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Synthesis and Structural Characterization of Methanide Silver(I) Complexes. Unprecedented Co-ordination of the Methanide Ligand in $[Ag_2(PPh_3)_2(SPPh_2CHPPh_2CHCO_2Me)]ClO_4\cdot4CH_2Cl_2$†

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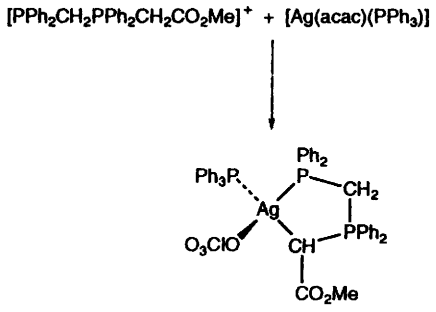
The mixed phosphine–phosphonium salt $[PPh_2CH_2PPh_2CH_2CO_2Me]ClO_4$ reacts with $[Ag(acac)(PPh_3)]$ (acac = acetylacetonate), with deprotonation of the ligand, displacing acac as acetylacetone and yielding the complex $[Ag(OClO_3)(PPh_3)(PPh_2CH_2PPh_2CHCO_2Me)]$, where the methanide ligand chelates the four-co-ordinate metal centre. The sulfide or oxide derivatives $[XPPh_2CH_2PPh_2R]ClO_4$ (X = S or O; R = Me or CH_2CO_2Me) also react with $[Ag(acac)(PPh_3)]$ in various stoichiometries to give $[Ag(PPh_3)(XPPh_2CHPPh_2Me)]ClO_4$ or $[Ag_2(PPh_3)_2(XPPh_2CHPPh_2CHCO_2Me)]ClO_4$; in the latter the methanide ligand co-ordinates both silver atoms through four donor centres (X, C, C, CO). Two of these derivatives have been characterized by X-ray analysis: $[Ag(OClO_3)(PPh_3)(PPh_2CH_2PPh_2CHCO_2Me)]$ crystallizes in the monoclinic space group $P2_1/n$, $a = 12.448(4)$, $b = 21.021(7)$, $c = 19.803(7)$ Å, $\beta = 108.60(3)°$, $Z = 4$, $T = -100$ °C; $[Ag_2(PPh_3)_2(SPPh_2CHPPh_2CHCO_2Me)]ClO_4$ crystallizes in the same space group with $a = 13.759(3)$, $b = 12.074(3)$, $c = 43.353(9)$ Å, $\beta = 92.62(2)°$, $Z = 4$, $T = -100$ °C.

Methanide complexes have received a great deal of attention in the last few years, and several synthetic routes have been developed in the preparation of such complexes.[1-4] We have previously concentrated on the synthesis of methanide gold species through reactions with bases such as NaH, $LiBu^n$ or Na_2CO_3 or with complexes that possess a ligand that can remove a proton of the corresponding phosphine derivative; these complexes include $[AuCl(CH_2PPh_3)]$[5] or $[Au(acac)(PPh_3)]$ (acac = acetylacetonate).[2,6,7] However very little attention has been paid to these types of complexes with silver(I). As far as we know only three examples have been reported, namely $[Ag_3\{(PPh_2)_2CH\}_3]$,[8] $[Ag\{(SPPh_2)_3C\}(PBu^n_3)]$[9] and the complex $[Ag_2(SPPh_2CHPPh_2Me)_2][ClO_4]_2$ previously described by us.[10]

Here we report the synthesis of silver(I) methanide complexes by reaction of $[Ag(acac)(PPh_3)]$ with various phosphine–phosphonium salts. Although $[Au(acac)(PPh_3)]$ has been previously used in the preparation of ylide[11] and methanide gold complexes, this is the first time that the corresponding acetylacetonate(triphenylphosphine)silver(I) complex has been used. The structure of the complex $[Ag_2(PPh_3)_2(SPPh_2CHPPh_2CHCO_2Me)]ClO_4$ reveals an unprecedented co-ordination mode of the ligand to the silver centres.

Results and Discussion

Reactions of $[Ag(acac)(PPh_3)]$ *with* $[PPh_2CH_2PPh_2R]ClO_4$.—The reactions of the salts $[PPh_2CH_2PPh_2R]ClO_4$ (R = Me or CH_2CO_2Me) with $[Ag(acac)(PPh_3)]$ in different stoichiometries have been studied. Thus treatment of $[PPh_2CH_2PPh_2CH_2CO_2Me]ClO_4$ with a slight excess of $[Ag(acac)(PPh_3)]$ leads to deprotonation of the ligand and formation of acetylacetone. There are two methylene groups in which the deprotonation can take place; in fact it occurs nearest to the ester group [equation (1)].



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(1)

Spectroscopic data confirm the chelate co-ordination of the ligand. The IR spectrum shows bands arising from the ClO_4^- anion (it is not possible to distinguish between T_d or C_{3v} co-ordination), and the ν(C=O) stretching frequency appears at 1640 cm^{-1}. This value is lower than in the free ligand (1736 cm^{-1}) as a consequence of the substitution of hydrogen in the CH_2CO_2Me group by a less electronegative group. The NMR spectra of this complex show broad signals at room temperature and therefore all data were measured at −80 °C in acetone. In the ^1H NMR spectrum the methylene and methine protons appear as multiplets and the methyl group as a singlet. The $^{31}P-\{^1H\}$ NMR spectrum shows three different phosphorus environments. The simplest is the PPh_2R group, which is a doublet by coupling to the nearest phosphorus. The PPh_3 appears as two

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† *Supplementary data available:* further details of the structure determinations (complete bond lengths and angles, H-atom coordinates, structure factors, thermal parameters) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, 76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference numbers CSD 401312 and 401313.

Table 1 NMR data (δ, J/Hz) for complexes **1–5**[a]

	^{31}P-$\{^1H\}$			^1H		
Complex	PPh_2	PPh_2R	PPh_3	Me	CH_2CO_2 ($CHCO_2$)	CH ($-CH_2-$)
1 $[Ag(OClO_3)(PPh_3)(PPh_2CH_2PPh_2$-$CHCO_2Me)]$	−9.5 (dddd), ^2J(PP) 33.0, 67.8 J(AgP) 335.7, 285.7	28.1 (d), ^2J(PP) 67.8	15.1 (ddd), ^2J(PP) 33.0 J(AgP) 579.4, 413.3	3.33 (s)	4.78 (m)	4.28 (m)
2 $[Ag(PPh_3)(SPPh_2CHPPh_2Me)]ClO_4$	41.3 (d), ^2J(PP) 8.4	21.1 (d), ^2J(PP) 8.4	10.0 (dm), J_{av}(AgP) 435	1.92 (m)		4.06 (m)
3 $[Ag(PPh_3)(OPPh_2CHPPh_2Me)]ClO_4$	30.2 (s)	21.1 (s)	15.5 (dd), J(AgP) 598.1, 527.1	2.55 (d), ^2J(PH) 12.94		3.9 (m)
4 $[Ag_2(PPh_3)_2(SPPh_2CHPPh_2CHCO_2$-$Me)]ClO_4$[b]	39.6 (s)	15.8 (s)	10.7 (dd), J(AgP) 630.9, 543.9 10.0 (dd), J(AgP) 542.1, 467.0	3.19 (s)	3.72 (m)	3.25 (m)
5 $[Ag_2(PPh_3)_2(OPPh_2CHPPh_2CHCO_2$-$Me)]ClO_4$	34.3 (s)	17.4 (s)	12.4 (dd), J(AgP) 597.2, 517.7 10.4 (dd), J(AgP) 617.7, 538.3	3.37 (s)	4.12 (m)	3.95 (m)

[a] s = Singlet, d = doublet, dd = doublet of doublets, ddd = two doublets of doublets, dddd = two doublets of doublet of doublets, dm = doublet of multiplets, m = multiplet; J(AgP) = $J(^{109}AgP)$ and $J(^{107}AgP)$. Spectra were recorded in $(CD_3)_2CO$ at −80 °C unless otherwise stated. [b] In CD_2Cl_2 at −80 °C.

doublets of doublets by coupling to the phosphorus and the two similar $I = \frac{1}{2}$ silver nuclei, ^{109}Ag and ^{107}Ag. Finally, the Ag–PPh_2 appears as two doublets of doublet of doublets because of the coupling with the other two phosphorus and the silver nuclei (see Table 1). Noteworthy are the different values of the coupling constants between both phosphorus to the silver nuclei: 335.7 and 285.7 Hz for the PPh_2 and 579.4 and 413.3 Hz for PPh_3. There are not many silver complexes with different phosphorus environments available to compare the coupling constants. Nevertheless, we have previously observed that in three-co-ordinated silver derivatives with a tertiary phosphine PR_3 and a diphosphine, the coupling constants are always higher for the tertiary phosphine: *e.g.* $[Ag(PPh_3)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$ (279.9 and 243.7 Hz, *vs.* 549.0 and 474.9 Hz).[12] If we regard complex **1** as distorted trigonal planar with an additional weak contact to the ClO_4^- anion (see comments on the crystal structure below) it is possible that a small difference in the bond lengths and the geometry could be responsible for this behaviour.

The FAB$^+$ mass spectrum shows the molecular cation peak at m/z = 827 $[Ag(PPh_3)(PPh_2CH_2PPh_2CHCO_2Me)]^+$ and other observed fragments correspond to $[Ag(PPh_3)_2]^+$, $[Ag(PPh_2CH_2PPh_2CHCO_2Me)]^+$ and $[Ag(PPh_3)]^+$.

The structure of complex **1** was confirmed by X-ray diffraction and is shown in Fig. 1. Atomic coordinates are collected in Table 2 and selected bond lengths and angles in Table 3. The silver(I) atom exhibits a very distorted tetrahedral geometry. The bite of the ligand, P(2)–Ag–C(2) 90.7(2)°, represents the major deviation from ideal geometry. The opposite angle O(3)–Ag–P(1) 91.0(5)° is also rather narrow, and both are compensated for by the angles C(2)–Ag–P(1) 124.6(2)° and O(3)–Ag–P(2) 126.1(5)°. The dihedral angle between the planes formed by Ag, P(2), C(2) and Ag, P(1), O(3) is 72°. The five-membered chelate ring displays an envelope conformation, with C(1) 0.73 Å out of the plane of the other four atoms.

The Ag–P distances, 2.426(2) and 2.470(2) Å, are smaller than those found in other four-co-ordinate silver complexes such as (*i*) $[Ag(PPh_3)_4]ClO_4$,[13] where the cation is situated on a crystallographic three-fold axis (*i.e.* two unique Ag–P bond distances); the Ag–P bond lengths are 1 × 2.650(2), 3 × 2.668(5) Å; (*ii*) $[Ag(dppe)_2]NO_3$ [dppe = 1,2-bis(diphenylphosphino)ethane],[14] where the Ag–P distances fall in the range 2.448(3)–2.527(3) Å; and (*iii*) $[Ag(phen)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$ (phen = 1,10-phenanthroline) [2.463(2) and 2.479(2) Å].[12]

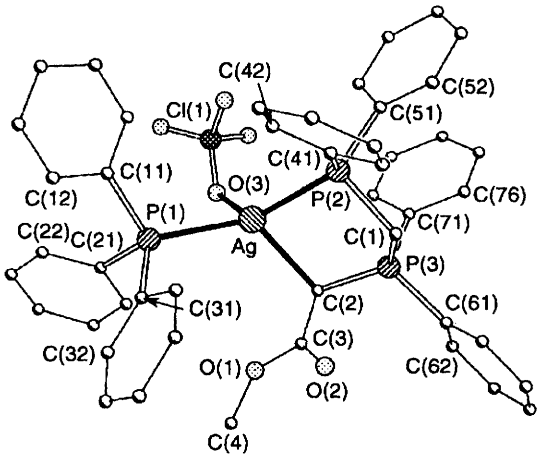


Fig. 1 Structure of complex **1** in the crystal. Hydrogen atoms are omitted for clarity; radii are arbitrary

The Ag–C bond is very long [2.414(6) Å] compared to $[Ag(C_6F_5)(CH_2PPh_3)]$ with a linear silver(I) atom [Ag–CH_2 2.131(6) Å].[15] However no comparison can be made with three- or four-co-ordinate complexes, where obviously these distances tend to be longer. The Ag–O(3) distance of 2.666(10) Å represents a weak bond to the perchlorate anion.

The reactions of $[PPh_2CH_2PPh_2CH_2CO_2Me]ClO_4$ with ⩾2 equivalents of $[Ag(acac)(PPh_3)]$ have been carried out but the same complex is obtained in all cases. We have also investigated the reaction of $[PPh_2CH_2PPh_2Me]ClO_4$ with $[Ag(acac)(PPh_3)]$, which leads to an irresolvable mixture of complexes. Probably the formation of an Ag–P–C three-membered chelate ring is not favoured, and competition for co-ordination to the phosphorus or the carbon atoms, or formation of oligomers may occur.

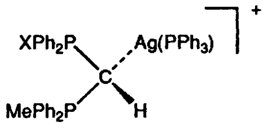
Reactions of $[Ag(acac)(PPh_3)]$ *with* $[XPPh_2CH_2PPh_2R]ClO_4$ (X = S *or* O).—In order to deprotonate this type of ligand further, we have used the oxide or sulfide derivatives, which make the methylene protons nearest to them more acidic. Therefore the reaction of $[XPPh_2CH_2PPh_2Me]ClO_4$ with $[Ag(acac)(PPh_3)]$ displaces acac as acetylacetone and the ligand is deprotonated giving $[Ag(PPh_3)(XPPh_2CHPPh_2Me)]ClO_4$ (X = S **2** or O **3**). There are two possible structures (**A** or **B**) for these complexes.

Table 2 Atomic coordinates (× 10^4) for complex **1**

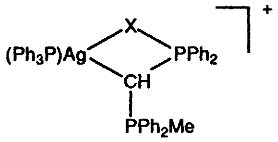
Atom	*x*	*y*	*z*
Ag	7 657.8(4)	2 298.7(2)	1 124.4(3)
P(1)	8 285.6(13)	1 687.0(7)	282.0(8)
P(2)	7 968.6(13)	2 101.5(7)	2 402.2(8)
P(3)	8 068.3(13)	3 513.1(7)	2 239.9(8)
C(1)	8 728(5)	2 844(2)	2 785(3)
C(2)	8 007(6)	3 420(3)	1 353(4)
C(3)	9 096(7)	3 497(3)	1 250(4)
C(4)	10 035(9)	3 646(5)	391(5)
O(1)	9 004(5)	3 605(3)	550(3)
O(2)	10 011(5)	3 476(3)	1 709(3)
C(11)	7 956(5)	839(3)	272(3)
C(12)	8 568(6)	383(3)	48(4)
C(13)	8 276(6)	−254(3)	22(4)
C(14)	7 370(6)	−442(3)	234(4)
C(15)	6 770(6)	14(3)	462(4)
C(16)	7 051(5)	646(3)	477(3)
C(21)	7 760(5)	1 939(3)	−655(3)
C(22)	7 501(6)	1 515(4)	−1 211(4)
C(23)	7 110(7)	1 734(4)	−1 911(4)
C(24)	6 985(6)	2 374(4)	−2 049(4)
C(25)	7 260(6)	2 802(4)	−1 500(4)
C(26)	7 640(6)	2 584(3)	−797(4)
C(31)	9 822(5)	1 705(3)	495(3)
C(32)	10 369(5)	1 911(3)	32(4)
C(33)	11 529(6)	1 945(3)	233(4)
C(34)	12 181(6)	1 767(3)	910(4)
C(35)	11 625(6)	1 551(4)	1 381(4)
C(36)	10 484(6)	1 531(3)	1 179(4)
C(41)	8 965(5)	1 476(3)	2 828(3)
C(42)	8 888(6)	908(3)	2 468(4)
C(43)	9 603(8)	403(3)	2 758(6)
C(44)	10 408(8)	474(4)	3 428(5)
C(45)	10 496(7)	1 036(4)	3 806(5)
C(46)	9 791(6)	1 542(3)	3 504(4)
C(51)	6 869(5)	2 030(2)	2 825(3)
C(52)	7 123(6)	1 943(3)	3 548(3)
C(53)	6 257(6)	1 875(3)	3 839(4)
C(54)	5 151(6)	1 896(3)	3 417(4)
C(55)	4 898(6)	1 981(3)	2 708(4)
C(56)	5 753(5)	2 046(3)	2 396(4)
C(61)	8 818(5)	4 215(3)	2 677(3)
C(62)	8 389(7)	4 794(3)	2 404(5)
C(63)	8 936(7)	5 354(3)	2 717(5)
C(64)	9 916(6)	5 325(3)	3 287(4)
C(65)	10 328(6)	4 748(3)	3 553(4)
C(66)	9 776(6)	4 192(3)	3 252(3)
C(71)	6 672(5)	3 580(3)	2 297(3)
C(72)	5 695(6)	3 528(3)	1 707(4)
C(73)	4 653(6)	3 567(4)	1 814(6)
C(74)	4 565(7)	3 665(4)	2 457(5)
C(75)	5 497(7)	3 717(4)	3 033(5)
C(76)	6 566(6)	3 680(3)	2 968(4)
Cl(1)	4 716(2)	2 181.9(10)	106.5(9)
O(3)	5 675(6)	2 526(5)	134(6)
O(4)	4 155(9)	1 898(4)	−526(4)
O(5)	4 955(6)	1 718(3)	659(3)
O(6)	3 932(6)	2 648(4)	219(5)
C(5)	1 171(15)	4 995(8)	1 992(9)
Cl(2)	2 560(4)	5 016(2)	2 667(2)
Cl(3)	1 252(5)	5 327(3)	1 213(3)
Cl(4)	8 664(8)	−19(5)	4 481(5)
Cl(5)	7 419(9)	663(5)	5 201(6)
Cl(6)	7 151(12)	70(7)	4 573(8)
Cl(7)	8 783(12)	815(7)	5 025(8)

Table 3 Selected bond lengths (Å) and angles (°) for complex **1**

Ag–C(2)	2.414(6)	Ag–P(1)	2.426(2)
Ag–P(2)	2.470(2)	Ag–O(3)	2.666(10)
P(1)–C(31)	1.829(6)	P(1)–C(11)	1.829(6)
P(1)–C(21)	1.837(7)	P(2)–C(41)	1.822(6)
P(2)–C(51)	1.828(6)	P(2)–C(1)	1.858(6)
P(3)–C(2)	1.744(7)	P(3)–C(71)	1.788(6)
P(3)–C(1)	1.803(6)	P(3)–C(61)	1.812(6)
C(2)–C(3)	1.447(9)	C(3)–O(2)	1.213(9)
C(3)–O(1)	1.371(8)	C(4)–O(1)	1.423(10)
C(2)–Ag–P(1)	124.6(2)	C(2)–Ag–P(2)	90.7(2)
P(1)–Ag–P(2)	129.49(6)	O(3)–Ag–P(1)	91.0(5)
O(3)–Ag–P(2)	126.1(5)	O(3)–Ag–C(2)	91.9(6)
C(31)–P(1)–C(11)	103.8(3)	C(31)–P(1)–C(21)	103.7(3)
C(11)–P(1)–C(21)	105.3(3)	C(31)–P(1)–Ag	112.1(2)
C(11)–P(1)–Ag	113.8(2)	C(21)–P(1)–Ag	116.8(2)
C(41)–P(2)–C(51)	103.3(3)	C(41)–P(2)–C(1)	103.5(3)
C(51)–P(2)–C(1)	104.1(3)	C(41)–P(2)–Ag	117.1(2)
C(51)–P(2)–Ag	126.0(2)	C(1)–P(2)–Ag	99.7(2)
C(2)–P(3)–C(71)	110.0(3)	C(2)–P(3)–C(1)	112.3(3)
C(71)–P(3)–C(1)	107.0(3)	C(2)–P(3)–C(61)	115.0(3)
C(71)–P(3)–C(61)	105.8(3)	C(1)–P(3)–C(61)	106.3(3)
P(3)–C(1)–P(2)	109.6(3)	C(3)–C(2)–P(3)	112.9(5)
C(3)–C(2)–Ag	101.8(4)	P(3)–C(2)–Ag	104.2(3)
O(2)–C(3)–O(1)	121.2(7)	O(2)–C(3)–C(2)	126.4(6)
O(1)–C(3)–C(2)	112.4(7)	C(3)–O(1)–C(4)	116.3(7)



A



B

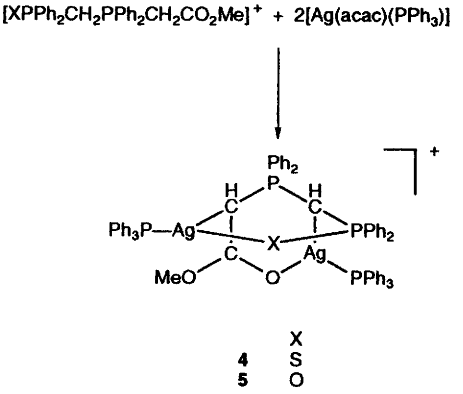
The structure found in [Au(PPh$_3$)(SPPh$_2$CHPPh$_2$Me)]ClO$_4$ corresponds to **A**;[2] however, although NMR data are compatible with both structures, we believe that complexes **2** and **3** possess the structure **B**, because the ν(P=S) band is displaced in the IR spectra to lower frequencies, as happens when the sulfur atom co-ordinates to a metal centre (587 *vs.* 605 cm^{-1} in the free ligand). The same comparison cannot be made with ν(P=O) because this band overlaps that of the ClO$_4^-$ anion. The bands for the ClO$_4^-$ are similar to those in complex **1**; thus it is difficult to distinguish whether a weak co-ordination to the metal centre occurs.

The ^{1}H NMR spectra of these compounds show the presence of multiplets for the methine proton and the methyl group. In the ^{31}P-{^{1}H} NMR spectrum of complex **2** a doublet is observed for each PPh$_2$ group and two multiplets for the PPh$_3$ group; the spectrum of complex **3** shows two broad singlets for the two PPh$_2$ groups and two doublets for the PPh$_3$ group coupled to the two silver nuclei.

The reaction of [Ag(acac)(PPh$_3$)] with [XPPh$_2$CH$_2$PPh$_2$CH$_2$CO$_2$Me]ClO$_4$ in 1 : 1 molar ratio gives a mixture of the monodeprotonated [Ag(PPh$_3$)(XPPh$_2$CHPPh$_2$CH$_2$CO$_2$Me)]ClO$_4$ and the dideprotonated complex [Ag$_2$(PPh$_3$)$_2$(XPPh$_2$CHPPh$_2$CHCO$_2$Me)]ClO$_4$, whereas reaction with 2 equivalents of [Ag(acac)(PPh$_3$)] gives pure dideprotonated complexes **4** and **5** [equation (2)].

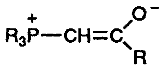
In the IR spectra of complexes **4** and **5** a substantial decrease in the carbonyl stretching frequency is observed, as a consequence of the oxygen bonding. Keto-stabilized ylides can co-ordinate to a metal centre through either the ylidic carbon atom or the oxygen atom (structure **C** or **D**), and both examples are known in transition-metal chemistry,[16,17] but as far as we are aware no examples have been reported where the ligand co-ordinates through both the oxygen and the carbon atom.

The ^{1}H NMR spectra of these derivatives show two multiplets for the methine protons and a singlet for the methyl

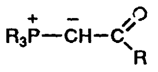


(2)

group. The ^{31}P-{^{1}H} NMR spectra show two broad singlets for the two different PPh_2 groups, mutually coupled. Both PPh_3 appear as two doublets because of the coupling with the silver nuclei ^{109}Ag and ^{107}Ag.



C



D

The structure of complex **4** has been established by X-ray diffraction, and the cation is shown in Fig. 2. Positional parameters are collected in Table 4 and selected bond lengths and angles in Table 5. Each silver atom is three-co-ordinate but their geometries differ. Ag(1) exhibits a slightly irregular trigonal-planar geometry, arising from the bite of the ligand C(2)–Ag(1)–S 107.8(3)°; the other angles are C(2)–Ag(1)–P(1) 129.0(3) and P(1)–Ag(1)–S 123.13(10)°, with the silver 0.02 Å out of the plane formed by the three co-ordinated atoms. However Ag(2) presents a very distorted trigonal-planar geometry; the bite of the ligand is far narrower with C(1)–Ag(2)–O(1) 93.2(3)°, compensated for by C(1)–Ag(2)–P(2) 160.0(3) and P(2)–Ag(2)–O(1) 106.4(2)°. The Ag(2) atom lies 0.06 Å out of the plane formed by the three donor atoms.

The Ag–P bonds, 2.372(3) and 2.404(3) Å, are shorter than those found in complex **1**, as would be expected on changing from four- to three-co-ordination. The Ag–C distances are Ag(1)–C(2) 2.289(11) and Ag(2)–C(1) 2.231(10) Å and are considerably shorter than in complex **1**, although still longer than in $[Ag(C_6F_5)(CH_2PPh_3)]$ where a more basic ylide ligand

Table 4 Atomic coordinates (× 10^4) for complex **4**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ag(1)	6 097.8(5)	800.3(7)	1 694.5(2)	C(63)	5 503(10)	1 389(14)	−75(3)
Ag(2)	3 932.5(6)	2 362.6(7)	1 128.4(2)	C(64)	6 378(11)	1 693(14)	56(3)
P(1)	7 475(2)	−256(2)	1 888.0(6)	C(65)	6 423(9)	2 195(14)	329(3)
P(2)	3 624(2)	2 368(3)	585.6(6)	C(66)	5 580(9)	2 416(13)	493(3)
P(3)	3 633(2)	706(2)	1 641.8(6)	C(71)	3 631(7)	180(9)	2 035(2)
P(4)	4 600(2)	2 919(2)	1 841.6(6)	C(72)	2 963(7)	640(10)	2 236(2)
S	4 648(2)	−59(2)	1 405.5(7)	C(73)	2 954(8)	302(10)	2 540(3)
C(1)	3 686(7)	2 165(9)	1 631(2)	C(74)	3 596(9)	−497(10)	2 645(3)
C(2)	5 802(7)	2 657(9)	1 741(2)	C(75)	4 264(9)	−957(9)	2 449(3)
C(3)	6 073(7)	3 094(9)	1 447(2)	C(76)	4 285(8)	−618(9)	2 148(2)
C(4)	7 379(8)	3 535(10)	1 137(2)	C(81)	2 448(7)	305(9)	1 472(2)
O(1)	5 521(5)	3 313(7)	1 226(2)	C(82)	2 231(7)	−818(10)	1 461(3)
O(2)	7 048(5)	3 215(6)	1 434(2)	C(83)	1 341(8)	−1 189(10)	1 330(3)
C(11)	7 685(8)	−1 555(9)	1 692(2)	C(84)	688(8)	−437(10)	1 216(3)
C(12)	8 613(8)	−1 939(9)	1 637(3)	C(85)	881(7)	687(10)	1 224(3)
C(13)	8 731(9)	−2 940(9)	1 487(3)	C(86)	1 764(7)	1 043(10)	1 352(2)
C(14)	7 948(8)	−3 565(9)	1 395(3)	C(91)	4 541(8)	2 717(9)	2 261(2)
C(15)	7 034(9)	−3 187(9)	1 447(3)	C(92)	5 165(7)	2 002(9)	2 426(2)
C(16)	6 889(8)	−2 190(9)	1 596(2)	C(93)	5 023(8)	1 799(10)	2 734(2)
C(21)	7 303(7)	−610(9)	2 288(2)	C(94)	4 288(8)	2 330(10)	2 878(2)
C(22)	7 029(8)	−1 652(10)	2 385(2)	C(95)	3 682(8)	3 049(10)	2 718(2)
C(23)	6 816(9)	−1 823(11)	2 692(3)	C(96)	3 797(8)	3 252(9)	2 409(2)
C(24)	6 887(8)	−992(10)	2 909(3)	C(101)	4 314(8)	4 372(9)	1 799(2)
C(25)	7 163(8)	52(10)	2 810(3)	C(102)	4 938(8)	5 117(9)	1 949(2)
C(26)	7 357(8)	241(10)	2 512(3)	C(103)	4 754(9)	6 234(10)	1 937(3)
C(31)	8 633(7)	471(9)	1 906(2)	C(104)	3 955(9)	6 635(10)	1 767(3)
C(32)	8 744(7)	1 374(9)	1 713(2)	C(105)	3 335(9)	5 907(9)	1 621(3)
C(33)	9 581(7)	1 999(9)	1 727(3)	C(106)	3 511(8)	4 765(9)	1 629(3)
C(34)	10 312(8)	1 726(10)	1 949(3)	Cl(1)	642(2)	4 650(3)	1 364.1(7)
C(35)	10 230(7)	833(10)	2 139(3)	O(3)	250(12)	4 796(11)	1 662(3)
C(36)	9 382(7)	208(9)	2 122(2)	O(4)	1 024(7)	5 672(8)	1 267(3)
C(41)	2 716(8)	1 346(11)	448(3)	O(5)	−165(8)	4 365(9)	1 178(3)
C(42)	2 663(10)	361(11)	609(3)	O(6)	1 318(8)	3 820(9)	1 392(4)
C(43)	2 002(9)	−437(12)	508(3)	C(5)	−559(11)	6 217(13)	628(5)
C(44)	1 400(10)	−258(13)	251(3)	Cl(2)	−1 717(4)	6 060(6)	499(2)
C(45)	1 463(8)	719(12)	87(3)	Cl(3)	−71(4)	7 512(4)	616.4(13)
C(46)	2 120(8)	1 507(12)	187(3)	C(6)	10 007(11)	2 663(13)	550(3)
C(51)	3 165(9)	3 702(11)	450(3)	Cl(4)	9 840(7)	3 456(6)	224(2)
C(52)	3 488(11)	4 210(11)	184(3)	Cl(5)	9 132(3)	1 666(6)	587.3(13)
C(53)	3 118(14)	5 243(12)	104(4)	C(7)	4 702(12)	5 925(13)	852(5)
C(54)	2 444(13)	5 774(13)	286(4)	Cl(6)	4 428(4)	7 347(5)	950.6(14)
C(55)	2 149(10)	5 254(12)	545(4)	Cl(7)	5 742(4)	5 841(5)	658.0(13)
C(56)	2 520(8)	4 241(12)	636(3)	C(8)	6 424(12)	−430(15)	820(5)
C(61)	4 698(9)	2 095(12)	369(3)	Cl(8)	7 230(6)	471(5)	1 036.4(12)
C(62)	4 636(10)	1 596(13)	86(3)	Cl(9)	7 187(9)	−1 293(9)	635(2)

Table 5 Selected bond lengths (Å) and angles (°) for complex **4**

Ag(1)–C(2)	2.289(11)	Ag(1)–P(1)	2.404(3)
Ag(1)–S	2.529(3)	Ag(2)–C(1)	2.231(10)
Ag(2)–P(2)	2.372(3)	Ag(2)–O(1)	2.488(7)
P(1)–C(11)	1.813(11)	P(1)–C(21)	1.814(11)
P(1)–C(31)	1.818(10)	P(2)–C(61)	1.816(11)
P(2)–C(51)	1.819(13)	P(2)–C(41)	1.835(12)
P(3)–C(1)	1.764(11)	P(3)–C(71)	1.821(11)
P(3)–C(81)	1.822(10)	P(3)–S	1.996(4)
P(4)–C(2)	1.758(10)	P(4)–C(1)	1.772(10)
P(4)–C(101)	1.805(11)	P(4)–C(91)	1.839(10)
C(2)–C(3)	1.445(14)	C(3)–O(1)	1.226(12)
C(3)–O(2)	1.353(11)	C(4)–O(2)	1.437(12)
C(2)–Ag(1)–P(1)	129.0(3)	C(2)–Ag(1)–S	107.8(3)
P(1)–Ag(1)–S	123.13(10)	C(1)–Ag(2)–P(2)	160.0(3)
C(1)–Ag(2)–O(1)	93.2(3)	P(2)–Ag(2)–O(1)	106.4(2)
C(11)–P(1)–C(21)	106.0(5)	C(11)–P(1)–C(31)	106.3(5)
C(21)–P(1)–C(31)	103.0(5)	C(11)–P(1)–Ag(1)	115.8(3)
C(21)–P(1)–Ag(1)	108.9(3)	C(31)–P(1)–Ag(1)	115.7(4)
C(61)–P(2)–C(51)	105.8(6)	C(61)–P(2)–C(41)	105.5(6)
C(51)–P(2)–C(41)	105.6(6)	C(61)–P(2)–Ag(2)	113.5(4)
C(51)–P(2)–Ag(2)	111.6(4)	C(41)–P(2)–Ag(2)	114.1(4)
C(1)–P(3)–C(71)	112.1(5)	C(1)–P(3)–C(81)	107.0(5)
C(71)–P(3)–C(81)	104.3(5)	C(1)–P(3)–S	114.6(4)
C(71)–P(3)–S	110.5(4)	C(81)–P(3)–S	107.7(4)
C(2)–P(4)–C(1)	115.7(5)	C(2)–P(4)–C(101)	110.6(5)
C(1)–P(4)–C(101)	107.5(5)	C(2)–P(4)–C(91)	107.7(5)
C(1)–P(4)–C(91)	112.3(5)	C(101)–P(4)–C(91)	102.2(5)
P(3)–S–Ag(1)	96.35(13)	P(3)–C(1)–P(4)	121.9(6)
P(3)–C(1)–Ag(2)	98.2(4)	P(4)–C(1)–Ag(2)	108.2(5)
C(3)–C(2)–P(4)	115.9(7)	C(3)–C(2)–Ag(1)	103.0(7)
P(4)–C(2)–Ag(1)	111.8(5)	O(1)–C(3)–O(2)	121.5(9)
O(1)–C(3)–C(2)	126.5(9)	O(2)–C(3)–C(2)	111.9(9)
C(3)–O(1)–Ag(2)	122.8(7)	C(3)–O(2)–C(4)	115.0(8)

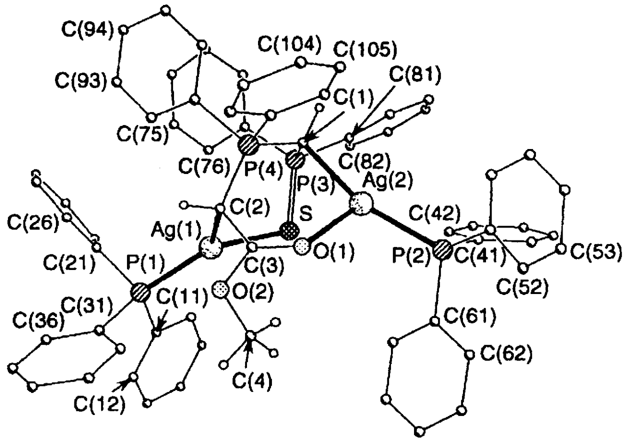


Fig. 2 Structure of the cation of complex **4** in the crystal with hydrogen atoms omitted for clarity; radii are arbitrary

is present, but are similar to those in [Ag{CH(PPh$_3$)COPh}$_2$]NO$_3$ [2.219(9)–2.256(8) Å, two independent molecules].[17] The Ag(1)–S bond length of 2.529(3) Å is slightly shorter than in [Ag{(PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$}{(SPPh$_2$)$_2$CH$_2$}]ClO$_4$ [2.540(2) and 2.588(2) Å] where the silver atom is four-co-ordinated. The Ag(2)–O(1) distance of 2.488(7) Å is similar to the shorter Ag–O to the nitrate group in [Ag(NO$_3$)(4-NO$_2$C$_5$H$_4$NO)$_2$] but longer than the Ag–O$_{\mathrm{NO}}$ distances of 2.364(3) and 2.318(3) Å.[18]

Experimental

General Data.—Instrumentation and general experimental techniques were as described earlier. The starting materials [Ag(acac)(PPh$_3$)],[19] [PPh$_2$CH$_2$PPh$_2$CH$_2$CO$_2$Me]ClO$_4$,[20] [SPPh$_2$CH$_2$PPh$_2$Me]ClO$_4$[21] and [SPPh$_2$CH$_2$PPh$_2$CH$_2$CO$_2$Me]ClO$_4$[20] were prepared according to published procedures.

Syntheses.—[OPPh$_2$CH$_2$PPh$_2$R]ClO$_4$ (R = Me *or* CH$_2$CO$_2$Me). To a solution of [PPh$_2$CH$_2$PPh$_2$Me]ClO$_4$ (0.449 g, 1 mmol) or [PPh$_2$CH$_2$PPh$_2$CH$_2$CO$_2$Me]ClO$_4$ (0.557 g, 1 mmol) in acetone (25 cm^3) at 0 °C was added H$_2$O$_2$ (0.12 cm^3, 1.2 mmol). The colourless solution was stirred for 1 h. The solvent was evaporated to dryness, redissolved in dichloromethane (20 cm^3) and anhydrous MgSO$_4$ was added. The suspension was filtered off and the solvent evaporated to *ca.* 5 cm^3. Addition of diethyl ether gave the salts as white solids. [OPPh$_2$CH$_2$PPh$_2$Me]ClO$_4$: Yield 85%. NMR (CDCl$_3$): ^{1}H, δ 2.67 [d, 3 H, *J*(PH) 13.87, Me], 4.25 [dd, 2 H, *J*(PH) 11.78 and 15.71 Hz, CH$_2$], 7.24–7.82 (m, 20 H, Ph); ^{31}P-{^{1}H}, δ 20.9 [d, ^2J(PP) 12.5, PPh$_2$Me], 25.1 [d, ^2J(PP) 12.5 Hz, OPPh$_2$]. Λ_M = 144 Ω^{-1} cm^2 mol^{-1} (Found: C, 60.25; H, 4.80. Calc. for C$_{26}$H$_{25}$ClO$_5$P$_2$: C, 60.65; H, 4.90%). [OPPh$_2$CH$_2$PPh$_2$CH$_2$CO$_2$Me]ClO$_4$: Yield 78%. NMR (CDCl$_3$): ^{1}H, δ 3.61 (s, 3 H, Me), 4.59 [d, 2 H, ^2J(PH) 13.43, C*H*$_2$CO$_2$Me], 4.53 [dd, 2 H, *J*(PH) 11.72 and 10.99 Hz, Ph$_2$PC*H*$_2$PPh$_2$]; ^{31}P-{^{1}H}, δ 20.65 [d, ^2J(PP) 12.5, PPh$_2$CH$_2$CO$_2$Me], 26.25 [d, ^2J(PP) 12.5 Hz, OPPh$_2$]. Λ_M = 141 Ω^{-1} cm^2 mol^{-1} (Found: C, 58.45; H, 4.70. Calc. for C$_{28}$H$_{27}$ClO$_7$P$_2$: C, 58.70; H, 4.75%).

[Ag(OClO$_3$)(PPh$_3$)(PPh$_2$CH$_2$PPh$_2$CHCO$_2$Me)]. To a dichloromethane solution (20 cm^3) of [PPh$_2$CH$_2$PPh$_2$CH$_2$CO$_2$Me]ClO$_4$ (0.111 g, 0.2 mmol) was added [Ag(acac)(PPh$_3$)] (0.112 g, 0.24 mmol). The mixture was stirred in the dark for 1 day. Concentration of the solvent (5 cm^3) and addition of diethyl ether (15 cm^3) gave complex **1** as a white solid. Yield 80%. Λ_M = 103 Ω^{-1} cm^2 mol^{-1} (Found: C, 59.10; H, 4.35. Calc. for C$_{46}$H$_{41}$AgClO$_6$P$_3$: C, 59.60; H, 4.65%).

[Ag(PPh$_3$)(XPPh$_2$CHPPh$_2$Me)]ClO$_4$ (X = S **2** *or* O **3**). To a solution of [SPPh$_2$CH$_2$PPh$_2$Me]ClO$_4$ (0.106 g, 0.2 mmol) or [OPPh$_2$CH$_2$PPh$_2$Me]ClO$_4$ (0.103 g, 0.2 mmol) in dichloromethane (25 cm^3) was added [Ag(acac)(PPh$_3$)] (0.188 g, 0.4 mmol) and the solution stirred for 1 day. Partial evaporation of the solvent to *ca.* 5 cm^3 and addition of diethyl ether (15 cm^3) gave complexes **2** and **3** as white solids. For **2**: yield 79%, Λ_M = 140 Ω^{-1} cm^2 mol^{-1} (Found: C, 59.20; H, 4.20; S, 3.35. Calc. for C$_{44}$H$_{39}$AgClO$_4$P$_3$S: C, 58.70; H, 4.35; S, 3.55%). For **3**: yield 85%, Λ_M = 133 Ω^{-1} cm^2 mol^{-1} (Found: C, 59.45; H, 4.55. Calc. for C$_{44}$H$_{39}$AgClO$_5$P$_3$: C, 59.80; H, 4.45%).

[Ag$_2$(PPh$_3$)$_2$(XPPh$_2$CHPPh$_2$CHCO$_2$Me)]ClO$_4$ (X = S **4** *or* O **5**). To a solution in dichloromethane (30 cm^3) of [SPPh$_2$CH$_2$PPh$_2$CH$_2$CO$_2$Me]ClO$_4$ (0.118 g, 0.2 mmol) or [OPPh$_2$CH$_2$PPh$_2$CH$_2$CO$_2$Me]ClO$_4$ (0.114 g, 0.2 mmol) was added [Ag(acac)(PPh$_3$)] (0.215 g, 0.46 mmol). The mixture was stirred for 1 day and then the solvent concentrated to *ca.* 5 cm^3. Addition of 15 cm^3 of diethyl ether afforded white solids of **4** and **5**. For **4**: yield 89%, Λ_M = 120 Ω^{-1} cm^2 mol^{-1} (Found: C, 57.90; H, 4.40; S, 2.20. Calc. for C$_{64}$H$_{55}$Ag$_2$ClO$_6$P$_4$S: C, 57.90; H, 4.15; S, 2.40%). For **5**: yield 79%, Λ_M = 129 Ω^{-1} cm^2 mol^{-1} (Found: C, 58.05; H, 4.20. Calc. for C$_{64}$H$_{55}$Ag$_2$ClO$_7$P$_4$: C, 58.55; H, 4.20%).

Crystal Structure Determination of Complex **1**.—*Crystal data*. C$_{48}$H$_{45}$AgCl$_5$O$_6$P$_3$, M_r = 1095.87, monoclinic, space group $P2_1/n$, a = 12.488(4), b = 21.021(7), c = 19.803(7) Å, β = 108.60(3)°, U = 4927(3) Å^3, Z = 4, D_c = 1.477 Mg m^{-3}, F(000) = 2232, T = −100 °C.

Data collection and reduction. A colourless prism 0.80 × 0.60 × 0.50 mm was mounted in inert oil (type RS3000, donated by Riedel de Haën) on a glass fibre. 14651 Reflections were measured on a Siemens R3 diffractometer (monochromated Mo-Kα radiation, λ = 0.710 73 Å), to $2\theta_{max}$ = 50°. Merging equivalents gave 8671 unique reflections (R_{int} 0.044), of which 8657 were used for all calculations (program system SHELXL 93).[22] Cell constants were refined from setting angles of 54 reflections in the range 2θ 20–22°.

Structure solution and refinement. The structure was solved by direct methods and subjected to anisotropic full-matrix leastsquares refinement on F^2. Hydrogen atoms were included using a riding model. Refinement proceeded to $R'(F^2) = 0.227$, conventional $R(F) = 0.071$ for 543 parameters and 448 restraints, $S = 1.008$; maximum Δ/σ 0.33, maximum $\Delta\rho$ 1.82 e Å^{-3}. Complex **1** crystallizes with two molecules of dichloromethane, one is disordered (four half chlorine sites). The slow convergence of the methyl group and the high thermal parameter of the perchlorate may also indicate disorder.

Crystal Structure Determination of Complex **4**.—*Crystal data*. $C_{68}H_{63}Ag_2Cl_9O_6P_4S$, $M_r = 1666.91$, monoclinic, space group $P2_1/n$, $a = 13.759(3)$, $b = 12.074(3)$, $c = 43.353(9)$ Å, $\beta = 92.62(2)°$, $U = 7194.5(28)$ Å^3, $Z = 4$, $D_c = 1.539$ Mg m^{-3}, $F(000) = 3368$, $T = -100$ °C.

Data collection and reduction. A total of 13 113 intensities were recorded from a colourless prism of 0.50 × 0.25 × 0.15 mm. An absorption correction based on ψ-scans was applied, with transmission factors 0.75–0.80. Merging equivalents gave 12 710 (R_{int} 0.079) unique reflections, of which 12 671 were used for all calculations. Other details as for complex **1**.

Structure solution and refinement. The structure was solved by direct methods and refined as above. Refinement proceeded to $R'(F^2) = 0.234$, conventional $R(F) = 0.068$ for 793 parameters and 602 restraints, $S = 1.073$, maximum Δ/σ 0.001, maximum $\Delta\rho$ 1.67 e Å^{-3}. The complex crystallizes with four molecules of dichloromethane.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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