.390(4)	Ag(1)−O(1)	2.265(11)
Ag(1)−O(3a)	2.485(10)	Ag(2)−P(2)	2.363(4)
Ag(2)−O(2)	2.397(11)	Ag(2)−O(3)	2.232(11)
C(1)−O(1)	1.272(19)	C(1)−O(2)	1.238(21)
C(1)−C(2)	1.516(23)	C(3)−O(3)	1.278(19)
C(3)−O(4)	1.254(19)	C(3)−C(4)	1.499(23)
P(1)−C(5)	1.879(13)	P(2)−C(5)	1.828(14)

Angles

O(1)−Ag(1)−P(1)	151.6(3)	O(1)−Ag(1)−O(3a)	79.9(4)
O(3a)−Ag(1)−P(1)	121.3(3)	O(2)−Ag(2)−P(2)	115.8(3)
O(2)−Ag(2)−O(3)	90.0(4)	O(3)−Ag(2)−P(2)	153.8(3)
Ag(1)−O(1)−C(1)	124.2(10)	Ag(3)−O(2)−C(1)	111.9(10)
O(1)−C(1)−O(2)	126.6(15)	O(1)−C(1)−C(2)	116.4(14)
O(2)−C(1)−C(2)	116.9(14)	Ag(2)−O(3)−C(3)	111.1(9)
Ag(2)−O(3)−Ag(1a)	117.2(4)	C(3)−O(3)−Ag(1a)	121.1(9)
O(3)−C(3)−O(4)	122.7(14)	O(3)−C(3)−C(4)	118.0(13)
O(4)−C(3)−C(4)	119.4(14)	Ag(1)−P(1)−C(5)	114.7(5)
Ag(2)−P(2)−C(5)	112.4(4)	P(1)−C(5)−P(2)	112.9(7)

(b) $[Ag(\eta^2\text{-}O_2CCH_3)(\mu\text{-}dppm)]_2$, **2**

Distances

Ag(1)−O(1)	2.611(3)	Ag(1)−O(2)	2.547(7)
Ag(1)−P(1)	2.473(3)	Ag(1)−P(2a)	2.437(3)
C(1)−C(2)	1.50(2)	C(2)−O(1)	1.24(1)
C(2)−O(2)	1.25(1)	P(1)−C(3)	1.841(8)
P(2)−C(3)	1.840(8)	O(2)⋯C(28)	3.07(2)
C(28)−Cl(1−3)	1.75(1) (Mean)	Ag(1)⋯Ag(1a)	3.194(2)

Angles

O(1)−Ag(1)−O(2)	50.4(2)	O(1)−Ag(1)−P(1)	82.2(2)
O(1)−Ag(1)−P(2a)	130.2(2)	O(2)−Ag(1)−P(1)	102.5(2)
O(2)−Ag(1)−P(2a)	106.7(2)	P(1)−Ag(1)−P(2a)	146.1(1)
C(1)−C(2)−O(1)	119.0(9)	C(1)−C(2)−O(2)	117.2(8)
O(1)−C(2)−O(2)	123.8(9)	Ag(1)−O(1)−C(2)	91.6(5)
Ag(1)−O(2)−C(2)	94.2(5)	Ag(1)−P(1)−C(3)	107.5(3)
Ag(1a)−P(2)−C(3)	113.0(3)	P(1)−C(3)−P(2)	111.6(5)

[a] Symmetry transformations: **1**, a($1 - x$, $-y$, $1 - z$); **2**, a($-x$, $-y$, $-z$).

of the crystal class, orientation matrices, and cell dimensions was performed according to established procedures.[13] Crystal data, data collection parameters, and results of the analyses are listed in Table 1. All data processing was performed on a DEC Micro VAX-II computer using the SHELXTL-PLUS system.[14] Analytical expressions of neutral-atom scattering factors were employed, and anomalous corrections were incorporated.[15] The raw data were processed with the learnt-profile procedure,[16] and absorption corrections using a program supplied in the SHELXTL-PC package were applied by fitting a pseudo absorption ellipsoid to the ψ-scan data for 12−20 selected strong reflections over a range of 2θ angles.[17]

Both structures were solved with the Patterson superposition method. The positions of all hydrogen atoms were generated geometrically (C−H bonds fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent C atoms. In the course of the analysis, **1** and **2** were found to contain solvent molecules of H_2O and $CHCl_3$, respectively. They were included in the analysis and satisfactorily refined. Atomic positional parameters of compounds **1** and **2** are listed in Table 2, and selected interatomic distances and bond angles, in Table 3. Tables of hydrogen atom positional parameters and anisotropic thermal parameters for structures **1** and **2** are available with the supplementary material.

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Supplementary Material Available: Details of the X-ray structural analyses for **1** and **2** including tables of crystallographic data, refined atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, and bond distances and angles (10 pages). Ordering information is given on any current masthead page. Listings of structure factors for **1** (12 pages) and **2** (12 pages) can be obtained from the corresponding authors.

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