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Synthesis of silver(I) complexes with carbonyl-stabilized phosphorus ylides: crystal structures of two $[Ag\{CH(PPh_3)C(O)R\}_2]^+$ derivatives

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Abstract

Reactions between AgX (X = ClO_4, NO_3) and ylides of the type $Ph_3P{=}CHC(O)R$ (R = Me, Ph, OMe, OPh) in the molar ratio 1/2 lead to complexes $[Ag\{CH(PPh_3)C(O)R\}_2]X$; X-ray structure determinations have been carried out on two such complexes (R = OEt, X = ClO_4 and R = OPh, X = NO_3). Two of the silver ylide complexes react with $[Au(acac)(PPh_3)]$ (acac = acetylacetonate) in the molar ratio 1/2 to give complexes $[Ag\{C(PPh_3)(CO_2R)(AuPPh_3)\}_2]ClO_4$ (R = Me, Et).

Introduction

Three types of ylide complexes of silver(I) have been reported: (i) mononuclear neutral $[AgCl(Y)]$ for $Y = Ph_3PCH_2$ [1], $(Ph_3P)_2C$ [2]; (ii) mononuclear cationic $[Ag(Y)_2]Cl$ for $Y = Ph_3PCH_2$, Ph_3PCHMe, Ph_3PCH^iPr [3], $Me_3PCH(SiMe_3)$ [4]; (iii) dinuclear neutral complexes $[Ag_2\{(CH_2)_2ERR'\}_2]$ for E = P, R = R' = Me [5], R = R' = Ph and R = Me, R' = Ph [4], R + R' = $(CH_2)_5$ [6], E = As, R = R' = Me [7]. The small number of such complexes contrasts with the large number known for gold(I) [8].

We have recently shown [9] that carbonyl-stabilized phosphorus ylides can be used to prepare stable gold(I) and gold(III) complexes in spite of their low basicity/nucleophilicity. The effect of a third resonance form (**c**), in addition to the usual ylide (**a**) and ylene (**b**) forms, is probably responsible for the low nucleophilic-

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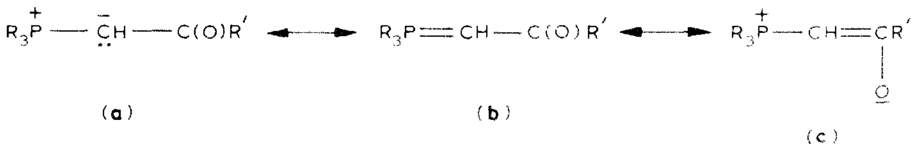
ity and for the ability of such ligands to act also as O-donors [10].



Here we report the synthesis of a series of stable complexes $[Ag(Y)_2]^+$, which are the first with carbonyl-stabilized phosphorus ylides, and the X-ray structures of two of them.

Results and discussion

Reactions between $AgClO_4$ or $AgNO_3$ and the ylides Ph_3P=CHC(O)R (Y_R) in the molar ratio $Y_R/Ag \geqslant 2$ gave the complexes $[Ag(Y_R)_2]X$ [R = Me (**1**), Ph (**2**), OMe (**3**), OEt (**4**); X = ClO_4 (**a**), NO_3 (**b**)]. These complexes are stable in the solid state and in acetone or dichloromethane solution if protected against daylight. Acetone solutions are conducting, but the molar conductivities of solutions of **1b** and **2b** are lower than expected for uni-univalent electrolytes (100–135 Ω^{-1} cm^2

Table 1

Analytical and other data for complexes **1**–**6**

Compound R	Compound X	M.p. (°C)	Λ_M [a]	Analyses (Found (calc) (%)) C	H	N	Yield (%)	ν(CO) [b] (cm^{-1})	$\Delta\nu$ [c]
[Ag{CH(PPh$_3$)COR}$_2$]X									
CH_3	ClO_4 (**1a**)	178(dec.)	100	59.68 (59.77)	4.62 (4.54)	-	88	1615	75
CH_3	NO_3 (**1b**)	160	58	62.88 (62.54)	4.98 (4.75)	1.87 (1.74)	88	1610	70
Ph	ClO_4 (**2a**)	150	123	63.47 (64.51)	4.48 (4.37)	–	50	1610	90
Ph	NO_3 (**2b**)	182	58	66.79 (67.12)	4.89 (4.55)	1.53 (1.50)	79	1610	90
OMe	ClO_4 (**3a**)	210	108	58.10 (57.58)	4.30 (4.37)	–	85	1670	70
OMe	NO_3 (**3b**)	182(dec.)	82	59.77 (60.15)	4.78 (4.57)	1.96 (1.67)	90	1670	70
OEt	ClO_4 (**4a**)	178	86	58.45 (58.45)	4.60 (4.68)	–	89	1665	65
OEt	NO_3 (**4b**)	153(dec.)	96	61.04 (60.98)	5.12 (4.88)	1.91 (1.62)	86	1665	65
[Ag{C(PPh$_3$)(COR)} (AuPPh$_3$)]X									
OMe	ClO_4 (**5**)	115	143	52.96 (52.26)	3.89 (3.71)	–	70	1630 1650sh	30
OEt	ClO_4 (**6**)	127	143	52.57 (52.76)	4.16 (3.82)	–	62	1630, 1650	50

[a] In ~10^{-4} *M* solutions in acetone (Ω^{-1} cm^2 mol^{-1}). [b] In complexes **3**–**6** the given data correspond to $\nu_{asym}(CO_2)$. [c] $\Delta\nu = \nu$(CO) complex − ν(CO) free ylide.

mol^{-1} [11]; see Table 1). This behaviour can be accounted for by assuming that the anion interacts with the cationic complex in solution; it is possible that an equilibrium between the two- and three-coordinate forms is set up.

In contrast to the more basic ylides such as $Ph_3P{=}CH_2$ [1] and $(Ph_3P)_2C$ [2], the ylide Y_{Me} does not react with AgCl.

Complexes **2a** and **4a** react with [AuCl(tht)] (tht = tetrahydrothiophene) or with $[AuCl(PPh_3)]$ to give $[Au\{CH(PPh_3)C(O)Ph\}_2]^+$ [12] and $[Au\{CH(PPh_3)C(O)\text{-}OEt\}(PPh_3)]$ [9], respectively. These transmetallations demonstrate the potential of the silver ylide complexes in preparing ylide complexes of other metals; they are among the first reported reactions in which two metal centres exchange an ylide ligand [13].

In all the complexes the ylide ligands bond to the silver atom through the methine carbon; this is indicated by the IR spectra, which show $\nu(CO)$ absorptions at higher frequency than in the uncoordinated ylides (Table 1). In the free ligands, the contribution of the three resonance forms (**a**–**c**) leads to a $\nu(CO)$ corresponding to a C–O bond order between 1 and 2. Coordination through the methine carbon, requiring resonance form **a**, would lead to a C–O bond order of 2. An opposite shift would be expected if coordination took place through the oxygen atom, effectively enforcing resonance form **c**.

Since the $\nu(CO)$ frequencies are almost the same for the ClO_4^- and NO_3^- salts, it seemed reasonable to postulate that any cation/NO_3 interaction must occur through the metal atom. This was confirmed for **2b** by a crystal structure determination (see below). The IR data were inconclusive in this respect because of overlap of $\nu(NO)$ and $\delta(NO_2)$ bands of the NO_3^- group with the ylide bands; the only differences between the spectra of compounds **1a**–**4a** and their counterparts **1b**–**4b** are the replacement of the ClO_4^- bands at 1100vs and 610s cm^{-1} by two new bands, also observed in the free ylide, at the same frequencies but with different intensities (1100s, 610vw). The $\nu(CO)$ band in these complexes appears at frequencies 10–40 cm^{-1} lower than those of the related $[Au(Y)_2]^+$ complexes [9,12], which is a consequence of the greater electronegativity of the gold atom.

^1H and $^{31}P\{^1H\}$ NMR data are presented in Table 2. Although two diastereoisomers (*RR/SS* and *RS*) are possible for each complex (because the methine carbons are chiral) NMR spectroscopy does not distinguish them at 80 MHz and room temperature. The methine resonances are intermediate between, and the $^2J(PH)$ values smaller than, those in the free ylides and the phosphonium salts; this was observed for other C-coordinated carbonyl-stabilized phosphorus ylide complexes [9,10b,14]. Values of $^2J(PH)$ much larger (ca. 20 Hz) have been observed in complexes where coordination is through the oxygen atom [10]. Neither H–Ag nor P–Ag coupling was observed at room temperature in the spectra of our complexes; the same was the case for $[Ag(C_6F_5)CH(PPh_3)CO_2Me]$ [13*]. It is possible that a fast equilibrium between complexes and free ylides is responsible for the failure to observe either the NMR couplings or the presence of two diastereoisomers.

As we have recently shown [9], the methine proton in these ylides has an acidic character when coordinated to gold(I). Thus $[Au\{CH(PPh_3)CO_2R\}PPh_3]ClO_4$ (R = Me, Et) react with $[Au(acac)(PPh_3)]$ to give acetylacetone (acacH) and [{Au-

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* Reference number with asterisk indicates a note in the list of references.

Table 2

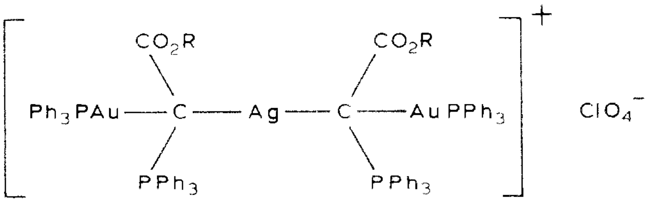
NMR data for complexes **1**–**4** and some ylides and phosphonium salts

Compound $[Ag\{CH(PPh_3)COR\}_2]X$	^1H NMR [a]				$^{31}P\{^1H\}$ NMR [a] δ(ppm)
	$\delta(CH)$ [b] or $\delta(CH_2)$ (ppm)	$^2J(PH)$ [b] (Hz)	$\delta(R)$ (ppm)	$\delta(Ph)$ (ppm)	
$R = CH_3$, $X = ClO_4$ (**1a**)	4.5(d)	7	1.84	7.4–7.6(m)	22.52
$R = CH_3$, $X = NO_3$ (**1b**)					21.32
$CH(PPh_3)COMe$	3.68(d)	27			15.3
$[CH_2(PPh_3)COMe]Cl$	6.15(d)	11			20.4
$R = Ph$, $X = ClO_4$ (**2a**)	5.06(d)	6	7.2–7.9(m)		25.12
$R = Ph$, $X = NO_3$ (**2b**)					24.99
$CH(PPh_3)COPh$	4.4(br)				17.0
$[CH_2(PPh_3)COPh]Br$	6.37(d)	11			21.9
$R = OMe$, $X = ClO_4$ (**3a**)	3.44(d)	9	3.39	7.2–7.9(m)	24.96
$R = OMe$, $X = NO_3$ (**3b**)					23.82
$CH(PPh_3)COOMe$	2.82(br)				17.67
$[CH_2(PPh_3)COOMe]Cl$	5.66(d)	13.8			20.68
$[CH_2(PPh_3)COOMe]ClO_4$	4.62(d)	14.6			
$R = OEt$, $X = ClO_4$ (**4a**)	3.44(br)		0.96(t), 3.84(q) $^3J(HH)$ 7 Hz	7.2–7.9(m)	25.06
$R = OEt$, $X = NO_3$ (**4b**)					24.53

[a] Recorded in $CDCl_3$ at 80 MHz, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal. When not stated signals are singlet. ^1H and ^{31}P NMR data referred to TMS and H_3PO_4, respectively.

[b] Most data corresponding to ylides and phosphonium salts are from ref. 14b.

$(PPh_3)\}_2\{\mu\text{-}C(PPh_3)CO_2R\}]ClO_4$. Similarly, **3a** and **4a** react with $[Au(acac)(PPh_3)]$ to give complexes **5** and **6**. Unfortunately neither complex is stable enough in solution to allow single crystals to be grown and these interesting species to be definitively characterized. We are currently studying their reactions in order to synthesize heteropolynuclear species.



(R = Me (**5**), Et (**6**))

Crystal structure determinations

Both structure determinations were rendered imprecise by the presence of disordered solvent and by the high temperature factors of some groups. Nevertheless, the basic features of both complexes **2b** and **4a** are clear.

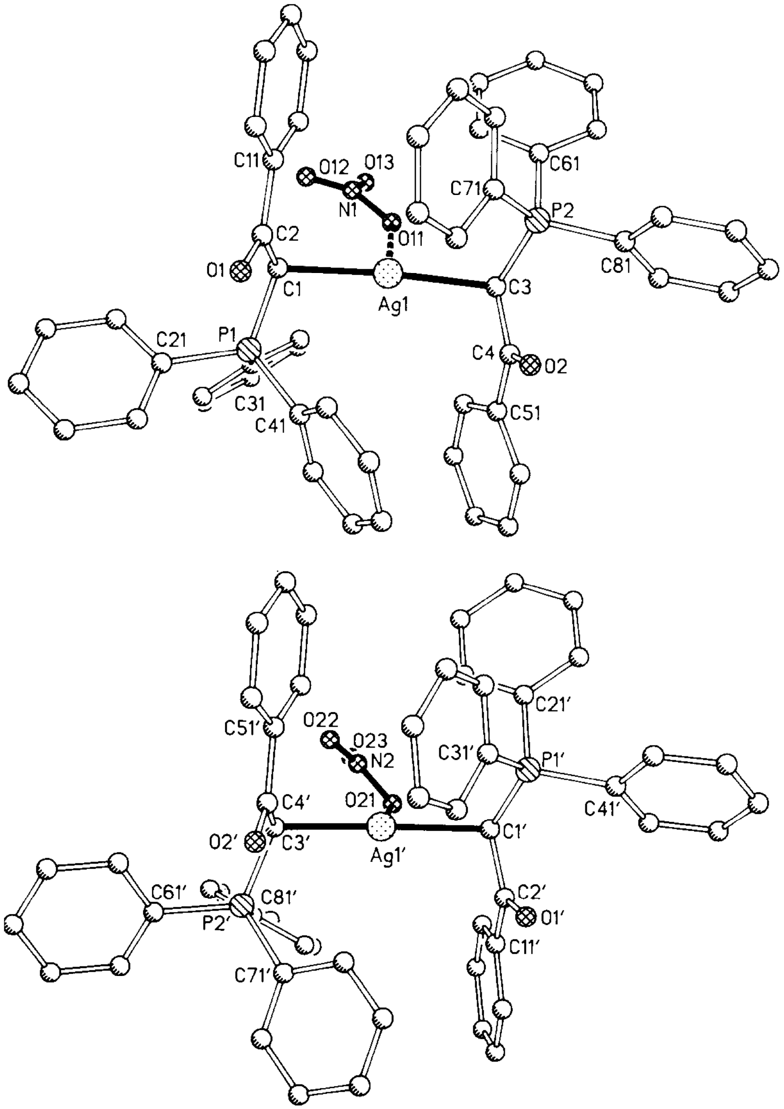


Fig. 1. The two independent complexes **2b** in the crystal, showing the atom numbering scheme. Radii arbitrary, H atoms omitted.

Complex 2b. There are two independent complexes in the asymmetric unit. In both of these (Fig. 1) the relative configurations at the chiral carbon atoms are *SS*. The nitrate ions are loosely associated with the metal centres, with Ag · · · O 2.75, 2.77(1) Å. The conformations about the central C(1) · · · C(3) axis are similar in both molecules (e.g. P(1)–C(1) · · · C(3)–P(2) −151, P(1′)–C(1′) · · · C(3′)–P(2′) 148°). There are some differences in the orientations of phenyl rings. The coordination geometry at silver (excluding the Ag · · · O interactions) is essentially linear, although the bond lengths and angles at the metal atom are appreciably different in both molecules (molecule 1: 2.21, 2.22 Å, 176°; molecule 2: 2.25, 2.26 Å, 168°).

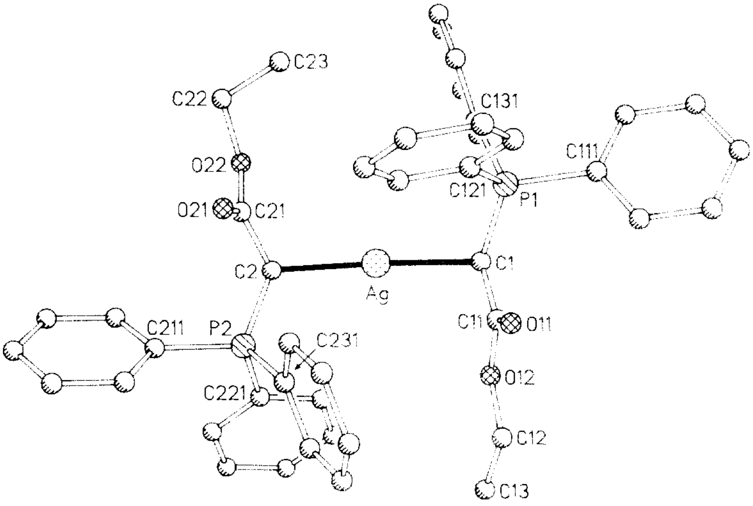


Fig. 2. Complex **4a** in the crystal, showing the atom numbering scheme. Radii arbitrary, H atoms omitted.

*Complex **4a**.* The relative configuration is *SS*. The coordination at silver is linear (Ag–C 2.18, 2.18 Å, C–Ag–C 174°) but there are no short Ag···$OClO_3$ interactions. The conformation about the molecular axis is almost eclipsed (C(21)–C(2)···C(1)–P(1) −8°). See Fig. 2.

Experimental

Infrared spectra, elemental analyses (C, H and N), conductance measurements, melting point determinations and NMR spectra were obtained as described elsewhere [9]. Reactions were carried out at room temperature with magnetic stirring; solutions were protected from light with aluminium foil.

All complexes were prepared in a similar manner. To a solution of $AgClO_4$ or $AgNO_3$ (100–300 mg) or of complex $[Ag(Y_R)_2]ClO_4$ (150–300 mg) in acetone (10 ml) or (for **2a**, **5**, **6**) dichloromethane (20 ml) were added two molar equivalents of the ylide [15] or $[Au(acac)(PPh_3)]$ [16], respectively. After 1–2 h the mixture was filtered through Celite or $MgSO_4$, and the filtrate concentrated to 3–5 ml. Addition of diethyl ether (15–30 ml) precipitated the product.

*X-Ray structure determination for complex **2b***

Colourless prisms were obtained by liquid diffusion of petroleum ether into a solution of **2b** in dichloromethane. They were sealed into capillaries to prevent loss of solvent of crystallization.

Crystal data. $C_{52}H_{42}AgNO_5P_2 \cdot 0.25CH_2Cl_2$, $M = 952.2$. Triclinic, space group $P\bar{1}$, a 11.781(3), b 19.407(4), c 19.517(5) Å, α 86.40(2), β 89.91(2), γ 89.65(2)°, V 4490 $Å^3$, $Z = 4$, D_x 1.41 g cm^{-3}, $F(000) = 1937$, $\mu(Mo\text{-}K_\alpha)$ 0.5 mm^{-1}.

Data collection. A crystal 0.7 × 0.7 × 0.3 mm was used to collect 14405 intensities on a Stoe-Siemens four-circle diffractometer in profile-fitting mode [17] to a maximum 2θ of 45°. Of 11701 unique reflections, 8070 with $F > 4\sigma(F)$ were used

(*Continued on p. 417*)

Table 3

Atomic coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for compound **2b**

Atom	x	y	z	U or U_{eq}
Ag(1)	1752(1)	2332(1)	1662(1)	54(1)
P(1)	−390(2)	3312(1)	1396(1)	46(1)
P(2)	3823(2)	1491(1)	2369(1)	50(1)
O(1)	1410(6)	4229(3)	1788(4)	64(3)
O(2)	2065(7)	1610(4)	3414(4)	79(3)
C(1)	1011(8)	3270(5)	1126(5)	52(4)
C(2)	1740(8)	3839(5)	1345(6)	53(4)
C(3)	2366(8)	1387(5)	2237(6)	56(4)
C(4)	1712(9)	1371(5)	2885(7)	65(5)
N(1)	1787(13)	1798(10)	−115(9)	146(5)
O(11)	1793(8)	1581(5)	513(5)	113(3)
O(12)	1749(11)	2387(8)	−250(7)	176(5)
O(13)	1736(16)	1367(10)	−477(10)	259(9)
C(12)	3307(7)	3502(4)	568(4)	70(5)
C(13)	4381	3618	296	110(7)
C(14)	5019	4169	504	104(7)
C(15)	4584	4603	984	104(7)
C(16)	3510	4486	1256	73(5)
C(11)	2872	3936	1048	56(4)
C(22)	−972(6)	4448(4)	571(3)	77(5)
C(23)	−1522	5072	397	78(5)
C(24)	−2137	5401	893	77(5)
C(25)	−2202	5107	1562	92(6)
C(26)	−1652	4483	1736	66(4)
C(21)	−1037	4154	1241	45(3)
C(32)	−2247(6)	2949(3)	643(5)	96(6)
C(33)	−2838	2533	212	112(7)
C(34)	−2367	1912	25	95(6)
C(35)	−1305	1707	268	122(7)
C(36)	−714	2123	698	97(6)
C(31)	−1185	2744	886	55(4)
C(42)	−1537(5)	2625(3)	2463(4)	60(4)
C(43)	−1725	2408	3149	81(5)
C(44)	−986	2603	3655	72(5)
C(45)	−59	3015	3477	74(5)
C(46)	128	3232	2791	63(4)
C(41)	−610	3036	2284	45(3)
C(52)	−7(9)	914(5)	2280(5)	131(8)
C(53)	−1097	651	2316	201(14)
C(54)	−1624	537	2952	209(16)
C(55)	−1062	687	3551	180(13)
C(56)	28	950	3515	117(7)
C(51)	556	1064	2879	90(6)
C(62)	4271(6)	1563(3)	993(5)	71(5)
C(63)	4746	1346	389	105(7)
C(64)	5459	771	410	110(8)
C(65)	5695	413	1036	106(7)
C(66)	5220	630	1641	87(6)
C(61)	4508	1205	1619	57(4)
C(72)	5273(5)	2605(3)	2192(3)	69(5)
C(73)	5593	3288	2258	79(5)
C(74)	4883	3737	2588	69(5)
C(75)	3852	3503	2853	74(5)

continued

Table 3 (continued)

Atom	x	y	z	U or U_{eq}
C(76)	3532	2820	2786	60(4)
C(71)	4243	2371	2456	50(4)
C(82)	5187(7)	1171(4)	3509(4)	82(5)
C(83)	5611	718	4031	117(7)
C(84)	5177	53	4129	132(9)
C(85)	4318	−160	3705	125(8)
C(86)	3894	293	3183	91(6)
C(81)	4329	958	3085	61(4)
Ag(1′)	3674(1)	7180(1)	3273(1)	58(1)
P(1′)	5627(2)	6005(1)	3672(1)	43(1)
P(2′)	2003(2)	8109(1)	2236(2)	54(1)
O(1′)	3816(6)	5360(3)	2895(4)	66(3)
O(2′)	4151(6)	8014(4)	1476(4)	79(3)
C(1′)	4152(7)	6141(4)	3773(5)	46(3)
C(2′)	3454(8)	5676(5)	3382(5)	47(4)
C(3′)	3378(8)	8131(5)	2573(5)	54(4)
C(4′)	4282(9)	8169(5)	2071(6)	59(4)
N(2)	3175(12)	7934(8)	4707(8)	123(4)
O(21)	2876(9)	7365(6)	4585(5)	133(4)
O(22)	3747(10)	8256(6)	4308(6)	145(4)
O(23)	2747(13)	8138(7)	5200(8)	198(6)
C(12′)	1566(8)	5202(4)	3201(4)	90(6)
C(13′)	448	5086	3392	119(8)
C(14′)	29	5347	3992	101(7)
C(15′)	728	5725	4401	85(5)
C(16′)	1846	5841	4209	73(5)
C(11′)	2265	5580	3609	54(4)
C(22′)	6035(5)	7114(3)	4449(3)	64(4)
C(23′)	6554	7456	4970	78(5)
C(24′)	7327	7105	5404	86(6)
C(25′)	7580	6413	5318	80(5)
C(26′)	7061	6072	4796	64(4)
C(21′)	6289	6422	4362	46(4)
C(32′)	5629(6)	6377(4)	2291(4)	67(4)
C(33′)	6088	6685	1690	100(7)
C(34′)	7151	6985	1701	118(8)
C(35′)	7755	6977	2314	102(6)
C(36′)	7296	6669	2916	71(5)
C(31′)	6232	6369	2904	49(4)
C(42′)	7058(5)	4887(3)	3500(3)	50(4)
C(43′)	7407	4204	3630	61(4)
C(44′)	6732	3743	4022	57(4)
C(45′)	5708	3967	4283	54(4)
C(46′)	5359	4650	4153	49(4)
C(41′)	6034	5110	3761	40(3)
C(52′)	5693(6)	8457(3)	2986(4)	67(5)
C(53′)	6761	8681	3164	89(6)
C(54′)	7548	8860	2652	92(6)
C(55′)	7265	8815	1963	94(6)
C(56′)	6197	8591	1785	76(5)
C(51′)	5411	8412	2297	56(4)
C(62′)	2490(5)	9316(4)	1457(4)	65(4)
C(63′)	2224	9888	1017	69(5)
C(64′)	1112	10006	809	85(5)

continued

Table 3 (continued)

Atom	x	y	z	U or U_{eq}
C(65′)	268	9551	1040	89(6)
C(66′)	535	8979	1479	82(5)
C(61′)	1646	8861	1688	57(4)
C(72′)	669(6)	7269(4)	1482(4)	92(6)
C(73′)	393	6648	1202	118(7)
C(74′)	1167	6103	1227	112(7)
C(75′)	2217	6180	1532	181(11)
C(76′)	2492	6801	1812	132(7)
C(71′)	1718	7345	1787	63(4)
C(82′)	811(7)	8754(3)	3210(5)	96(6)
C(83′)	149	8774	3800	123(8)
C(84′)	−262	8162	4119	116(7)
C(85′)	−11	7531	3848	116(8)
C(86′)	651	7511	3258	92(6)
C(81′)	1062	8122	2940	62(4)
Cl(1)	7606(13)	9226(8)	5046(8)	251(6)
C(100)	10000	10000	5000	244(16)
Cl(2)	11903(23)	9698(13)	4711(13)	495(14)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

for all calculations (program SHELX-76). Cell constants were refined from 2θ values of 56 reflections in the range 20–23°.

Structure solution and refinement. The structure was solved by the heavy-atom method and refined to R 0.082, R_w 0.080. Phenyl rings were refined as rigid groups with C–C 1.395, C–H 0.96 Å, all angles 120°. Ag, P, C and ylide O atoms were refined anisotropically (877 parameters). The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0006F^2$.

Final atomic coordinates are presented in Table 3, and selected bond lengths and angles in Table 4 [18*].

*X-Ray structure determination for complex **4a***

Colourless, extremely thin plates were obtained by liquid diffusion of diethyl ether into a solution of **4a** in dichloromethane. They were sealed into capillaries to prevent loss of solvent of crystallization.

Crystal data. $C_{44}H_{42}AgClO_8P_2 \cdot 0.5CH_2Cl_2$, $M = 946.58$. Triclinic, space group $P\bar{1}$, a 9.832(3), b 10.965(4), c 21.798(7) Å, α 77.10(3), β 78.23(4), γ 73.07(2)°, V 2167 Å^3, $Z = 2$, D_x 1.45 g cm^{-3}, $F(000) = 953$, μ(Mo-K_α) 0.6 mm^{-1}.

Data collection. As for **2b**, with following differences: 7643 reflections, 5652 unique, 2666 with $|F| > 4\sigma(F)$. Cell constants from 34 reflections. Crystal size $0.6 \times 0.25 \times$ ca. 0.002 mm. Structure solution and refinement: R 0.103, R_w 0.083. Ag, P, Cl, O and ester C atoms anisotropic (261 parameters). Weighting scheme $w^{-1} = \sigma^2(F) + 0.0005F^2$.

Final atomic coordinates are presented in Table 5, and selected bond lengths and angles in Table 6 [18].

(Continued on p. 420)

Table 4

Selected bond lengths (Å) and angles (°) for compound **2b**

Ag(1)–C(1)	2.219(9)	Ag(1′)–C(1′)	2.256(8)
Ag(1)–O(11)	2.751(10)	Ag(1′)–O(21)	2.773(10)
P(1)–C(21)	1.810(7)	P(1′)–C(21′)	1.797(7)
P(1)–C(41)	1.802(7)	P(1′)–C(41′)	1.799(6)
P(2)–C(61)	1.791(9)	P(2′)–C(61′)	1.804(7)
P(2)–C(81)	1.789(8)	P(2′)–C(81′)	1.771(10)
O(2)–C(4)	1.233(16)	O(2′)–C(4′)	1.228(14)
C(2)–C(11)	1.471(13)	C(2′)–C(11′)	1.489(13)
C(4)–C(51)	1.502(15)	C(4′)–C(51′)	1.501(13)
N(1)–O(12)	1.158(24)	N(2)–O(22)	1.184(19)
Ag(1)–C(3)	2.210(9)	Ag(1′)–C(3′)	2.253(9)
P(1)–C(1)	1.748(10)	P(1′)–C(1′)	1.783(9)
P(1)–C(31)	1.803(8)	P(1′)–C(31′)	1.770(8)
P(2)–C(3)	1.765(10)	P(2′)–C(3′)	1.762(10)
P(2)–C(71)	1.799(7)	P(2′)–C(71′)	1.804(8)
O(1)–C(2)	1.246(13)	O(1′)–C(2′)	1.239(12)
C(1)–C(2)	1.491(14)	C(1′)–C(2′)	1.477(13)
C(3)–C(4)	1.481(17)	C(3′)–C(4′)	1.451(15)
N(1)–O(11)	1.269(20)	N(2)–O(21)	1.199(19)
N(1)–O(13)	1.131(28)	N(2)–O(23)	1.178(22)
C(3)–Ag(1)–C(1)	175.6(4)	C(3′)–Ag(1′)–C(1′)	167.7(4)
O(11)–Ag(1)–C(1)	94.7(3)	O(21)–Ag(1′)–C(1′)	81.2(3)
O(11)–Ag(1)–C(3)	86.8(3)	O(21)–Ag(1′)–C(3′)	111.1(3)
C(31)–P(1)–C(21)	105.2(3)	C(31′)–P(1′)–C(21′)	106.3(3)
C(41)–P(1)–C(1)	114.3(4)	C(41′)–P(1′)–C(1′)	113.3(3)
C(41)–P(1)–C(31)	107.4(4)	C(41′)–P(1′)–C(31′)	107.8(3)
C(71)–P(2)–C(3)	114.2(4)	C(71′)–P(2′)–C(3′)	113.6(4)
C(81)–P(2)–C(3)	112.1(4)	C(81′)–P(2′)–C(3′)	107.1(5)
C(81)–P(2)–C(71)	109.7(3)	C(81′)–P(2′)–C(71′)	107.9(4)
C(2)–C(1)–Ag(1)	103.6(6)	C(2′)–C(1′)–Ag(1′)	101.2(6)
C(1)–C(2)–O(1)	120.7(9)	C(1′)–C(2′)–O(1′)	123.5(9)
C(11)–C(2)–C(1)	120.1(9)	C(11′)–C(2′)–C(1′)	116.9(8)
C(4)–C(3)–Ag(1)	103.6(6)	C(4′)–C(3′)–Ag(1′)	107.5(6)
C(3)–C(4)–O(2)	123.1(10)	C(3′)–C(4′)–O(2′)	122.6(10)
C(51)–C(4)–C(3)	117.4(10)	C(51′)–C(4′)–C(3′)	117.9(9)
C(21)–P(1)–C(1)	114.1(4)	C(21′)–P(1′)–C(1′)	105.9(4)
C(31)–P(1)–C(1)	107.2(4)	C(31′)–P(1′)–C(1′)	116.1(4)
C(41)–P(1)–C(21)	108.0(3)	C(41′)–P(1′)–C(21′)	106.8(3)
C(61)–P(2)–C(3)	106.2(4)	C(61′)–P(2′)–C(3′)	113.4(4)
C(71)–P(2)–C(61)	107.1(3)	C(71′)–P(2′)–C(61′)	109.0(4)
C(81)–P(2)–C(61)	107.1(4)	C(81′)–P(2′)–C(61′)	105.3(3)
P(1)–C(1)–Ag(1)	106.5(4)	P(1′)–C(1′)–Ag(1′)	109.2(4)
C(2)–C(1)–P(1)	114.9(7)	C(2′)–C(1′)–P(1′)	113.5(7)
C(11)–C(2)–O(1)	119.1(9)	C(11′)–C(2′)–O(1′)	119.6(8)
P(2)–C(3)–Ag(1)	107.1(4)	P(2′)–C(3′)–Ag(1′)	109.2(4)
C(4)–C(3)–P(2)	112.6(8)	C(4′)–C(3′)–P(2′)	115.8(8)
C(51)–C(4)–O(2)	119.5(11)	C(51′)–C(4′)–O(2′)	119.5(9)
O(12)–N(1)–O(11)	118.9(17)	O(22)–N(2)–O(21)	119.9(15)
O(13)–N(1)–O(12)	127.9(19)	O(23)–N(2)–O(22)	126.3(16)
O(13)–N(1)–O(11)	112.9(18)	O(23)–N(2)–O(21)	113.2(15)
N(1)–O(11)–Ag(1)	128.8(10)	N(2)–O(21)–Ag(1′)	104.8(9)

Table 5

Atomic coordinates ($\times 10^4$) and isotropic displacement parameters (Å$^2 \times 10^3$) for compound **4a**

Atom	x	y	z	U or U_{eq}
Ag	1026(2)	3447(2)	2341(1)	48(1)
P(1)	798(5)	2462(5)	3881(2)	43(2)
C(112)	−679(12)	2489(11)	5121(6)	73(6)
C(113)	−873	2681	5747	80(7)
C(114)	122	3133	5947	73(6)
C(115)	1311	3394	5521	94(7)
C(116)	1505	3201	4894	79(7)
C(111)	510	2749	4694	45(5)
C(122)	2895(13)	323(12)	4352(5)	70(6)
C(123)	4048	−764	4291	90(7)
C(124)	4591	−1124	3696	73(6)
C(125)	3980	−396	3162	82(7)
C(126)	2826	691	3222	61(6)
C(121)	2284	1051	3817	46(5)
C(132)	−915(11)	800(11)	3926(5)	64(6)
C(133)	−2201	531	3899	82(7)
C(134)	−3384	1538	3735	67(6)
C(135)	−3280	2816	3598	78(7)
C(136)	−1994	3086	3625	69(6)
C(131)	−811	2078	3789	45(5)
P(2)	2693(5)	3556(5)	916(2)	50(3)
C(212)	4947(13)	2274(11)	92(5)	63(6)
C(213)	5514	1645	−430	77(7)
C(214)	4595	1479	−798	61(6)
C(215)	3110	1942	−644	91(7)
C(216)	2544	2571	−122	77(7)
C(211)	3462	2737	246	55(5)
C(222)	2218(11)	5701(11)	−35(5)	68(6)
C(223)	1675	7015	−262	70(6)
C(224)	931	7850	164	88(7)
C(225)	731	7372	816	78(7)
C(226)	1275	6059	1042	64(6)
C(221)	2018	5223	617	45(5)
C(232)	4731(13)	4457(10)	1280(5)	63(6)
C(233)	5889	4313	1592	82(7)
C(234)	6454	3129	1964	83(7)
C(235)	5861	2090	2025	95(8)
C(236)	4703	2234	1713	76(7)
C(231)	4138	3418	1340	48(5)
C(1)	1038(18)	3803(16)	3287(7)	36(8)
O(11)	3411(14)	3523(13)	3493(6)	67(7)
O(12)	2309(14)	5355(15)	2906(6)	62(7)
C(11)	2351(24)	4172(25)	3267(9)	50(12)
C(12)	3506(20)	5825(21)	2824(9)	68(11)
C(13)	3316(22)	7076(19)	2353(11)	102(13)
C(2)	1281(20)	3015(19)	1389(8)	53(10)
O(21)	2442(15)	798(14)	1523(6)	75(8)
O(22)	41(15)	1420(14)	1551(6)	67(7)
C(21)	1342(22)	1624(24)	1476(9)	51(11)
C(22)	−26(23)	76(22)	1748(11)	84(13)
C(23)	−315(26)	−243(21)	2435(12)	123(16)
Cl	2261(8)	3339(7)	7516(3)	74(4)

continued

Table 5 (continued)

Atom	x	y	z	U or U_{eq}
O(1)	3026(22)	2211(21)	7763(8)	180(13)
O(2)	2659(28)	3661(18)	6895(9)	221(16)
O(3)	2104(25)	4337(20)	7814(9)	197(16)
O(4)	912(27)	3251(23)	7563(14)	231(20)
Cl(2)	5435(26)	4348(25)	5478(10)	495(14)
C(100)	4237(57)	4273(58)	4791(28)	319(26)

Table 6

Selected bond lengths (Å) and angles (°) for compound **4a**

Ag–C(1)	2.184(14)	Ag–C(2)	2.181(16)
P(1)–C(111)	1.819(13)	P(1)–C(121)	1.801(13)
P(1)–C(131)	1.810(13)	P(1)–C(1)	1.768(17)
P(2)–C(211)	1.803(13)	P(2)–C(221)	1.773(13)
P(2)–C(231)	1.802(14)	P(2)–C(2)	1.722(18)
C(1)–C(11)	1.451(23)	O(11)–C(11)	1.208(20)
O(12)–C(11)	1.352(21)	O(12)–C(12)	1.382(19)
C(12)–C(13)	1.507(22)	C(2)–C(21)	1.480(24)
O(21)–C(21)	1.198(19)	O(22)–C(21)	1.333(20)
O(22)–C(22)	1.457(21)	C(22)–C(23)	1.448(24)
C(2)–Ag–C(1)	173.4(7)	C(11)–C(1)–Ag	107.6(11)
C(131)–P(1)–C(111)	105.7(5)	P(1)–C(1)–Ag	111.3(8)
C(1)–P(1)–C(111)	114.8(6)	C(11)–C(1)–P(1)	114.4(14)
C(1)–P(1)–C(131)	107.7(7)	O(11)–C(11)–C(1)	127.4(22)
C(121)–P(1)–C(111)	107.3(5)	O(12)–C(11)–O(11)	121.6(20)
C(131)–P(1)–C(121)	108.4(5)	P(2)–C(2)–Ag	109.5(9)
C(1)–P(1)–C(121)	112.6(7)	C(21)–C(2)–P(2)	118.2(14)
C(231)–P(2)–C(211)	107.2(5)	O(21)–C(21)–C(2)	122.0(19)
C(2)–P(2)–C(211)	113.4(7)	O(22)–C(21)–O(21)	125.4(22)
C(2)–P(2)–C(231)	113.4(7)	C(12)–O(12)–C(11)	117.7(17)
C(221)–P(2)–C(211)	107.9(5)	O(12)–C(11)–C(1)	110.8(19)
C(231)–P(2)–C(221)	107.3(6)	C(13)–C(12)–O(12)	109.7(17)
C(2)–P(2)–C(221)	107.3(8)	C(21)–C(2)–Ag	106.1(11)
		C(22)–O(22)–C(21)	115.9(17)
		O(22)–C(21)–C(2)	112.3(19)
		C(23)–C(22)–O(22)	110.4(18)

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