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FULL PAPER

Co-ordination chemistry of 1,1′-bis(diphenylthiophosphoryl)ferrocene (dptpf) towards silver(I). Crystal structure of the polymeric complex $[Ag_2(\mu\text{-dptpf})\{(SPPh_2)_2CH_2\}_2]_n[ClO_4]_{2n}$ ‡

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The ligand 1,1′-bis(diphenylthiophosphoryl)ferrocene, dptpf, reacted with various silver complexes to afford two-, three- or four-co-ordinate species. Thus the reaction of dptpf with $[Ag(OClO_3)(PPh_3)]$ in 1 : 1 or 1 : 2 molar ratio gave the three-co-ordinate $[Ag(dptpf)(PPh_3)]ClO_4$ or the linear $[Ag_2(dptpf)(PPh_3)_2][ClO_4]_2$ derivatives. Similarly, the treatment of dptpf with $AgClO_4$ in 2 : 1 or 1 : 1 molar ratio afforded the homoleptic compounds $[Ag(dptpf)_2]ClO_4$ or $[Ag(dptpf)]ClO_4$; in the latter dptpf acts as a *trans*-chelating ligand. The complex $[Ag(dptpf)]ClO_4$ can react further with bidentate ligands such as 2,2′-bipyridine (bipy) or bis(diphenylthiophosphoryl)methane, $(SPPh_2)_2CH_2$, leading to the four-co-ordinate $[Ag(dptpf)(bipy)]ClO_4$ or the four-co-ordinate polymeric species $[Ag_2(\mu\text{-dptpf})\{(SPPh_2)_2CH_2\}_2]_n[ClO_4]_{2n}$, which was characterised by X-ray diffraction.

The diphosphine 1,1′-bis(diphenylphosphine)ferrocene (dppf), although synthesised more than two decades ago,[1] has recently received much attention in view of its chemical uniqueness and industrial importance. The ability of this ligand to confer the qualities of the ferrocenyl group on the resultant complexes without disturbing the inherent characteristics of the latter has widened the scope of metal complexes in the design of catalysts, drugs and materials.[2] One of the more important features of dppf is its flexibility; it can modify its steric bite in order to adapt to different geometric requirements of the metal centres. This fact has allowed the synthesis of a great variety of complexes with uncommon geometries, *e.g.* trigonal planar or tetrahedral gold(I) derivatives,[3] and is likely to play a role in the activity of various dppf-based metalloorganic catalysts.[4]

The oxidation of dppf with sulfur to give the bis(diphenylthiophosphoryl)ferrocene (dptpf) ligand provides a new derivative with a longer and more flexible backbone. We have previously demonstrated the bonding ability of dptpf towards Au^I or Ag^I by preparing the species $[M(dptpf)]^+$ with dptpf acting as a *trans*-chelating ligand,[5] and recently the analogous copper derivative has been obtained.[6] Here we report on the co-ordination chemistry of dptpf with silver(I) complexes. The use of $[Ag(dptpf)]^+$ as starting material has allowed not only the increase in the co-ordination number of the silver centre but the synthesis of the novel polymeric species $[Ag_2(\mu\text{-dptpf})\{(SPPh_2)_2CH_2\}_2]_n[ClO_4]_{2n}$.

Results and Discussion

The reaction of dptpf with $[Ag(OClO_3)(PPh_3)]$ in dichloromethane allows the synthesis of the three-co-ordinate $[Ag(dptpf)(PPh_3)]ClO_4$ **1** or the linear $[Ag_2(\mu\text{-dptpf})(PPh_3)_2][ClO_4]_2$ **2** derivatives in high yield (Scheme 1). Complexes **1** and **2** are air- and moisture-stable solids that behave as 1 : 1 or 1 : 2 electrolytes, respectively, in acetone solutions.

Their IR spectra are very similar and show bands arising from the PPh_3 and dptpf ligands and those of the perchlorate anion at 1100vs (br) and 620s cm^{-1}. In the ^1H NMR spectra three multiplets appear in the ratio 4 : 4 : 35 or 4 : 4 : 50, corresponding to the α and β protons of the cyclopentadienyl ring and to those in the phenyl groups. The $^{31}P\text{-}\{^1H\}$ NMR spectra at room temperature show a sharp resonance for the phosphorus of the dptpf and a broad signal for the PPh_3. At −55 °C a singlet (dptpf) and two doublets (PPh_3) are observed with an approximate ratio of 2 : 1 or 1 : 1 for complexes **1** or **2**, respectively (see Experimental). The two doublets arise from the coupling of the phosphorus with the two silver nuclei, ^{107}Ag and ^{109}Ag. In the positive-ion liquid secondary ion mass spectra (LSIMS) for complexes **1** or **2** the cation molecular peak appears only for the monocationic species $[Ag(dptpf)(PPh_3)]^+$ at $m/z = 987$ (1%). The most intense peak in both spectra is the fragment $[Ag(dptpf)]^+$, which appears at $m/z = 727$.

The treatment of dptpf with $AgClO_4$ in molar ratio 2 : 1 or 1 : 1 gives the homoleptic derivatives $[Ag(dptpf)_2]ClO_4$ **3** or $[Ag(dptpf)]ClO_4$ **4**. Compound **3** is probably tetrahedral while **4**, which we have previously reported,[5] has a silver centre linearly co-ordinated by the dptpf as a *trans*-chelating ligand, representing the first example of this type of complex for silver.

Compound **3** is a yellow air- and moisture-stable solid that behaves as a 1 : 1 electrolyte in acetone solutions. The ^1H NMR spectrum shows the resonances for the cyclopentadienyl and phenyl ring in the appropriate ratio. The $^{31}P\text{-}\{^1H\}$ spectrum is a singlet because of the equivalence of the phosphorus atoms. In the positive-ion LSIMS the cation molecular peak appears at $m/z = 1345$ (4%), although the most intense peak corresponds to the fragment $[Ag(dptpf)]^+$ at $m/z = 727$.

Taking into account the linear co-ordination of the silver centre in complex **4**, we surmised that this could easily react with further ligands, increasing the co-ordination number of the silver atom. Indeed, the reaction with bipy (2,2′-bipyridine) leads to the four-co-ordinate species $[Ag(dptpf)(bipy)]ClO_4$. Complex **5** is an air- and moisture-stable yellow solid that behaves as a 1 : 1 electrolyte in acetone solutions. Its IR spectrum presents, apart from the bands arising from dptpf and the anion ClO_4^-, the vibrations ν(C=N) at 1655m and 1687m cm^{-1} from the bipy ligand. The ^1H NMR spectrum shows two multiplets for the Cp protons and four resonances, two doublets and two virtual triplets, for the bipy protons. The positive-ion

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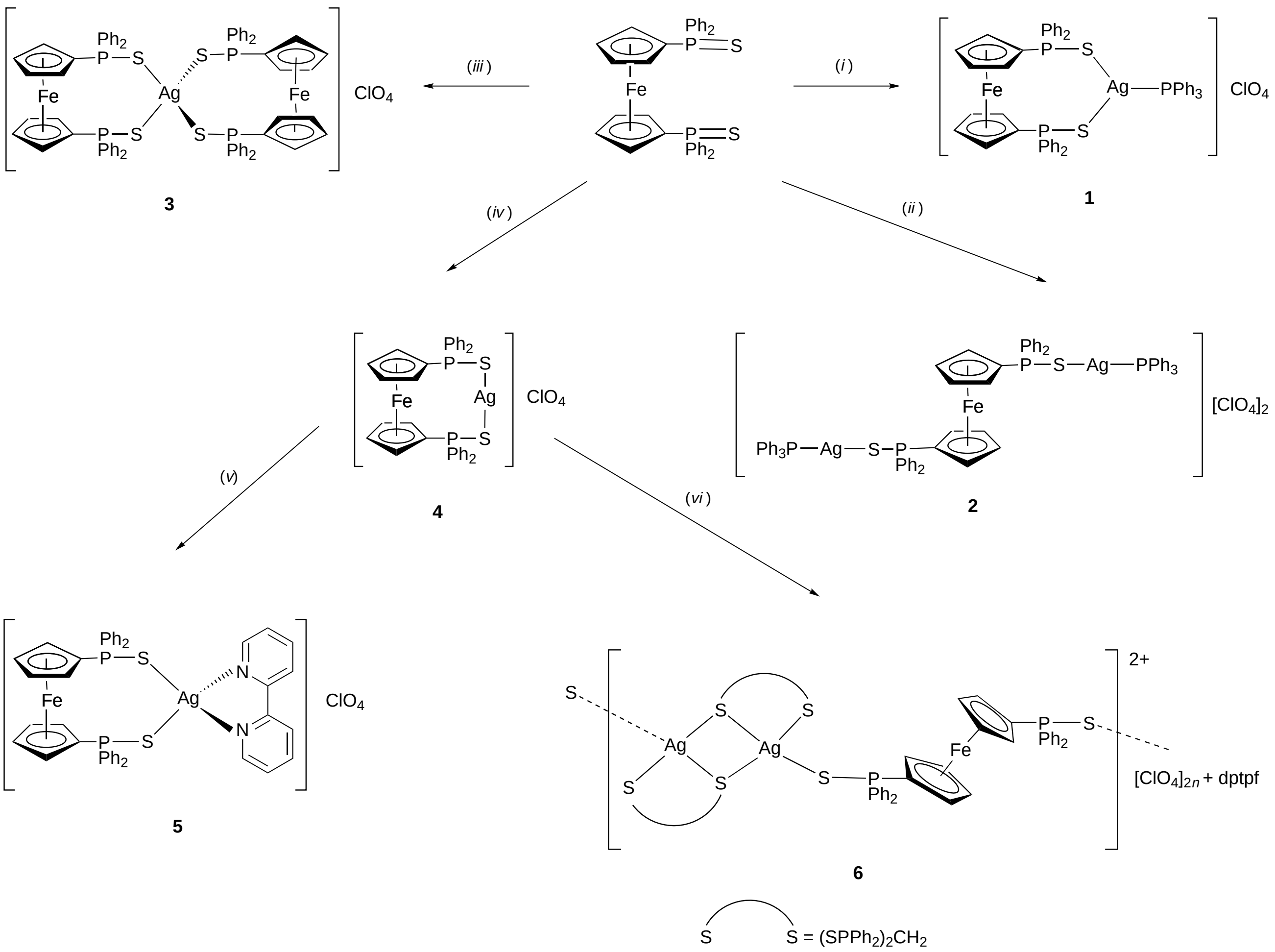
‡ Dedicated to Professor Pascual Royo on the occasion of his 60th birthday.



Scheme 1 (*i*) $[Ag(OClO_3)(PPh_3)]$; (*ii*) 2 $[Ag(OClO_3)(PPh_3)]$; (*iii*) $\frac{1}{2}$ $AgClO_4$; (*iv*) $AgClO_4$; (*v*) bipy; (*vi*) $(SPPh_2)_2CH_2$

LSIMS shows the cationic peak, $[Ag(dptpf)(bipy)]^+$, at $m/z = 982$ (1%). Again the most intense peak corresponds to the fragment $[Ag(dptpf)]^+$.

We have also carried out the reaction of $[Ag(dptpf)]ClO_4$ with $(SPPh_2)_2CH_2$. However, in contrast to the reaction mentioned above we obtained a complex of stoichiometry $[Ag_2(dptpf)\{(SPPh_2)_2CH_2\}_2][ClO_4]_2$ **6** and the free ligand dptpf. The ^1H NMR spectrum of **6** shows a triplet for the methylene protons of $(SPPh_2)_2CH_2$, two multiplets for the cyclopentadienyl protons and a multiplet for phenyl protons. The ratio is 1:1:1:15 which agrees with the proposed formula. The $^{31}P-\{^1H\}$ NMR spectrum presents two singlets for the equivalent phosphorus atoms of dptpf and $(SPPh_2)_2CH_2$, respectively, with an approximate ratio of 1:2. The positive-ion LSIMS shows neither the molecular peak, $[Ag_2(dptpf)\{(SPPh_2)_2CH_2\}_2][ClO_4]_2$, nor the $[M]^{2+}$ peak as expected for dicationic species. However some fragmentation peaks are present at $m/z = 1281$ (6%, $[Ag_2(dptpf)\{(SPPh_2)_2CH_2\}]^+$), 1173 (7%, $[Ag(dptpf)\{(SPPh_2)_2CH_2\}]^+$), 1111 (10%, $[Ag_2\{(SPPh_2)_2CH_2\}_2]^+$) and 727 (100%, $[Ag(dptpf)]^+$).

With these spectroscopic data we imagined a dinuclear structure with two chelating $(SPPh_2)_2CH_2$ and one bridging dptpf ligand. However, when we solved the crystal structure of complex **6** by X-ray diffraction, it turned out to be the polymeric species shown in Fig. 1. It is possible that in solution complex **6** is monomeric, because it is very soluble in common organic solvents and no higher peaks appear in the positive-ion FAB mass spectrum. In the solid state the polymeric chain arises through the connection of the $[Ag_2(dptpf)\{(SPPh_2)_2CH_2\}_2]^{2+}$ units through one of the sulfur atoms of the $(SPPh_2)_2CH_2$ ligand (see Fig. 2).

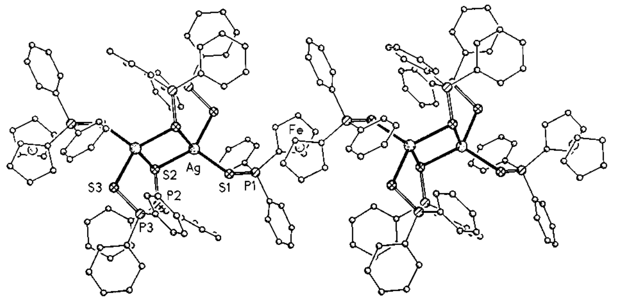


Fig. 1 Part of the polymeric chain of the cation of complex **6** in the crystal showing the atom numbering scheme, radii are arbitrary; H atoms are omitted for clarity

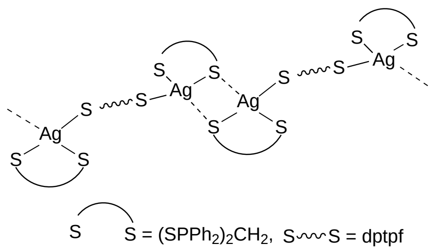


Fig. 2 Formation of the polymeric complex **6** in the solid state

The structure of the cation of **6** consists of a monomeric '$Ag_2(\mu\text{-}dptpf)\{(SPPh_2)_2CH_2\}_2$' unit that repeats to form a polymeric chain, although the asymmetric unit is only half the formula because the iron atom lies on an inversion centre. The single independent silver atom displays a distorted tetrahedral geometry; it is co-ordinated by a chelating $(SPPh_2)_2CH_2$ ligand

Table 1 Selected bond lengths (Å) and angles (°) for complex **6**

Ag–S3#	2.514(2)	Ag–S2	2.530(2)
Ag–S1	2.534(2)	Ag–S2#	2.801(2)
P1–C11	1.780(7)	P1–C21	1.804(7)
P1–C31	1.817(7)	P1–S1	1.982(2)
P2–C41	1.800(7)	P2–C51	1.806(7)
P2–C1	1.840(7)	P2–S2	1.997(2)
P3–C61	1.809(7)	P3–C71	1.816(7)
P3–C1	1.822(7)	P3–S3	1.972(2)
S3#–Ag–S2	129.81(6)	S3#–Ag–S1	104.99(6)
S2–Ag–S1	120.23(6)	S3#–Ag–S2#	96.93(6)
S2–Ag–S2#	96.57(6)	S1–Ag–S2#	98.81(6)
C11–P1–C21	106.8(3)	C11–P1–C31	104.7(3)
C21–P1–C31	107.1(3)	C11–P1–S1	112.9(2)
C21–P1–S1	110.6(2)	C31–P1–S1	114.3(2)
C41–P2–C51	105.8(3)	C41–P2–C1	109.1(3)
C51–P2–C1	107.7(3)	C41–P2–S2	110.6(2)
C51–P2–S2	110.5(2)	C1–P2–S2	112.8(2)
C61–P3–C71	106.3(3)	C61–P3–C1	106.5(3)
C71–P3–C1	105.1(3)	C61–P3–S3	111.5(2)
C71–P3–S3	111.6(2)	C1–P3–S3	115.2(2)
P1–S1–Ag	106.01(9)	P2–S2–Ag	106.91(9)
P2–S2–Ag#	103.95(9)	Ag–S2–Ag#	83.43(6)
P3–S3–Ag#	107.74(9)	P3–C1–P2	117.7(4)

Symmetry transformation used to generate equivalent atoms: # $-x + \frac{1}{2}, -y + \frac{3}{2}, -z$.

(atoms S2 and S3), whereby one sulfur atom (S2) also forms a bridge to an adjacent silver atom, leading to four-membered Ag_2S_2 rings with inversion symmetry. This type of co-ordination for the $(SPPh_2)_2CH_2$ ligand has not been previously reported. A search of the Cambridge Database revealed no other cases where one sulfur atom of the ligand co-ordinates one, and the other two, metal atoms.[7] The fourth co-ordination site is occupied by one sulfur atom (S1) of the dptpf ligand, which then links (*via* its second symmetry-related S1) the monomeric units to form the polymer. Table 1 lists bond lengths and angles for complex **6**; three of the Ag–S distances are similar Ag–S1 2.534(2), Ag–S2 2.530(2) and Ag–S3# 2.514(2) Å. These distances are slightly shorter than in other tetrahedral silver complexes such as $[AgBr([18]aneS_6)]$[8] ([18]-aneS_6 = 1,4,7,10,13,16-hexathiacyclooctadecane) [2.514(1)–2.636(1) Å], $[Ag\{(SPPh_2)_2CH_2\}\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$[9] [2.540(2), 2.588(2) Å], $[Ag_2\{S_2C_2(CN)_2\}(PPh_3)_4]$[10] [2.568(7), 2.653(7) Å for the silver atom in a tetrahedral geometry]. The other distance Ag–S2# is longer, 2.801(2) Å, and corresponds to the three-co-ordinate sulfur atom; this agrees with our proposed pathway for polymer formation. A search of the Cambridge Database revealed 426 Ag–S bonds involving four-co-ordinate silver; the bond lengths ranged from 2.360–3.008 Å. The Ag–S2# distance of 2.801(2) Å can thus reasonably be regarded as a bonding interaction. Within the four-membered ring, the independent angles are 96.57(6)° at Ag and 83.43(6)° at S2, the Ag–Ag# distance is 3.554(1) Å, too long to be considered an interaction. The angles at silver vary between 96.57(6) (as above) and 129.81(6)° [S2–Ag–S3#]; the bite angle of the $(SPPh_2)_2CH_2$ ligand is 96.93(6)°. Owing to the imposed symmetry, the cyclopentadienyl rings ideally stagger and the phosphorus atoms are antiperiplanar.

Experimental

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in *ca.* 5 x 10^{-4} mol dm^{-3} solutions with a Philips 9509 conductimeter, C and H analyses were carried out with a Perkin-Elmer 2400 microanalyzer. Mass spectra were recorded on a VG Autospec, with the liquid secondary-ion mass spectra (LSIMS) technique, using nitrobenzyl alcohol as matrix, NMR spectra were recorded on a Varian Unity 300 spectrometer and a Bruker ARX 300 spectrometer in $CDCl_3$. Chemical shifts are cited relative to $SiMe_4$ (^1H, external) and 85% H_3PO_4 (^{31}P, external). The starting materials dptpf,[1b] $[Ag(OClO_3)(PPh_3)]$[11] and $(SPPh_2)_2CH_2$[12] were prepared by published procedures. All other chemicals used were commercially available and used without further purification. **CAUTION:** perchlorate salts with organic cations may be explosive.

Syntheses

$[Ag(dptpf)(PPh_3)]ClO_4$ 1. To a solution of $[Ag(OClO_3)(PPh_3)]$ (0.047 g, 0.1 mmol) in dichloromethane (20 cm^3) was added dptpf (0.062 g, 0.1 mmol) and the mixture stirred for 1 h. Concentration of the solution to *ca.* 5 cm^3 and addition of diethyl ether (10 cm^3) gave **1** as an orange solid. Yield 80%. Λ_M 142 Ω^{-1} cm^2 mol^{-1} (Found: C, 56.15; H, 3.96; S, 6.06. Calc. for $C_{52}H_{43}AgClFeO_4P_3S_2$: C, 57.40; H, 3.98; S, 5.89%). NMR data, ^1H: δ 4.40 (m, 4 H, C_5H_4), 4.61 (m, 4 H, C_5H_4), 7.1–7.8 (m, 35 H, Ph); ^{31}P-{^1H}: δ 44.9 (s, dptpf), 8.1 [dd, PPh_3, $J(^{109}AgP)$ 543.0, $J(^{107}AgP)$ 447.1 Hz].

$[Ag_2(\mu\text{-dptpf})(PPh_3)_2][ClO_4]_2$ 2. To a solution of $[Ag(OClO_3)(PPh_3)]$ (0.094 g, 0.2 mmol) in dichloromethane (20 cm^3) was added dptpf (0.062 g, 0.1 mmol) and the mixture stirred for 1 h. Concentration of the solution of *ca.* 5 cm^3 and addition of diethyl ether (10 cm^3) gave **2** as an orange solid. Yield 89%. Λ_M 253 Ω^{-1} cm^2 mol^{-1} (Found: C, 52.75; H, 3.67; S, 4.42. Calc. for $C_{70}H_{58}Ag_2Cl_2FeO_8P_4S_2$: C, 52.91; H, 3.71; S, 4.00%). NMR data, ^1H: δ 4.36 (m, 4 H, C_5H_4), 4.63 (m, 4 H, C_5H_4), 7.1–8.0 (m, 50 H, Ph); ^{31}P-{^1H}: δ 50.9 (s, dptpf), 17.1 [dd, PPh_3, $J(^{109}AgP)$ 566.8, $J(^{107}AgP)$ 493.6 Hz].

$[Ag(dptpf)_2]ClO_4$ 3. To a dichloromethane solution (20 cm^3) of $AgClO_4$ (0.021 g, 0.1 mmol) was added dptpf (0.124 g, 0.2 mmol) and the mixture stirred for 1 h. Evaporation of the solvent to *ca.* 5 cm^3 and addition of diethyl ether (10 cm^3) gave **3** as a yellow solid. Yield 62%. Λ_M 129 Ω^{-1} cm^2 mol^{-1} (Found: C, 54.48; H, 4.13; S, 7.58. Calc. for $C_{44}H_{56}AgClFe_2O_4P_4S_4$: C, 54.97; H, 3.95; S, 8.38%). NMR data, ^1H: δ 4.38 (m, 8 H, C_5H_4), 4.53 (m, 8 H, C_5H_4), 7.4–7.8 (m, 40 H, Ph); ^{31}P-{^1H}: δ 46.1 (s, dptpf).

$[Ag(dptpf)(bipy)]ClO_4$ 5. To a dichloromethane solution (20 cm^3) of $[Ag(dptpf)]ClO_4$ (0.081 g, 0.1 mmol) was added bipy (0.011 g, 0.1 mmol) and the mixture stirred for 2 h. Evaporation of the solvent to *ca.* 5 cm^3 and addition of diethyl ether (10 cm^3) gave **5** as a yellow solid. Yield 78%. Λ_M 133 Ω^{-1} cm^2 mol^{-1} (Found: C, 53.52; H, 3.78; N, 2.76; S, 6.75. Calc. for $C_{44}H_{26}AgClFeN_2O_4P_2S_2$: C, 53.76; H, 3.66; N, 2.85; S, 6.51%). NMR data, ^1H: δ 4.38 (m, 4 H, C_5H_4), 4.61 (m, 4 H, C_5H_4), 7.37 (t, 2 H, bipy), 7.4–7.7 (m, 20 H, Ph), 7.94 (t, 2 H, bipy), 8.27 (d, 2 H, bipy), 8.41 (d, 2 H, bipy), ^{31}P-{^1H}: δ 44.8 (s, dptpf).

$[Ag_2(\mu\text{-dptpf})\{(SPPh_2)_2CH_2\}_2]_n[ClO_4]_{2n}$ 6. To a dichloromethane solution (20 cm^3) of $[Ag(dptpf)]ClO_4$ (0.081 g, 0.1 mmol) was added $(SPPh_2)_2CH_2$ (0.045 g, 0.1 mmol) and the mixture stirred for 30 min. Evaporation of the solvent to *ca.* 5 cm^3 and addition of diethyl ether (10 cm^3) gave **6** as a yellow solid. Yield 72%. Λ_M 133 Ω^{-1} cm^2 mol^{-1} (Found: C, 52.03; H, 3.51; S, 10.01. Calc. for $C_{84}H_{72}Ag_2Cl_2FeO_8P_6S_6$ (monomeric unit): C, 52.27; H, 3.76; S, 9.96%). NMR data, ^1H: δ 4.03 (t, 4 H, CH_2), 4.43 (m, 4 H, C_5H_4), 4.47 (m, 4 H, C_5H_4), 7.4–7.9 (m, 60 H, Ph); ^{31}P-{^1H}: δ 40.6 (s, dptpf), 34.2 [s, $(SPPh_2)_2CH_2$].

Crystallography

The crystal was mounted in inert oil on a glass fibre and transferred to the cold gas stream of a Siemens P4 diffractometer equipped with an LT-2 low temperature attachment. Data were

Table 2 Details of data collection and structure refinement for complex **6**

Compound	**6**·$3CH_2Cl_2$
Chemical Formula	$C_{84}H_{72}Ag_2Cl_2FeO_8P_6S_6 \cdot 3CH_2Cl_2$
M	2184.86
Crystal habit	Orange tablet
Crystal size/mm	0.75 × 0.40 × 0.12
Crystal system	Monoclinic
Space group	$C2/c$
a/Å	26.933(4)
b/Å	11.2087(12)
c/Å	31.404(3)
β/°	105.737(8)
U/Å^3	9125(2)
Z^a	4
D_c/Mg m^{-3}	1.590
F(000)	4424
T/°C	−100
$2\theta_{max}$/°	50
μ(Mo-Kα)/mm^{-1}	1.113
No. of reflections measured	8146
No. of unique reflections	8001
R_{int}	0.034
R^b [F, $F > 4\sigma(F)$]	0.059
wR^c (F^2, all reflections)	0.156
No. of reflections used	7996
No. of parameters	526
No. of restraints	425
S^d	0.866
Maximum $\Delta\rho$/e Å^{-3}	2.5

[a] Based on formula with one Fe atom. [b] $R(F) = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [c] $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program. [d] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$, where n is the number of data and p the number of parameters.

collected using monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å), scan type ω. Cell constants were refined from setting angles of 58 reflections in the range 2θ 7–25°; ψ scans displayed no significant intensity variations, therefore no absorption correction could be applied. The structure was solved by direct methods and refined on F^2 using the program SHELXL 93.[13] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. Special refinement details: because of the rather weak data, an effect attributable to the dichloromethane of solvation, a system of restraints to light-atom displacement-factor components and local ring symmetry was used. The major features of residual density are associated with one of the solvent molecules, which may be disordered. Further details of the data collection and structure refinement are given in Table 2.

CCDC reference number 186/911.

See http://www.rsc.org/suppdata/dt/1998/1277/ for crystallographic files in .cif format.

Acknowledgements

We thank the Dirección General de Investigación Científica y Técnica (No. PB94-0079) and the Fonds der Chemischen Industrie for financial support.

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Received 12*th December* 1997; *Paper* 7/08959G