Synthesis of Silver(I) Complexes with 1,1′-Bis(diphenylphosphino)ferrocene (dppf). Crystal Structures of $[Ag(dppf)(PPh_3)]ClO_4{\cdot}2CH_2Cl_2$, $[Ag(dppf)_2]ClO_4{\cdot}2CHCl_3$ and $[Ag(dppf)(phen)]ClO_4$ (phen = 1,10-phenanthroline)†

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Addition of 1,1′-bis(diphenylphosphino)ferrocene (dppf) to a solution of $AgClO_4$ in 1:1 molar ratio led to the complex $[Ag(OClO_3)(dppf)]$ **1**. Substitution of the perchlorate anion in **1** by monodentate ligands gave $[Ag(dppf)(L)]ClO_4$ (L = PPh_3 **2** or $SPPh_3$ **3**), or with the less sterically demanding phosphine PPh_2Me the four-co-ordinate silver(I) complex $[Ag(dppf)(PPh_2Me)_2]ClO_4$ **4**. Direct reaction of dppf with $[Ag(OClO_3)(PPh_3)]$ also affords complex **2**. The homoleptic derivative $[Ag(dppf)_2]ClO_4$ **5** can be synthesized by reaction of dppf and $AgClO_4$ using a molar ratio of 2:1, or by substitution of the ClO_4^- by dppf in complex **1**. Treatment of **1** with other bidentate ligands such as 1,10-phenanthroline (phen), 2,2′-bipyridine (bipy) or bis(diphenylphosphino)methane disulfide (SdppmS) gave mixed cationic four-co-ordinate complexes $[Ag(dppf)(L\text{–}L)]ClO_4$ (L–L = phen **6**, bipy **7** or SdppmS **8**); with sodium dithiocarbamates $Na(S_2CNR_2)$ the neutral species $[Ag(S_2CNR_2)(dppf)]$ (R = Et **9** or Me **10**) were obtained. The crystal structures of complexes **2**, **5** and **6** have been established by X-ray diffraction. Compound **2** shows a trigonal-planar silver(I) centre, whereas in complexes **5** and **6** the silver atom exhibits a tetrahedral geometry.

The synthesis and reactivity of transition-metal complexes with the ligand 1,1′-bis(diphenylphosphino)ferrocene (dppf) are of current interest, mainly because of the catalytic properties displayed by some of the complexes.[1–4]

We have previously studied the co-ordination behaviour of this ligand towards gold-(I) and -(III) centres;[5] our aim here was to compare or contrast its reactivity towards silver(I). It is well known that gold(I) and silver(I) exhibit different co-ordination modes in their diphosphine complexes.[6] However, we report here mononuclear three- or four-co-ordinate silver(I) complexes similar to those we described for gold(I). In these derivatives the 1,1′-bis(diphenylphosphino)ferrocene ligand acts as a chelate rather than a bridge, in contrast to the findings of Hor *et al.*[7] in studies carried out with silver carboxylate complexes. This shows the ability of this metalloligand to modify its steric bite in order to adapt to different geometric requirements of the metal centres.

Results and Discussion

The reaction of $AgClO_4$ with dppf in diethyl ether in a 1:1 molar ratio gives a yellow solution from which $[Ag(OClO_3)(dppf)]$ **1** can be isolated (see Scheme 1). The IR spectrum shows bands at 1100s br, 1060s, 910m and 624m cm^{-1} arising from covalent perchlorate, apart from those of the dppf.[8] The NMR data are consistent with the formula; thus in the ^1H NMR spectrum three multiplets with a ratio 1:1:5 appear corresponding to the cyclopentadienyl protons (two different environments in each ring) and the phenyl groups, respectively. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **1** consists of a broad singlet at room temperature, which sharpens to a doublet of doublets consistent with the abundance and gyromagnetic ratio for ^{107}Ag and ^{109}Ag (see Table 1).

The positive-ion FAB mass spectrum shows the cation peak $[Ag(dppf)]^+$ as the most intense at *m/z* 661, other fragments correspond to $[AgO(dppf)]^+$ (677, 11) and dppf (554, 13%). Additionally, a peak with low intensity (8%) appears at *m/z* 1423, which corresponds to the fragment $[Ag_2(OClO_3)(dppf)_2]^+$ and could indicate the presence of a dimer. Hor *et al.*[7] have prepared and characterized the compound $[\{Ag(NO_3)(dppf)\}_2]$, its structure shows a dimer with the dppf ligands bridging both silver centres and co-ordinated nitrato groups (**A**).

Molecular weight data of **1** in $CHCl_3$ (1528) also suggest the presence of a dimer. However, we believe that the solid-state structure could be different from that found in $[\{Ag(NO_3)(dppf)\}_2]$ for two reasons: (*i*) the flexibility of the dppf ligand allows it to adopt different geometries, but the chelated form is very well represented, (*ii*) the fragment $[Ag(dppf)]^+$ is very stable as deduced from the mass spectrum and from the reactivity of complex **1**, which shows that this unit is preserved in all derivatives.

We therefore propose structure **B** for complex **1**.

Form **B** has been also found in $[\{Ag(NO_3)(PPh_3)_2\}_2]$ where the nitrato groups bridge both silver atoms,[9] although we cannot rule out the possibility of the structural framework **A** that was found in the nitrato salt. Unfortunately no crystals of suitable quality could be grown.

We have studied the reactivity of complex **1** with

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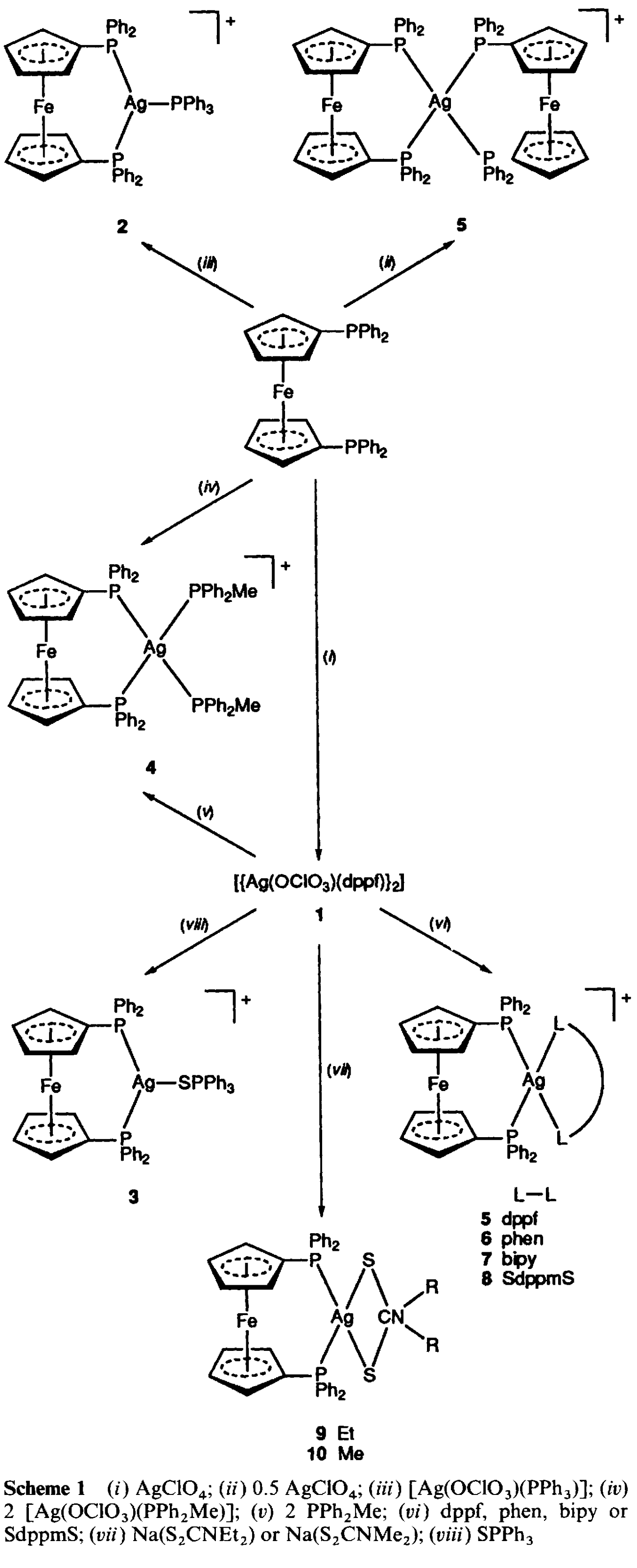
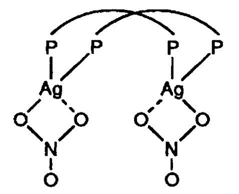
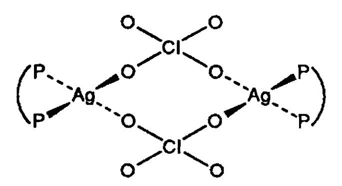
† *Supplementary data available:* Further details of the structure determinations (complete bond lengths and angles, H-atom coordinates, structure factors, thermal parameters) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, 76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference number CSD 401493 (**2**), 401444 (**5**) and 401445 (**6**).



Scheme 1 (*i*) $AgClO_4$; (*ii*) 0.5 $AgClO_4$; (*iii*) $[Ag(OClO_3)(PPh_3)]$; (*iv*) 2 $[Ag(OClO_3)(PPh_2Me)]$; (*v*) 2 PPh_2Me; (*vi*) dppf, phen, bipy or SdppmS; (*vii*) $Na(S_2CNEt_2)$ or $Na(S_2CNMe_2)$; (*viii*) $SPPh_3$



A



B

monodentate ligands such as PPh_2Me, PPh_3 or $SPPh_3$, and the reaction of equimolecular amounts of **1** with the latter two gives the complexes $[Ag(dppf)(L)]ClO_4$ (L = PPh_3 **2** or $SPPh_3$ **3**). With the less sterically demanding phosphine PPh_2Me a mixture of $[Ag(dppf)(PPh_2Me)]ClO_4$ and $[Ag(dppf)(PPh_2Me)_2]ClO_4$ is obtained, but when the reaction is carried out with 2 equivalents of PPh_2Me the pure complex $[Ag(dppf)(PPh_2Me)_2]ClO_4$ **4** is isolated. Complex **2** has also been prepared by an alternative procedure, by reaction of $[Ag(OClO_3)(PPh_3)]$ with dppf, which shows the great tendency of this diphosphine to act as a chelate rather than a bridge in silver(I) complexes (the 2:1 reaction proceeds with formation of the same complex). These complexes are analogous to those that we reported previously for gold.[5]

The ^1H NMR spectra of complexes **2**–**4** show two multiplets for the cyclopentadienyl protons and a doublet for the methyl group in complex **4**. The $^{31}P\text{-}\{^1H\}$ NMR spectra are very different. Complex **2** presents an AX_2 system with coupling between A and X, whereby both are coupled with the silver nuclei ^{107}Ag and ^{109}Ag, thus A appears as a doublet of doublets of triplets and X as a doublet of doublet of doublets [see Fig. 1(*a*)]; **3** displays a doublet of doublets for the phosphorus of the dppf and a singlet for the $SPPh_3$, with $^2J(AgP)$ and $^3J(AgP)$ absent; the spectrum of **4** corresponds to an A_2X_2 system, both coupled to ^{107}Ag and ^{109}Ag, and two doublets of doublets of triplets are observed for the two phosphorus environments [see Fig. 1(*b*)].

In the positive-ion FAB mass spectra molecular cation peaks appear at *m*/*z* 925 (**2**, 17%) and 955 (**3**, 7%) while in complex **4** this peak is not present although the fragment $[Ag(dppf)(PPh_2Me)]^+$ appears at *m*/*z* 863 (14%). The most intense peak in every spectrum corresponds to $[Ag(dppf)]^+$.

The structure of complex **2** was confirmed by X-ray diffraction analysis (Fig. 2). Atomic coordinates are given in Table 2, with selected bond lengths and angles in Table 3. The compound crystallizes with two molecules of dichloromethane; the chlorine atoms Cl(3) $\cdots$ Cl(5) have a contact of 3.810 Å. The complex is isostructural with the trigonal-planar gold analogue $[Au(dppf)(PPh_3)]ClO_4$.[5] The bite angle of the diphosphine, P(1)–Ag–P(2) 109.63(4)°, is (necessarily) similar to that in the gold complex [109.5(1)°] and represents an enforced deviation from ideal geometry; the other angles are P(3)–Ag–P(1) 131.19(4) and P(3)–Ag–P(2) 119.12(4)°. The silver atom lies 0.03 Å out of the plane of the three phosphorus atoms. The cyclopentadienyl rings are staggered by 5.8° around the Cp $\cdots$ Cp axis (Cp = centre of cyclopentadienyl ring) defined by the torsion angles C(1)–Cp–Cp–C(7). The Ag–P distances are Ag–P(1) 2.4312(12), Ag–P(2) 2.4802(12) and Ag–P(3) 2.4244(12) Å, the shortest being to the monodentate phosphine. The longest is similar to those found in four-co-ordinate silver complexes $[Ag(dppe)_2]NO_3$, [dppe = 1,2-bis(diphenylphosphino)ethane] [2.488(3)–2.527(3) Å][10] and the others approach values found in the complexes [AgX(L′)] {L′ = 2,11-bis[(diphenylphosphino)methyl]benzo[*c*]phenanthrene, X = Cl, $SnCl_3$, NO_3 or ClO_4}, which range from 2.401(3) to 2.455(1) Å.[11]

Treatment of complex **1** with bidentate ligands such as dppf, 2,2′-bipyridine(bipy), 1,10-phenanthroline(phen) or bis(diphenylphosphino)methane disulfide (SdppmS) affords the four-co-ordinate complexes $[Ag(dppf)(L\text{–}L)]ClO_4$ (L–L = dppf **5**, phen **6**, bipy **7** or SdppmS **8**). The homoleptic complex $[Ag(dppf)_2]ClO_4$ can also be synthesized by direct reaction of $AgClO_4$ and 2 equivalents of dppf. Recently, in a parallel study, the PF_6 salt of this complex was reported but the crystal structure was not determined.[12]

The ^1H NMR spectra of complexes **5**–**8** show the α and β protons of the ferrocenyl ring as multiplets or broad singlets; in the $^{31}P\text{-}\{^1H\}$ NMR spectra two doublets are observed as a consequence of chemically equivalent phosphorus atoms coupled to both silver nuclei.

Table 1 $^{31}P-\{^1H\}$ and ^1H NMR data for complexes **1**–**10** *

	$^{31}P-\{^1H\}$ NMR		^1H NMR	
Complex	dppf	L	C_5H_4	L
1 $[\{Ag(OClO_3)(dppf)\}_2]$	1.8 (d, br) J_{av} (AgP) 519		4.19 (m), 4.37 (m)	
2 $[Ag(dppf)(PPh_3)]ClO_4$	2.4 (ddd) J(AgP) 413.3, 385.5	14.3 (ddt) J(AgP) 349.6, 305.2 ^2J(PP) 96.6	4.20 (m), 4.46 (m)	
3 $[Ag(dppf)(SPPh_3)]ClO_4$	−1.7 (dd) J(AgP) 420.5, 369.5	44.3 (s)	4.02 (m), 4.39 (m)	
4 $[Ag(dppf)(PPh_2Me)_2]ClO_4$	−0.1 (ddt) J(AgP) 268.5, 232.1	−14.0 (ddt) J(AgP) 263.8, 229.3 ^2J(PP) 57.8	4.03 (m), 4.35 (m)	
5 $[Ag(dppf)_2]ClO_4$	−2.8 (dd) J(AgP) 267.6, 234.1		4.11 (m), 4.41 (m)	
6 $[Ag(dppf)(phen)]ClO_4$	−2.6 (dd) J(AgP) 425.3, 368.3		4.33 (m), 4.49 (m)	7.84 (m), 8.05 (m) 8.56 (m), 8.89 (m)
7 $[Ag(dppf)(bipy)]ClO_4$	−1.7 (dd) J(AgP) 427.0, 372.9		4.28 (m), 4.47 (m)	7.42 (m), 8.09 (m) 8.45 (m), 8.50 (m)
8 $[Ag(dppf)(SdppmS)]ClO_4$	−4.0 (dd) J(AgP) 385.8, 336.9	36.3 (s)	4.14 (m), 4.28 (m)	1.56 (s)
9 $[Ag(S_2CNEt_2)(dppf)]$	−7.6 (dd) J(AgP) 378.5, 328.4		4.16 (m), 4.24 (m)	1.30 (t), 4.01 (q) ^3J(HH) 7.14
10 $[Ag(S_2CNMe_2)(dppf)]$	−7.7 (dd) J(AgP) 378.8, 329.7		4.28 (m), 4.20 (m)	3.61 (s)

* Recorded in $CDCl_3$ at −55 °C, coupling constants in Hz; s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublets of doublets, ddt = doublet of doublets of triplets, m = multiplet, br = broad.

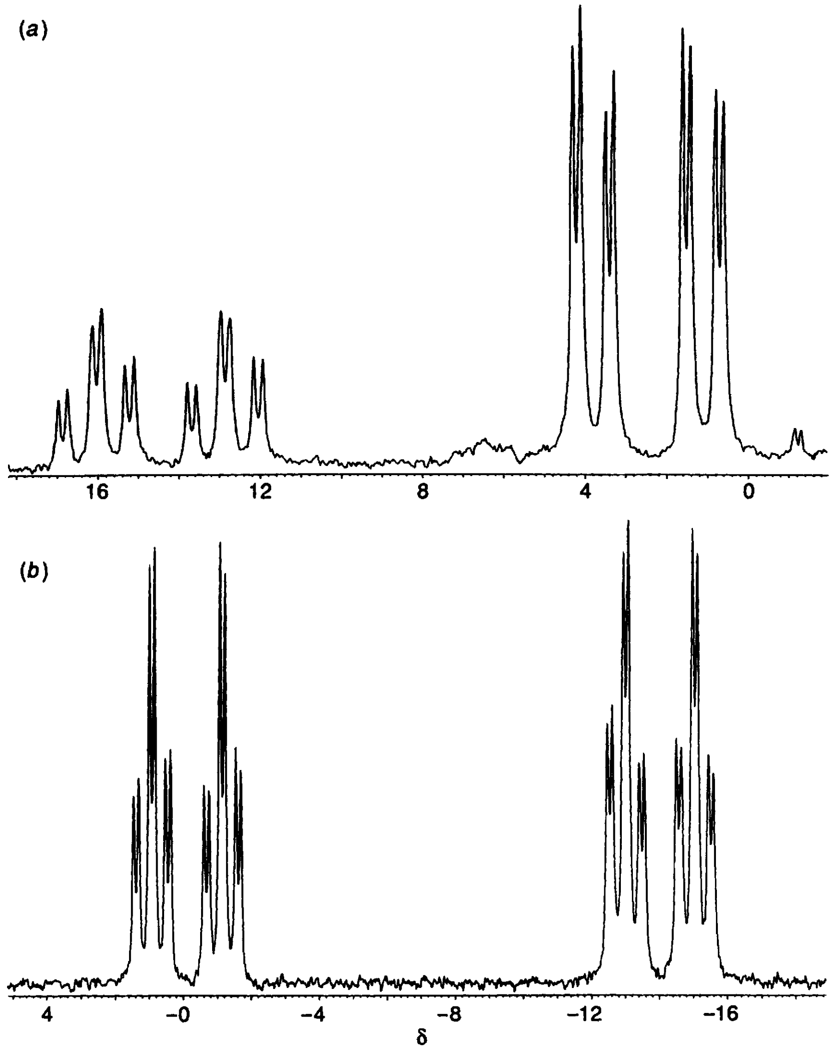


Fig. 1 (*a*) $^{31}P-\{^1H\}$ NMR spectrum of complex **2** at −55 °C, (*b*) $^{31}P-\{^1H\}$ NMR spectrum of compound **4** at −55 °C

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

Atom	*x*	*y*	*z*
Ag	7 303(1)	3 232(1)	4 992(1)
Fe	7 457(1)	5 643(1)	4 958(1)
P(1)	7 626(1)	4 011(1)	4 081(1)
P(2)	7 310(1)	4 095(1)	5 935(1)
P(3)	7 059(1)	1 830(1)	5 108(1)
C(1)	8 037(3)	4 992(3)	4 291(2)
C(2)	7 721(4)	5 734(3)	4 023(2)
C(3)	8 211(3)	6 335(3)	4 398(2)
C(4)	8 826(3)	5 977(3)	4 888(2)
C(5)	8 718(3)	5 152(3)	4 828(2)
C(6)	6 901(3)	5 060(3)	5 668(2)
C(7)	6 216(3)	5 149(3)	5 124(2)
C(8)	6 079(3)	5 963(3)	5 005(2)
C(9)	6 683(4)	6 383(3)	5 463(2)
C(10)	7 189(3)	5 827(3)	5 881(2)
C(11)	6 603(3)	4 115(3)	3 488(2)
C(12)	6 664(4)	4 446(3)	2 896(2)
C(13)	5 872(4)	4 469(3)	2 447(3)
C(14)	5 027(4)	4 154(3)	2 590(3)
C(15)	4 952(4)	3 828(3)	3 169(3)
C(16)	5 741(3)	3 807(3)	3 623(3)
C(21)	8 518(3)	3 571(3)	3 646(2)
C(22)	8 333(4)	2 816(3)	3 400(3)
C(23)	8 989(4)	2 423(3)	3 096(3)
C(24)	9 860(4)	2 766(3)	3 047(3)
C(25)	10 053(4)	3 503(3)	3 291(2)
C(26)	9 394(3)	3 909(3)	3 590(2)
C(31)	8 422(3)	4 215(3)	6 441(2)
C(32)	8 472(4)	4 637(3)	7 001(2)
C(33)	9 304(4)	4 662(4)	7 406(3)
C(34)	10 086(4)	4 250(4)	7 256(3)
C(35)	10 043(4)	3 839(4)	6 704(3)
C(36)	9 208(4)	3 810(3)	6 296(3)
C(41)	6 512(3)	3 760(3)	6 491(2)
C(42)	5 626(3)	4 072(3)	6 527(2)
C(43)	5 013(4)	3 714(3)	6 889(2)
C(44)	5 270(4)	3 036(3)	7 223(2)
C(45)	6 163(4)	2 723(3)	7 203(2)
C(46)	6 775(4)	3 073(3)	6 839(2)
C(51)	5 967(3)	1 568(3)	5 415(2)
C(52)	5 363(3)	2 180(3)	5 552(2)
C(53)	4 521(4)	2 018(3)	5 774(3)
C(54)	4 261(4)	1 246(3)	5 871(3)
C(55)	4 848(4)	636(3)	5 735(3)
C(56)	5 695(4)	796(3)	5 508(2)
C(61)	8 033(4)	1 583(3)	5 707(2)
C(62)	7 926(4)	1 306(3)	6 305(2)
C(63)	8 715(4)	1 203(4)	6 750(3)
C(64)	9 603(4)	1 373(4)	6 596(3)
C(65)	9 721(4)	1 649(3)	6 002(3)
C(66)	8 933(4)	1 758(3)	5 556(3)
C(71)	7 177(3)	1 133(3)	4 469(2)
C(72)	6 690(4)	1 272(3)	3 872(2)
C(73)	6 766(4)	747(3)	3 383(3)
C(74)	7 326(4)	101(3)	3 471(3)
C(75)	7 822(4)	−41(3)	4 057(3)
C(76)	7 745(4)	467(3)	4 557(3)
Cl(1)	7 669(1)	7 116(1)	7 868(1)
O(1)	6 736(4)	7 191(6)	7 763(4)
O(2)	7 902(8)	6 483(4)	7 498(4)
O(3)	8 171(4)	7 766(3)	7 696(3)
O(4)	7 965(4)	6 893(3)	8 505(3)
Cl(2)	5 844(2)	8 429(1)	5 982(1)
Cl(3)	7 436(2)	9 338(1)	6 555(1)
C(100)	6 754(7)	8 492(6)	6 579(5)
Cl(4)	9 627(2)	9 473(2)	5 715(2)
Cl(5)	8 505(5)	8 166(2)	5 287(2)
C(101)	9 351(15)	8 536(11)	5 808(7)

Table 3 Selected bond lengths (Å) and angles (°) for complex **2**

Ag–P(3)	2.4244(12)	Ag–P(1)	2.4312(12)
Ag–P(2)	2.4802(12)	P(1)–C(1)	1.806(5)
P(1)–C(11)	1.821(5)	P(1)–C(21)	1.820(5)
P(2)–C(6)	1.810(5)	P(2)–C(31)	1.819(5)
P(2)–C(41)	1.825(5)	P(3)–C(51)	1.814(5)
P(3)–C(61)	1.819(5)	P(3)–C(71)	1.823(5)
P(3)–Ag–P(1)	131.19(4)	P(3)–Ag–P(2)	119.12(4)
P(1)–Ag–P(2)	109.63(4)	C(1)–P(1)–C(11)	106.9(2)
C(1)–P(1)–C(21)	106.2(2)	C(11)–P(1)–C(21)	104.0(2)
C(1)–P(1)–Ag	113.2(2)	C(11)–P(1)–Ag	113.0(2)
C(21)–P(1)–Ag	112.9(2)	C(6)–P(2)–C(31)	108.1(2)
C(6)–P(2)–C(41)	106.4(2)	C(31)–P(2)–C(41)	102.8(2)
C(6)–P(2)–Ag	108.2(2)	C(31)–P(2)–Ag	117.5(2)
C(41)–P(2)–Ag	113.1(2)	C(51)–P(3)–C(61)	108.1(2)
C(51)–P(3)–C(71)	105.4(2)	C(61)–P(3)–C(71)	103.8(2)
C(51)–P(3)–Ag	114.7(2)	C(61)–P(3)–Ag	101.0(2)
C(71)–P(3)–Ag	122.4(2)	C(2)–C(1)–P(1)	129.6(4)
C(5)–C(1)–P(1)	122.7(3)	C(10)–C(6)–P(2)	131.2(4)
C(7)–C(6)–P(2)	120.9(3)	C(12)–C(11)–P(1)	122.3(4)
C(16)–C(11)–P(1)	118.5(4)	C(26)–C(21)–P(1)	124.2(4)
C(22)–C(21)–P(1)	116.9(4)	C(32)–C(31)–P(2)	121.2(4)
C(36)–C(31)–P(2)	119.3(4)	C(42)–C(41)–P(2)	124.1(3)
C(46)–C(41)–P(2)	116.8(3)	C(56)–C(51)–P(3)	123.3(4)
C(52)–C(51)–P(3)	117.8(3)	C(62)–C(61)–P(3)	124.3(4)
C(66)–C(61)–P(3)	116.1(4)	C(72)–C(71)–P(3)	119.2(4)
C(76)–C(71)–P(3)	122.1(4)		

In the positive-ion FAB mass spectra of **5–8** the molecular cation peaks appear at *m*/*z* 1215 (**5**, 18%), 843 (**6**, 19%), 817 (**7**, 7%) and 1111 (**8**, 18%). The fragmentation peaks are very similar for the three complexes, the most intense corresponding to [Ag(dppf)]$^+$, for **6** and **7** the peak assigned to [AgN(dppf)]$^+$ and for complex **8** the peak [AgS(dppf)]$^+$ are observed.

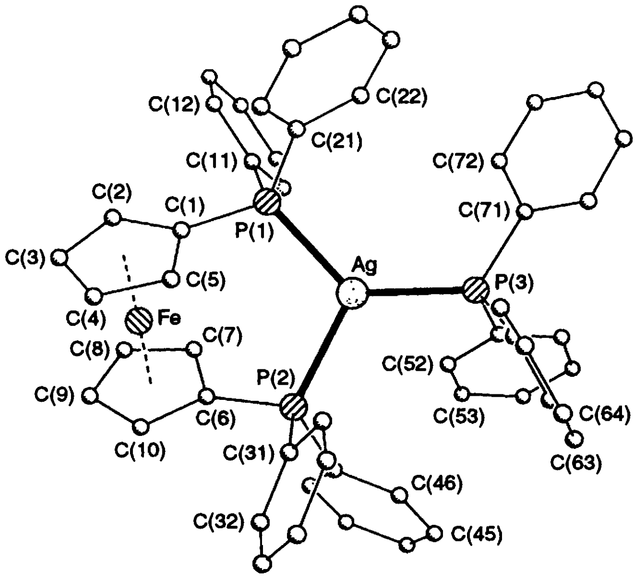


Fig. 2 Structure of the cation of compound **2** in the crystal; hydrogen atoms are omitted for clarity, radii are arbitrary

We have carried out reactions of complex **1** with other bidentate phosphines such as 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane and *o*-phenylene bis(diphenylphosphine), in an attempt to obtain the mixed

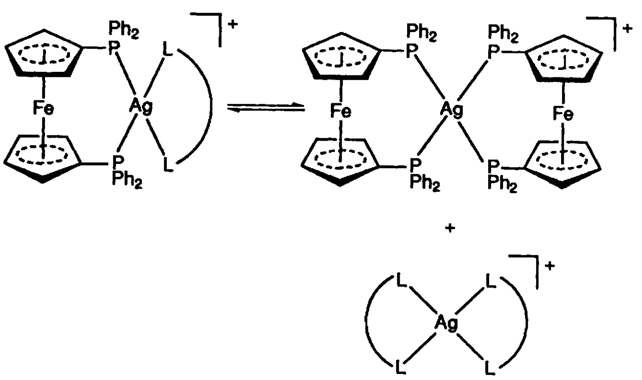


Fig. 3 Equilibria in silver(I)–dppf–diphosphine complexes; diphosphine = $Ph_2P(CH_2)_nPPh_2$ (n = 2 or 3), or $Ph_2PC_6H_4PPh_2$

diphosphine silver derivatives [Ag(L–L)(dppf)]ClO_4. In the FAB mass spectra the molecular cation peaks [Ag(L–L)(dppf)]$^+$ and the fragments [Ag(L–L)]$^+$ and [Ag(dppf)]$^+$ are present. However the NMR spectra, carried out in $CDCl_3$ solution, show that an equilibrium exists between the homoleptic and the mixed complexes (Fig. 3).

Consequently, in the $^{31}P-\{^1H\}$ NMR spectra the mixed species present an A_2X_2 system with coupling to the silver nuclei and appear as two doublets of doublets of triplets, and the homoleptic species show doublet of doublets typical of equivalent phosphorus atoms coupled to ^{107}Ag and ^{109}Ag.

The neutral derivatives [Ag(S_2CNR_2)(dppf)] (R = Et **9** or Me **10**) can be synthesized by reaction of **1** with Na(S_2CNR_2) in dichloromethane.

The NMR data of complexes **9** and **10** are in agreement with their formulation, and are similar to those of the other derivatives, except for the ^1H NMR, where a singlet for the methyl and a triplet and a quartet for the ethyl groups appear. In the FAB mass spectra of complexes **9** and **10** the molecular cation peaks are not present, but peaks corresponding to $[M + Ag]^+$ appear. This association has been previously observed by us in other neutral silver complexes.[13] The molecular weight determination in chloroform (isopiestic method) gives values corresponding to monomers, 811 (810.55) for complex **9** and 780 (783.47) for compound **10**.

The crystal structures of complexes [Ag(dppf)$_2$]ClO_4 **5** and [Ag(dppf)(phen)]ClO_4 **6** have been determined by X-ray diffraction. The molecular structure of the cation of complex **5** is shown in Fig. 4. Atomic coordinates are collected in Table 4 and selected bond lengths and angles in Table 5. The complex crystallizes with two molecules of chloroform in the asymmetric unit, some of the chlorine atoms have contacts with the oxygen atoms of the perchlorate group, the shortest being at 3.398, 3.452 and 3.630 Å; there are also contacts between chlorines in different asymmetric units [Cl(2) ··· Cl(2i) 3.834, Cl(2) ··· Cl(3i) 3.792 Å, i = $-x$, $-y + 2$, $-z + 1$]. The silver atom exhibits an almost regular tetrahedral geometry, with small deviations arising from the bite angles of the diphosphine P(1)–Ag–P(2) 105.71(4) and P(3)–Ag–P(4) 98.39(4)°. These angles are slightly narrower than in complex **2**, although much wider than in related four-co-ordinate bisphosphine complexes; *e.g.* [Ag(dppe)$_2$]NO_3 [84.5(1) and 83.8(1)°].[10] The dihedral angle between the planes Ag–P(1)–P(2) and Ag–P(3)–P(4) is 88.3°, close to the ideal value of 90°. The cyclopentadienyl rings are staggered by 12.5 and 11.9° at Fe(1) and Fe(2) around the Cp ··· Cp axis, defined by the torsion angles C(101)–Cp–Cp–C(92) and C(122)–Cp–Cp–C(112), respectively. The Ag–P distances lie in the range 2.549(2)–2.602(2) Å, between those in the four-co-ordinate [Ag(PPh_3)$_4$]ClO_4 [2.650(2), 3 × 2.668(5) Å][14] and [Ag(dppe)$_2$]NO_3 [2.488(3)–2.527(3) Å].[10]

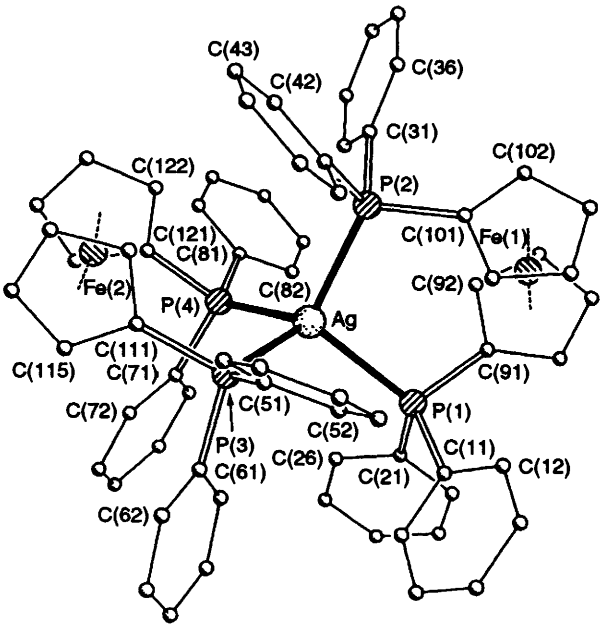


Fig. 4 Structure of the cation of compound **5** in the crystal; hydrogen atoms are omitted for clarity, radii are arbitrary

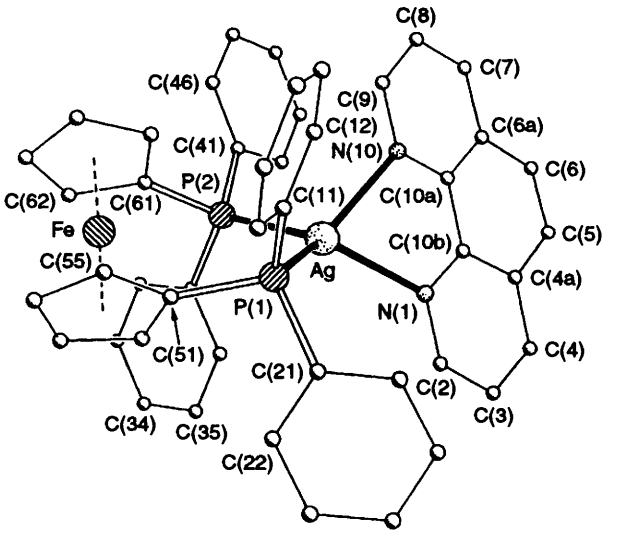


Fig. 5 Structure of the cation of compound **6** in the crystal; hydrogen atoms are omitted for clarity, radii are arbitrary

The molecular structure of the cation of complex **6** is shown in Fig. 5, with atomic coordinates in Table 6 and selected bond lengths and angles in Table 7. The silver atom is chelated by one diphosphine and one phenanthroline ligand and has a distorted tetrahedral geometry. The distortion arises from the restricted bite of the phenanthroline ligand N(1)–Ag–N(10) 70.85(10)°, whereas the diphosphine bite angle P(1)–Ag–P(2) 110.59(3) is larger than that in complex **5**. The dihedral angle between the planes Ag–P(1)–P(2) and Ag–N(1)–N(10) is 69.4°. The cyclopentadienyl rings are staggered by 15.3° around the Cp ··· Cp axis defined by the torsion angle C(61)–Cp–Cp–C(52). The Ag–P distances are 2.4112(10) and 2.5067(10) Å, smaller than in complex **5**, but similar to those in [Ag(phen){(PPh_2)$_2C_2B_{10}H_{10}$}]ClO_4 [2.463(2) and 2.479(2) Å], previously reported by us.[15] The Ag–N bond lengths of 2.343(3) and 2.361(3) Å are also similar to those in the compound [Ag(phen){(PPh_2)$_2C_2B_{10}H_{10}$}]ClO_4.

Table 4 Atomic coordinates (× 10^4) for complex **5**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ag	5 982.9(3)	3 016.2(2)	2 230.6(2)	C(72)	3 877(5)	1 170(3)	3 454(3)
Fe(1)	9 047.9(6)	5 033.2(4)	1 883.7(3)	C(73)	3 357(6)	989(4)	4 085(3)
Fe(2)	3 089.1(6)	706.6(4)	1 276.2(4)	C(74)	4 068(6)	897(4)	4 679(3)
P(1)	7 245.7(11)	4 350.6(8)	3 165.3(6)	C(75)	5 294(5)	971(3)	4 644(3)
P(2)	6 836.9(11)	3 242.5(8)	1 003.9(6)	C(76)	5 814(5)	1 134(3)	4 012(3)
P(3)	3 686.7(11)	2 865.4(8)	2 022.3(6)	C(81)	7 090(4)	1 089(3)	2 619(3)
P(4)	5 775.4(11)	1 510.0(8)	2 572.1(7)	C(82)	8 192(5)	1 578(3)	3 058(3)
C(11)	6 602(4)	5 242(3)	3 343(2)	C(83)	9 158(5)	1 248(4)	3 149(3)
C(12)	6 897(5)	5 972(3)	3 013(3)	C(84)	9 058(5)	435(4)	2 803(3)
C(13)	6 269(6)	6 564(4)	3 141(3)	C(85)	7 995(5)	−42(4)	2 355(3)
C(14)	5 356(6)	6 453(4)	3 581(3)	C(86)	7 010(5)	281(3)	2 262(3)
C(15)	5 062(5)	5 732(4)	3 917(3)	C(91)	8 766(4)	4 776(3)	2 902(2)
C(16)	5 681(5)	5 130(3)	3 806(3)	C(92)	9 337(4)	4 199(3)	2 531(2)
C(21)	7 569(4)	4 185(3)	4 105(2)	C(93)	10 490(4)	4 704(3)	2 352(3)
C(22)	8 343(5)	4 843(3)	4 636(3)	C(94)	10 635(5)	5 577(4)	2 601(3)
C(23)	8 518(5)	4 723(3)	5 354(3)	C(95)	9 595(5)	5 633(3)	2 951(3)
C(24)	7 895(5)	3 952(3)	5 537(3)	C(101)	7 757(4)	4 347(3)	1 015(2)
C(25)	7 127(5)	3 292(3)	5 018(3)	C(102)	8 958(4)	4 690(3)	786(2)
C(26)	6 982(5)	3 410(3)	4 300(3)	C(103)	9 343(5)	5 598(3)	983(2)
C(31)	7 872(4)	2 645(3)	712(2)	C(104)	8 411(5)	5 836(3)	1 328(3)
C(32)	8 197(4)	2 136(3)	1 170(3)	C(105)	7 436(4)	5 066(3)	1 350(2)
C(33)	9 001(5)	1 673(3)	969(3)	C(111)	2 679(4)	1 849(3)	1 495(2)
C(34)	9 477(5)	1 729(3)	320(3)	C(112)	2 682(4)	1 592(3)	730(3)
C(35)	9 164(4)	2 239(3)	−145(3)	C(113)	1 788(5)	768(3)	493(3)
C(36)	8 348(4)	2 687(3)	49(3)	C(114)	1 231(4)	507(3)	1 117(3)
C(41)	5 685(4)	3 003(3)	190(2)	C(115)	1 780(4)	1 175(3)	1 729(3)
C(42)	5 358(4)	2 217(3)	−290(3)	C(121)	4 694(4)	716(3)	1 865(2)
C(43)	4 408(5)	2 020(3)	−866(3)	C(122)	4 809(4)	683(3)	1 096(3)
C(44)	3 770(5)	2 596(4)	−955(3)	C(123)	3 902(5)	−80(3)	712(3)
C(45)	4 073(5)	3 364(4)	−487(3)	C(124)	3 231(5)	−501(3)	1 224(3)
C(46)	5 017(4)	3 569(3)	84(3)	C(125)	3 694(4)	−29(3)	1 929(3)
C(51)	3 294(4)	3 675(3)	1 565(2)	Cl(1)	108.1(12)	8 291.4(8)	2 207.4(7)
C(52)	4 026(5)	4 526(3)	1 806(3)	O(1)	−478(4)	8 556(3)	1 613(2)
C(53)	3 809(5)	5 186(3)	1 483(3)	O(2)	810(4)	7 762(3)	1 919(2)
C(54)	2 850(5)	4 994(4)	920(3)	O(3)	898(4)	9 027(3)	2 705(2)
C(55)	2 109(5)	4 153(3)	686(3)	O(4)	−818(5)	7 796(3)	2 588(3)
C(56)	2 319(4)	3 500(3)	1 011(3)	C(131)	48(6)	8 378(4)	4 355(4)
C(61)	2 991(4)	2 986(3)	2 866(2)	Cl(2)	1 081(2)	9 313.5(13)	4 858(2)
C(62)	1 816(5)	3 081(3)	2 864(3)	Cl(3)	−1 465(2)	8 321.1(15)	4 508.8(13)
C(63)	1 367(5)	3 240(4)	3 518(3)	Cl(4)	398(2)	7 483.8(12)	4 612.9(11)
C(64)	2 070(6)	3 284(3)	4 177(3)	C(132)	3 453(6)	8 126(4)	2 756(3)
C(65)	3 213(6)	3 180(4)	4 180(3)	Cl(5)	4 958(2)	8 793.6(14)	3 069.3(14)
C(66)	3 680(5)	3 044(3)	3 522(3)	Cl(6)	3 454(2)	7 225.7(13)	2 130.9(11)
C(71)	5 110(4)	1 241(3)	3 410(3)	Cl(7)	2 673(2)	7 798.6(11)	3 487.5(8)

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

Ag–P(3)	2.549(2)	Ag–P(1)	2.561(2)
Ag–P(2)	2.584(2)	Ag–P(4)	2.602(2)
P(1)–C(91)	1.802(5)	P(1)–C(21)	1.832(5)
P(1)–C(11)	1.835(5)	P(2)–C(101)	1.807(5)
P(2)–C(31)	1.820(5)	P(2)–C(41)	1.837(5)
P(3)–C(111)	1.815(5)	P(3)–C(61)	1.826(5)
P(3)–C(51)	1.826(5)	P(4)–C(121)	1.802(5)
P(4)–C(81)	1.834(5)	P(4)–C(71)	1.840(5)
P(3)–Ag–P(1)	113.15(4)	P(3)–Ag–P(2)	106.81(4)
P(1)–Ag–P(2)	105.71(4)	P(3)–Ag–P(4)	98.39(4)
P(1)–Ag–P(4)	117.84(4)	P(2)–Ag–P(4)	114.54(4)
C(91)–P(1)–C(21)	103.4(2)	C(91)–P(1)–C(11)	107.9(2)
C(21)–P(1)–C(11)	99.9(2)	C(91)–P(1)–Ag	109.5(2)
C(21)–P(1)–Ag	116.7(2)	C(11)–P(1)–Ag	118.0(2)
C(101)–P(2)–C(31)	102.6(2)	C(101)–P(2)–C(41)	103.3(2)
C(31)–P(2)–C(41)	102.9(2)	C(101)–P(2)–Ag	112.5(2)
C(31)–P(2)–Ag	117.1(2)	C(41)–P(2)–Ag	116.53(14)
C(111)–P(3)–C(61)	104.1(2)	C(111)–P(3)–C(51)	103.8(2)
C(61)–P(3)–C(51)	101.0(2)	C(111)–P(3)–Ag	116.1(2)
C(61)–P(3)–Ag	114.0(2)	C(51)–P(3)–Ag	116.0(2)
C(121)–P(4)–C(81)	101.7(2)	C(121)–P(4)–C(71)	102.4(2)
C(81)–P(4)–C(71)	101.5(2)	C(121)–P(4)–Ag	107.3(2)
C(81)–P(4)–Ag	121.9(2)	C(71)–P(4)–Ag	119.2(2)

We have investigated the redox behaviour of some of these complexes, **5**–**7** and **9**, and, in contrast to our observations with the gold derivatives, the cyclic voltammograms (in CH_2Cl_2, scan rate 100 mV s^{-1}) show quasireversible oxidation waves (the cathodic to anodic ratio i_{pc}/i_{pa} is *ca.* 0.8:1 with peak potentials at 0.97, 0.88, 0.88 and 0.93 V, respectively). These values are similar to those for the gold complexes, and the oxidation is associated with the ferrocene moiety.

Experimental

Instrumentation and general experimental techniques were as described earlier.[5] All the reactions were carried out at room temperature. The yields, analysis, conductivities and melting points for the new complexes are listed in Table 8. The starting materials [Ag($OClO_3$)(PPh_3)][16] and SdppmS[17] were prepared by published methods. All other reagents were obtained commercially.

Syntheses.—[{Ag($OClO_3$)(dppf)}$_2$] **1**. To a solution of $AgClO_4$ (0.041 g, 0.2 mmol) in diethyl ether (30 cm^3) was added dppf (0.111 g, 0.2 mmol), forming immediately a yellow precipitate of **1**. The reaction mixture was stirred for 30 min and then the solid was filtered off and washed with diethyl ether (2 × 5 cm^3).

Table 6 Atomic coordinates (× 10^4) for complex **6**

Atom	*x*	*y*	*z*
Ag	5835.2(2)	6731.9(1)	6436.2(1)
Fe	5608.9(5)	8425.1(3)	7800.1(2)
P(1)	5910.0(8)	8120.9(5)	6227.7(4)
P(2)	5904.4(8)	6476.3(5)	7612.7(4)
N(1)	6875(3)	5861(2)	5816.2(13)
C(2)	7977(3)	5966(2)	5630(2)
C(3)	8622(4)	5381(2)	5342(2)
C(4)	8109(4)	4660(2)	5244(2)
C(4a)	6948(3)	4523(2)	5436(2)
C(5)	6367(4)	3770(2)	5375(2)
C(6)	5265(4)	3660(2)	5585(2)
C(6a)	4607(3)	4283(2)	5852(2)
C(7)	3437(4)	4194(2)	6053(2)
C(8)	2868(4)	4816(2)	6294(2)
C(9)	3467(3)	5541(2)	6336(2)
N(10)	4566(3)	5649(2)	6152.6(12)
C(10a)	5143(3)	5032(2)	5912.0(15)
C(10b)	6348(3)	5146(2)	5716.9(14)
C(11)	4541(3)	8595(2)	5867.6(15)
C(12)	3470(3)	8161(2)	5775(2)
C(13)	2397(3)	8505(2)	5520(2)
C(14)	2401(3)	9289(2)	5357(2)
C(15)	3456(3)	9728(2)	5441(2)
C(16)	4526(3)	9387(2)	5697(2)
C(21)	7093(3)	8395(2)	5713(2)
C(22)	7963(3)	8960(2)	5875(2)
C(23)	8903(4)	9090(2)	5492(2)
C(24)	8958(4)	8679(2)	4937(2)
C(25)	8079(4)	8123(2)	4762(2)
C(26)	7167(4)	7975(2)	5154(2)
C(31)	7412(3)	6398(2)	8042(2)
C(32)	7607(3)	6286(2)	8700(2)
C(33)	8777(4)	6315(2)	8998(2)
C(34)	9760(4)	6436(2)	8649(2)
C(35)	9582(4)	6523(2)	7998(2)
C(36)	8414(3)	6507(2)	7694(2)
C(41)	5019(3)	5640(2)	7855(2)
C(42)	5447(4)	4896(2)	7753(2)
C(43)	4756(4)	4238(2)	7855(2)
C(44)	3627(4)	4325(3)	8063(2)
C(45)	3170(4)	5065(3)	8157(2)
C(46)	3868(4)	5722(3)	8058(2)
C(51)	6289(3)	8678(2)	6952.5(15)
C(52)	7242(3)	8436(2)	7419(2)
C(53)	7258(4)	8969(2)	7939(2)
C(54)	6335(4)	9531(2)	7804(2)
C(55)	5730(4)	9356(2)	7193(2)
C(61)	5190(3)	7293(2)	7971(2)
C(62)	5467(3)	7702(2)	8560(2)
C(63)	4647(4)	8334(2)	8586(2)
C(64)	3835(4)	8316(2)	8021(2)
C(65)	4166(3)	7686(2)	7643(2)
Cl	722.6(8)	6837.5(5)	6346.6(4)
O(1)	929(3)	6820(2)	5683.9(13)
O(2)	−317(3)	7313(2)	6437.3(14)
O(3)	503(3)	6052(2)	6554.7(14)
O(4)	1770(3)	7157(2)	6713.2(15)

Table 7 Selected bond lengths (Å) and angles (°) for complex **6**

Ag–N(1)	2.343(3)	Ag–N(10)	2.361(3)
Ag–P(1)	2.4112(10)	Ag–P(2)	2.5067(10)
P(1)–C(51)	1.813(3)	P(1)–C(11)	1.817(3)
P(1)–C(21)	1.828(3)	P(2)–C(61)	1.798(3)
P(2)–C(31)	1.824(4)	P(2)–C(41)	1.826(3)
N(1)–C(2)	1.322(4)	N(1)–C(10b)	1.358(4)
C(2)–C(3)	1.395(5)	C(3)–C(4)	1.361(5)
C(4)–C(4a)	1.396(5)	C(4a)–C(10b)	1.408(5)
C(4a)–C(5)	1.436(5)	C(5)–C(6)	1.343(6)
C(6)–C(6a)	1.428(5)	C(6a)–C(7)	1.401(5)
C(6a)–C(10a)	1.409(5)	C(7)–C(8)	1.353(5)
C(8)–C(9)	1.401(5)	C(9)–N(10)	1.317(4)
N(10)–C(10a)	1.351(4)	C(10a)–C(10b)	1.438(5)
N(1)–Ag–N(10)	70.85(10)	N(1)–Ag–P(1)	119.69(7)
N(10)–Ag–P(1)	138.69(7)	N(1)–Ag–P(2)	117.74(7)
N(10)–Ag–P(2)	94.52(7)	P(1)–Ag–P(2)	110.59(3)
C(51)–P(1)–C(11)	103.8(2)	C(51)–P(1)–C(21)	103.9(2)
C(11)–P(1)–C(21)	104.4(2)	C(51)–P(1)–Ag	111.78(11)
C(11)–P(1)–Ag	118.14(11)	C(21)–P(1)–Ag	113.37(11)
C(61)–P(2)–C(31)	105.2(2)	C(61)–P(2)–C(41)	102.9(2)
C(31)–P(2)–C(41)	106.9(2)	C(61)–P(2)–Ag	107.65(11)
C(31)–P(2)–Ag	116.60(12)	C(41)–P(2)–Ag	116.15(11)
C(2)–N(1)–C(10b)	118.0(3)	C(2)–N(1)–Ag	125.9(2)
C(10b)–N(1)–Ag	115.5(2)	N(1)–C(2)–C(3)	123.3(4)
C(4)–C(3)–C(2)	119.4(4)	C(3)–C(4)–C(4a)	119.1(3)
C(4)–C(4a)–C(10b)	118.2(3)	C(4)–C(4a)–C(5)	122.5(3)
C(10b)–C(4a)–C(5)	119.3(3)	C(6)–C(5)–C(4a)	120.3(4)
C(5)–C(6)–C(6a)	122.1(3)	C(7)–C(6a)–C(10a)	117.4(3)
C(7)–C(6a)–C(6)	123.5(3)	C(10a)–C(6a)–C(6)	119.1(3)
C(8)–C(7)–C(6a)	119.9(4)	C(7)–C(8)–C(9)	118.9(4)
N(10)–C(9)–C(8)	123.1(4)	C(9)–N(10)–C(10a)	118.5(3)
C(9)–N(10)–Ag	125.1(2)	C(10a)–N(10)–Ag	114.5(2)
N(10)–C(10)–C(6a)	122.2(3)	N(10)–C(10a)–C(10b)	118.7(3)
C(6a)–C(10a)–C(10b)	119.2(3)	N(1)–C(10b)–C(4a)	122.0(3)
N(1)–C(10b)–C(10a)	118.1(3)	C(4a)–C(10b)–C(10a)	119.9(3)

[Ag(dppf)(L)]ClO$_4$ (L = PPh$_3$ **2** *or* SPPh$_3$ **3**). To a solution of **1** (0.076 g, 0.05 mmol) in dichloromethane (20 cm^3) was added PPh$_3$ (0.026 g, 0.1 mmol) or SPPh$_3$ (0.029 g, 0.1 mmol) and the mixture stirred for 30 min. The solution was concentrated to *ca.* 5 cm^3 and addition of diethyl ether (15 cm^3) gave yellow solids of **2** or **3**. Complex **2** was also obtained by another procedure: to a dichloromethane solution of [Ag(OClO$_3$)(PPh$_3$)] (0.047 g, 0.1 mmol) was added dppf (0.055 g, 0.1 mmol) and the solution stirred for 30 min. Concentration to *ca.* 5 cm^3 and addition of diethyl ether (15 cm^3) gave a yellow solid **2**.

[Ag(dppf)(PPh$_2$Me)$_2$]ClO$_4$ **4**. To a solution of **1** (0.076 g, 0.05 mmol) in tetrahydrofuran (20 cm^3) was added PPh$_2$Me (0.037 cm^3, 0.2 mmol). The mixture was stirred for 30 min, whereupon concentration to *ca.* 5 cm^3 and addition of diethyl ether (15 cm^3) gave **4** as a yellow solid.

[Ag(dppf)(L–L)]ClO$_4$ (L–L = dppf **5**, phen **6**, bipy **7** *or* SdppmS **8**). To a solution of **1** (0.076 g, 0.05 mmol) in dichloromethane (20 cm^3) was added dppf (0.055 g, 0.1 mmol), phen (0.018 g, 0.1 mmol), bipy (0.015 g, 0.1 mmol) or SdppmS (0.045 g, 0.1 mmol). The solution was stirred for 30 min and then concentrated to *ca.* 5 cm^3. Addition of diethyl ether (15 cm^3) gave yellow-orange solids of the complexes **5**–**8**. Another synthetic route was also used to prepare compound **5**: to a solution of AgClO$_4$ (0.021 g, 0.1 mmol) in acetone (20 cm^3) was added dppf (0.111 g, 0.2 mmol) and the mixture stirred for 30 min. Concentration to *ca.* 5 cm^3 and addition of diethyl ether afforded complex **5** as a yellow solid.

[Ag(S$_2$CNR$_2$)(dppf)] (R = Et **9** *or* Me **10**). To a solution of **1** (0.076 g, 0.05 mmol) in dichloromethane (25 cm^3) was added Na(S$_2$CNEt$_2$) (0.017 g, 0.1 mmol) or Na(S$_2$CNMe$_2$) (0.014 g, 0.1 mmol). The solution was stirred for 2 h, during which white NaClO$_4$ precipitated. The solution was filtered through Celite. Concentration to *ca.* 5 cm^3 and addition of hexane yielded yellow solids of **9** or **10**.

X-Ray Structure Determinations.—Crystals were mounted in inert oil on glass fibres. Data were collected using monochromated Mo-Kα radiation (λ = 0.710 73 Å). Diffractometer type: Siemens-Stoe AED-2 (**2**), Stoe STADI-4 (**5** and **6**), with an Oxford or Siemens low-temperature attachment, respectively. Scan type ω–θ. Cell constants were refined from

Table 8 Analytical data and other properties for complexes **1**–**10**

Complex	Yield (%)	Analysis[a] (%) C	H	N	Λ_M[b]/Ω^{-1} cm^2 mol^{-1}	M.p./°C
1 $[\{Ag(OClO_3)(dppf)\}_2]$	70	53.20 (53.60)	3.60 (3.70)		132	195[c]
2 $[Ag(dppf)(PPh_3)]ClO_4$	99	60.75 (61.00)	4.00 (4.25)		143	90
3 $[Ag(dppf)(SPPh_3)]ClO_4 \cdot 0.5CH_2Cl_2$	78	57.55 (57.40)	4.30 (4.05)		132	185
4 $[Ag(dppf)(PPh_2Me)_2]ClO_4$	86	61.85 (62.00)	4.90 (4.70)		140	125
5 $[Ag(dppf)_2]ClO_4$	88	62.60 (62.30)	4.55 (4.30)		132	215[c]
6 $[Ag(dppf)(phen)]ClO_4$	56	58.15 (58.65)	3.95 (3.85)	2.65 (2.95)	134	215[c]
7 $[Ag(dppf)(bipy)]ClO_4 \cdot 0.5CH_2Cl_2$	84	55.65 (55.65)	4.15 (3.90)	2.95 (2.90)	135	180
8 $[Ag(dppf)(SdppmS)]ClO_4$	79	57.70 (57.65)	4.35 (4.10)		135	175
9 $[Ag(S_2CNEt_2)(dppf)]$	62	57.85 (57.80)	5.20 (4.70)	1.80 (1.70)	0.3[d]	190[c]
10 $[Ag(S_2CNMe_2)(dppf)]$	43	56.80 (56.70)	4.40 (4.35)	1.80 (1.80)	10.76	120

[a] Calculated values in parentheses. [b] In acetone. [c] With decomposition. [d] In nitromethane.

Table 9 Details of data collection and structure refinement for complexes **2**, **5** and **6**

Compound	$2 \cdot 2CH_2Cl_2$	$5 \cdot 2CHCl_3$	**6**
Chemical formula	$C_{54}H_{49}AgCl_5FeO_4P_3$	$C_{70}H_{58}AgCl_7Fe_2O_4P_4$	$C_{46}H_{36}AgClFeN_2O_4P_2$
Crystal habit	Orange tablet	Yellow tablet	Yellow prism
Crystal size/mm	0.90 × 0.90 × 0.38	0.85 × 0.35 × 0.10	0.40 × 0.35 × 0.23
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a/Å	14.275(2)	11.411(2)	11.027(4)
b/Å	16.997(2)	16.517(3)	17.050(3)
c/Å	21.219(3)	18.600(4)	21.029(5)
α/°	–	98.20(2)	–
β/°	96.76(2)	94.59(2)	95.09(3)
γ/°	—	107.45(2)	—
U/Å^3	5112.6(12)	3282.0(11)	3938(2)
Z	4	2	4
D_c/Mg m^{-3}	1.554	1.573	1.589
M	1195.81	1554.76	941.88
F(000)	2432	1576	1912
T/°C	−100	−130	−130
$2\theta_{max}$/°	45	50	50
μ(Mo-Kα)/mm^{-1}	1.07	1.16	1.06
Transmission	0.67–0.81	0.78–0.85	0.77–0.85
No. of reflections measured	7047	11481	9143
No. of unique reflections	6725	11441	6953
R_{int}	0.125	0.042	0.023
$R[F, F > 4\sigma(F)]$	0.055	0.047	0.035
wR (F^2, all refl.)	0.154	0.113	0.076
a,b in $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$	0.1022, 14.5720	0.0275, 7.9238	0.0173, 4.1986
No. of parameters	613	793	515
No. of restraints	452	0	0
S	1.024	1.051	1.079
Max. $\Delta\rho$/e Å^{-3}	1.84	0.67	0.34

±ω angles of *ca.* 50 reflections in the range 2θ 20–23°. Absorption corrections were applied on the basis of ψ-scans. Structures were solved by the heavy-atom method (**2** and **5**) and direct methods (**6**) and refined anisotropically on F^2 using the program SHELXL 93.[18] Hydrogen atoms were included using a riding model. Other data are collected in Table 9.

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

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