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Note

# *trans*-Chelating ligating ability of 1,1'-bis(diphenylselenophosphoryl)ferrocene (dpspf) towards silver(I). Crystal structure of [Ag(dpspf)]ClO<sub>4</sub>

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#### Abstract

The ligand 1,1'-bis(diphenylselenophosphoryl)ferrocene,  $Fe[\eta^5-C_5H_4P(Se)Ph_2]_2$  (dpspf), reacted readily with  $[Ag(MeCN)_4]ClO_4$ in CH<sub>2</sub>Cl<sub>2</sub> to quantitatively give the monomeric two-coordinated complex  $[Ag(dpspf)]ClO_4$ . The solution behavior of the complex has been probed by variable-concentration and/or -temperature multinuclear NMR spectroscopy (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>77</sup>Se), which revealed extreme lability. Single-crystal X-ray structural analysis shows that the complex (orthorhombic, *Pna2*<sub>1</sub>, *a* = 26.34(1), *b* = 12.363(6), *c* = 11.209(6) Å, *Z* = 4) exists as mononuclear species in an almost linear two-coordination environment around the silver atom with an Se(1)–Ag–Se(2) angle of 176.5(1)°. The Ag–Se bond distances (2.456(4) and 2.449(3) Å) and the Ag–Se–P angles (98.1(2) and 102.6(2)°) point towards a substantially sp<sup>3</sup> hybridization of the selenium donor atoms. © 2000 Elsevier Science S.A. All rights reserved.

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

#### 1. Introduction

One of the most interesting features of ferrocenebased ligands in coordination chemistry is their flexibility, possibly due to the organometallic 'ball-joint'. The skeletal flexibility of these metalloligands confers the ability to stabilize complexes of varied metal geometry under a variety of coordinative bonding modes [1]. In this connection, the unique capability of 1,1'-bis(diphenylthiophosphoryl)ferrocene (dptpf) to function as a *trans*-chelating ligand has recently been documented on the basis of X-ray authenticated examples of the species  $[M(dptpf)]^+$  (M = Cu(I) [2], Ag(I) and Au(I) [3]). The novel selenium analogue (dpspf), at variance with the oxygen congener, was similarly assigned to bind to Cu(I) in the *trans*-chelate fashion mainly on the basis of NMR spectroscopy [2]. In fact, owing to the exceeding sensitivity to moisture and reactivity towards coordinating solvents of solutions of the complex [Cu(dpspf)]BF<sub>4</sub> [2], several attempts to obtain suitable crystals for X-ray analysis failed.

However, we were successful in obtaining single crystals of the more stable and tractable silver derivative. Herein reported are the synthesis, the solution multinuclear NMR characterization and the solid-state X-ray structural characterization of the closely related complex  $[Ag(dpspf)]ClO_4$  (1).

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## 2. Experimental

## 2.1. General procedures and materials

All reactions and manipulations of solutions were performed under a dinitrogen atmosphere. 1,1'-bis-(diphenylselenophosphoryl)ferrocene (dpspf) was prepared as previously reported [2]. Tetrakis(acetonitrile)silver(I) perchlorate was obtained by metathesis between AgNO<sub>3</sub> and NaClO<sub>4</sub> in acetonitrile. The precipitate of NaNO<sub>3</sub> was filtered and the resulting solution was concentrated by rotary evaporation until transparent crystals began to form. Upon cooling in the refrigerator and addition of Et<sub>2</sub>O the product precipitated as a white microcrystalline powder, which was collected by filtration, rinsed with Et<sub>2</sub>O and dried under a gentle stream of nitrogen. All other reagents were of reagent-grade quality and were used as supplied.

#### 2.2. Apparatus

The IR spectra were recorded as Nujol mulls on KBr plates using a Nicolet 5SXC-FTIR spectrometer. <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>77</sup>Se NMR experiments were obtained in CDCl<sub>3</sub> solution at 298 K in 5 mm sample tubes on a Jeol 90 MHz and/or a Bruker AC-200 spectrometer equipped with a variable temperature apparatus. The <sup>1</sup>H and <sup>13</sup>C spectra were referenced by assigning the <sup>1</sup>H impurity in the solvent at  $\delta$  7.24 and the <sup>13</sup>C multiplet at  $\delta$  77.0. The external references were  $H_3PO_4$  (85% w/w) for <sup>31</sup>P and selenophene, adjusted to  $\delta$  605 from Me<sub>2</sub>Se [4], for <sup>77</sup>Se.

# 2.3. Preparation of the complex [Ag(dpspf)]ClO4 (1)

To a solution of dpspf (1.14 g, 1.60 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) was added [Ag(MeCN)<sub>4</sub>]ClO<sub>4</sub> (0.595 g, 1.60 mmol) and the mixture was stirred at room temperature under nitrogen. After 1 h the cloudy solution was filtered and the filtrate concentrated under vacuum to a small volume. Addition of Et<sub>2</sub>O caused the precipitation of a brick-red solid which was collected by filtration, washed with Et<sub>2</sub>O and dried under vacuum to constant weight. The yield (1.50 g) was essentially quantitative. The solid product contained CH<sub>2</sub>Cl<sub>2</sub> of crystallization as determined by <sup>1</sup>H NMR spectroscopy and confirmed by elemental analysis. Anal. Found: C, 42.6; H, 2.95; Ag, 11.1. Calc. for C<sub>34</sub>H<sub>28</sub>AgClFeO<sub>4</sub>-P<sub>2</sub>Se<sub>2</sub>·0.7CH<sub>2</sub>Cl<sub>2</sub>: C, 42.6; H, 3.00; Ag, 11.0%. IR: 568 cm<sup>-1</sup> (P=Se) ( $\Delta v = -5$  cm<sup>-1</sup> with respect to uncoordinated dpspf). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K):  $\delta$  7.8–7.6 (m, 10H, Ph), 4.70 (q,  $J_{\rm HH}$  and  $J_{\rm HP} \approx 2$  Hz, 2H,  $C_5H_4$ ), 4.26 (q,  $J_{\text{HH}}$  and  $J_{\text{HP}} \approx 2$  Hz, 2H, C<sub>5</sub>H<sub>4</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (saturated solution):  $\delta$  33.25 (s with  $^{77}\text{Se}$  satellites,  $^1\!J_{\rm PSe}$ 599 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  133.4 (d,  $J_{CP}$  = 3.3 Hz,  $C_{\delta}$ ), 131.9 (d,  $J_{CP} = 11.0$  Hz,  $C_{\beta}$ ), 129.3 (d,  $J_{CP} = 13.2$  Hz,  $C_{\gamma}$ ), 129.1 (d,  $J_{CP} = 80.7$  Hz,  $C_{\alpha}$ ), phenyl resonances;  $\delta$  76.1

(d,  $J_{CP} = 8.8$  Hz,  $C_{\beta}$ ), 75.7 (d,  $J_{CP} = 4.4$  Hz,  $C_{\gamma}$ ), 74.2 (d,  $J_{\rm CP} = 87.3$  Hz,  $C_{\alpha}$ ), cyclopentadienyl resonances. <sup>77</sup>Se{<sup>1</sup>H} NMR:  $\delta$  - 303 (d, <sup>1</sup> $J_{SeP}$  = 598 Hz).

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive.

# 2.4. X-ray crystallography

Complex 1 crystallizes as a CH<sub>2</sub>Cl<sub>2</sub> monosolvate from dichloromethane-pentane. Single crystals of the complex were grown in a refrigerator by layering pentane onto the sample solution in dichloromethane. The experimental X-ray data, collected on a Nicolet Siemens R3m/V diffractometer using the  $\omega$ -2 $\theta$  technique at a varied scan rate, are summarized in Table 1, and some selected bond lengths and angles are reported in Table 2. Further details are provided in Section 4.

Table 1 Crystallographic data for the structure determination and refinement

Empirical formula	[C <sub>34</sub> H <sub>28</sub> AgFeP <sub>2</sub> Se <sub>2</sub> ]ClO <sub>4</sub> ·CH <sub>2</sub> Cl <sub>2</sub>
Crystal system	orthorhombic
Space group	<i>Pna</i> 2 <sub>1</sub> (no. 33)
a (Å)	26.34(1)
b (Å)	12.363(6)
c (Å)	11.209(6)
$V(Å^3)$	3650(3)
$D_{\rm calc}$ (g cm <sup>-3</sup> )	1.828
Ζ	4
λ (Mo Kα) (Å)	0.71073
$\mu  ({\rm cm}^{-1})$	32.7
<i>F</i> (000)	1976
$2\theta$ Range (°)	4.5-50.0
T (K)	293
Observed reflections $(I \ge 2\sigma(I))$	1394
R <sup>a</sup>	0.060
wR <sub>2</sub> <sup>b</sup>	0.188
GOF °	0.947

<sup>a</sup>  $R = \Sigma ||F_{o}| - |F_{o}|| / \Sigma |F_{o}|.$ 

<sup>b</sup>  $wR_2 = [\Sigma(w(|F_o|^2 - |F_c|^2)^2) / \Sigma(w(|F_o|^2))]^{1/2}.$ <sup>c</sup> GOF =  $[\Sigma(w(|F_o|^2 - |F_c|^2)^2) / (n-p)]^{1/2}.$ 

Table 2		
Selected bond lengths (Å) an	d angles (°) for	[Ag(dpspf)]ClO <sub>4</sub> ·CH <sub>2</sub> Cl <sub>2</sub>

Ag Se(1)	2.456(A)	P(1) C(11)	1.85(2)
Ag=SU(1)	2.430(4)	P(1) = C(11)	1.03(2)
Ag-Se(2)	2.449(3)	P(2) = C(31)	1.74(2)
Se(1) - P(1)	2.131(6)	P(1)-C(21)	1.81(2)
Se(2) - P(2)	2.133(6)	P(2)-C(41)	1.81(2)
P(1)-C(1)	1.82(2)	Fe-C <sub>mean</sub>	2.04(1)
P(2)-C(6)	1.79(2)		
Bond angles			
Se(1)–Ag–Se(2)	176.5(1)	Se(2) - P(2) - C(31)	115.5(6)
Ag-Se(1)-P(1)	98.1(2)	Se(1)-P(1)-C(21)	114.8(7)
Ag-Se(2)-P(2)	102.6(2)	Se(2)-P(2)-C(41)	106.9(7)
Se(1)-P(1)-C(1)	112.2(6)	Fe-C(1)-P(1)	129(1)
Se(2)-P(2)-C(6)	112.2(7)	Fe-C(6)-P(2)	128(1)
Se(1) - P(1) - C(11)	106.9(7)		



Fig. 1. ORTEP view of the complex. The thermal ellypsoids are drawn at 40% probability.

The final unit-cell parameters were determined from 50 high-angle data ( $2\theta > 22^\circ$ ). Corrections were applied for Lorentz, polarization and long-term intensity fluctuations, the latter on the basis of the intensities of two reflections repeatedly measured during data collection. Corrections for absorption effects were not applied, since azimuthal scan data for some reflections at  $\chi$  near 90° proved to be unnecessary. The structure was solved by heavy-atom methods and refined by full-matrix leastsquares against  $F^2$ . The nine heavy atoms were assigned anisotropic displacement parameters and all hydrogen atoms were constrained to ideal geometries with C-H 0.96 Å and variable isotropic thermal parameters. The Flack [5] parameter for the absolute configuration was 0.01(3). The thermal parameters for the solvate molecule were large, indicating possible disorder, a feature quite common to complexes containing CH<sub>2</sub>Cl<sub>2</sub> solvent. However, the final difference Fourier map was featureless, the maximum residual density being of 0.6 e  $Å^{-3}$  in the vicinity of the silver atom. The structure was solved and refined using SHELXTL/PC [6] and SHELXL-93 [7] program packages.

## 3. Results and discussion

Complex 1 can be readily obtained in high yield as a brick-red solid by ligand-exchange reaction from the labile precursor  $[Ag(MeCN)_4]ClO_4$  and equimolar amounts of dpspf in CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature. The crystal structure of 1 has been established by X-ray diffraction. The compound crystallizes as a CH<sub>2</sub>Cl<sub>2</sub> monosolvate from dichloromethane-pentane The ORTEP drawing of complex 1·CH<sub>2</sub>Cl<sub>2</sub> is shown in Fig. 1. The environment about silver is that of the expected linear two-coordination geometry, with a slight deviation from the ideal 180° because of the Se(1)–Ag–Se(2) angle of 176.5(1)° imposed by the ligand bite. The metal is only marginally involved in interac-

tions with a symmetrically-related perchlorate oxygen (at 3.40 Å) (Fig. 2) and the iron atom (at 3.875 Å). The structural features closely parallel those of the parent complex containing the dptpf ligand [3] and the only differences in the bond lengths arise from the difference in the covalent radii of the donor atoms ( $r_{se} = 1.17$ ;  $r_{\rm s} = 1.04$  Å) [8]. The Ag–Se distance (mean value of 2.453(3) Å) represents the minimum value found among the 99 observations retrieved in the version 5.16 of October 1998 of the Cambridge Structural Database [9] and scattered through a large range (from 2.473 to 3.051 Å), while the Se-P distance (mean value of 2.132(6) Å) slightly increases upon coordination, and it is consistent with the lower P=Se stretching frequency observed in the IR spectrum. In fact, in the uncoordinated ligand this length is 2.103(6) Å [2] and shows no substantial variation for comparable selenides (2.111(3) Å for Me<sub>3</sub>PSe [10]; 2.108(1) Å for Cy<sub>3</sub>PSe [11]; 2.106(1) Å for Ph<sub>3</sub>PSe [12]; 2.109(7) Å for (*m*-tolyl)<sub>3</sub>PSe [13] and 2.116(5) Å for (o-tolyl)<sub>3</sub>PSe [14]). However, to accommodate the silver atom the ligand destroys the centrosymmetric arrangement found in the solid state and in the resulting Ag-Se(1)-P(1)-C(1)-Fe-C(6)-P(2)-Se(2)eight-membered ring the four heavy atoms are virtually coplanar, while P(1) and C(6) lie below this plane (by 0.63 and 0.38 Å, respectively) and P(2) and C(1) above (by 0.55 and 0.35 Å, respectively). In the ferrocene moiety the cyclopentadienyl rings are staggered, forming an angle of 23.2°, and slightly tilted away from the Fe center with a dihedral angle of 8.9°. The C(1)-(5) ring makes dihedral angles of 84.4 and 58.5° with the phenyl rings at P(1), while for C(6)–(10) the values, relative to the phenyl rings at P(2), are 75.9 and 56.1°.

The solid-state mononuclear structure of **1** appears not to be maintained in solution, as is evident from the multinuclear (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>77</sup>Se) NMR spectra in chlorinated solvents. Thus, the <sup>31</sup>P NMR spectrum in  $CDCl_3$  at 25°C (Fig. 3) consists of one major signal, due to the phosphorus atoms bonded to magnetically



Fig. 2. Packing diagram of the complex showing the intermolecular Ag···O(4) (at x, y, z-1) interaction of 3.40 Å.

inactive Se nuclei, and of a doublet stemming from the phosphorus nucleus bonded to <sup>77</sup>Se (7.6% natural abundance, I = 1/2) with the expected relative intensities. A splitting pattern arising from coupling to <sup>13</sup>C nuclei of the cyclopentadienyl and phenyl groups is also apparent. It is worth noting, within this set of resonances, that the doublet attributable to the ortho and meta carbon atoms of the phenyl substituents shows a separation of 12.2 Hz and an intensity almost identical with that of the <sup>77</sup>Se satellites. Remarkably, no coupling of the phosphorus nuclei to the metal center (<sup>107</sup>Ag 51.8%, I = 1/2 and <sup>109</sup>Ag 48.2%, I = 1/2) is observable. Moreover, the chemical shift of the main signal is strongly effected by the concentration of the solution moving at higher field by up to 1.077 ppm as the solute concentration is gradually increased 25 times. Conversely, only minor effects on the  ${}^{1}J_{PSe}$  are detectable, with higher values for more concentrated solutions. For instance,  $\delta$ (<sup>31</sup>P) 34.327 (<sup>1</sup>J<sub>PSe</sub> 591.2 Hz), 34.024 (592.5 Hz), 33.385 (598.0 Hz) and 33.250 (599.4 Hz) for 8, 41, 170 and 210 mmol  $dm^{-3}$  CDCl<sub>3</sub> solutions of 1, respectively. For comparison, the uncoordinated dpspf ligand in CDCl<sub>3</sub> exhibits its <sup>31</sup>P resonance at  $\delta$  30.93 (<sup>1</sup>J<sub>PSe</sub> 743 Hz), with negligible effects on the concentration [2].

A smaller concentration effect is also observed in the corresponding <sup>1</sup>H NMR spectrum, which displays the usual pair of multiplets typical of two sets of  $C_5H_4$  protons arranged in a symmetrical environment. The two sets of equally intense signals occur as apparent

1:3:3:1 quartets centered at  $\delta$  4.70 and 4.26 ( $J_{\rm HH} \cong 2$  Hz), the first of which is well resolved and remains substantially unchanged throughout the concentration range shown, whereas the quartet at higher field is poorly resolved and moves slightly to higher frequency as the solute concentration is increased.

Since the two bond  $^{107/109}$ Ag $^{-31}$ P coupling constant is expected to be approximately 10 Hz [15], it should be clearly detectable in the presence of kinetically stable metal-ligand bonds. Hence, these observations point unambiguously to the occurrence of rapid dissociation



Fig. 3.  ${}^{31}P{}^{1}H$  NMR spectrum of the complex in CDCl<sub>3</sub> (saturated solution) at 25°C.

and intermolecular association processes involving the Ag–Se bonds. The low-energy exchange process is still operational at  $-95^{\circ}$ C as is evident from variable temperature <sup>31</sup>P NMR studies. Upon cooling a saturated CD<sub>2</sub>Cl<sub>2</sub> solution of 1 from 27 to  $-95^{\circ}$ C, the sharp resonance at  $\delta$  33.75 (<sup>1</sup>J<sub>PSe</sub> 595.7 Hz) begins moving slowly to higher field ( $\delta$  33.14 at  $-60^{\circ}$ C) while retaining the unresolved fine structure, but still no evidence is found at the lowest temperature for the expected two doublets in the <sup>31</sup>P resonance. Thus, at  $-95^{\circ}$ C the signal is still a singlet ( $\delta$  32.43), though quite large (line width  $\Delta v_{1/2}$ ) = 7.5 Hz), with sharp pertinent <sup>77</sup>Se satellites (<sup>1</sup>J<sub>PSe</sub> 598.3 Hz).

The kinetic lability of the Ag–Se bond in complex 1 is confirmed by the <sup>77</sup>Se NMR spectrum. The sharp doublet is centered at  $\delta$  – 303, slightly shifted upfield with respect to the uncoordinated ligand ( $\delta$  – 297.5, <sup>1</sup>J<sub>SeP</sub> 743 Hz), and the separation of the signals is 598 Hz, in good agreement with the <sup>1</sup>J<sub>PSe</sub> value already found in the corresponding <sup>31</sup>P spectrum. Upon cooling the solution to – 65°C, the one observable alteration is a broadening of the signals without any significant change of the chemical shift values. Similarly extreme lability has recently been noted in silver complexes with bis(selenoethers) [16].

The facile fluxionality exhibited by silver complex 1 seems to be in remarkable contrast with the rigidity claimed for its copper(I) analogue [2]. As a matter of fact, the kinetic stability of the Cu-Se bond was merely inferred by the clear presence in the <sup>31</sup>P NMR spectrum of the complex of a couple of satellites symmetrically flanking the main resonance (J = 12 Hz) in the appropriate  $\approx 8\%$ intensity ratio, just as expected for a three-bond (<sup>31</sup>P–Se–Cu–<sup>77</sup>Se) interaction. Now, the similar NMR features shared by very labile complex 1 are conclusively rationalized in terms of coupling of <sup>31</sup>P nuclei to fortuitously overlapping  ${}^{13}C_{\beta}$  and  ${}^{13}C_{\gamma}$  of the phenyl substituents (see Section 2) [17]. Our former statement of kinetically stable Cu–Se bonds lacks <sup>77</sup>Se NMR support, and in the light of these additional findings may, consequently, result in an invalid assumption.

## 4. Supplementary material

A CIF file containing tables of crystal data and experimental conditions, final atomic positional parame-

ters, bond lengths, bond angles and thermal parameters has been deposited at the Cambridge Crystallographic Data Centre (CCDC no. 137140). Copies of this information may 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 or www: http://www.ccdc.cam.ac.uk).

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