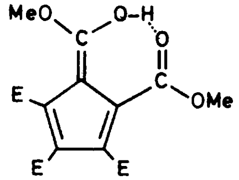
Pentakis(methoxycarbonyl)cyclopentadiene Chemistry. Part 4.[1] Some Silver(I) Complexes: Crystal and Molecular Structures of $[\{Ag[C_5(CO_2Me)_5](OH_2)\}_n]\cdot 1.5nH_2O$, $[\{Ag[C_5(CO_2Me)_5](PPh_3)\}_2]$, and $[Ag\{C_5(CO_2Me)_5\}(PPh_3)_2]$ †

Michael I. Bruce * and Michael L. Williams
Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia, 5001
Brian W. Skelton and Allan H. White *
Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia, 6009

A series of silver(I) derivatives of pentakis(methoxycarbonyl)cyclopentadiene has been prepared (from the diene and silver acetate), including $[\{Ag[C_5(CO_2Me)_5](OH_2)\}_n]\cdot 1.5_nH_2O$, $[\{Ag[C_5(CO_2Me)_5](PPh_3)\}_2]$, $[Ag\{C_5(CO_2Me)_5\}(PPh_3)_2]$, $[Ag\{C_5(CO_2Me)_5\}(dppe)]$ [dppe = 1,2-bis(diphenylphosphino)ethane], and $[Ag\{C_5(CO_2Me)_5\}(tppme)]$ [tppme = 1,1,1-tris(diphenylphosphinomethyl)ethane]. In polar solvents, some of these complexes form conducting solutions. Structural studies by single-crystal *X*-ray diffraction have given the following results: $[\{Ag[C_5(CO_2Me)_5](OH_2)\}_n]\cdot 1.5nH_2O$ forms a one-dimensional polymer, centrosymmetrically related silver atoms being bridged by a similarly related pair of water molecules [Ag–O 2.450(5), 2.437(5) Å], and also by a $C_5(CO_2Me)_5$ ligand, alternately bonded through a pair of carboxylate oxygen atoms [Ag–O 2.391(5), 2.417(6) Å] and an interaction with two of the $C_5(CO_2Me)_5$ ring carbons [2.586(7), 2.807(7) Å]; in $[\{Ag[C_5(CO_2Me)_5](PPh_3)\}_2]$, the silver atom is essentially four-co-ordinated by a phosphine ligand [Ag–P 2.397(1) Å], a chelating $C_5(CO_2Me)_5$ ligand [Ag–O 2.415(3), 2.613(3) Å], and an interaction with one of the π bonds in the C_5 ring of the $C_5(CO_2Me)_5$ ligand [Ag–C 2.632(4), 2.472(4) Å], the whole species being bridged by $C_5(CO_2Me)_5$ ligands to give a centrosymmetric dimer; $[Ag\{C_5(CO_2Me)_5\}(PPh_3)_2]$ is monomeric, with silver four-co-ordinated by two phosphine ligands [Ag–P 2.428(2), 2.414(2) Å] and a chelating $C_5(CO_2Me)_5$ ligand [Ag–O 2.465(4), 2.594(5) Å].

In previous Parts of this series, we have described the syntheses of several compounds containing ligands derived from pentakis(methoxycarbonyl)cyclopentadiene, $HC_5(CO_2Me)_5$ (1).



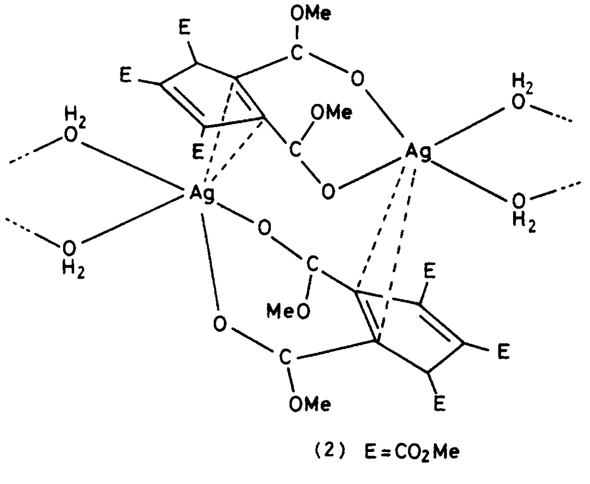
(1) E = CO_2Me

This diene is a strong organic acid, and we have been interested to determine the effect of the five electron-withdrawing CO_2Me groups on the bonding of the $[C_5(CO_2Me)_5]^-$ anion to metals. To this end, we have determined and reported the molecular structures of the diene (1) and its lithium, potassium, thallium, and barium salts,[2,3] in which the proton or metal atoms are bonded to carboxyl oxygens. In $[Ru(\eta\text{-}C_5H_5)\{\eta\text{-}C_5(CO_2Me)_5\}]$[4] and $[Rh\{\eta\text{-}C_5H_2(CO_2Me)_3\}_2][C_5(CO_2Me)_5]$,[5] the C_5 rings are attached to the metal atoms in the η^5 mode found with the classical cyclopentadienyl complexes.

Although the acidic proton in (1) is *O*-bonded, we recall that alkylation of the silver derivative of (1) affords a ring-carbon substituted derivative.[6] Accordingly, we considered that it would be instructive to investigate derivatives of the Group 1B metals: this account describes some of our results obtained with silver(I) compounds.

Results and Discussion

We have used the ready displacement of acetate from silver acetate by the strong organic acid, pentakis(methoxycarbonyl)cyclopentadiene, to synthesise the silver(I) derivative (2) of diene (1). Compound (2) is a white solid, which is both light and heat sensitive. It is soluble only in polar solvents such as water, the lower alcohols, or acetone; both the solid and solutions turn red quickly in light. If solutions are u.v.



(2) E = CO_2Me

---

† *Supplementary data available* (No. SUP 23518, 54 pp.): thermal parameters, structure factors, H-atom parameters, phenyl ring-planes and geometries. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Infrared spectra (cm^{-1}) obtained from Nujol mulls

Compound	ν(CO)	Other bands
(2) $[\{Ag[C_5(CO_2Me)_5](OH_2)\}_n]\cdot 1.5nH_2O$	ν(C=O) 1 722s, 1 705s 1 660vs ν(C–O) 1 284s, 1 245s, 1 214vs, 1 180s	1 475 (sh), 1 432 (sh), 1 420w, 1 403w, 1 164w, 1 155w, 1 080m, 1 009m, 991w, 969vw, 943w, 882w, 854w, 833w, 784 (sh), 782m, 754w, 744m, 718vw, 696w
(3) $[\{Ag[C_5(CO_2Me)_5](PPh_3)\}_2]$	ν(C=O) 1 726s, 1 720s, 1 698 (sh), 1 694s, 1 670m ν(C–O) 1 278s, 1 220s, 1 208s	1 586vw, 1 572vw, 1 488w, 1 482w, 1 435m, 1 425vw, 1 413m, 1 362m, 1 329vw, 1 306w, 1 175s, 1 168 (sh), 1 155w, 1 099w, 1 095w, 1 074m, 1 069 (sh), 1 025w, 1 006m, 994m, 963w, 943w, 922vw, 879w, 852w, 833w, 805vw, 793w, 778m, 753m, 750m, 745m, 720w, 705w, 700m, 694m
(4) $[Ag\{C_5(CO_2Me)_5\}(PPh_3)_2]$	ν(C=O) 1 700 (sh), 1 698w, 1 693vs, 1 685 (sh), 1 621s ν(C–O) 1 290s, 1 220vs, 1 203vs	1 587w, 1 570vw, 1 555vw, 1 491w, 1 478w, 1 455s, 1 448m, 1 434m, 1 426w, 1 392w, 1 366 (sh), 1 330vw, 1 308w, 1 179w, 1 172m, 1 163 (sh), 1 095m, 1 070m, 1 025w, 1 011m, 996w, 990m, 965w, 954w, 938vw, 920vw, 866w, 857w, 835w, 790w, 782w, 761 (sh), 753 (sh), 746m, 721w, 705w, 693m
(5) $[Ag\{C_5(CO_2Me)_5\}(dppe)]$	ν(C=O) 1 749w, 1 723s, 1 704 (sh), 1 699 (sh), 1 690s, 1 684 (sh), 1 677 (sh), 1 674vs, 1 645 (sh), 1 637s ν(C–O) 1 288m, 1 210s, 1 195s	1 588w, 1 573w, 1 555vw, 1 455w, 1 437w, 1 425 (sh), 1 415w, 1 367w, 1 170s, 1 159vw, 1 150 (sh), 1 100w, 1 075 (sh), 1 070m, 1 025 (sh), 1 009m, 1 000w, 940w, 920vw, 880vw, 849w, 838w, 790m, 748m, 731vw, 720m, 691m
(6) $[Ag\{C_5(CO_2Me)_5\}(tppme)]$	ν(C=O) 1 710s, 1 690s, 1 683w ν(C–O) 1 274m, 1 200vs, 1 170s	1 585vw, 1 571vw, 1 465 (sh), 1 455 (sh), 1 436w, 1 367w, 1 305 (sh), 1 095w, 1 068m, 1 024vw, 1 014w, 998w, 971vw, 939w, 833w, 787w, 740m, 730w, 694m

Table 2. Metal atom environments in (2), (3), and (4). Atoms derived from $C_5(CO_2Me)_5$ ligands are italicized. The first column for each entry is the metal–ligand distance (Å); the other entries are the angles (°) subtended at the metal by the ligand atoms in question

(2)	*r*	*O*(21)	*O*(31)	O(0$^{\mathrm{I}}$)	*C*(2$^{\mathrm{II}}$)	*C*(3$^{\mathrm{II}}$)
O(0)	2.450(5)	87.0(2)	156.8(2)	85.3(2)	108.3(2)	85.1(2)
O(21)	2.391(5)		74.4(2)	127.3(2)	133.1(2)	113.9(2)
O(31)	2.417(6)			95.0(2)	94.7(2)	114.9(2)
O(0$^{\mathrm{I}}$)	2.437(5)				98.6(2)	117.2(2)
C(2$^{\mathrm{II}}$)	2.586(7)					30.7(2)
C(3$^{\mathrm{II}}$)	2.807(7)					

(3)	*r*	*C*(4)	*C*(5)	*O*(11$^{\mathrm{III}}$)	*O*(51$^{\mathrm{III}}$)
P	2.397(1)	119.94(7)	146.2(1)	123.39(8)	88.32(7)
C(4)	2.632(4)		32.1(1)	110.3(1)	136.45(9)
C(5)	2.472(4)			90.3(1)	106.99(9)
O(11$^{\mathrm{III}}$)	2.415(3)				70.9(1)
O(51$^{\mathrm{III}}$)	2.613(3)				

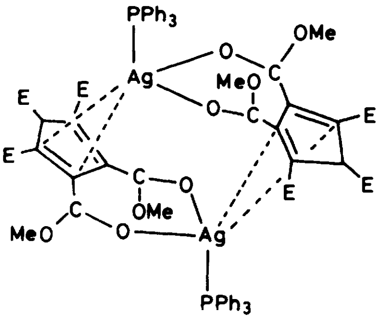
(4)	*r*	P(2)	*O*(11)	*O*(51)
P(1)	2.428(2)	136.64(5)	96.9(1)	109.4(1)
P(2)	2.414(2)		120.9(1)	102.5(1)
O(11)	2.465(4)			71.8(2)
O(51)	2.594(5)			

Symmetry transformations: I $2 - x, 2 - y, 1 - z$; II $2 - x, 2 - y, \bar{z}$; III $\bar{x}, \bar{y}, \bar{z}$.

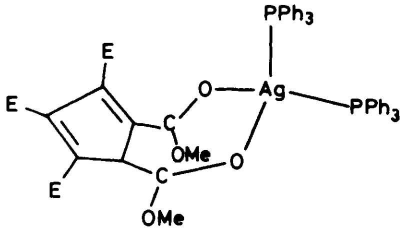
irradiated, a silver mirror is formed on the vessel; the dark red solution gave at least ten fractions on attempted purification by preparative t.l.c. on silica gel. While no pure products were isolated, the mass spectrum of a sample which had partially decomposed contained an ion at *m*/*e* 710, that is, corresponding to a dimer of $C_5(CO_2Me)_5$, which might be formed by coupling of two C_5 radicals formed in the primary decomposition process. An analogous feature has been described in the chemistry of C_5Cl_5;[7] the C_{10} product is formed by decomposition of $Tl(C_5Cl_5)$.

Complex (2) reacts readily with iodomethane to give the ring-methylated methylpentakis(methoxycarbonyl)cyclopentadiene; this compound has been obtained previously by methylating the solution obtained from the diene (1) and silver oxide, although complex (2) was not isolated from the latter reaction.

Reactions between silver acetate and (1) in the presence of tertiary phosphines gave complexes (3)—(6). These were obtained as white solids which were stable to air and water; some decomposition occurred if they were exposed to light or heat (>40 °C) for prolonged periods. These compounds are all insoluble in water or light petroleum, but will dissolve in polar solvents such as methanol, ethanol, or acetone; unlike $Ag[C_5(CO_2Me)_5]$, they are also soluble in benzene, dichloromethane, and chloroform. Solutions in polar solvents have conductivities consistent with the solutes being 1 : 1 electrolytes.



(3) E = CO_2Me



(4) E = CO_2Me

The formulations of complexes (3)—(6) follow from conventional analytical and spectroscopic studies. In particular, the n.m.r. spectra reveal that the $C_5(CO_2Me)_5$ groups are either highly fluxional or present as the symmetrical C_{5v} anions: only one sharp resonance is found for each of four sets of magnetically active nuclei (CH_3, and ring C, CO, and CH_3). This observation is at variance with the solid-state structures (see below), but is consistent with the solution conductivities; we favour the interpretation involving formation of a $[C_5(CO_2Me)_5]^-$ anion and a silver-containing cation. This probably occurs also for solutions of $Ag[C_5(CO_2Me)_5]$ in water since the solid-state structure reveals the presence of μ-H_2O molecules. The cations are probably tetrahedrally co-ordinated solvated [Ag(tertiary phosphine)]$^+$ systems.

Structural Studies.—(*a*) $[\{Ag[C_5(CO_2Me)_5](OH_2)\}_n]\cdot 1.5nH_2O$ (2). Analytically pure samples of $Ag[C_5(CO_2Me)_5]$, obtained by drying recrystallised samples, are no longer suitable for diffraction studies. The crystal for the *X*-ray structure determination was chosen from a sample which had been recrystallised from water. The unit-cell contents (see Figure 1), as determined by the structural study, showed that the stoicheiometry of the complex system was $Ag[C_5(CO_2Me)_5](OH_2)$; however, other molecules of solvent, modelled as partially populated oxygen fragments in the refinement, also exist independently of the complex, in lattice interstices, raising the degree of solvation to $Ag[C_5(CO_2Me)_5]\cdot$*ca.*$2.5H_2O$, one formula unit comprising the asymmetric unit.

Table 3. Ligand least-squares planes, calculated through the C_5 ring skeleton, given in the form $pX + qY + rZ = s$, where the right hand orthogonal Å frame (X, Y, Z) is defined with X parallel to a, Z in the ac plane. σ (defining atoms) and atom deviations, δ, are in Å. θ° is the dihedral angle to the C–CO–O carboxyl plane

	(2)	(3)	(4)
$10^4\ p$	8 879	−4 343	1 208
$10^4\ q$	−1 352	8 989	9 406
$10^4\ r$	−4 397	0 586	−3 175
s	6.811	−1.538	4.082
σ	0.005	0.002	0.003
δC(1)	−0.005	0.001	0.004
δC(2)	0.005	−0.002	−0.004
δC(3)	−0.004	0.002	0.004
δC(4)	0.000	−0.001	−0.001
δC(5)	0.003	0.000	−0.001
δC(11)	0.031	0.025	0.133
δC(21)	−0.259	0.143	−0.024
δC(31)	−0.018	0.198	−0.088
δC(41)	0.200	−0.121	0.035
δC(51)	0.054	−0.384	−0.080
δO(11)	1.052	0.696	0.095
δO(21)	−0.575	1.063	0.683
δO(31)	0.556	0.456	−1.018
δO(41)	1.217	0.760	0.215
δO(51)	0.287	−0.607	0.826
δO(12)	−1.159	−0.790	0.352
δO(22)	−0.161	−0.889	−0.961
δO(32)	−0.700	0.069	1.012
δO(42)	−0.899	−1.355	−0.181
δO(52)	−0.189	−0.521	−1.317
δC(12)	−1.204	−0.717	0.466
δC(22)	−0.406	−0.747	−0.993
δC(32)	−0.794	0.245	0.991
δC(42)	−0.781	−1.572	−0.102
δC(52)	−0.225	−0.829	−1.529
θ(1)	86.3	42.0	9.1
θ(2)	14.8	62.5	48.4
θ(3)	34.6	12.3	68.3
θ(4)	72.1	74.3	10.3
θ(5)	12.4	15.9	77.6

The basic unit of the well defined portion of the structure is a dimeric $[\{C_5(CO_2Me)_5\}Ag(OH_2)_2Ag\{C_5(CO_2Me)_5\}]$ species located about the (0, 0, $\frac{1}{2}$) inversion centres with the two silver atoms bridged by a pair of symmetrically disposed water oxygen atoms [Ag–O 2.450(5), 2.437(5) Å; Ag–O–Ag 94.7(2)° (Table 2)]. The silver atom is also co-ordinated by O(*n*1) type oxygen atoms from adjacent $C_5(CO_2Me)_5$ carboxylate substituents [Ag–O 2.391(5), 2.417(6) Å; Ag–O(21,31)–C 132.4(4), 139.5(4)°]. As expected, these carboxylate planes are approximately coplanar with the C_5 ring, which is itself a good plane (σ, 0.005 Å), and, as expected, a pair of non-adjacent, non-co-ordinated carboxylate planes (1 and 4) lie approximately normal to the ring. Atoms C(21) and C(41) lie −0.259 and 0.200 Å from the C_5 plane respectively (Table 3); moreover, the C_5 geometry (see Table 4) is rather irregular with four C–C bonds ranging between 1.387(9) and 1.415(8) Å, and the fifth, C(2)–C(3), lying between the co-ordinating carboxylates, longer at 1.441(8) Å. The four oxygen atoms co-ordinated to the silver are disposed all to one side of the atom; the void thus created is occupied by an approach from the C(2)–C(3) bond of an inversion-related $C_5(CO_2Me)_5$ ring, with Ag–C(2,3)

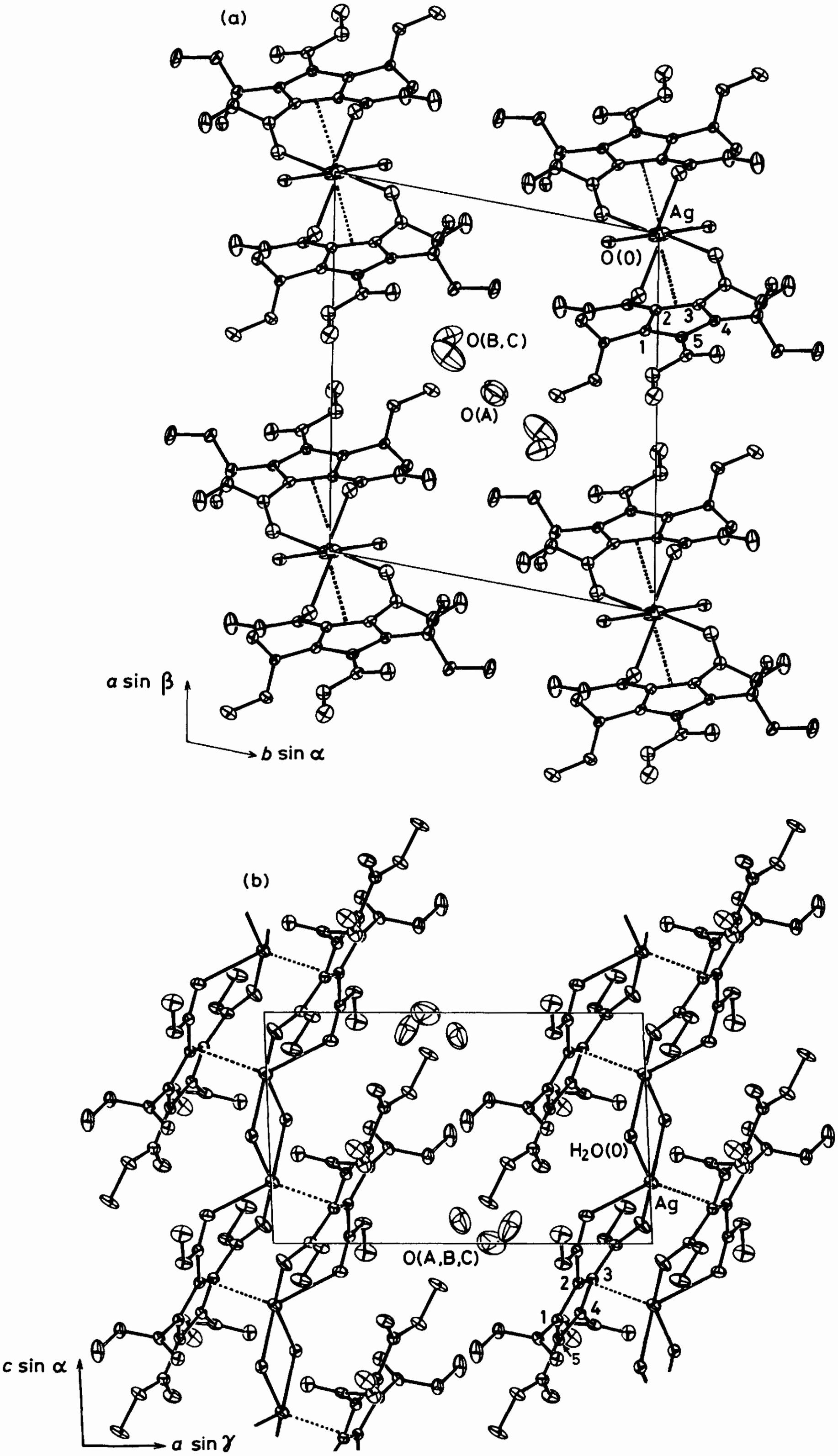


Figure 1. Unit-cell contents of (2) projected down (*a*) the *c* axis and (*b*) the *b* axis

Table 4. $C_5(CO_2Me)_5$ ligand geometries: distances (Å), angles (°)

	(2)	(3)	(4)
C(1)–C(2)	1.410(8)	1.380(6)	1.444(9)
C(2)–C(3)	1.441(8)	1.414(5)	1.386(10)
C(3)–C(4)	1.387(9)	1.407(6)	1.423(9)
C(4)–C(5)	1.415(8)	1.421(5)	1.393(9)
C(5)–C(1)	1.397(9)	1.442(5)	1.402(9)
C(1)–C(11)	1.493(8)	1.460(5)	1.411(9)
C(2)–C(21)	1.460(9)	1.490(6)	1.468(10)
C(3)–C(31)	1.485(8)	1.461(5)	1.487(9)
C(4)–C(41)	1.483(9)	1.492(5)	1.469(10)
C(5)–C(51)	1.472(9)	1.469(5)	1.476(9)
C(11)–O(11)	1.210(8)	1.199(6)	1.227(8)
C(21)–O(21)	1.220(7)	1.179(6)	1.176(9)
C(31)–O(31)	1.211(9)	1.204(6)	1.165(9)
C(41)–O(41)	1.199(8)	1.193(5)	1.192(9)
C(51)–O(51)	1.197(8)	1.205(4)	1.204(8)
C(11)–O(12)	1.305(8)	1.343(4)	1.341(9)
C(21)–O(22)	1.323(7)	1.319(6)	1.344(9)
C(31)–O(32)	1.321(8)	1.329(5)	1.308(9)
C(41)–O(42)	1.332(9)	1.332(6)	1.322(9)
C(51)–O(52)	1.329(7)	1.330(5)	1.332(9)
O(12)–C(12)	1.455(10)	1.438(6)	1.452(11)
O(22)–C(22)	1.434(10)	1.448(7)	1.411(11)
O(32)–C(32)	1.439(9)	1.439(4)	1.432(11)
O(42)–C(42)	1.450(9)	1.432(6)	1.426(11)
O(52)–C(52)	1.447(9)	1.441(7)	1.445(10)

	(2)	(3)	(4)
C(5)–C(1)–C(2)	108.7(8)	108.2(3)	106.3(5)
C(1)–C(2)–C(3)	106.5(5)	109.1(3)	108.6(5)
C(2)–C(3)–C(4)	108.3(5)	107.8(3)	107.6(5)
C(3)–C(4)–C(5)	108.2(5)	108.3(3)	108.2(6)
C(4)–C(5)–C(1)	108.3(5)	106.6(3)	109.2(5)
C(5)–C(1)–C(11)	124.2(7)	126.8(4)	123.1(6)
C(2)–C(1)–C(11)	127.0(6)	125.0(3)	130.3(6)
C(1)–C(2)–C(21)	125.0(5)	124.2(3)	128.7(6)
C(3)–C(2)–C(21)	126.8(5)	126.3(3)	122.7(6)
C(2)–C(3)–C(31)	128.1(6)	124.3(4)	123.7(6)
C(4)–C(3)–C(31)	123.7(6)	127.2(3)	128.4(6)
C(3)–C(4)–C(41)	125.8(5)	125.6(3)	128.5(6)
C(5)–C(4)–C(41)	125.2(6)	125.9(3)	123.3(6)
C(4)–C(5)–C(51)	123.5(6)	126.0(3)	125.3(6)
C(1)–C(5)–C(51)	128.2(5)	124.4(3)	125.4(6)
C(1)–C(11)–O(11)	123.8(6)	127.4(4)	124.9(7)
C(2)–C(21)–O(21)	124.8(6)	123.5(4)	124.2(7)
C(3)–C(31)–O(31)	126.1(6)	124.5(3)	123.6(6)
C(4)–C(41)–O(41)	124.5(5)	125.1(4)	123.1(7)
C(5)–C(51)–O(51)	124.2(5)	125.3(4)	126.5(6)
C(1)–C(11)–O(12)	112.4(5)	110.5(4)	115.5(7)
C(2)–C(21)–O(22)	113.0(5)	112.7(4)	113.6(6)
C(3)–C(31)–O(32)	111.1(6)	112.7(4)	112.3(6)
C(4)–C(41)–O(42)	112.2(6)	110.4(3)	113.6(6)
C(5)–C(51)–O(52)	111.7(5)	112.2(3)	111.0(6)
O(11)–C(11)–O(12)	123.8(5)	122.1(3)	119.6(7)
O(21)–C(21)–O(22)	122.1(6)	123.8(4)	122.1(7)
O(31)–C(31)–O(32)	122.7(5)	122.8(4)	124.1(7)
O(41)–C(41)–O(42)	123.2(6)	124.5(4)	123.3(7)
O(51)–C(51)–O(52)	124.0(6)	122.5(4)	122.5(6)
C(11)–O(12)–C(12)	116.0(6)	115.7(4)	116.0(6)
C(21)–O(22)–C(22)	116.6(5)	114.7(5)	118.1(6)
C(31)–O(32)–C(32)	115.9(6)	116.5(4)	115.7(6)
C(41)–O(42)–C(42)	117.1(6)	116.4(4)	116.4(6)
C(51)–O(52)–C(52)	117.0(5)	115.6(3)	117.0(6)

2.586(7), 2.807(7) Å (Table 2). The silver atom is closer to C(2) but the interaction appears to be weak and insufficient to perturb the planarity of the C_5 ring. It may, however, influence the non-coplanarity of two of the substituent carbon atoms described above. The silver atom is thus unusually five-co-ordinate, with approximate square-pyramidal geometry; the four oxygens are approximately coplanar (σ, 0.36 Å) with the silver atom some 0.76 Å above this plane. The close interaction with C(2) has the effect of generating an infinite polymer of dimers along *b*, and the asymmetry (towards a σ-bonded form) presumably activates the ring carbon towards alkylation. Estimates of the hydrogen atom positions suggest strong hydrogen bonding to nearby O(*n*1) oxygen atoms (Table 5).

(*b*) $[\{Ag[C_5(CO_2Me)_5](PPh_3)\}_2]$ (3). The unit-cell contents (see Figure 2) confirm the stoicheiometry as $Ag[C_5(CO_2Me)_5](PPh_3)$ with one formula unit as the asymmetric unit. The silver atom interacts with both phosphine and $C_5(CO_2Me)_5$ ligands, and in particular with the latter in a manner which leads to bridging about a crystallographic inversion centre, so that a dimer of the type $[(Ph_3P)Ag\{C_5(CO_2Me)_5\}_2Ag(PPh_3)]$ is formed.

The silver atom is essentially four-co-ordinate. One of the bonds is to the triphenylphosphine ligand: Ag–P is 2.397(1) Å, to be compared with 2.35(1) Å in $[Ag\{P(C_6H_4Me\text{-}p)_3\}\{BH_2(pz)_2\}]$ (pz = pyrazolyl), 2.37(9) Å in $[\{AgCl(PPh_3)\}_4]$,[9] 2.42(2) Å in $[\{AgBr(PPh_3)\}_4]$,[9] and 2.48(0) Å (average) in $[Ag(PPh_3)_2]_2[Ni\{S_2C{=}C(CN)_2\}_2]$.[10] The triphenylphosphine ligand geometry shows no unusual features. The $C_5(CO_2Me)_5$ ligand chelates the silver *via* atoms O(11) and O(51) [Ag–O 2.415(3), 2.613(3) Å (Table 2)]. These parameters may be compared with the Ag–O bonds in $[\{Ag(O_2CMe)(PPh_3)\}_4]$, where those to bridging acetate groups range between 2.226(12) and 2.26(1) Å, and in the Ag–O–Ag system are 2.320(7), 2.475(7) Å;[11] Ag–O bonds to the chelating nitrate group in $[Ag(NO_3)L]$ ($L = MeSCH_2CMe_2CH{=}CH_2$) are 2.537(7) and 2.647(10) Å.[12] The fourth bond to silver is an asymmetric interaction with the C(4)–C(5) double bond, with Ag–C bonds of 2.632(4) and 2.472(4) Å. Similar asymmetric Ag–C=C interactions are found in $[Ag(cod)_2]BF_4$ (cod = cyclo-octa-1,5-diene) [2.48(1)—2.52(1) Å],[13] and in the above-mentioned $[Ag(NO_3)L]$ [2.466(7), 2.522(6) Å].[12] The silver approaches almost normal to the C_5 ring plane. There is only a small effect on the ring geometry, however: the C(4)–C(5) bond is marginally longer at 1.421(5) Å, while the C_5 ring remains planar (σ, 0.002 Å). In the C_5 ring C(1)–C(5) is the longest bond as might be expected from earlier studies, and the O–C–O angles are smallest for C(11) and C(51). The dihedral angle for the C(1) carboxylate substituent to the C_5 ring plane is 42.0°, which is rather larger than usual, and may result from the Ag–ring carbon interaction.

(*c*) $[Ag\{C_5(CO_2Me)_5\}(PPh_3)_2]$ (4). This complex is monomeric, the unit-cell contents (see Figure 3) confirming the stoicheiometry $Ag[C_5(CO_2Me)_5](PPh_3)_2$; the monomer comprises the asymmetric unit of the structure. The space group is chiral, as are the molecules when ligand dispositions are taken into account, but it would not be expected, and there is no evidence to suggest, that in solution the chiral perturbations will be other than fluxional.

As in (3), the silver atom is essentially four-co-ordinate. The two tertiary phosphine ligands are attached to silver by slightly longer Ag–P bonds [2.428(2), 2.414(2) Å (Table 2)] than those found in (3). The P–Ag–P angle [136.64(5)°] is considerably

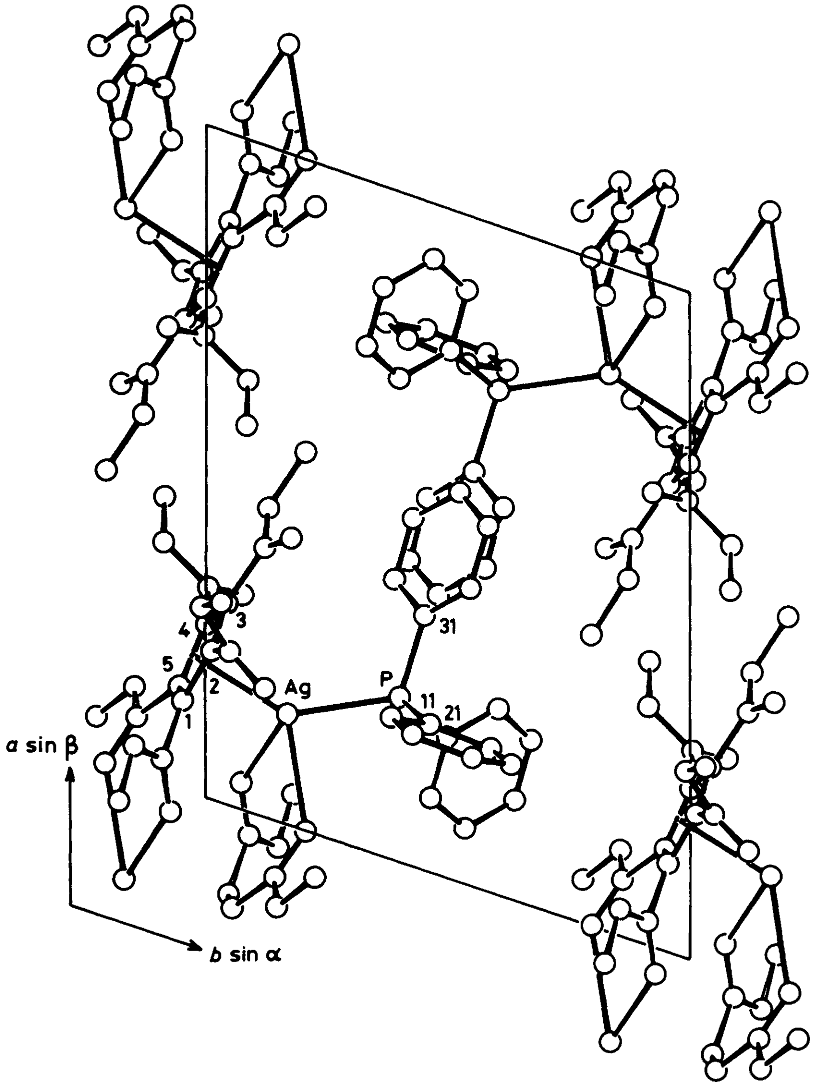


Figure 2. Unit-cell contents of (3) projected down *c*. Key-atom labelling is given

larger than the ideal tetrahedral angle, probably as a result of steric interaction between the two phosphine ligands. We note that in $[Ag(PPh_3)_2]_2[Ni\{S_2C{=}C(CN)_2\}_2]$, which formally contains an ' $[Ag(PPh_3)_2]^+$ ' cation, there is a strong Ag–S interaction between the ' cation ' and ' anion ', with a resulting P–Ag–P angle of 118.5°.[10] As expected, the Ag–P distance becomes shorter as the P–Ag–P angle enlarges.

The other two-co-ordinate sites about the silver are occupied by O(11) and O(51) [Ag–O(11,51) 2.465(4), 2.594(5) Å], the $C_5(CO_2Me)_5$ ligand again behaving as a chelate. Here, the C(5) carboxylate substituent is one of the two that lies pseudo-normal to the C_5 plane, and we note that in this case, in regard to carboxylate 5, and in (3) in regard to carboxylate 4, the longer of the two Ag–O(*n*1) bonds in each case is associated with the carboxylate with the greatest dihedral angle to the C_5 plane. This may be a consequence of the fact that the Ag–O bonds in both (3) and (4) must be quite weak and are insufficient to maintain close coplanarity of both of the chelating carboxylates relative to the C_5 plane, and with O(11) · · · O(51) at the van der Waals distances. Moreover, we now find that C(1)–C(5) in this case is no longer the longest bond of the C_5 ring.

Conclusions

This paper describes the preparation and characterisation of some silver(I) derivatives of the strong organic acid (1). Structural studies of three of these have revealed four-co-ordinate silver atoms chelated by two carboxylate carbonyl groups, with the remaining positions occupied by water [in (2)] or tertiary phosphines [in (3) and (4)], and by a weak asymmetric interaction with a C=C double bond in the C_5 ring in (2) and (3). Both the chelate oxygen, and the olefinic, bonds to silver are weak, as shown by their behaviour in polar solvents: ionisation to symmetrical $[C_5(CO_2Me)_5]^-$ anions and solvated silver cations occurs. However, in solution of (2) there appears to be sufficient interaction to activate the ring carbon towards alkylation, *e.g.* by iodomethane.

Experimental

General experimental details have been described in previous papers in this series. All reactions were run under nitrogen, and were protected from light. Infrared spectra are collected in Table 1.

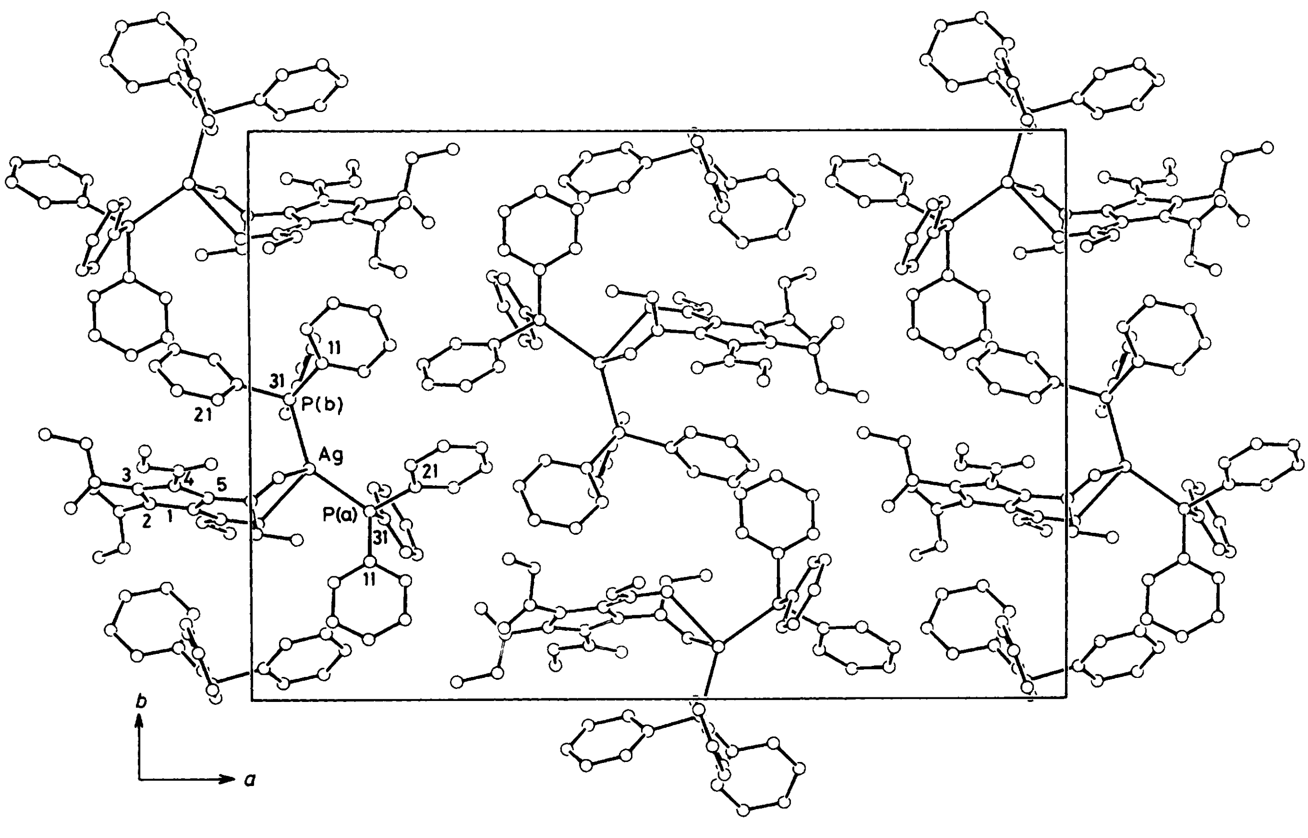


Figure 3. Unit-cell contents of (4) projected down *c*. Key-atom labelling is given

Table 5. Non-hydrogen atom co-ordinates for $[\{Ag[C_5(CO_2Me)_5](OH_2)\}_n]\cdot 1.5nH_2O$ (2)

Atom	*x*	*y*	*z*
Ag	1.003 31(5)	1.012 12(6)	0.266 41(7)
ligand anion			
C(1)	0.740 0(5)	0.963 3(6)	−0.332 3(8)
C(11)	0.687 3(5)	0.835 2(6)	−0.411 9(8)
O(11)	0.734 4(4)	0.764 9(4)	−0.500 9(6)
O(12)	0.584 0(4)	0.809 0(4)	−0.378 5(6)
C(12)	0.523 1(7)	0.693 0(8)	−0.469 5(14)
C(2)	0.799 8(5)	0.992 6(6)	−0.170 1(8)
C(21)	0.799 7(5)	0.907 1(6)	−0.031 4(8)
O(21)	0.828 1(4)	0.940 1(4)	0.122 3(5)
O(22)	0.762 0(4)	0.787 6(4)	−0.087 5(6)
C(22)	0.759 2(9)	0.697 3(7)	0.040 8(12)
C(3)	0.836 8(5)	1.127 5(6)	−0.152 9(8)
C(31)	0.901 7(5)	1.206 3(6)	−0.004 4(8)
O(31)	0.974 2(4)	1.176 2(4)	0.082 5(7)
O(32)	0.874 2(4)	1.319 5(4)	0.017 6(6)
C(32)	0.931 1(8)	1.403 7(7)	0.159 7(10)
C(4)	0.801 1(5)	1.176 1(6)	−0.302 2(8)
C(41)	0.835 0(6)	1.307 0(6)	−0.350 7(8)
O(41)	0.925 8(4)	1.351 1(4)	−0.387 6(6)
O(42)	0.753 5(4)	1.372 4(4)	−0.343 9(7)
C(42)	0.773 8(8)	1.497 1(7)	−0.407 2(12)
C(5)	0.741 4(5)	1.074 7(6)	−0.414 0(8)
C(51)	0.694 1(5)	1.089 8(6)	−0.588 1(8)
O(51)	0.714 0(5)	1.184 1(5)	−0.662 5(6)
O(52)	0.626 5(4)	0.986 0(4)	−0.653 0(6)
C(52)	0.570 9(7)	0.990 9(8)	−0.820 7(10)
Water			
O(0) [a]	0.954 2(4)	0.846 0(4)	0.465 0(6)
O(A) [b]	0.494 1(17)	0.496 7(22)	0.099 9(28)
O(B) [b]	0.574 8(33)	0.357 1(42)	0.002 8(49)
O(C) [b]	0.625 0(25)	0.355 2(31)	0.074 5(46)

[a] Estimated *x*, *y*, *z* values for H(1) and H(2) respectively: 0.879(—), 0.805(—), 0.452(—); 0.998(—), 0.781(—), 0.454(—). Associated hydrogen bonds, H(1) ··· O(11) ($x, y, 1 + z$): 1.8(3) Å, O–H ··· O 160°; H(2) ··· O(41) ($2 - x, 2 - y, \bar{z}$): 1.8(8) Å, O–H ··· O, 169°. [b] Population: 0.5.

Preparation of $Ag[C_5(CO_2Me)_5]$.—A solution of $HC_5(CO_2Me)_5$ (500 mg, 1.4 mmol) in methanol (20 cm^3) was added to a stirred suspension of silver acetate (234 mg, 1.4 mmol) in the same solvent (10 cm^3). After 1 h at ambient temperature (20 °C), filtration and removal of solvent (rotary evaporator) afforded a white solid, which was recrystallised (methanol–diethyl ether, at 0 °C) to give light sensitive and thermally unstable *crystals* of $Ag[C_5(CO_2Me)_5]$, decomp. 150—160 °C, which were stored at −15 °C (Found: C, 39.45; H, 3.50. $C_{15}H_{15}AgO_{10}$ requires C, 38.90; H, 3.25%).

The structure determination (see below) of a sample recrystallised from water indicated that the composition of this material was $Ag[C_5(CO_2Me)_5](OH_2)\cdot 1.5H_2O$.

Preparation of $[\{Ag[C_5(CO_2Me)_5](PPh_3)\}_2]$ (3).—A mixture of $HC_5(CO_2Me)_5$ (500 mg, 1.4 mmol), silver acetate (240 mg,

Table 6. Non-hydrogen atom co-ordinates for $[\{Ag[C_5(CO_2Me)_5](PPh_3)\}_2]$ (3)

Atom	*x*	*y*	*z*
Ag	0.164 05(2)	0.167 23(3)	0.113 09(3)
Ligand anion			
C(1)	0.132 2(3)	−0.046 4(3)	−0.137 9(3)
C(11)	0.035 0(3)	−0.089 3(4)	−0.230 8(3)
O(11)	−0.039 4(2)	−0.073 0(3)	−0.211 7(3)
O(12)	0.039 0(2)	−0.147 6(3)	−0.348 4(3)
C(12)	−0.048 9(4)	−0.178 4(7)	−0.451 7(5)
C(2)	0.220 6(3)	0.011 5(3)	−0.161 5(3)
C(21)	0.228 7(3)	0.049 3(4)	−0.282 1(3)
O(21)	0.190 6(3)	0.121 1(3)	−0.319 9(3)
O(22)	0.280 2(2)	−0.009 6(3)	−0.343 8(3)
C(22)	0.296 8(5)	0.032 0(6)	−0.456 0(5)
C(3)	0.298 8(3)	0.042 3(3)	−0.048 8(3)
C(31)	0.400 7(3)	0.121 5(4)	−0.031 9(4)
O(31)	0.428 0(2)	0.175 3(4)	−0.108 8(3)
O(32)	0.461 5(2)	0.128 9(3)	0.079 1(3)
C(32)	0.563 7(3)	0.205 0(5)	0.103 8(5)
C(4)	0.257 4(3)	0.001 6(3)	0.046 6(3)
C(41)	0.314 3(3)	0.004 7(3)	0.176 7(3)
O(41)	0.319 7(2)	0.078 0(3)	0.275 8(2)
O(42)	0.358 7(2)	−0.086 3(3)	0.166 9(2)
C(42)	0.425 6(4)	−0.084 2(6)	0.282 7(5)
C(5)	0.153 2(3)	−0.054 0(3)	−0.006 6(3)
C(51)	0.085 1(3)	−0.141 1(3)	0.043 9(3)
O(51)	0.000 6(2)	−0.205 8(3)	−0.013 3(3)
O(52)	0.128 4(2)	−0.146 0(3)	0.160 5(3)
C(52)	0.065 1(4)	−0.224 1(5)	0.219 8(5)
Triphenylphosphine ligand			
P	0.246 12(7)	0.397 94(9)	0.162 13(9)
C(11)	0.221 2(3)	0.460 6(4)	0.024 1(3)
C(12)	0.215 7(3)	0.585 3(4)	0.031 5(4)
C(13)	0.201 6(4)	0.628 6(5)	−0.077 1(4)
C(14)	0.191 8(3)	0.546 6(5)	−0.194 4(4)
C(15)	0.196 8(3)	0.422 9(5)	−0.203 7(4)
C(16)	0.211 5(3)	0.379 7(4)	−0.095 3(4)
C(21)	0.210 7(3)	0.496 5(3)	0.287 7(3)
C(22)	0.278 7(3)	0.601 7(4)	0.384 4(4)
C(23)	0.247 9(4)	0.669 6(5)	0.480 6(4)
C(24)	0.150 9(4)	0.634 9(5)	0.479 1(4)
C(25)	0.082 5(4)	0.531 8(5)	0.383 5(5)
C(26)	0.111 9(3)	0.461 9(4)	0.287 3(4)
C(31)	0.380 3(3)	0.448 9(4)	0.219 8(4)
C(32)	0.418 9(3)	0.388 5(4)	0.305 8(4)
C(33)	0.518 6(4)	0.425 0(5)	0.358 6(5)
C(34)	0.581 8(4)	0.522 3(6)	0.326 4(5)
C(35)	0.545 2(4)	0.580 8(6)	0.239 9(6)
C(36)	0.443 8(3)	0.544 1(5)	0.185 2(5)

Table 7. Non-hydrogen atom co-ordinates for $[Ag\{C_5(CO_2Me)_5\}(PPh_3)_2]$ (4)

Atom	*x*	*y*	*z*
Ag	0.072 12(2)	0.407 91(2)	0.439 20(5)
Ligand anion			
C(1)	−0.068 7(2)	0.337 3(3)	0.532 3(6)
C(11)	−0.036 3(2)	0.319 4(3)	0.420 2(8)
O(11)	0.009 3(1)	0.310 8(2)	0.431 0(6)
O(12)	−0.058 1(2)	0.314 1(3)	0.293 5(5)
C(12)	−0.025 3(4)	0.294 7(5)	0.177 7(9)
C(2)	−0.122 6(2)	0.347 1(3)	0.534 4(7)
C(21)	−0.159 2(2)	0.333 3(4)	0.422 1(8)
O(21)	−0.191 0(2)	0.373 7(3)	0.388 6(6)
O(22)	−0.154 1(2)	0.268 5(3)	0.361 7(6)
C(22)	−0.184 8(3)	0.252 2(5)	0.244 9(10)
C(3)	−0.136 4(2)	0.372 6(3)	0.665 7(8)
C(31)	−0.189 5(3)	0.384 7(4)	0.709 4(8)
O(31)	−0.219 1(2)	0.338 9(3)	0.720 0(7)
O(32)	−0.199 5(2)	0.452 6(3)	0.729 2(7)
C(32)	−0.249 5(3)	0.468 6(5)	0.775 4(16)
C(4)	−0.092 0(2)	0.378 5(3)	0.748 4(7)
C(41)	−0.086 8(3)	0.404 5(4)	0.893 5(8)
O(41)	−0.047 1(2)	0.416 7(4)	0.946 8(6)
O(42)	−0.130 1(2)	0.411 6(3)	0.960 2(5)
C(42)	−0.127 9(4)	0.439 7(5)	1.099 5(10)
C(5)	−0.051 4(2)	0.356 9(3)	0.666 2(7)
C(51)	0.001 1(3)	0.351 2(4)	0.715 1(7)
O(51)	0.034 8(2)	0.392 3(3)	0.689 5(5)
O(52)	0.007 5(2)	0.293 2(3)	0.795 0(6)
C(52)	0.056 9(3)	0.282 5(6)	0.855 2(10)
Triphenylphosphine ligand a			
P	0.146 05(6)	0.332 49(8)	0.414 74(19)
C(11)	0.145 4(3)	0.243 9(3)	0.491 7(7)
C(12)	0.101 4(3)	0.207 2(4)	0.504 6(9)
C(13)	0.099 4(3)	0.138 3(4)	0.559 5(12)
C(14)	0.143 3(4)	0.107 0(4)	0.601 6(9)
C(15)	0.188 0(3)	0.141 7(4)	0.590 2(11)
C(16)	0.188 6(3)	0.209 7(4)	0.536 1(10)
C(21)	0.201 3(3)	0.375 8(4)	0.489 3(7)
C(22)	0.248 2(3)	0.374 0(5)	0.428 5(10)
C(23)	0.287 9(3)	0.409 9(7)	0.490 4(13)
C(24)	0.282 1(5)	0.444 3(6)	0.610 4(15)
C(25)	0.236 1(5)	0.447 3(5)	0.676 1(12)
C(26)	0.195 9(3)	0.413 6(5)	0.612 8(9)
C(31)	0.163 2(2)	0.319 4(4)	0.231 2(7)
C(32)	0.150 6(3)	0.373 4(4)	0.135 6(8)
C(33)	0.164 2(3)	0.368 5(5)	−0.004 3(8)
C(34)	0.189 9(3)	0.308 4(5)	−0.049 7(9)
C(35)	0.202 8(3)	0.256 0(4)	0.042 6(10)
C(36)	0.189 4(3)	0.260 2(4)	0.181 8(8)
Triphenylphosphine ligand b			
P	0.049 29(6)	0.529 85(9)	0.382 09(19)
C(11)	0.088 7(2)	0.592 5(3)	0.480 2(6)
C(12)	0.070 2(3)	0.652 4(3)	0.548 2(7)
C(13)	0.102 8(3)	0.697 8(4)	0.620 8(8)
C(14)	0.153 2(3)	0.683 6(4)	0.625 3(9)
C(15)	0.171 5(3)	0.624 0(4)	0.558 3(9)
C(16)	0.139 6(3)	0.578 5(4)	0.488 2(8)
C(21)	−0.015 2(2)	0.556 3(3)	0.414 9(8)
C(22)	−0.042 0(3)	0.599 4(5)	0.327 8(9)
C(23)	−0.091 3(3)	0.617 1(6)	0.355 7(12)
C(24)	−0.114 4(3)	0.588 2(6)	0.473 6(13)
C(25)	−0.088 4(3)	0.545 7(4)	0.562 3(13)
C(26)	−0.038 7(3)	0.529 6(4)	0.533 8(10)
C(31)	0.059 1(2)	0.552 6(3)	0.197 9(7)
C(32)	0.077 0(3)	0.617 8(3)	0.154 2(7)
C(33)	0.079 4(4)	0.634 2(4)	0.012 1(8)
C(34)	0.064 7(3)	0.583 6(5)	−0.085 4(7)
C(35)	0.047 8(3)	0.518 8(4)	−0.042 8(8)
C(36)	0.044 0(3)	0.504 5(4)	0.098 5(7)

1.44 mmol), and triphenylphosphine (390 mg, 1.5 mmol) in methanol (50 cm^3) was stirred for 20 h at ambient temperature. Filtration and evaporation gave a white solid, which was recrystallised (MeOH) to give white rod-like *crystals* of $Ag[C_5(CO_2Me)_5](PPh_3)$ (650 mg, 65%), m.p. 198—200 °C, which were light-sensitive and thermally unstable (Found: C, 54.90; H, 4.00. $C_{33}H_{30}AgO_{10}P$ requires C, 54.65; H, 4.15%). ^1H N.m.r.: $\delta(CDCl_3)$ 3.75 (s, 15 H, OMe), 7.35, 7.45 (both m, 15 H, Ph). ^{13}C N.m.r.: $\delta(CDCl_3)$ 52.0 (s, OMe), 117.9 (s, ring C), 129.0—134.4 (m, Ph), 168.8 (s, CO_2Me). Conductivity (acetone) 56 ohm^{-1} cm^2 mol^{-1}.

Preparation of $[Ag\{C_5(CO_2Me)_5\}(PPh_3)_2]$ (4).—A similar reaction to the above used silver acetate (120 mg, 0.7 mmol), $HC_5(CO_2Me)_5$ (250 mg, 0.7 mmol), and PPh_3 (380 mg, 1.5 mmol) in methanol (30 cm^3). After 18 h, evaporation and washing with boiling light petroleum (b.p. 40—60 °C; 2 × 50 cm^3) gave a white solid, which was recrystallised to give white *rods* of complex (4) (560 mg, 81%), darkening and melting at 213—217 °C (Found: C, 62.20; H, 4.50. $C_{51}H_{45}AgO_{10}P_2$ requires C, 62.00; H, 4.60%). ^1H N.m.r.: $\delta(CDCl_3)$ 3.58 (s, 15 H, OMe), 7.38 (m, 30 H, Ph). ^{13}C N.m.r.: $\delta(CDCl_3)$ 51.1 (s, OMe), 117.8 (s, ring C), 128.9—134.0 (m, Ph), 168.5 (s, CO_2Me). Conductivity (acetone) 86 ohm^{-1} cm^2 mol^{-1}.

Preparation of $[Ag\{C_5(CO_2Me)_5\}(dppe)]$ (5).—A mixture of $HC_5(CO_2Me)_5$ (250 mg, 0.7 mmol), silver acetate (120 mg, 0.72 mmol), and 1,2-bis(diphenylphosphino)ethane (dppe) (300 mg, 0.75 mmol) in methanol (30 cm^3) was stirred at room temperature for 18 h. After this time, the white solid was filtered off, washed with MeOH (2 × 5 cm^3) and diethyl ether (2 × 5 cm^3) and dried. Evaporation of the filtrate to *ca.* 15 cm^3 and cooling afforded a second crop (total yield 560 mg, 93%). Recrystallisation from methanol afforded pure complex (5) as a white *powder*, m.p. 194—197 °C (darkens at 180 °C) (Found: C, 56.20; H, 4.50. $C_{41}H_{39}AgO_{10}P_2$ requires C, 57.15; H, 4.55%). ^1H N.m.r.: $\delta(CDCl_3)$ 1.72 (s br, 4 H, CH_2), 3.68 (s, 15 H, OMe), 7.30 (s br, 20 H, Ph). ^{13}C N.m.r.: $\delta(CDCl_3)$ 51.6 (s, OMe), 118.0 (s, ring C), 129.6—132.9 (m, Ph), 168.9 (s, CO_2Me). Conductivity (acetone) 84.7 ohm^{-1} cm^2 mol^{-1}.

Preparation of $[Ag\{C_5(CO_2Me)_5\}(tppme)]$ (6).—A similar reaction using $HC_5(CO_2Me)_5$ (130 mg, 0.37 mmol), silver acetate (60 mg, 0.36 mmol), and 1,1,1-tris(diphenylphosphinomethyl)ethane (tppme) (220 mg, 0.35 mmol) afforded a white solid which was recrystallised [methanol-diethyl ether (1:1)] to give complex (6) as a white *powder* (270 mg, 70%), m.p. 147—153 °C (Found: C, 61.15; H, 5.10. $C_{56}H_{54}AgO_{10}P_3$ requires C, 61.85; H, 5.00%). ^1H N.m.r.: $\delta(CDCl_3)$ 1.31 (s, 3 H, Me), 2.57, (s br, 6 H, CH_2), 3.60 (s, 15 H, OMe), 7.11 (s br, 30 H, Ph). Conductivity (acetone) 70.7 ohm^{-1} cm^2 mol^{-1}.

Reaction between $Ag[C_5(CO_2Me)_5]$ *and Iodomethane.*—Iodomethane (3 cm^3, excess) in methanol (15 cm^3) was added to a solution of $Ag[C_5(CO_2Me)_5]$ [prepared *in situ* from silver acetate (120 mg, 0.72 mmol) and $HC_5(CO_2Me)_5$ (250 mg, 0.7 mmol) in methanol (20 cm^3)]; an olive green precipitate formed immediately. After stirring at room temperature for 6 h, the solution was filtered, and the solid washed with methanol (2 × 10 cm^3). The combined filtrates were evaporated to give $MeC_5(CO_2Me)_5$ (240 mg, 93%) as a white solid; recrystallisation (methanol) afforded clear colourless crystals, m.p. 99—100 °C (lit.,[6] 101—102 °C). ^1H N.m.r.: $\delta(CDCl_3)$ 1.70 (s, 3 H, Me), 3.67 (s, 3 H, OMe), 3.83, 3.88 (both s, 6 H, OMe).

Crystallography.—General details are given in ref. 2. Atomic parameters for complexes (2), (3), and (4) are shown in Tables 5, 6, and 7 respectively. Phosphorus environments in (3) and (4) are shown in Table 8.

Table 8. Phosphorus environments in complexes (3) and (4)

Atom	(3)	(4)/a	(4)/b
P-C(11)	1.809(4)	1.805(7)	1.826(6)
P-C(21)	1.828(4)	1.820(7)	1.811(7)
P-C(31)	1.819(4)	1.820(7)	1.821(7)
Ag-P-C(11)	112.6(1)	118.8(2)	110.1(2)
Ag-P-C(21)	113.9(1)	111.1(2)	117.1(2)
Ag-P-C(31)	114.9(1)	111.9(2)	113.6(2)
C(11)-P-C(21)	105.4(2)	104.8(3)	106.3(3)
C(11)-P-C(31)	105.1(2)	105.6(3)	105.0(3)
C(21)-P-C(31)	104.0(2)	103.3(3)	103.8(3)

Crystal data. $[\{Ag[C_5(CO_2Me)_5](OH_2)\}_n]\cdot 1.5nH_2O$ (2), $(C_{15}H_{20}AgO_{12\cdot 5})_n$, $M = 508.2$, Triclinic, space group $P\bar{1}(C_i^1$, no. 2), $a = 12.45(1)$, $b = 10.776(9)$, $c = 7.624(8)$ Å, $\alpha = 94.91(7)$, $\beta = 91.50(7)$, $\gamma = 99.90(7)°$, $U = 1\,003(2)$ Å^3, $D_m = 1.68(1)$, $Z = 2$, $D_c = 1.68$ g cm^{-3}, $F(000) = 514$, specimen size 0.04 × 0.07 × 0.37 mm, $\mu(\text{Mo-}K_\alpha) = 10.1$ cm^{-1}, $\lambda = 0.710\,69$ Å, $2\theta_{max.} = 50°$, $N = 3\,554$, $N_o = 2\,059$; $R,R',S = 0.041, 0.049, 1.25$.

$[\{Ag[C_5(CO_2Me)_5](PPh_3)\}_2]$ (3), $(C_{33}H_{30}AgO_{10}P)_2$, $M = 725.5$, Triclinic, space group $P\bar{1}(C_i^1$, no. 2), $a = 14.595(6)$, $b = 11.043(4)$, $c = 11.024(5)$ Å, $\alpha = 101.91(3)$, $\beta = 101.79(3)$, $\gamma = 105.56(3)°$, $U = 1\,610(1)$ Å^3, $Z = 2$, $D_c = 1.50$ g cm^{-3}, $F(000) = 740$, specimen size 0.40 × 0.24 × 0.08 mm, $\mu(\text{Mo-}K_\alpha)$ 6.9 cm^{-1}, $\lambda = 0.710\,69$ Å, $2\theta_{max.} = 50°$, $N = 5\,715$, $N_o = 4\,446$; $R,R',S = 0.039, 0.049, 1.42$.

$[Ag\{C_5(CO_2Me)_5\}(PPh_3)_2]$ (4), $C_{51}H_{45}AgO_{10}P_2$, $M = 987.7$, Orthorhombic, space group $P2_12_12_1$ (D_2^4, no. 19), $a = 26.592(8)$, $b = 18.638(6)$, $c = 9.507(2)$ Å, $U = 4\,712(2)$ Å^3, $D_m = 1.38(1)$, $Z = 4$, $D_c = 1.39$ g cm^{-3}, $F(000) = 2\,032$, specimen size 0.13 × 0.22 × 0.38 mm, $\mu(\text{Mo-}K_\alpha) = 5.2$ cm^{-1}, $\lambda = 0.710\,69$ Å, $2\theta_{max.} = 50°$, $N = 4\,679$, $N_o = 3\,148$; $R,R',S = 0.035, 0.039, 1.06$.

Abnormal features. The specimen of (2) was mounted in a capillary. All data for compounds (2)—(4) were corrected for absorption (analytical correction).

In the phosphine ligands, ring carbon atoms are numbered $C(n1)$—$C(n6)$ for ring n; $C(n1)$ is attached to phosphorus. The $C_5(CO_2Me)_5$ ligand numbering follows that employed previously [1-3] with ring atoms designated $C(n)$, $n = 1$—5 and attached carbon and oxygen atoms designated $C,O(n1,n2)$ in order from the point of attachment. For clarity in presentation of the Figures in this paper and following papers, only the numbering of the $C_5(CO_2Me)_5$ ring atoms is shown, together with $C(n1)$ of the phosphine phenyl rings.

Acknowledgements

We gratefully acknowledge support of this work by grants from the Australian Research Grants Committee.

References

1 Part 3, M. I. Bruce, J. K. Walton, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1982, 2227.

2 Part 1, M. I. Bruce, J. K. Walton, M. L. Williams, S. R. Hall, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1982, 2209.

3 Part 2, M. I. Bruce, J. K. Walton, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1982, 2221.

4 M. I. Bruce, B. W. Skelton, R. C. Wallis, J. K. Walton, A. H. White, and M. L. Williams, *J. Chem. Soc., Chem. Commun.*, 1981, 428.

5 M. I. Bruce, J. R. Rodgers, and J. K. Walton, *J. Chem. Soc., Chem. Commun.*, 1981, 1253.

6 E. LeGoff and R. B. LaCount, *J. Org. Chem.*, 1964, **29**, 423; P. Schmidt, R. W. Hoffmann, and J. Backes, *Angew. Chem.*, 1972, **84**, 534; *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 513.

7 G. Wulfsberg and R. West, *J. Am. Chem. Soc.*, 1972, **94**, 6069.

8 M. I. Bruce, J. D. Walsh, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1981, 956.

9 M. R. Churchill, J. Donahue, and F. J. Rotella, *Inorg. Chem.*, 1976, **15**, 2752.

10 D. Coucouvanis, N. C. Baenziger, and S. M. Johnson, *Inorg. Chem.*, 1974, **13**, 1191.

11 E. T. Blues, M. G. B. Drew, and B. Femi-Onadeko, *Acta Crystallogr., Sect. B*, 1977, **33**, 3965.

12 E. C. Alyea, G. Ferguson, A. McAlees, R. McCrindle, R. Myers, P. Y. Siew, and S. A. Dias, *J. Chem. Soc., Dalton Trans.*, 1981, 481.

13 A. Albinati, S. V. Meille, and G. Carturan, *J. Organomet. Chem.*, 1979, **182**, 269.

Received 23*rd July* 1982; *Paper* 2/1262