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1,1'-Bis(diphenyloxophosphoryl)ferrocene (dpopf) as ligand in silver(I) complexes. Crystal structure of [Ag(dpopf)(PPh₃)₂]ClO₄

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Abstract

The ligand 1,1'-bis(diphenyloxophosphoryl)ferrocene, dpopf, reacted with silver derivatives to afford mononuclear complexes, $[Ag(OClO_3)(dpopf)]$ (1), $[Ag(dpopf)_2]ClO_4$, $[Ag(dpopf)(PPh_3)]ClO_4$, or the dinuclear complex, $[Ag(PPh_3)\}_2(dpopf)](ClO_4)_2$. From 1, other three-, $[Ag(dpopf)(SPPh_3)]ClO_4$, and four-coordinated derivatives, $[Ag(dpopf)(PPh_3)_2]ClO_4$ (6) $[Ag(dpopf)(L-L)]ClO_4$ [L-L = bipy, $(SPPh_2)_2CH_2$] were obtained by substitution reactions. The crystal structure of 6 was solved and revealed the expected distorted tetrahedral coordination at silver, with a ligand bite angle of 96.10(13)°. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Silver complexes; Ferrocene complexes; Diphosphine complexes; Crystal structures

1. Introduction

The chemistry of 1,1'-bis(diphenylphosphine)ferrocene (dppf) is currently receiving much attention associated with its increasing applications [1]. It has a strong bonding ability based on the two PPh₂ groups and it is a very flexible ligand that can modify its steric bite in order to adapt to different geometric requirements of various metal centres. This has facilitated the synthesis of a great number of mono or polynuclear gold or silver derivatives with different geometries [2,3].

The oxidation of dppf to give bis(diphenyloxophosphoryl)ferrocene (dpopf), provides a new ligand with a longer and more flexible backbone. The presence of O-donor atoms could favour the coordination to copper or silver centres, rather than gold. Some copper complexes, such as $[Cu(dppf)(dpopf)]BF_4$ [4], [Cu- $(dpopf)_2](BF_4)_2$, or $[Cu(dpopf)_2(EtOH)](BF_4)_2$ [5], with dpopf as chelating ligand, have been recently reported. Here we report on the coordination chemistry of dpopf with silver centres. Mono and dinuclear derivatives are reported in which the oxygen donor ligand acts as bridging or chelating ligand.

2. Results and discussion

The reaction of dpopf with AgClO₄, in a molar ratio or 2:1, gives the mononuclear complexes 1:1 $[Ag(OClO_3)(dpopf)]$ (1) or $[Ag(dpopf)_2]ClO_4$ (2), respectively (See Scheme 1). They are yellow, air- and moisture-stable solids and behave as 1:1 electrolytes in acetone solution. Their IR spectrum shows, apart from the bands arising from the dpopf ligand, those of the perchlorate at 1097(vs, br), 1073(s), 919(w) and 623(m) cm^{-1} (1) or 1096(vs, br) and 625(m) cm^{-1} (2). The positive-ion LSI MS exhibits a peak corresponding to the cation $[Ag(dpopf)]^+$ or $[Ag(dpopf)_2]^+$ at m/z = 693(25%, 1) or 1279 (2%, 2), respectively. The ¹H NMR spectra show, apart from the multiplet from the phenyl protons, two multiplets for the α and β protons of the substituted cyclopentadienyl rings at approximately 4.2 and 4.6 ppm. The ${}^{31}P{}^{1}H{}$ NMR spectra at room temperature show a singlet at 28.7 (1) or 34.4 ppm (2).

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Scheme 1. (i) $AgClO_4$; (ii) $1/2 AgClO_4 (L-L = dpopf)$; (iii) $[Ag(OClO_3)(PPh_3)]$ (L = PPh₃); (iv) 2 $[Ag(OClO_3)(PPh_3)]$; (v) 2 PPh₃; (vi) PPh₃ or SPPh₃; (vii) bipy or (SPPh₂)₂CH₂ or NaS₂CNEt₂.

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The treatment of dpopf with $[Ag(OClO_3)(PPh_3)]$, in the molar ratio 1:1 or 1:2, gives the ionic mononuclear [Ag(dpopf)(PPh₃)]ClO₄ (3) or the dinuclear $[{Ag(PPh_3)}_2(dpopf)](ClO_4)_2$ (4) derivative as a vellow solid. Complexes 3 and 4 behave as 1:1 or 2:1 electrolytes, respectively. The positive-ion LSI MS exhibit a peak corresponding to the cation $[Ag(PPh_3)(dpopf)]^+$ at m/z = 957 (10%, 3; 22%, 4). The ³¹P{¹H} NMR spectrum of 3, at -55° , shows a broad singlet at 36.6 ppm (dpopf) and a poorly resolved doublet of doublets (PPh₃) at 11.4 ppm. Complex 4 shows, at room temperature, a singlet at 38.4 (dpopf) and two doublets at 15.1 ppm [PPh₃, J(PAg) 714.2 and 823.9 Hz].

Complex 1 reacts readily with further ligands. The reaction with monodentate ligands leads to the threecoordinate $[Ag(dpopf)L]ClO_4 [L = PPh_3 (3), SPPh_3 (5)]$ or to the four-coordinate $[Ag(dpopf)(PPh_3)_2]ClO_4$ (6) complexes (Scheme 1). The reaction with bidentate ligands leads to the four-coordinate [Ag(dpopf)(L-L))]- ClO_4 [L-L = bipy (7), (SPPh₂)₂CH₂ (8)]. These are airand moisture-stable yellow solids that behave as 1:1 electrolytes in acetone solutions. The positive-ion LSI MS show the cation molecular peak, $[M - ClO_4]^+$, except for complex 7 [m/z = 989 (5, 1%), 1219 (6, 1%),1143 (8, 4%)]. The cation $[Ag(dpopf)]^+$ is observed in all the complexes (m/z = 693). The vibration v(P=S)appears in the IR spectra at 591(m) (5) or 568(m) cm⁻¹ (8). The ${}^{31}P{}^{1}H$ NMR spectra present only a singlet for complex 7 (32.4 ppm), two singlets for complexes 5 or 8, corresponding to the different phosphorus of the two ligands (31.0 and 46.3 ppm (5) or 29.5 and 38.5 ppm (8)) or a singlet and a doublet of doublets for complex 6 [-55° C, 36.6 and 11.4 ppm, *J*(PAg) 368.0 and 318.7 Hz]. The ¹H NMR spectra are in agreement with the proposed structures (see Section 3). A complex similar to 6, but with copper, [Cu(dpopf)(PPh_3)_2]NO_3 (9), can be obtained by reaction of dpopf and [Cu(NO₃)(PPh₃)₂]. (³¹P{¹H} NMR spectrum: two singlets at 28.4 and -0.02 ppm).

The yellow, neutral complex $[Ag(dpopf)(S_2CNEt_2)]$ (10) can be obtained by reaction of complex 1 and Na(S₂CNEt₂). The ¹H NMR spectrum shows a multiplet at 4.37 (8H, C₃H₄), a quartet at 4.01 (4H, CH₂), and a triplet at 1.31 ppm (6H, CH₃). The ³¹P{¹H} NMR spectrum presents only a singlet at 29.2 ppm.

The structure of complex 6 has been confirmed by an X-ray crystal diffraction study. A selection of bond

Table I									
Selected	bond	lengths	[Å]	and	angles	[°]	for	derivativ	ve 6

Ag–O(2)	2.397(4)
Ag-O(1)	2.410(4)
Ag-P(2)	2.437(2)
Ag–P(1)	2.443(2)
O(2)-Ag-O(1)	96.10(13)
O(2)–Ag–P(2)	97.13(10)
O(1)-Ag-P(2)	120.49(10)
O(2)–Ag–P(1)	115.68(11)
O(1)-Ag-P(1)	91.24(10)
P(2)-Ag-P(1)	131.93(6)



Fig. 1. The cation of compound 6 with the atom numbering scheme. Hydrogen atoms have been omitted for clarity. Radii are arbitrary.

lengths and angles are collected in Table 1. Complex **6** crystallises with one molecule of dichloromethane. The silver centre displays a highly distorted tetrahedral geometry; the angles around Ag range from 91.24(10) [O(1)-Ag-P(1)] to 131.93(6) [P(2)-Ag-P(1)]. The P-Ag-P angle is appreciably larger than the ideal tetrahedral angle, possibly reflecting a tendency towards strong linear bonding between silver(I) centres and phosphine ligands. The metal-metal distance Ag…Fe is 4.905 Å. (Fig. 1)

The Ag–P bond distances, 2.437(2) and 2.443(2) Å, are in line with those found in other tetrahedral silver complexes such as $[Ag(dppe)_2]NO_3$ [6] (range 2.488(3)–2.527(3) Å), $[Ag(phen)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$ [7] (2.463(2), 2.479(2) Å) or $[Ag\{C_5(CO_2Me)_5\}(PPh_3)_2]$ [8] (2.428(2), 2.414(2) Å). The Ag–O bond lengths (2.397(4), 2.410(4) Å) compare well with literature values for four-coordinated silver complexes [8–11].

The perchlorate oxygens, which are well-defined (U values approximately 0.07 Å²), act as acceptors in non-classical hydrogen bonds C199–H199…O3 [H…O 2.24 Å, C–H…O 156°], C43–H43…O5 [2.48 Å, 144°], C73–H73…O5 [2.44 Å, 163°] and C14–H14…O6 [2.40 Å, 142°].

3. Experimental

Infrared spectra were recorded on a Perkin–Elmer 883 spectrophotometer, over the range $4000-200 \text{ cm}^{-1}$, using Nujol mulls between polyethylene sheets. Conductivities were measured in approximately 5×10^{-4} mol dm⁻³ solutions with a Philips 9509 conductimeter. C, H, N and S analyses were carried out with a Perkin–Elmer 2400 microanalyser. Mass spectra were recorded on a VG Autospec, with the Liquid secondary-ion mass spectra (LSI MS) technique, using nitrobenzyl alcohol as matrix. ¹H and ³¹P{¹H} NMR spectra were recorded on a Varian UNITY 300, Bruker ARX300 or GEMINI 2000 apparatus in CDCl₃ solu-

tions (kept with Na₂CO₃), if no other solvent is stated; chemical shifts are quoted relative to SiMe₄ (external, ¹H) and 85% H_3PO_4 (external, ³¹P).

The starting materials $[Ag(OCIO_3)(PPh_3)]$ [12], dpopf [13] and $(SPPh_2)_2CH_2$ [14] were prepared by published procedures. Caution: perchlorate salts with organic cations may be explosive.

3.1. Syntheses

3.1.1. $[Ag(OClO_3)(dpopf)]$ (1) or $[Ag(dpopf)_2]ClO_4$ (2)

To a solution of $AgClO_4$ (0.021 g, 0.1 mmol) in dichloromethane (20 cm³) was added dpopf (0.058 g, 0.1 mmol or 0.029 g, 0.05 mmol) and the mixture stirred for 1 h. Concentration of the solution to approximately 5 cm³ and addition of diethyl ether (10 cm³) gave complex **1** or **2** as a yellow solid. Complex **1**: Yield 89%. Λ_M 121 ohm⁻¹ cm² mol⁻¹. Elemental analysis: *Anal.* Found: C, 51.2; H, 3.35. Calc. for C₃₄H₂₈AgClFeO₆P₂: C, 51.45; H, 3.55%. Complex **2**: Yield 65%. Λ_M 140 ohm⁻¹ cm² mol⁻¹. Elemental analysis: *Anal.* Found: C, 59.3; H, 3.9. Calc. for C₆₈H₅₆AgClFe₂O₈P₄: C, 59.2; H, 4.05%.

3.1.2. $[Ag(dpopf)(PPh_3)]ClO_4$ (3) or $[{Ag(PPh_3)}_2(dpopf)](ClO_4)_2$ (4)

To a solution of dpopf (0.059 g, 0.1 mmol) in dichloromethane (20 cm³) was added [Ag(OClO₃)-(PPh₃)] (0.047 g, 0.1 mmol or 0.094 g, 0.2 mmol) and the mixture stirred for 90 min. Concentration of the solution to approximately 5 cm³ and addition of diethyl ether (10 cm³) gave complex **3** or **4** as a yellow solid. Complex **3**: Yield 80%. $A_{\rm M}$ 130 ohm⁻¹ cm² mol⁻¹. Elemental analysis: *Anal.* Found: C, 59.3; H, 3.85. Calc. for C₅₂H₄₃AgClFeO₆P₃: C, 59.15; H, 4.05%. Complex **4**: Yield 82%. $A_{\rm M}$ 189 ohm⁻¹ cm² mol⁻¹. Elemental analysis: *Anal.* Found: C, 55.25; H, 3.75. Calc. for C₇₀H₅₈Ag₂Cl₂FeO₁₀P₄: C, 55.15; H, 3.85%.

3.1.3. $[Ag(dpopf)L]ClO_4$ ($L = PPh_3$, (3); $SPPh_3$, (5)), $[Ag(dpopf)(PPh_3)_2]ClO_4$ (6) or $[Ag(dpopf)(L-L)]ClO_4$ $(L-L = bipy, (7); (SPPh_2)_2CH_2, (8))$

To a solution of complex 1 (0.079 g, 0.1 mmol) in dichloromethane (20 cm³) was added the neutral ligand [PPh₃, 0.026 g, 0.1 mmol or 0.052, 0.2 mmol; SPPh₃, 0.029 g, 0.1 mmol; bipy, 0.011 g, 0.1 mmol or (SPPh₂)₂CH₂, 0.045 g, 0.1 mmol] and the mixture stirred for 90 min. Concentration of the solution to approximately 5 cm³ and addition of diethyl ether (10 cm³) gave complexes **3**, or **5**–**8** as yellow solids. Complex **3**: Yield 60%. Complex **5**: Yield 50%. $\Lambda_{\rm M}$ 114 ohm⁻¹ cm² mol⁻¹. Elemental analysis: *Anal.* Found: C, 57.3; H, 3.85; S, 2.95. Calc. for C₅₂H₄₃AgClFeO₆P₃S: C, 57.45; H, 4.05; S, 3.4%. Complex **6**: Yield 70%. $\Lambda_{\rm M}$ 138 ohm⁻¹ cm² mol⁻¹. Elemental analysis: *Anal.* Found: C, 63.7; H, 4.45. Calc. for C₇₀H₅₈AgClFeO₆P₄:

C, 63.8; H, 4.4%. Complex 7: Yield 82%. $\Lambda_{\rm M}$ 122 ohm⁻¹ cm² mol⁻¹. Elemental analysis: *Anal*. Found: C, 55.4; H, 3.7; N, 3.45. Calc. for C₄₄H₃₆AgCl-FeN₂O₆P₂: C, 55.65; H, 3.8; N, 2.95%. Complex 8: Yield 85%. $\Lambda_{\rm M}$ 122 ohm⁻¹ cm² mol⁻¹. Elemental analysis: *Anal*. Found: C, 57.3; H, 4.1; S, 5.6. Calc. for C₅₉H₅₀AgClFeO₆P₄S₂: C, 57.05; H, 4.0; S, 5.15%.

3.1.4. $[Cu(dpopf)(PPh_3)_2]NO_3$ (9)

To a solution of dpopf (0.059 g, 0.1 mmol) in dichloromethane (20 cm³) was added [Cu(NO₃)(PPh₃)₂] (0.065 g, 0.1 mmol) and the mixture stirred for 45 min. Concentration of the solution to approximately 5 cm³ and addition of diethyl ether (10 cm³) gave complex **9** as a yellow solid. Yield 69%. $\Lambda_{\rm M}$ 26 ohm⁻¹ cm² mol⁻¹. Elemental analysis: *Anal*. Found: C, 67.5; H, 4.4; N, 1.25. Calc. for C₇₀H₅₈CuFeNO₅P₄: C, 68.05; H, 4.75; N, 1.15%.

3.1.5. $[Ag(dpopf)(S_2CNEt_2)]$ (10)

To a solution of complex 1 (0.079 g, 0.1 mmol) in dichloromethane (20 cm³) was added NaS_2CNEt_2

Table 2

Details of data collection and structure refinement for comp	ex 6	
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Compound	6 ·CH ₂ Cl ₂			
Chemical formula	$\mathrm{C_{71}H_{60}AgCl_{3}FeO_{6}P_{4}}$			
Crystal habit	yellow tablet			
Crystal size (mm)	0.6 imes 0.6 imes 0.2			
Crystal system	orthorhombic			
Space group	$Pca2_1$			
a (Å)	34.026(4)			
b (Å)	12.169(2)			
<i>c</i> (Å)	15.674(3)			
$U(Å^3)$	6490(2)			
Ζ	4			
D_{calc} (Mg m ⁻³)	1.436			
M	1403.14			
<i>F</i> (000)	2872			
T (°C)	-100			
$2\theta_{\max}$ (°)	50			
μ (Mo K α) (mm ⁻¹)	0.800			
Transmission	0.740-0.849			
Number of reflections measured	10855			
Number of unique reflections	9524			
R _{int}	0.0408			
$R^{a}(F, F > 4\sigma(F))$	0.0439			
$wR^{b}(F^{2}, \text{ all reflections})$	0.0797			
Number of parameters	775			
Number of restraints	683			
S ^c	0.83			
Maximum $\Delta \rho$ (eÅ ⁻³)	0.53			

^a $R(F) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|.$

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

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

(0.023 g, 0.1 mmol) and the mixture stirred for 3 h. The suspension was filtered to remove the NaClO₄ formed. Concentration of the solution to approximately 5 cm³ and addition of diethyl ether (10 cm³) gave complex **10** as a yellow solid. Yield 75%. Elemental analysis: *Anal.* Found: C, 56.1; H, 4.95; N, 1.7; S, 8.25. Calc. for $C_{39}H_{38}AgFeNO_2P_2S_2$: C, 55.6; H, 4.5; N, 1.65; S, 7.6%.

3.2. 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 collected using monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Scan type ω . An absorption correction was based on Ψ -scans. The structure was solved by the heavy-atom method, and refined on F^2 using the program SHELXL-93 [15]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. Further details are given in Table 2.

3.2.1. Special refinement details

A system of restraints to light-atom displacementfactor components and local ring symmetry was used. The absolute structure (polar axis direction) was determined by the method of Flack [16]; the x parameter refined to -0.01(2).

4. Supplementary material

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the number CCDC 155759. Copies can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk

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