Synthesis of Pentafluorophenyl(ylide)silver(I) Complexes: *X*-Ray Structures of two Modifications of $[Ag(C_6F_5)(CH_2PPh_3)]$ *

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Monomeric silver ylide complexes $[Ag(C_6F_5)(CH_2ER_3)]$ ($ER_3 = PPh_3$, PPh_2Me, $PPhMe_2$, or $AsPh_3$) can be prepared by the reaction of $Ag(CF_3CO_2)$ with $Li(C_6F_5)$ and $[ER_3Me][CF_3CO_2]$. The free ylides CH_2PPh_3, CH_2PPh_2Me, or $CH(CO_2Me)PPh_3$ react with $Ag(C_6F_5)$ or $AgClO_4$ to afford $[Ag(C_6F_5)(ylide)]$ or $[Ag(CH_2PPh_3)_2]ClO_4$ respectively. Several novel ylide-transfer reactions from silver ylides to other silver or gold centres are reported. The structures of two forms of $[Ag(C_6F_5)(CH_2PPh_3)]$ have been established. The molecules differ mainly in the orientation of one phenyl ring. The C_6F_5 groups are highly distorted at the *ipso* carbon [C–C–C 113.1(5) and 112.5(5)°].

Few monomeric silver complexes containing ylide ligands [AgCl(ylide)] [ylide = CH_2PPh_3 [1] or $C(PPh_3)_2$ [2]] and $[Ag(ylide)_2]Cl$ [ylide = CH_2PPh_3, $CH(Me)PPh_3$, $CH(Pr^i)PPh_3$,[3] or $CH(SiMe_3)PMe_3$ [4]] have been described. They were all prepared by the reaction of AgCl with the free ylide.

In this paper we describe the preparation of $[Ag(C_6F_5)(ylide)]$ [ylide = CH_2PPh_3, CH_2PPh_2Me, CH_2PPhMe_2, CH_2AsPh_3, or $CH(CO_2Me)PPh_3$] and their ylide-transfer reactions with other silver or gold compounds. Some of us recently[5] reported the first observed ylide-transfer reactions (between gold centres), the scope of which has now been extended. We also report the crystal structure determination of $[Ag(C_6F_5)(CH_2PPh_3)]$.

Results and Discussion

When $[ER_3Me][CF_3CO_2]$ [$ER_3 = PPh_3$, PPh_2Me, $PPhMe_2$, or $AsPh_3$] is added to diethyl ether solutions obtained by mixing at −78 °C freshly prepared $Li(C_6F_5)$ with $Ag(CF_3CO_2)$ (3:1 ratio) and stirring for 1 h the solutions turn yellow-orange. On warming the colour slowly disappears and the solutions are colourless at room temperature. From these solutions neutral ylide complexes can be isolated [equation (1); ER_3 =

$$Ag(CF_3CO_2) + 2Li(C_6F_5) + [ER_3Me][CF_3CO_2] \longrightarrow 2Li(CF_3CO_2) + C_6F_5H + [Ag(C_6F_5)(CH_2ER_3)] \quad (1)$$

PPh_3 (**1**), PPh_2Me (**2**), $PPhMe_2$ (**3**), or $AsPh_3$ (**4**)]. We propose that this process consists of several steps. (*a*) Formation of $[Ag(C_6F_5)_2]^-$, in agreement with previous observations on similar reactions forming the corresponding NBu_4^+ [6] or $[N(PPh_3)_2]^+$ [7] salts. (*b*) Further reaction of the excess of $Li(C_6F_5)$ with the phosphonium or arsonium salt, to afford the corresponding free ylide [equation (2)]. This is supported by the

$$[ER_3Me][CF_3CO_2] + Li(C_6F_5) \longrightarrow CH_2ER_3 + Li(CF_3CO_2) + C_6F_5H \quad (2)$$

following observation: if the process is carried out as described above [equation (1)] but the excess of $Li(C_6F_5)$ is destroyed by hydrolysis before the addition of $[AsPh_3Me][CF_3CO_2]$, the ionic complex (**5**) is obtained [equation (3)]. With

$$Ag(CF_3CO_2) + 2Li(C_6F_5) + [AsPh_3Me][CF_3CO_2] \longrightarrow 2Li(CF_3CO_2) + \underset{(\mathbf{5})}{[AsPh_3Me][Ag(C_6F_5)_2]} \quad (3)$$

$[ER_3Me][CF_3CO_2]$ ($ER_3 = PPh_2Me$ or $PPhMe_2$) non-crystallizable oils are obtained; their i.r. spectra, however, are as expected for $[ER_3Me][Ag(C_6F_5)_2]$. (*c*) The free ylide [equation (2)] displaces one C_6F_5 group from $[Ag(C_6F_5)_2]^-$ [equation (4)]. To confirm this, we have treated free CH_2PPh_3 (obtained

$$Li[Ag(C_6F_5)_2] + CH_2ER_3 \longrightarrow Li(C_6F_5) + [Ag(C_6F_5)(CH_2ER_3)] \quad (4)$$

by reaction of $[PPh_3Me]ClO_4$ with LiBu) with diethyl ether suspensions of $[NBu_4][Ag(C_6F_5)_2]$. One C_6F_5 group is indeed displaced and the ylide complex (**1**) can be isolated.

Reaction of the diarylargentate (**5**) with NaH affords complex (**4**) [equation (5)] a process previously used to synthesize (pentafluorophenyl)(ylide)gold complexes.[8]

$$[AsPh_3Me][Ag(C_6F_5)_2] + NaH \longrightarrow [Ag(C_6F_5)(CH_2AsPh_3)] + Na(C_6F_5) + H_2 \quad (5)$$

Complexes (**1**)—(**4**) are air- and moisture-stable white solids at room temperature, though sensitive to light. Their dichloromethane or chloroform solutions decompose with precipitation of metallic silver. The conductivity of their acetone solutions increases slowly and reaches (after 3 h) values corresponding to 1:1 electrolytes, but no precipitation is observed. The i.r. spectra (Table 1) show an intense absorption at 594—543 cm^{-1} which can be assigned to ν(Ag–C), by analogy to the gold complexes.[8] In the ^1H n.m.r. spectra the $Ag-CH_2-E$ group resonates as a doublet of doublets [(**1**)], pseudo-triplet [(**2**)], or doublet [(**3**) and (**4**)] at 1.36—0.78 p.p.m. (Table 1).

Recrystallization of $[Ag(C_6F_5)(CH_2PPh_3)]$ from several solvents affords two types of crystals: square prisms and plates (**A**) or hexagonal prisms (**B**) whose i.r. spectra (Nujol mulls) differ, principally in the 900—800 cm^{-1} region. Crystals (**A**) give

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* Pentafluorophenyl(triphenylphosphoniomethanide)silver(I).

Supplementary data available: complete bond lengths and angles, thermal parameters, H-atom co-ordinates, and structure factors are available from the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2, W. Germany, by quoting the reference number CSD 52419 and a full literature citation.

Table 1. Analytical data for the complexes

Complex	Yield (%)	Analysis (%)[a]		M.p. (°C)	ν(Ag–C) (cm^{-1})	^{1}H N.m.r.[b]	^{31}P N.m.r.[c]
		C	H				
(**1**) $[Ag(C_6F_5)(CH_2PPh_3)]$	83[d]	54.6	3.2	139	586, 575	1.23	37.90
		(54.5)	(3.1)	(decomp.)		(12.0, 10.3)	(8.4)
(**2**) $[Ag(C_6F_5)(CH_2PPh_2Me)]$	81[d]	48.9	3.15	81	594	0.97	28.67
		(49.1)	(3.1)	(decomp.)		(8.2, 8.2)	(6.5)
(**3**) $[Ag(C_6F_5)(CH_2PPhMe_2)]$	60[d]	42.05	3.0	109	580	0.78	25.28
		(42.2)	(3.1)	(decomp.)		(12.7)	(8.6)
(**4**) $[Ag(C_6F_5)(CH_2AsPh_3)]$	70[d]	50.6	2.7	160	543	1.36	
		(50.45)	(2.9)	(decomp.)		(5.4)	
(**5**) $[AsPh_3Me][Ag(C_6F_5)_2]$	70	48.1	2.4	82			
		(48.8)	(2.4)	(decomp.)			
(**6**) $[Ag(C_6F_5)\{CH(CO_2Me)PPh_3\}]$	87	53.2	3.2	110			25.55
		(53.2)	(3.1)	(decomp.)			
(**7**) $[Ag(CH_2PPh_3)_2]ClO_4$	82	59.7	4.25		590, 534	1.10	33.8
		(60.1)	(4.5)			(11.6, 11.6)	(9.8)

[a] Calculated values are given in parentheses. [b] Values for δ(CH_2) with *J*(PH) and *J*(AgH)/Hz in parentheses. [c] δ Values with *J*(AgP)/Hz in parentheses. [d] From reaction (1).

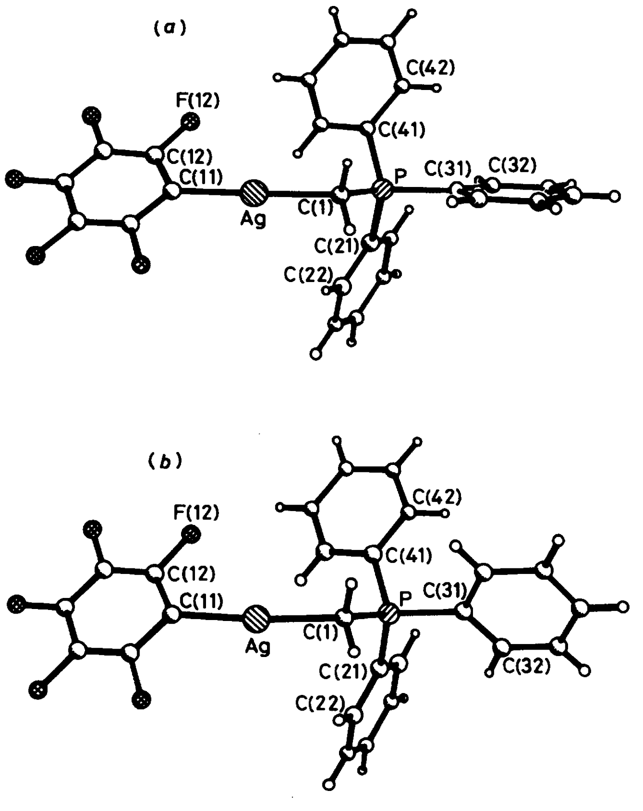

Figure 1. Structures of both modifications of compound (**1**) in the crystal: (*a*) triclinic form, (*b*) monoclinic form. Radii are arbitrary

two bands at 870s and 835s cm^{-1}, whilst (**B**) show bands at 890s, 848m, 842m, and 828s cm^{-1}. A specimen of each form has been studied by single-crystal *X*-ray crystallography (see Figure 1): (**A**) are triclinic, (**B**) monoclinic.

The two modifications display very similar molecular structures; the only major difference is in the orientation of the phenyl ring C(31)—C(36) [torsion angle C(1)–P–C(31)–C(32) −177.8 and +126.5° respectively for the triclinic and monoclinic forms]. The co-ordination at silver is linear [178.2(2) and 175.4(3)°]. (Attempts to increase the co-ordination number by adding pyridine or 2,2′-bipyridyl failed, unchanged starting materials being recovered.) The Ag–C(1) bond lengths are 2.144(5) and 2.131(6) Å and the angles Ag–C(1)–P 112.2(3) and 115.0(3)°; the latter difference is statistically significant. A notable feature of both structures is the distortion of the C_6F_5 rings at the *ipso* carbon; the angles C(12)–C(11)–C(16) are as low as 113.1(5) and 112.5(5)°. It appears to be a general property of the M–C_6F_5 moiety that this angle is well below 120°, although we have only studied compounds with M = Au, Pd, or Pt; as far as we know, (**1**) is the first silver ylide complex and also the first pentafluorophenylsilver complex to be crystallographically characterized. The molecular packing of both modifications in the crystal is shown in Figure 2.

The ionic complex (**5**) is a white solid. In acetone solution it shows the expected conductivity (Λ_M = 108 ohm^{-1} cm^2 mol^{-1}, in 5 × 10^{-4} mol dm^{-3} solution) for a 1:1 electrolyte. Its ^{1}H n.m.r. spectrum shows a signal (methyl group) at 2.72 p.p.m.

Complexes (**1**) and (**2**) can also be obtained by addition of free ylide to diethyl ether solutions of $Ag(C_6F_5)$, though in lower yields (60 and 30% respectively) even if an excess of ylide (2.5:1 ratio) is used.

Addition of $CH(CO_2Me)PPh_3$ to $Ag(C_6F_5)$ gives $[Ag(C_6F_5)\{CH(CO_2Me)PPh_3\}]$ (**6**), an air- and moisture-stable white solid at room temperature, albeit sensitive to light. Its i.r. spectrum shows ν(CO) at 1 656vs cm^{-1}. The ^{1}H n.m.r. spectrum shows a singlet at 3.59 p.p.m. (OMe) and a doublet at 3.55 p.p.m. [CH, *J*(PH) or *J*(AgH) = 2.6 Hz].

The (1:2) reaction between $AgClO_4$ and CH_2PPh_2 in tetrahydrofuran solution causes precipitation of $[Ag(CH_2PPh_3)_2]ClO_4$ (**7**). It is a white solid, unstable at room temperature, which can be stored for months at −20 °C. In dichloromethane or chloroform solution metallic silver slowly precipitates. The i.r. spectrum of this compound shows two bands at 1 100s, br and 620m cm^{-1} from the ClO_4^- anion.[9] It reacts with equimolar amounts of $[NBu_4][Ag(C_6F_5)_2]$ with ylide transfer [equation (6)] to give the neutral complex (**1**).

$$[NBu_4][Ag(C_6F_5)_2] + [Ag(CH_2PPh_3)_2]ClO_4 \longrightarrow [NBu_4]ClO_4 + 2[Ag(C_6F_5)(CH_2PPh_3)] \quad (6)$$

This is the first ylide-transfer reaction observed between two silver centres. Other similar reactions involving ylide transfer (*a*) from a silver to another silver centre [equation (7)] and (*b*) from

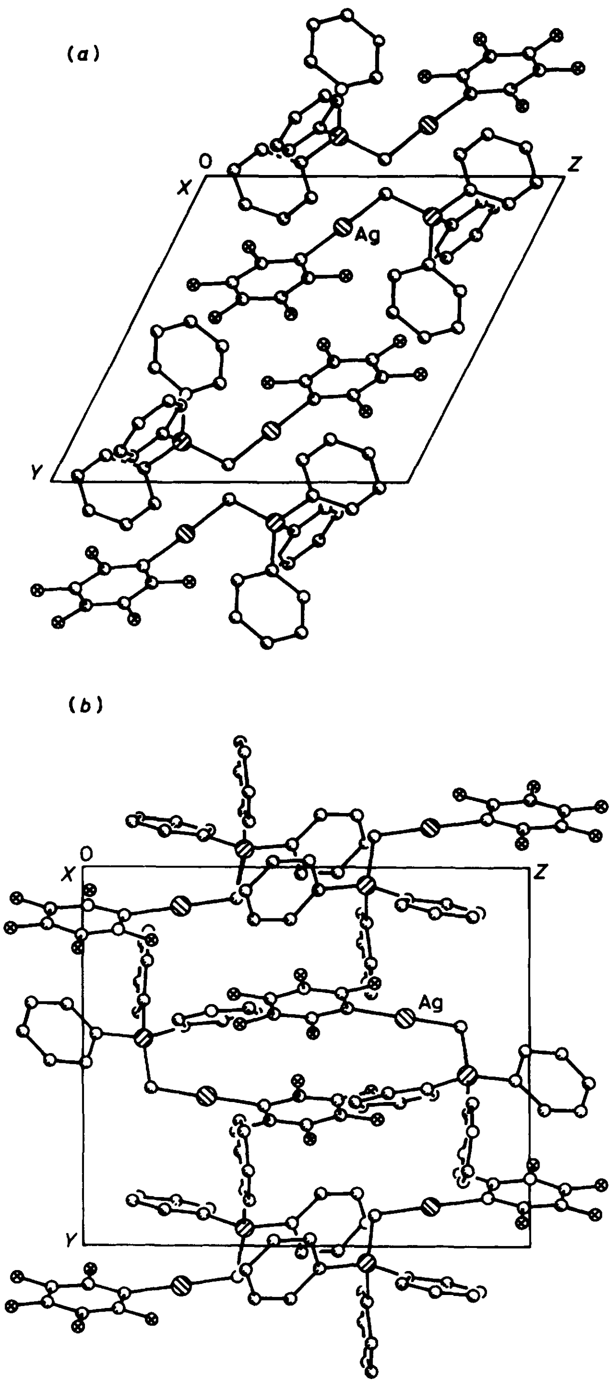

Figure 2. Packing diagrams of both modifications of compound (1): (*a*) triclinic form, (*b*) monoclinic form. Hydrogen atoms are omitted. Both projections are along *x*. The Ag atom of the reference molecule is labelled

a silver to a gold centre [equation (8)] have also been established (see Experimental section).

$$2[Ag(C_6F_5)(CH_2PPh_3)] + AgClO_4 \longrightarrow 2Ag(C_6F_5) + [Ag(CH_2PPh_3)_2]ClO_4 \quad (7)$$

$$[Ag(C_6F_5)(CH_2PPh_3)] + [AuCl(PPh_3)] \longrightarrow [Au(C_6F_5)(CH_2PPh_3)] + [AgCl(PPh_3)] \quad (8)$$

Experimental

The instrumentation and general experimental technique were as described earlier.[8,10] Phosphorus-31 n.m.r. spectra were recorded on a Varian XL-200 apparatus (in $CDCl_3$ solution, H_3PO_4 as external reference). Yields, melting points, C and H analyses, and some other relevant i.r. and n.m.r. data for the novel complexes are listed in Table 1.

Preparation of the Complexes.—$[Ag(C_6F_5)(CH_2ER_3)]$ [ER_3 = PPh_3 (**1**), PPh_2Me (**2**), $PPhMe_2$ (**3**), or $AsPh_3$ (**4**)]. The following procedures were used.

(*a*) To a diethyl ether solution (45 cm^3) of $Li(C_6F_5)$ (9 mmol)[11] at −78 °C was added $Ag(CF_3CO_2)$ (0.663 g, 3 mmol) and the mixture was stirred for 60 min under a nitrogen atmosphere. Then $[ER_3Me][CF_3CO_2]$ (4 mmol) was added [ER_3 = PPh_3 (1.561 g), PPh_2Me (1.313 g), $PPhMe_2$ (1.065 g), or $AsPh_3$ (1.737 g)], stirring was continued for 10 min, and the mixture allowed to warm to room temperature (*ca.* 60 min). Complexes (**1**), (**3**), and (**4**) precipitated and were filtered off, washed with water (3 × 5 cm^3), and dissolved in diethyl ether (130 cm^3). The solutions were filtered through a (0.5-cm thick) layer of anhydrous $MgSO_4$ and evaporated to *ca.* 15 cm^3. Upon addition of n-hexane (20 cm^3), complexes (**1**) (83), (**3**) (60), and (**4**) (70% yield) precipitated as white solids.

Complex (**2**) is more soluble. The solution was filtered to remove the excess of phosphonium salt and concentrated to *ca.* 10 cm^3. Addition of n-hexane (20 cm^3) gave (**2**) as a white solid, which was recrystallized as above.

(*b*) To a CH_2PPh_3 solution [prepared by reaction between $[PPh_3Me]ClO_4$ (0.151 g, 0.4 mmol) and LiBu (0.4 mmol) in diethyl ether (20 cm^3)] was added $[NBu_4][Ag(C_6F_5)_2]$[6] (0.240 g, 0.35 mmol) and the mixture was stirred under a nitrogen atmosphere for 5 h. Thereafter, the solution was exposed to air and diethyl ether (30 cm^3) was added, then the solution was filtered and evaporated to dryness. The residue was washed with water (3 × 5 cm^3) and extracted with diethyl ether (40 cm^3). After filtering through a (1.0-cm thick) layer of anhydrous $MgSO_4$, the solution was evaporated to *ca.* 10 cm^3. Upon addition of n-hexane (20 cm^3) complex (**1**) was isolated (45% yield).

(*c*) To a diethyl ether suspension (15 cm^3) of NaH (0.2 g, 20% in paraffin) was added complex (**5**) (0.229 g, 0.3 mmol). The mixture was stirred at room temperature and under a nitrogen atmosphere for 1 h. The excess of NaH was filtered off and the solution was evaporated to *ca.* 5 cm^3. Addition of n-hexane gave complex (**4**) (80% yield).

(*d*) To a diethyl ether solution (15 cm^3) of $Ag(C_6F_5)$[6] (0.3 mmol) was added a CH_2PR_3 solution {prepared by treating in diethyl ether (20 cm^3) $[PPh_3Me]ClO_4$ (0.301 g, 0.8 mmol) or, respectively, $[PPh_2Me_2]ClO_4$ (0.252 g, 0.8 mmol) with LiBu (0.8 mmol)} and the mixture was stirred for 1 h at room temperature and under a nitrogen atmosphere. Thereafter, the mixture was exposed to air and diethyl ether (20 cm^3) was added. The mixture was filtered through a (0.5-cm thick) layer of anhydrous $MgSO_4$ and the filtrate was evaporated to dryness. The residue was washed (3 × 5 cm^3) and dissolved in diethyl ether (50 cm^3), and the solution was filtered through (0.5 cm) $MgSO_4$ and evaporated to *ca.* 5 cm^3. Upon addition of n-hexane (30 cm^3) complexes (**1**) (60% yield) and (**2**) (30% yield) were isolated.

(*e*) To a diethyl ether suspension (50 cm^3) of $[NBu_4][Ag(C_6F_5)_2]$[6] (0.171 g, 0.25 mmol) was added complex (**7**) 0.190 g, 0.25 mmol) and the mixture was stirred at room temperature for 8 h. The precipitated $[NBu_4]ClO_4$ was filtered off and the solution was concentrated to *ca.* 5 cm^3. Addition of n-hexane (10 cm^3) caused precipitation of complex (**1**) (85% yield).

$[AsPh_3Me][Ag(C_6F_5)_2]$ (**5**). To a diethyl ether solution (40 cm^3) of $Li(C_6F_5)$[11] (9 mmol, −78 °C) was added $Ag(CF_3CO_2)$

(0.663 g, 3 mmol). The mixture was stirred at −78 °C for 60 min then allowed to warm to 0 °C. Three drops of water were added and the mixture stirred during 15 min. The salt [AsPh$_3$Me][CF$_3$CO$_2$] was added (1.737 g, 4 mmol) and the mixture was allowed to warm to room temperature and stirred for another 45 min. Thereafter, the mixture was evaporated to dryness, the residue was washed with water (3 × 10 cm^3), extracted with diethyl ether (100 cm^3), and the extract was filtered through a (1-cm thick) layer of anhydrous MgSO$_4$. Evaporation of the solution to *ca.* 8 cm^3 and subsequent addition of n-hexane (20 cm^3) rendered a white solid (**5**) (70% yield).

[Ag(C$_6$F$_5$){CH(CO$_2$Me)PPh$_3$}] (**6**). To a diethyl ether solution (30 cm^3) of Ag(C$_6$F$_5$)[6] (0.5 mmol) was added CH(CO$_2$Me)(PPh$_3$)[12] (0.167 g, 0.5 mmol) and the mixture was stirred at room temperature for 45 min. Thereafter, the solution was evaporated to *ca.* 5 cm^3 and n-hexane (20 cm^3) was added to obtain a white solid (**6**).

[Ag(CH$_2$PPh$_3$)$_2$]ClO$_4$ (**7**). (*a*) To a tetrahydrofuran solution (25 cm^3) of CH$_2$PPh$_3$ (1 mmol) (obtained as described above from [PPh$_3$Me]ClO$_4$ and LiBu) was added AgClO$_4$ (0.104 g, 0.5 mmol) and the mixture was stirred at room temperature and under a nitrogen atmosphere for 3 h. A precipitate of complex (**7**) was filtered off. Evaporation of the filtrate to *ca.* 5 cm^3 and addition of n-hexane (20 cm^3) rendered a second crop. Both crops were recrystallized from CH$_2$Cl$_2$–n-hexane (82% yield).

(*b*) To a diethyl ether solution (20 cm^3) of complex (**1**) (0.276 g, 0.5 mmol) was added dropwise a diethyl ether solution (20 cm^3) of AgClO$_4$ (0.052 g, 0.25 mmol). After stirring at room temperature for 15 min the white solid [complex (**7**)] was filtered off (60% yield).

[Au(C$_6$F$_5$)(CH$_2$PPh$_3$)]. To a diethyl ether solution (40 cm^3) of complex (**1**) (0.220 g, 0.4 mmol) was added [AuCl(PPh$_3$)][13] (0.198 g, 0.4 mmol). After stirring for 2 h at room temperature the precipitated [AgCl(PPh$_3$)] was filtered off and the filtrate was evaporated to *ca.* 5 cm^3. Addition of n-hexane (20 cm^3) caused the precipitation of [Au(C$_6$F$_5$)(CH$_2$PPh$_3$)] (86% yield).

X-*Ray Structure Determination of* [Ag(C$_6$F$_5$)(CH$_2$PPh$_3$)] (**1**).—The following conditions were common to the structure

Table 2. Data collection and structure refinement for complex (**1**)

	Modification A (triclinic)	Modification B (monoclinic)
Space group	$P\bar{1}$	$P2_1/n$
a/Å	8.891(3)	12.139(2)
b/Å	11.685(4)	12.487(2)
c/Å	12.636(5)	15.023(3)
α/°	112.74(3)	90
β/°	108.89(3)	103.06(2)
γ/°	97.28(3)	90
U/Å^3	1 096.8	2 218.4
Z	2	4
D_c/g cm^{-3}	1.67	1.65
M	551.26	551.26
F(000)	548	1 096
μ(Mo-K_α)/mm^{-1}	1.0	1.0
Crystal size (mm)	0.6 × 0.3 × 0.08	0.55 × 0.45 × 0.35
Reflections measured	4 625	4 093
Unique reflections	3 850	3 902
Observed reflections [$F > 4\sigma(F)$]	3 112	2 887
R	0.037	0.044
R'	0.036	0.040
g	0.0002	0.0002
Parameters	289	289

Table 3. Atom co-ordinates (× 10^4) for compound (**1**) (triclinic modification)

Atom	x	y	z
Ag	1 158.3(0.4)	1 686.1(0.3)	4 546.2(0.3)
P	3 488(1)	1 329(1)	6 890(1)
C(11)	−239(5)	2 737(4)	3 813(4)
C(12)	−1 277(5)	3 310(4)	4 291(4)
C(13)	−2 273(5)	3 952(4)	3 809(4)
C(14)	−2 255(5)	4 025(4)	2 754(4)
C(15)	−1 236(5)	3 474(4)	2 231(4)
C(16)	−282(5)	2 850(4)	2 760(4)
F(12)	−1 375(3)	3 260(3)	5 334(2)
F(13)	−3 268(4)	4 494(3)	4 330(3)
F(14)	−3 220(3)	4 623(3)	2 243(3)
F(15)	−1 213(3)	3 557(3)	1 192(3)
F(16)	698(3)	2 328(3)	2 185(3)
C(1)	2 513(5)	562(3)	5 259(3)
C(21)	4 925(4)	2 891(3)	7 466(3)
C(22)	5 388(5)	3 230(4)	6 664(4)
C(23)	6 529(5)	4 430(4)	7 130(5)
C(24)	7 186(5)	5 256(4)	8 373(5)
C(25)	6 734(5)	4 932(4)	9 184(4)
C(26)	5 586(5)	3 749(4)	8 727(4)
C(31)	4 673(4)	436(3)	7 558(3)
C(32)	5 486(5)	882(4)	8 846(4)
C(33)	6 406(5)	188(5)	9 310(4)
C(34)	6 518(5)	−957(5)	8 504(5)
C(35)	5 739(6)	−1 405(4)	7 234(5)
C(36)	4 799(5)	−717(4)	6 759(4)
C(41)	1 947(4)	1 593(3)	7 540(3)
C(42)	1 482(4)	841(4)	8 067(3)
C(43)	233(5)	1 012(5)	8 478(4)
C(44)	−560(5)	1 916(5)	8 368(4)
C(45)	−121(5)	2 656(4)	7 839(4)
C(46)	1 142(5)	2 511(3)	7 429(3)

Table 4. Atom co-ordinates (× 10^4) for compound (**1**) (monoclinic modification)

Atom	x	y	z
Ag	9 020.5(0.3)	3 954.2(0.3)	7 218.5(0.2)
P	8 015(1)	5 462(1)	8 630(1)
C(1)	8 482(4)	4 177(3)	8 461(3)
C(11)	9 413(4)	3 713(3)	5 941(3)
C(12)	8 673(4)	3 962(4)	5 136(3)
C(13)	8 895(4)	3 871(4)	4 288(3)
C(14)	9 915(4)	3 472(4)	4 210(3)
C(15)	10 696(4)	3 201(4)	4 982(3)
C(16)	10 434(4)	3 329(4)	5 809(3)
F(12)	7 631(2)	4 364(3)	5 167(2)
F(13)	8 106(3)	4 132(3)	3 526(2)
F(14)	10 158(3)	3 358(3)	3 389(2)
F(15)	11 717(3)	2 838(3)	4 899(2)
F(16)	11 266(2)	3 048(3)	6 558(2)
C(21)	9 091(3)	6 459(3)	8 632(2)
C(22)	10 212(3)	6 185(4)	8 735(3)
C(23)	11 005(4)	6 967(5)	8 728(3)
C(24)	10 701(4)	8 017(5)	8 620(3)
C(25)	9 583(4)	8 297(4)	8 520(3)
C(26)	8 785(4)	7 523(3)	8 529(3)
C(31)	7 561(3)	5 598(3)	9 691(3)
C(32)	7 977(5)	6 381(4)	10 339(3)
C(33)	7 653(6)	6 390(4)	11 153(3)
C(34)	6 909(5)	5 642(5)	11 338(4)
C(35)	6 494(5)	4 868(5)	10 725(3)
C(36)	6 831(4)	4 827(4)	9 905(3)
C(41)	6 834(3)	5 830(3)	7 709(3)
C(42)	5 756(4)	5 966(4)	7 851(3)
C(43)	4 869(4)	6 192(4)	7 108(3)
C(44)	5 054(4)	6 281(4)	6 265(3)
C(45)	6 126(4)	6 181(4)	6 114(3)
C(46)	7 017(4)	5 949(3)	6 845(3)

Table 5. Selected bond lengths (Å) and angles (°) for compound (**1**)

	Triclinic modification	Monoclinic modification
Ag–C(11)	2.105(6)	2.102(6)
Ag–C(1)	2.144(5)	2.131(6)
C(1)–P	1.738(4)	1.739(6)
C(21)–P	1.809(5)	1.804(5)
C(31)–P	1.816(5)	1.808(6)
C(41)–P	1.813(5)	1.813(5)
C(11)–Ag–C(1)	178.2(2)	175.4(3)
C(1)–P–C(21)	111.2(3)	112.1(3)
C(1)–P–C(31)	114.5(3)	113.0(3)
C(1)–P–C(41)	109.6(3)	110.5(3)
C(21)–P–C(31)	106.2(3)	107.4(3)
C(21)–P–C(41)	107.9(3)	105.9(3)
C(31)–P–C(41)	107.1(3)	107.6(3)
Ag–C(1)–P	112.2(3)	115.0(3)
C(12)–C(11)–C(16)	113.1(5)	112.5(5)

determinations of both modifications: Stoe-Siemens four-circle diffractometer, monochromated Mo-K_α radiation, profile-fitting mode,[14] $2\theta_{max.}$ 50°, absorption correction based on ψ scans, and cell constants refined from 2θ values of 50 reflections in the range 20—23°. Solutions by heavy-atom method (using SHELX system[15]), anisotropic refinement on F, H atoms included using riding model, weighting scheme $w^{-1} = \sigma^2(F) + gF^2$. Further details are given in Table 2, atom co-ordinates in Tables 3 and 4, and bond lengths and angles in Table 5.

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References

1 Y. Yamamoto and H. Schmidbaur, *J. Organomet. Chem.*, 1975, **97**, 479.
2 H. Schmidbaur, C. E. Zybill, G. Müller, and C. Krüger, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 729.
3 Y. Yamamoto and H. Schmidbaur, *J. Organomet. Chem.*, 1975, **96**, 133.
4 H. Schmidbaur, J. Adlkofer, and M. Heimann, *Chem. Ber.*, 1974, **107**, 3697.
5 R. Usón, A. Laguna, M. Laguna, A. Usón, and M. C. Gimeno, *Organometallics*, 1987, **6**, 682.
6 R. Usón, A. Laguna, and J. A. Abad, *J. Organomet. Chem.*, 1983, **246**, 341.
7 R. Usón, A. Laguna, and E. Fernández, unpublished work.
8 R. Usón, A. Laguna, M. Laguna, and A. Usón, *Inorg. Chim. Acta*, 1983, **73**, 63.
9 B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1961, 3091.
10 R. Usón, A. Laguna, M. Laguna, A. Usón, and M. C. Gimeno, *Inorg. Chim. Acta*, 1986, **114**, 91.
11 P. L. Coe, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1962, 3227; R. Usón and A. Laguna, *Inorg. Synth.*, 1982, **21**, 71.
12 W. J. Considine, *J. Org. Chem.*, 1962, **27**, 647.
13 M. L. Malvano, *Atti. Accad. Naz. Lincei*, 1908, **17**, 847.
14 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.
15 G. M. Sheldrick, SHELX program system, University of Cambridge, 1976.

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