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Synthesis and crystallographic characterisation of silver complexes with the ligand diferrocenylphenylphosphine

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Abstract—Diferrocenylphosphine (PFc₂Ph) reacts with Ag(TfO) or [Ag(TfO)(PR₃)] (TfO = trifluoromethanesulfonate) to afford the three-coordinate complexes [Ag(TfO)(PFc₂Ph)₂] or [Ag(TfO)(PFc₂Ph)(PR₃)] (PR₃ = PPh₂Me, PPh₃), respectively. The complex [Ag(TfO)(PFc₂Ph)₂] further reacts with bidentate ligands, such as bis(diphenylthiophosphoryl)methane (dptpm) or S₂CNEt₂⁻ leading to the cationic, [Ag(PFc₂Ph)₂(dptpm)]TfO, or neutral, [Ag(S₂CNEt₂)(PFc₂Ph)₂], four-coordinate complexes. The reaction with 1,10-phenanthroline (phen) gives to the four-coordinate [Ag(TfO)(PFc₂Ph)(phen)]. © 1998 Elsevier Science Ltd. All rights reserved. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: Silver; Ferrocene; Diferrocenylphenylphosphine

The study of the coordination chemistry of ferrocenylphosphines, such as the diphosphine 1,1'bis(diphenylphosphino)ferrocene, has attracted a great deal of interest because the resultant complexes often find applications in homogeneous catalysis, in organic synthesis, manipulation of materials and production of fine chemicals [1, 2]. However, diferrocenylphenylphosphine (PFc₂Ph), although synthesised more than three decades ago, by interaction of ferrocene with dichlorophenylphosphine in the presence of anhydrous aluminium chloride [3], has scarcely been studied. Only very few complexes, such as $[M(CO)_5(PFc_2Ph)]$ (M = Mo or W), [CoMe $(DH)_2(PFc_2Ph)$] (DH = dimethylglioximate), [Ni $(acac)_2(PFc_2Ph)$ [4] or the gold derivative [AuCl(PFc₂Ph)] [5], have been reported, but no silver derivative has been described so far.

Here we report on the synthesis of mononuclear three- or four coordinate silver(I) complexes that contain one or two diferrocenylphenylphosphine ligands.

RESULTS AND DISCUSSION

The reaction of Ag(TfO) (TfO trifluoromethanesulfonate) with diferrocenylphenylphosphine (PFc₂Ph) in diethyl ether, in a 1:2 molar ratio, gives a suspension from which [Ag(TfO)(PFc₂Ph)₂] 1 can be isolated (Scheme 1). Other mononuclear complexes with two different phosphines, $[Ag(TfO)(PFc_2Ph)(PR_3)](PR_3 = PPh_2Me$ 2, PPh_3 3), can be prepared by reaction of [Ag(TfO)(PR₃)] with the ferrocenylphosphine in dichloromethane. Complexes 1-3 are yellow solids, air- and moisture stable. They behave as 1:1 electrolytes in acetone solution, which confirms an ionic nature, [Ag(PFc₂Ph)(PR₃)]TfO, in solution. In the IR spectra, the trifluoromethanesulfonate group gives rise to strong absorptions at 1625 (br) [v(SO₃)], 1225 $[v_{sym}(CF_3)]$ and 1559 $[v_{as}(CF_3)]$ cm⁻¹.

In the positive-ion liquid secondary ion mass spectra (LSIMS) the cation peaks $[Ag(PFc_2Ph)(PR_3)]^+$ appear at m/z 1063 (1, 50) and 847 (3, 57%). Additionally, other fragments in the spectrum of 3 correspond to $[Ag(PPh_3)_2]^+$ (633, 85) and $[Ag(PFc_2Ph)_2]^+$ (1063, 25%).

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Scheme 1. (i) 1/2 Ag(TfO) or [Ag(TfO)(PR₃)], (ii) 1+P(S)Ph₂CH₂PPh₂(S) or NaS₂CNEt₂, (iii) 1+phen.

The ¹H NMR spectra of complexes 1–3 show the four different protons of the $P(C_5H_4)$ rings as four multiplets or as a broad multiplet and the equivalent protons of the C_5H_5 rings as a singlet (see Table 1). In the spectrum of complex 3 the resonances due to complex 1 are also present. In the ${}^{31}P{}^{1}H$ NMR spectrum of 1, CDCl₃ at -55° C, two doublets are observed as a consequence of chemically equivalent phosphorus atoms coupled to ¹⁰⁷Ag and ¹⁰⁹Ag nuclei. Complexes 2 and 3 present an AB system, both coupled to the two silver nuclei (Table 1). In the spectrum of 3 the resonances due to complex 1 and $[Ag(PPh_3)_2]^+$ [two doublets at $\delta - 3.2$, J(AgP) 604.3, 524.0 Hz] are also observed, indicating the existence of a ligand exchange equilibrium of 3 and the corresponding homoleptic species, although complex 3 is predominant. In complex 2 only signals of very low intensity at $\delta -2$ ([Ag(PFc_2Ph)_2]⁺) and -4 $([Ag(PPh_2Me)_2]^+)$ are present.

The structure of complex 1 was confirmed by X-ray diffraction analysis. The molecule is shown in Fig. 1, with selected bond lengths and angles in Table 2. The trifluoromethanesulfonate is coordinated by one oxygen to the silver atom. The silver presents a somewhat distorted trigonal-planar coordination, probably due to the steric requirements of the phosphines, with angles P(2)–Ag–P(1) of 135.20(6), O(1)–Ag–P(1) of 104.6(2) and O(1)-Ag-P(2) of 120.2(2)°. The silver atom lies only 0.01 Å out of the plane of the two phosphorus and oxygen atoms. The Ag-P distances [2.450(2) and 2.445(2) Å] are similar to those found other tri-coordinate silver complexes in $[Ag(dppf)(PPh_3)]ClO_4$ [dppf=1,1'-bis(diphenylphosphino)ferrocene] [6] which range from 2.424(1) to 2.480(1) Å and slightly longer than those found in $[Ag_2(PPh_3)_2(SPPh_2CHPPh_2CHCO_2Me)]CIO_4$, 2.372(3) and 2.404(3) Å [7]. The Ag–O bond length of 2.345(7) Å is smaller than in the preceding dinuclear compound, 2.488(7) Å [7], but longer than in $[Ag(NO_3)(4-NO_2C_5H_4NO)_2]$, 2.364(3) and 2.318(3) Å [8]. The cyclopentadienyl rings are as expected parallel and planar. The rings are staggered by 13, 18 and 13° for Fe(2), Fe(3) and Fe(4), respectively, but by 29° for Fe(1), around the Cp · · · Cp axis (Cp = centre of cyclopentadienyl ring) defined by the torsion angles C–Cp–Cp–C. The Fe–Cp distances are in the range 1.639(3)–1.650(3) Å.

We have studied the reactivity of complex 1 with bidentate ligands such as bis(diphenylthiophosphoryl)methane (dptpm), S₂CNEt₂⁻ (from NaS₂ CNEt₂) or 1,10-phenanthroline (phen). Treatment of equimolecular amounts of 1 with the first two ligands affords the four-coordinate cationic or neutral complexes. $[Ag(PFc_2Ph)_2(dptpm)]TfO$ (4) and $[Ag(S_2CNEt_2)(PFc_2Ph)_2]$ (5). They are air- and moisture stable yellow solids. The IR spectrum of 4 shows bands at 1258 (s, br), 1224 (s) and 1157 (s) cm⁻¹, from the TfO anion, and the v(P=S) vibration appears at $557 (m) cm^{-1}$. A band at $1515 (m) cm^{-1}$ in the IR spectrum of 5 is attributable to v(C=N) of the dithiocarbamate ligand. In the LSIMS spectra the molecular peak does not appear, but the peaks assigned to the fragments $[Ag(PFc_2Ph)(L-L)]^+$ at m/z1035 (1, 50) and 847 (3, 57%) are present. Complex 4 is an 1:1 electrolyte in acetone solution, but 5 behaves as nonconductor in solution.

The ¹H NMR spectra of complexes 4 and 5 show the expected four resonances for the $P(C_5H_4)$ protons

			¹ H		³¹ P
Complex	$P(C_5H_4)$	(C ₅ H ₅)	L	PFc ₂ Ph	L
1 [Ag(TfO)(PFc ₂ Ph) ₂]	4.27(m) 4.46(m) 4.52(m) 4.67(m)	4.07(m)		-2(dd) ^a J(AgP) 577.0, 501.1	
2 [Ag(TfO)(PFc ₂ Ph)(PPh ₂ Me)]	4.17(m) 4.28(m) 4.34(m) 4.37(m)	3.90(m)	2.26(s) 7–8(m)	-2 ^a J(AB) 35.8 J(AgP) 603.3, 519.8	-3.8 J(AgP) 566.0, 470.2
3 [Ag(TfO)(PFc ₂ Ph)(PPh ₃)]	4–5(m)	4.04(m)	7–8(m)	11.05 ^a J(AB) 35.8 J(AgP) 604.3, 444.6	11.8 J(AgP) 582.9, 422.2
4 [Ag(PFc ₂ Ph) ₂ (dptpm)]TfO	4.09(m) 4.29(m) 4.36(m) 4.40(m)	4.04(m)	4.57(t) <i>J</i> (PH) 14.3	4.5(dd) ^b J(AgP) 640.9, 555.7	45.8(s)
$\textbf{5} \left[Ag(S_2CNEt_2)(PFc_2Ph)_2\right]$	4.08(m) 4.30(m) 4.31(m) 4.34(m)	4.10(m)	1.37(t) 4.07(q) <i>J</i> (HH) 6.96	7.1 (dd) ^b J(AgP) 598.1, 517.8	
6 [Ag(TfO)(PFc ₂ Ph)(phen)]	4.18(m) 4.22(m) 4.40(m) 4.43(m)	4.05(m)	7.44(m) 7.94(d) 8.56(d) 9.32(m)	-5.4(d, br) ^a J _{aver.} 442	

Table 1. ¹H and ³¹P-{¹H} NMR data for complexes 1–6

^a Recorded in CDCl₃ at -55° C, ^b Recorded in (CD₃)₂CO at -85° C, coupling constant in Hz; s = singlet, d = doublet, dd = two doublets, t = triplet, m = multiplet, br = broad.



Fig. 1. The molecule of complex 1 in the crystal showing the atom-numbering scheme, radii are arbitrary. H atoms are omitted for clarity.

Ag-O(1)	2.345(7)	Ag-P(2)	2.445(2)
Ag-P(1)	2.450(2)	P(1)-C(11)	1.805(7)
P(1)-C(21)	1.812(6)	P(1)-C(51)	1.829(6)
P(2)–C(31)	1.803(6)	P(2)–C(41)	1.812(6)
P(2)–C(61)	1.824(6)	S-O(1)	1.399(7)
O(1)–Ag–P(2)	120.2(2)	O(1)-Ag- $P(1)$	104.6(2)
P(2)-Ag-P(1)	135.20(6)	C(11)–P(1)–C(21)	102.9(3)
C(11) - P(1) - C(51)	103.2(3)	C(21)–P(1)–C(51)	105.2(3)
C(11)–P(1)–Ag	120.9(2)	C(21)–P(1)–Ag	110.6(2)
C(51)–P(1)–Ag	112.5(2)	C(31)–P(2)–C(41)	101.5(3)
C(31) - P(2) - C(61)	103.5(3)	C(41)–P(2)–C(61)	103.4(3)
C(31)–P(2)–Ag	130.0(2)	C(41)–P(2)–Ag	109.8(2)
C(61)–P(2)–Ag	105.7(2)	S–O(1)–Ag	125.0(4)

Table 2. Selected bond lengths [Å] and angles [°] for complex 1.

and a singlet for the C_5H_5 rings (Table 1). The CH_2 groups of **4** appears as a triplet at 4.57 ppm [*J*(PH), 14.3 Hz] and ethyl groups of **5** are present as a quartet (CH₂, 4.07 ppm, *J*(HH) 6.96 Hz) and a triplet (CH₃, 1.37 ppm). The ³¹P{¹H} NMR spectrum of **4**, (CD₃)₂CO at -85° C, shows a singlet for the two phosphorus of the diphosphine and two doublets for the phosphorus of the ferrocenylphosphine coupled with the ¹⁰⁷Ag and ¹⁰⁹Ag nuclei. In complex **5** only the resonance due to the phosphorus coupled to the silver nuclei (two doublets) is observed.

The crystal structure of complex 5 has been established by X-ray diffraction. The compound crystallises as a chloroform solvate. The molecule is shown in Fig. 2, with selected bond lengths and angles in Table 3. The silver atom is coordinated to two phosphines and one chelating dithiocarbamate ligand and has a distorted tetrahedral geometry. The distortion arises from the restricted bite of the dithiocarbamate, S(1)-Ag–S(2) 67.40(6) $^{\circ}$, whereas the other angles are wider than ideal, P(2)-Ag-S(2) 131.73(7) or P(1)-Ag-S(1) $126.87(7)^{\circ}$. The dihedral angle between the planes Ag– P(1)-P(2) and Ag-S(1)-S(2) is 66° . The cyclopentadienyl rings of Fe(1), Fe(2), Fe(3) and Fe(4) are staggered by 10, 2, 19 and 15°, respectively, around the Cp $\cdot \cdot \cdot$ Cp axis. The Ag–P distances are 2.500(2) 2.528(2) Å, similar and to those in $[Ag{(PPh_2)_2C_2B_{10}H_{10}}(dptpm)]ClO_4,$ 2.526(2)and 2.532(2) A [9], or in other four-coordinate complexes, such as $[Ag(dppe)_2]^+$ [10]. However the two different Ag-S distances, 2.605(2) and 2.739(2) Å, are longer than in $[Ag{(PPh_2)_2C_2B_{10}H_{10}}(dptpm)]ClO_4$, 2.540(2) and 2.588(2) Å [9].

Complex 1 reacts with equimolecular amounts of 1,10-phenanthroline in a different way; substitution of one ferrocenylphosphine is now observed to give $[Ag(TfO)(PFc_2Ph)(phen)]$ (6). Complex 6 is an airand moisture stable light orange solid. It behaves as an 1:1 electrolyte in acetone solution, which indicates the dissociation of the trifluoromethanesulfonate ligand to give the ions $[Ag(PFc_2Ph)(phen)]^+$

TfO⁻. In the LSIMS spectrum the cation peak $[Ag(PFc_2Ph)(phen)]^+$ appears at m/z 765 as the most intense one.

The ¹H NMR spectrum of **6** shows the expected resonances of the ferrocenylphosphine (Table 1) and four multiplets at 7.44, 7.94, 8.56 and 9.32 ppm due to the eight protons of the phenanthroline. The phosphorus atom appears as a broad doublet (CDCl₃, -55° C), due to the coupling with the silver nuclei, in the ³¹P{¹H} NMR spectrum.

The molecule of complex 6 is shown in Fig. 3 with selected bond lengths and angles in Table 4. The silver atom presents a distorted tetrahedral geometry, lying 0.39 Å out of the plane formed by the two nitrogen and phosphorus atoms in the direction of the triflate oxygen O(1), with Ag-O(1) 2.626(3) Å. The interplanar angle between AgN(1)N(2) and AgPO(1) is 88°. The restricted "bite" of the phenanthroline, N(1)-Ag–N(2) 72.12(10) $^{\circ}$, represents one major deviation from ideal geometry. The Ag-P bond, 2.3445(12) Å, is shorter than in complex 1 or in other three-coordinate derivatives, such as [Ag(dppf)(PPh₃)]ClO₄, 2.424(1) to 2.480(1)Å [6], or $[Ag\{(PPh_2)_2C_2B_9H_{10}\}(PPh_3)],$ 2.3974(10) to 2.4942(10) Å [11], reflecting the correspondingly weak Ag coordination to N and O atoms in 6. The phenanthroline is asymmetrically coordinated through two different Ag-N bonds of 2.289(3) and 2.351(3)Å which are of the same order as those found in other phenanthroline complexes, such as $[Ag{(PPh_2)_2C_2B_{10}H_{10}}(phen)]ClO_4$ [9] or [Ag(dppf)](phen)]ClO₄ [6]. The shorter Ag–N distance is associated with the widest angle, P-Ag-N(1) 142.11(7)°. The ferrocene systems display twists of 7 and 17° for Fe(1) and Fe(2), respectively.

EXPERIMENTAL

General

Infrared spectra were recorded in the range 4000– 200 cm⁻¹ on a Perkin-Elmer 883 spectrophotometer



Fig. 2. Molecular structure of complex 5 in the crystal. H atoms are omitted for clarity.

Ag-P(1)	2.500(2)	Ag–P(2)	2.528(2)
Ag-S(1)	2.605(2)	Ag-S(2)	2.739(2)
P(1)-C(1)	1.799(7)	P(1)–C(11)	1.811(7)
P(1)–C(41)	1.853(7)	P(2)–C(21)	1.807(7)
P(2)–C(31)	1.823(7)	P(2)–C(51)	1.835(7)
S(1)-C(60)	1.733(8)	S(2)-C(60)	1.721(8)
N–C(60)	1.340(9)	N-C(63)	1.450(10)
N–C(61)	1.482(9)		
P(1)-Ag-P(2)	115.95(7)	P(1)-Ag-S(1)	126.86(7)
P(2)-Ag-S(1)	105.70(7)	P(1)–Ag–S(2)	103.06(7)
P(2)-Ag-S(2)	131.73(7)	S(1)-Ag-S(2)	67.40(6)
C(1)–P(1)–Ag	116.5(2)	C(11)–P(1)–Ag	118.9(2)
C(41)–P(1)–Ag	112.7(2)	C(21)–P(2)–Ag	117.9(2)
C(31)–P(2)–Ag	120.0(3)	C(51)–P(2)–Ag	112.1(2)
C(60)–S(1)–Ag	89.1(3)	C(60)-S(2)-Ag	85.0(3)
C(60)–N–C(63)	122.5(7)	C(60)–N–C(61)	120.9(7)
C(63)–N–C(61)	116.6(6)	N-C(60)-S(2)	121.4(6)
N-C(60)-S(1)	120.1(6)	S(2)-C(60)-S(1)	118.4(4)
N-C(61)-C(62)	114.9(7)	N-C(63)-C(64)	112.3(7)

Table 3. Selected bond lengths [Å] and angles [°] for complex 5.

using Nujol mulls between polyethylene sheets. Conductivities were measured in $ca. 5 \times 10^{-4}$ mol dm⁻³ solutions with a Philips 9509 conductimeter. C and H analyses were carried out with a Perkin-Elmer 2400 microanalyser. Mass spectra were recorded on a VG autospec, with the LSIMS technique, using nitrobenzyl alcohol as matrix. NMR spectra were recorded on a Varian Unity 300 spectrometer and a Bruker ARX 300 spectrometer in $CDCl_3$ or $(CD_3)_2CO$. Chemical shifts are cited relative to $SiMe_4$ (¹H, external) and 85% H₃PO₄ (³¹P, external). The starting complexes [Ag(TfO)(PR₃)] (PR₃=PPh₂Me, PPh₃) where prepared by reaction of equimolar amounts of Ag(TfO) and the ligand PR₃ in dichloromethane.



Fig. 3. The molecule of complex 6 in the crystal. H atoms are omitted for clarity.

Ag-N(1)	2.289(3)	Ag–P	2.3445(21)
Ag–N(2)	2.351(3)	Ag-O(1)	2.626(3)
P-C(21)	1.800(3)	P-C(11)	1.800(3)
P-C(31)	1.820(3)	N(1)-C(2)	1.316(4)
N(1)-C(10B)	1.362(4)	N(2)-C(9)	1.326(4)
N(2)-C(10A)	1.355(5)	C(2)–C(3)	1.394(5)
C(3)–C(4)	1.359(6)	C(4)–C(4A)	1.395(6)
C(4A)-C(10B)	1.410(5)	C(4A) - C(5)	1.433(5)
C(5)–C(6)	1.342(6)	C(6)-C(6A)	1.421(6)
C(6A)-C(7)	1.402(6)	C(6A)-C(10A)	1.417(5)
C(7)–C(8)	1.363(6)	C(8)–C(9)	1.394(5)
C(10A)-C(10B)	1.435(5)		
N(1)–Ag–P	1.42.11(7)	N(1)-Ag-N(2)	72.12(10)
P-Ag-N(2)	135.01(7)	N(1)-Ag-O(1)	90.28(9)
P-Ag-O(1)	110.19(7)	N(2)-Ag-O(1)	92.63(10)
C(21)–P–C(11)	101.2(2)	C(21)–P–C(31)	102.0(2)
C(11)–P–C(31)	105.05(14)	C(21)–P–Ag	115.73(11)
C(11)–P–Ag	115.54(11)	C(31)–P–Ag	115.37(12)
C(2)-N(1)-C(10B)	118.3(3)	C(2)–N(1)–Ag	125.4(2)
C(10B)-N(1)-Ag	116.3(2)	C(9)-N(2)-C(10A)	118.1(3)
C(9)-N(2)-Ag	127.5(3)	C(10A)-N(2)-Ag	114.2(2)
N(1)-C(2)-C(3)	123.5(4)	C(4)-C(3)-C(2)	118.8(4)
C(3)-C(4)-C(4A)	119.9(4)	C(4)-C(4A)-C(10B)	117.8(3)
C(4)-C(4A)-C(5)	123.5(4)	C(10B)-C(4A)-C(5)	118.7(4)
C(6)-C(5)-C(4A)	121.2(4)	C(5)-C(6)-C(6A)	121.7(4)
C(7)-C(6A)-C(10A)	117.3(4)	C(7)-C(6A)-C(6)	123.5(4)
C(10A)-C(6A)-C(6)	119.2(4)	C(8)-C(7)-C(6A)	120.2(4)
C(7)-C(8)-C(9)	118.6(4)	N(2)-C(9)-C(8)	123.7(4)
N(2)-C(10A)-C(6A)	122.2(3)	N(2)-C(10A)-C(10B)	118.7(3)
C(6A)-C(10A)-C(10B)	119.1(3)	N(1)-C(10B)-C(4A)	121.6(3)
N(1)-C(10B)-C(10A)	118.3(3)	C(4A)-C(10B)-C(10A)	120.1(3)

Table 4. Selected bond lengths [Å] and angles [°] for complex 6.

Compound	1	$5 \cdot \text{CHCl}_3$	6
Chemical Formula	$C_{53}H_{46}AgF_3Fe_4O_3P_2S$	$C_{58}H_{57}AgCl_3Fe_4NP_2S_2$	$C_{39}H_{31}AgF_3Fe_2N_2O_3PS$
Crystal habit	yellow prism	yellow plate	yellow plate
Crystal size/mm	$0.70 \times 0.50 \times 0.20$	$0.40 \times 0.40 \times 0.10$	$0.40 \times 0.30 \times 0.15$
Crystal system	Triclinic	Triclinic	Triclinic
Space group	ΡĪ	ΡĪ	ΡĪ
$a/ m \AA$	11.719(4)	11.395(2)	11.152(4)
$b/ m \AA$	13.595(4)	12.154(2)	11.720(4)
$c/ m \AA$	15.698(4)	20.030(3)	14.024(5)
$\alpha/^{\circ}$	73.56(3)	77.771(14)	77.95(3)
$\beta/^{\circ}$	76.58(3)	79.167(10)	89.26(3)
$\gamma/^{\circ}$	89.58(3)	77.981(14)	80.37(3)
$U/Å^3$	2328.7(12)	2621.6(7)	1768.8(11)
Ζ	2	2	2
$D_c/\mathrm{g~cm^{-3}}$	1.730	1.687	1.720
M	1213.17	1331.73	915.26
<i>F</i> (000)	1224	1352	920
$T/^{\circ}\mathrm{C}$	-100	-100	-130
$2 heta_{ m max}/^{\circ}$	50	50	55
μ (Mo- $K\alpha$)/cm ⁻¹	18.0	17.82	15.21
Transmission	0.75-0.93	—	0.748-0.886
No. of reflections measured	8614	9410	8406
No. of unique reflections	8177	8964	8134
$R_{\rm int}$	0.034	0.068	0.127
$R^{\rm a}\left(F > 4\sigma(F)\right)$	0.054	0.054	0.038
$wR^{\rm b}$ (F^2 , all refl.)	0.145	0.123	0.089
No. of reflections used	8177	8925	8101
No. of parameters	604	642	469
No. of restraints	452	478	0
S ^c	1.016	0.951	1.096
Max. $\Delta \rho / e \AA^{-3}$	1.263	0.8	0.441

Table 5. Details of data collection and structure refinement for the complexes 1, 5 and 6.

^a $R(F) = \Sigma ||F_{o}| - |F_{c}|| / \Sigma ||F_{o}|,$

^b $wR(F^2) = [\Sigma\{w(F_o^2 - F_o^2)2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}; w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_o^2]/3$ and *a* and *b* are constants adjusted by the program

^c $S = [\Sigma \{w(F_o^2 - F_c^2)^2\}/(n-p)]^{0.5}$, where *n* is the number of data and *p* the number of parameters.

$[Ag(TfO)(PFc_2Ph)_2]$ (1)

To a suspension of PFc₂Ph [3] (0.096 g, 0.2 mmol) in diethyl ether (20 cm³) was added Ag(TfO) (0.021 g, 0.1 mmol). The mixture was stirred for 1 h and then filtered. The product was dissolved in dichloromethane (20 cm³) and the solution was concentrated to *ca*. 5 cm³. Addition of diethyl ether (15 cm³) gave complex **1** as a yellow solid. Yield 79%, $\Lambda_{\rm M}$ 121 Ω^{-1} cm² mol⁻¹ (Found: C, 52.05; H, 3.5; S, 3.0. Calc. for C₅₃H₄₆AgF₃Fe₄O₃P₂S: C, 52.5; H, 3.7; S, 2.6%).

$[Ag(TfO)(PFc_2Ph)(PR_3)](PR_3 = PPh_2Me(\mathbf{2}), PPh_3(\mathbf{3}))$

To a solution of PFc₂Ph (0.048 g, 0.1 mmol) in dichloromethane (25 cm³) was added [Ag(TfO)(PR₃)] (0.046 g, PR₃=PPh₂Me; 0.052, PR₃=PPh₃; 0.1 mmol) and the mixture was stirred for 1 h. The solution was concentrated to *ca*. 5 cm³ and addition of hexane (15 cm³) gave complex **2** and **3** as a yellow solids. Complex **2**: Yield 65%, $\Lambda_{\rm M}$ 106 Ω^{-1} cm²mol⁻¹

[Ag(PFc₂Ph)₂(dptpm)]TfO (4)

To a solution of complex 1 (0.121 g, 0.1 mmol) in dichloromethane (20 cm³) was added P(S)Ph₂CH₂PPh₂(S) [12] (0.045 g, 0.1 mmol) and the mixture was stirred for 1 h. The solution was concentrated to *ca*. 5 cm³ and addition of diethyl ether (15 cm³) gave complex 4 as a yellow solid. Yield 60%, $\Lambda_{\rm M}$ 140 Ω^{-1} cm² mol⁻¹ (Found: C, 56.25; H, 4.15; S, 6.3. Calc. for C₇₈H₆₈AgF₃Fe₄O₃P₄S₃: C, 56.35; H, 4.1; S, 5.8%).

$[Ag(S_2CNEt_2)(PFc_2Ph)_2] (5)$

To a dichloromethane solution (20 cm³) of complex 1 (0.121 g, 0.1 mmol) was added NaS₂CNEt₂ (0.023 g, 0.1 mmol). The mixture was stirred for 4 h and then filtered off to remove the sodium tri-fluoromethanesulfonate. The solvent was evaporated under vacuum to *ca*. 5 cm³; addition of diethyl ether (15 cm³) afforded complexes **5** as a yellow solid. Yield 68% (Found: C, 55.9; H, 4.3; N, 1.15; S, 5.1. Calc. for $C_{57}H_{56}AgFe_4NP_2S_2$: C, 56.45; H, 4.65; N, 1.15; S, 5.2%).

$[Ag(TfO)(PFc_2Ph)(phen)]$ (6)

To a dichloromethane solution (20 cm^3) of complex **1** (0.121 g, 0.1 mmol) was added 1,10-phenanthroline (0.018 g, 0.1 mmol). The mixture was stirred for 1 h and then the solution was concentrated under vacuum to *ca*. 5 cm³; addition of diethyl ether (15 cm³) afforded complexes **6** as a light orange solid. Yield 75%, Λ_M 140 Ω^{-1} cm² mol⁻¹ (Found: C, 51.9; H, 3.45; N, 3.05; S, 3.75. Calc. for C₃₉H₃₁AgF₃Fe₂N₂O₃PS: C, 52.6; H, 3.4; N, 3.05; S, 3.5%).

Crystal Structure Determinations

The crystals were mounted in inert oil on glass fibres and transferred to the cold gas stream of a Siemens R3 (1) or P4 (5) or a STOE Stadi4 (6) diffractometers equipped with an LT-2 low temperature attachment. Data were collected using monochromated MoK α radiation ($\lambda = 0.71073$ Å). Scan type ω (1,5) or ω/θ (6). Cell constants were refined from setting angles (1,5) or $\pm \omega$ angles of *ca*. 60 reflections in the range $2\theta \ 10^{-1}$ 25°. Absorption corrections were applied on the basis of Ψ -scans (1,6). Structures were solved by the heavyatom method and refined on F² using the program SHELXL-93 [13]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. A system of restraints to light-atom displacement-factor components was used. Special refinement details for 1: The high displacement parameters of O(1) may indicate some disorder (flexibility of coordination geometry at silver). Crystal data are given in Table 5.

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