ELSEVIER

Inorganica Chimica Acta 277 (1998) 163–170

Inorganica Chimica Acta

Variable coordination modes for 1,1′-bis(diphenylphosphino)ferrocene (dppf) mono- and di-chalcogenides or -oxides (dppfE and dppfE$_2$; E = O, S or Se) in copper(I) complexes. Crystal structure of $[\{Cu(dppf)\}_2(\mu\text{-}dppfS_2)](BF_4)_2$ and $[Cu(dppfSe)_2]BF_4$

Giuseppe Pilloni [a,*], Bruno Longato [b,d], Giuliano Bandoli [c]

[a] *Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Via Marzolo 1, 35131 Padua, Italy*
[b] *Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Via Marzolo 1, 35131 Padua, Italy*
[c] *Dipartimento di Scienze Farmaceutiche, Via Marzolo 5, 35131 Padua, Italy*
[d] *Centro di Studio sulla Stabilita' e Reattivita' dei Composti di Coordinazione, CNR, Via Marzolo 1, 35131 Padua, Italy*

Received 19 September 1997; accepted 28 October 1997

Abstract

Reaction of $[Cu(MeCN)_4]BF_4$ with the phosphine $Fe[\eta^5\text{-}C_5H_4PPh_2]_2$ (dppf) and its disulfide (dppfS$_2$) sequentially in chlorinated solvents led to the dinuclear tricoordinate complex $[\{Cu(dppf\text{-}P,P')\}_2(\mu\text{-}dppfS_2\text{-}S,S')](BF_4)_2$ (**1**), whereas reaction of the copper reagent with dppf and its diselenide (dppfSe$_2$) gave the bis-chelate dppf-monoselenide compound $[Cu(dppfSe\text{-}P,Se)_2]BF_4$ (**2**). Similarly, the E = O or S relevant complexes $[Cu(dppfE\text{-}P,E)_2]BF_4$ were obtained by reaction of the copper(I) precursor with the dppf-monoderivatives $[\eta^5\text{-}C_5H_4PPh_2]Fe[\eta^5\text{-}C_5H_4P(E)Ph_2]$ (dppfE). The complexes have been characterized by ^1H and ^{31}P NMR spectroscopy. Single-crystal X-ray structure determinations were performed for complexes **1** and **2**. Complex **1** crystallizes as $CHCl_3$ (**1a**) or $CHBr_3$ (**1b**) monosolvates. The cation of **1** is exactly centrosymmetric and shows a distorted trigonal planar coordination at copper with a P–Cu–P angle of 115.7(1)° and the S–Cu–P angles of 138.6(1) and 104.3(6)°, as mean values from **1a** and **1b**. In complex **2** the coordination geometry around the metal atom is markedly distorted tetrahedral with the two dppfSe moieties acting as chelating ligands with bite angles of 111.5(2) and 116.8(2)°. The Se(1)–Cu–Se(2) angle (103.4(2)°) approaches the value for tetrahedral geometry, while the remaining angles differ significantly from the ideal value ranging from 96.1(2) to 121.9(3)°. The Cu–Se–P angles (124.5(2) and 132.9(2)°) point towards a substantially sp^2 hybridization of the selenium atom. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Copper complexes; Chalcogenide complexes; Ferrocene complexes; Crystal structures

1. Introduction

As a part of our current studies on the coordination ability of the phosphine oxides and chalcogenides $Fe[\eta^5\text{-}C_5H_4\text{-}P(E)Ph_2]_2$ (E = nothing (dppf), O (dppfO$_2$), S (dppfS$_2$) or Se (dppfSe$_2$)), we recently reported on the synthesis and the solution chemistry of the homoleptic complexes $[Cu(dppfE_2)]BF_4$ and $[Cu_4(\mu\text{-}dppfE_2)_6X]X_3$ (E = S, Se; X = BF$_4$, PF$_6$ or ClO$_4$) [1]. In these compounds the coordinative bonding mode of the chalcogenophosphoryl ligands towards Cu(I) appeared to span from *trans*-chelating to symmetrical bridging modes, at variance with the oxygen analogue (dppfO$_2$) which was found to bind to Cu(I) in the chelate fashion [2a,b]. Here, we argued that the different ligating behaviour was unlikely to be merely attributed to the well-known difference in the dative bonding features of the heavier phosphine chalcogenides from that for the phosphine oxides [3]. As a matter of fact, we anticipated that the mono-oxo, -thio and -seleno derivatives, $[\eta^5\text{-}C_5H_4PPh_2]Fe[\eta^5\text{-}C_5H_4P(E)Ph_2]$ (dppfE), were all found to bind to Cu(I) in the chelating mode. Several copper(I) complexes of diphosphine disulfides or -selenides have been reported [4], but complexes containing only diphosphine monochalcogenides or -oxides are to date unknown.

Herein reported are the synthesis and solution ^1H and ^{31}P NMR characterization of the four-coordinated copper(I) complexes of general formula $[Cu(dppfE)_2]BF_4$ (E = O, S or Se) and of the tricoordinate dicopper(I) salt

---

[*] Corresponding author. Tel.: +39-49-827 5230.

0020-1693/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved.
PII S0020-1693(97)06129-X

$[\{Cu(dppf)\}_2(\mu\text{-}dppfS_2)](BF_4)_2$, including the solid-state X-ray structural characterization of $[Cu(dppfSe)_2]BF_4$ and $[\{Cu(dppf)\}_2(\mu\text{-}dppfS_2)](BF_4)_2$.

2. Experimental

2.1. General procedures and materials

All reactions and manipulations of solutions were performed under a dinitrogen atmosphere. Anhydrous dichloromethane and 1,2-dichloroethane (Fluka), and 1,1′-bis(diphenylphosphino)ferrocene (dppf) (Aldrich) were obtained commercially and used without purification. Tetrakis(acetonitrile)copper(I) tetrafluoroborate [5], 1,1′-bis(diphenylselenophosphoryl)ferrocene ($dppfSe_2$) [1] and 1-(diphenylphosphino)-1′-(diphenyloxophosphoryl)-ferrocene (dppfO) [6] were prepared as previously reported. The compound 1,1′-bis(diphenylthiophosphoryl)ferrocene ($dppfS_2$) was synthesized by the literature procedure [7]. The compound 1-(diphenylphosphino)-1′-(diphenylthiophosphoryl)ferrocene (dppfS) was obtained from the addition of 1 mol equivalent of sulfur to dppf in toluene and purified by a procedure similar to that devised for the strictly related octamethylferrocene derivative [8]. A solution of sublimed sulfur (0.058 g, 1.80 mmol) in toluene (5 cm^3) was added to a solution of dppf (1.0 g, 1.80 mmol) in toluene (15 cm^3) and the mixture was stirred at room temperature. After 2 h the orange solution was evaporated to dryness under vacuum and the crude mixture of dppf, dppfS and $dppfS_2$ in approximately 1:2:1 ratio chromatographed on silica gel. The unreacted diphosphine, the mono- and disulfide species were separated in the sequence by eluting initially with 1:1 toluene/hexane, then with 2:1 toluene/hexane and finally with chloroform. The second fraction of eluted was concentrated to ~ 10 cm^3 on a rotary evaporator, and addition of pentane led to dppfS in 50% yield (0.53 g) as a yellow, crystalline solid. *Anal.* Found: C, 69.7; H, 4.75; S, 5.5. Calc. for $C_{34}H_{28}FeP_2S$: C, 69.35; H, 4.80; S, 5.45%. IR: 656 cm^{-1} (P=S). NMR ($CDCl_3$, 300 K): ^1H, δ 7.8–7.2 (m, 10H, Ph), 4.47 (t, J_{HH} ~ 2 Hz, 1H, C_5H_4), 4.34 (q, J_{HH} ~ 2 Hz, 2H, C_5H_4), 3.98 (q, J_{HH} ~ 2 Hz, 1H, C_5H_4); $^{31}P\{^1H\}$, δ 41.16 (s, P^V), −17.56 (s, P^{III}). All other reagents and starting materials were of reagent-grade quality and were used as supplied.

2.2. Apparatus

Proton (89.55 MHz) and $^{31}P\{^1H\}$ (36.23 MHz) NMR spectra were run on a JEOL 90 Q spectrometer equipped with a variable-temperature apparatus. Chemical shifts are reported in ppm relative to internal $SiMe_4$ and external H_3PO_4 (85% w./w.), respectively. IR spectra were recorded as Nujol mulls on KBr plates using a Nicolet 5SXC-FTIR spectrometer.

2.3. Preparation of the copper(I) complexes

2.3.1. $[\{Cu(dppf)\}_2(\mu\text{-}dppfS_2)](BF_4)_2$ (1)

To a solution of dppf (0.880 g, 1.59 mmol) in anhydrous 1,2-dichloroethane (20 cm^3) was added $[Cu(MeCN)_4]BF_4$ (0.500 g, 1.59 mmol) and the mixture was stirred at room temperature in an inert atmosphere until a clear solution was formed. After addition of $dppfS_2$ (0.980 g, 1.59 mmol), the resulting mixture was refluxed for about 15 min. The solution was cooled to room temperature and evaporated to dryness under vacuum. At the end, addition of CH_2Cl_2 (25 cm^3) to the residue dissolved in the minimum volume of chloroform afforded in a few minutes a deep yellow precipitate which was recovered by filtration, washed with CH_2Cl_2 and dried under vacuum. The solid product invariably contained CH_2Cl_2 of crystallization, as determined by ^1H NMR spectroscopy. Most of the clathrate solvent could be removed by heating in vacuo at 60°C for 48 h to give pure **1**. Yield: 1.46 g (91%). *Anal.* Found: C, 60.9; H, 4.15; S, 3.25. Calc. for $C_{102}H_{84}B_2Cu_2F_8Fe_3P_6S_2$: C, 60.4; H, 4.15; S, 3.15%. IR: 631 cm^{-1} (P=S) ($\Delta\nu = -24$ cm^{-1} with respect to uncoordinated $dppfS_2$). NMR ($CDCl_3$, 300 K): ^1H, δ 7.5–7.3 (m, 15H, Ph), 4.48 (m, 1H, C_5H_4), 4.41 (br s, 2H, C_5H_4), 4.22 (m, 1H, C_5H_4), 4.10 (br s, 2H, C_5H_4); $^{31}P\{^1H\}$, δ 41.63 (s, 1P, P^V), −12.24 (s, 2P, P^{III}); NMR ($CDCl_3/CH_2Cl_2$ 3:1 vol./vol., 183 K): $^{31}P\{^1H\}$, δ 40.78 (t, $^3J_{PP}$ 20.8 Hz, 1P, P^V), −13.00 (d, $^3J_{PP}$ 20.8 Hz, 2P, P^{III}).

2.3.2. $[Cu(dppfSe)_2]BF_4$ (2)

To a solution of dppf (0.820 g, 1.48 mmol) in anhydrous 1,2-dichloroethane (20 cm^3) was added $[Cu(MeCN)_4]BF_4$ (0.465 g, 1.48 mmol) and the mixture was stirred at room temperature in an inert atmosphere until a clear solution was formed. After addition of $dppfSe_2$ (1.05 g, 1.48 mmol), the resulting mixture was refluxed for about 10 min. The solution was cooled to room temperature and the solvent removed under vacuum. An oily, orange product was obtained which upon gently heating converted into a yellow foamy solid. The crude product was dissolved in ethanol (20 cm^3) and heated with stirring until a yellow solid was precipitated. After cooling in the refrigerator, the solid was collected by filtration, washed with cold EtOH, Et_2O and then dried under vacuum. Yield: 2.0 g (95%). *Anal.* Found: C, 57.4; H, 3.85. Calc. for $C_{68}H_{56}BCuF_4Fe_2P_4Se_2$: C, 57.6; H, 3.95%. IR: 563 cm^{-1} (P=Se). NMR ($CDCl_3$, 300 K): ^1H, δ 7.8–7.2 (m, 10H, Ph), 4.43 (m, 2H, C_5H_4), 4.13 (m, 2H, C_5H_4); $^{31}P\{^1H\}$, δ 30.37 (m with ^{77}Se satellites, $^1J_{PSe}$ 670 Hz), −7.90 (br s, P^{III}); NMR ($CDCl_3$, 208 K): $^{31}P\{^1H\}$, δ 30.66 (dd with ^{77}Se satellites, $^1J_{PSe}$ 710 Hz, $^3J_{PP}$ 15.9 and 25.6 Hz), −7.55 (dd, $^3J_{PP}$ 15.9 and 25.6 Hz).

2.3.3. $[Cu(dppfS)_2]BF_4$ (3)

Complex **3** was obtained upon treating a CH_2Cl_2 solution (10 cm^3) of dppfS (0.246 g, 0.42 mmol) with $[Cu(MeCN)_4]BF_4$ (0.066 g, 0.21 mmol) with stirring. After 1 h the yellow solution was evaporated to dryness under vacuum. Redissolution in the minimum volume of CH_2Cl_2, followed by the gradual addition of toluene (10 cm^3) gave a yellow solid, which was filtered, washed with pentane and dried under vacuum at 60°C to constant weight. Yield: 0.25 g (90%). *Anal.* Found: C, 61.45; H, 4.2; S, 4.9. Calc. for $C_{68}H_{56}BCuF_4Fe_2P_4S_2$: C, 61.7; H, 4.25; S, 4.85%. IR: 634 cm^{-1} (P=S) ($\Delta\nu = -22$ cm^{-1} with respect to uncoordinated dppfS). NMR (CD_2Cl_2, 300 K): ^1H, δ 7.8–7.2 (m, 10H, Ph), 4.54 (br s, 1H, C_5H_4), 4.45 (q, J_{HH} ~2 Hz, 1H, C_5H_4), 4.17 (m, 2H, C_5H_4); $^{31}P\{^1H\}$, δ 40.87 (dd, $^3J_{PP}$ 18.2 and 13.4 Hz, P^V), −8.65 (br s, P^{III}); NMR (CD_2Cl_2, 183 K): $^{31}P\{^1H\}$, δ 40.65 (dd, $^3J_{PP}$ 23.2 and 15.9 Hz, P^V), −8.99 (unresolved m, P^{III}).

2.3.4. $[Cu(dppfO)_2]BF_4$ (4)

Complex **4** was obtained upon treating a CH_2Cl_2 solution (10 cm^3) of dppfO (0.228 g, 0.40 mmol) with $[Cu(MeCN)_4]BF_4$ (0.063 g, 0.20 mmol) with stirring. After 1 h the orange solution was evaporated to dryness under vacuum. The oily, orange product was dissolved in ethanol (10 cm^3) and heated to reflux for a few minutes. Upon cooling a yellow precipitate separated which was collected by filtration, washed with cold EtOH, Et_2O and then dried under vacuum. Yield: 0.21 g (81%). *Anal.* Found. C, 63.0; H, 4.3. Calc. for $C_{68}H_{56}BCuF_4Fe_2P_4O_2$: C, 63.25; H, 4.35%. IR: 1156 cm^{-1} (P=O) ($\Delta\nu = -12$ cm^{-1} with respect to uncoordinated dppfO). NMR (CD_2Cl_2, 300 K): ^1H, δ 7.8–7.0 (m, 10H, Ph), 4.68 (s, 1H, C_5H_4), 4.28 (s, 3H, C_5H_4); $^{31}P\{^1H\}$, δ 33.71 (t, $^3J_{PP}$ 6.1 Hz, P^V), −12.2 (br s, P^{III}); NMR (CD_2Cl_2, 183 K): $^{31}P\{^1H\}$, δ 34.15 (t, $^3J_{PP}$ 6.1 Hz, P^V), −13.06 (s, P^{III}).

2.4. X-ray crystallography

Complex **1** crystallizes as $CHCl_3$ (**1a**) or $CHBr_3$ (**1b**) monosolvates from chloroform–methanol or bromoform–methanol, respectively. Single crystals of the complexes were grown by layering methanol onto the sample solution in chloroform (**1a**) or bromoform (**1b**). Suitable crystals of complex **2**, analysing as $[Cu(dppfSe)_2]BF_4 \cdot C_7H_8$, were grown by layering toluene onto the sample solution in nitromethane. Details of the crystal data, intensity measurements and data processing for the three structures are summarized in Table 1. Cell parameters were determined from 40 high-angle data ($2\theta > 22°$). For **2** extensive decay (up to 30%) in the intensity of the standard reflections occurred during data collection (4 days), owing either to solvent loss or to radiation decay (or to a combination of both); the data were corrected for the decay, while no correction for absorption was applied to **2**. On the contrary, absorption corrections were applied to the data sets of **1a** and **1b**, based on azimuthal scans of five reflections with an Eulerian angle χ near 90°. The structures were solved by standard heavy-atom methods, with subsequent Fourier difference maps yielding the positions of the light atoms, and refined by full-matrix least-squares against F^2. To ensure a good observation-to-variable ratio all the light atoms of **2** were treated isotropically, while in **1a** and **1b** isotropy was applied only to the solvent molecule and the BF_4^- ion, which in the three structures has been found to be severely disordered and was modelled with partial occupancy atom sites. In addition, the toluene molecule of **2** occupies in the crystal two positions with a population ratio of about 1:1, as evidenced by the refinement routine. Difference maps, calculated after the refinement, were essentially featureless. No attempt was made to locate hydrogen atoms. The least-squares residuals and other relevant parameters are given in Table 1, while selected bond distances and angles are reported in Tables 2 and 3. The SHELXTL/PC and SHELXL-93 program packages [9] were employed for the solution and refinement of the three structures and ORTEP [10] used to plot the molecular structures.

3. Results and discussion

The controlled replacement of the MeCN ligands in $[Cu(MeCN)_4]^+$ with dppf and $dppfE_2$ sequentially in chlorinated solvents leads to the dinuclear tricoordinate complex $[\{Cu(dppf\text{-}P,P')\}_2(\mu\text{-}dppfE_2\text{-}E,E')]^{2+}$ (E = S, **1**) or bischelate dppf-monochalcogenide derivative $[Cu(dppfE\text{-}P,E)_2]^+$ (E = Se, **2**), at variance with the E = O analogue which was found to produce under identical experimental conditions the four-coordinated species $[Cu(dppf\text{-}P,P')(dppfO_2\text{-}O,O')]^+$ [2a].

The crystal structure of complex **1** has been established by X-ray diffraction. The compound crystallizes as the chloroform (**1a**) or the bromoform (**1b**) monosolvate. The ORTEP drawing of the dication complex $[\{Cu(dppf)\}_2(\mu\text{-}dppfS_2)]^{2+}$ of **1** is depicted in Fig. 1. Complex **1** reveals a centrosymmetric dimeric structure where the Fe(2) atom of the bridging ligand lies on an inversion centre at 1/2, 1/2, 0. The copper atoms are three-coordinated being trigonally bonded to one chelating dppf ligand and symmetrically bridged by one $dppfS_2$ molecule. The CuP_2S moieties are nearly planar, with the metal ion lying 0.15 Å out of the plane of the three donor atoms. Sizable deviation from idealized trigonal-planar coordination geometry around Cu is observed. The P(1)–Cu–P(2) angle (116.0(1)° in **1a**) is markedly smaller than the P(2)–Cu–S angle of 138.3(1)° but significantly larger than the P(1)–Cu–S angle of 104.2(1)° (the corresponding values in **1b** are 115.5(1), 138.3(1) and 104.1(1)°). This distortion is possibly due to geometrical constraints imposed by the ferrocenyl framework. The Cu–P distances (2.229(2)–2.228(3) and 2.269(2)–2.277(3) Å) fall in the range observed for related compounds (mean value of 2.252(8) Å for 53 $Cu\text{-}PPh_3$ entries retrieved from CSD) [11]. In particular, the Cu–P(1) distances can be compared with the mean value (2.274(4) Å) measured for the chelating dppf ligand in the isostructural derivative $[\{Cu(dppf)\}_2(\mu\text{-}dppf)]^{2+}$ [12]. The Cu–S bond length (2.238(5)–2.236(4) Å) is somewhat longer than those of 2.144(5) and 2.140(5) Å observed for

Table 1
Structure determination summary [a]

	$[\{Cu(dppf)\}_2(\mu\text{-}dppfS_2)](BF_4)_2\cdot CHCl_3$ (**1a**)	$[\{Cu(dppf)\}_2(\mu\text{-}dppfS_2)](BF_4)_2\cdot CHBr_3$ (**1b**)	$[Cu(dppfSe)_2]BF_4\cdot C_6H_5Me$, **2**$\cdot C_6H_5Me$
Crystal data			
Empirical formula	$C_{51.5}H_{42.5}BCl_{1.5}CuF_4Fe_{1.5}P_3S$	$C_{51.5}H_{42.5}BBr_{1.5}CuF_4Fe_{1.5}P_3S$	$C_{75}H_{64}BCuF_4Fe_2P_4Se_2$
M	1073.6	1140.3	1509.1
Colour, habit	yellow needles	yellow irregularly shaped prisms	orange spheres
Crystal size (mm)	0.1×0.2×0.1	0.1×0.15×0.15	spherical, *r*=0.1
Crystal system	triclinic	triclinic	orthorhombic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_12_12_1$ (No. 19)
a (Å)	10.137(3)	10.180(5)	17.019(6)
b (Å)	14.354(5)	14.378(5)	20.594(7)
c (Å)	17.391(8)	17.482(7)	20.560(6)
α (°)	98.96(3)	98.92(3)	90
β (°)	92.86(3)	92.68(3)	90
γ (°)	95.31(3)	95.93(3)	90
U (Å^3)	2484(2)	2509(2)	7206(4)
D_c (Mg m^{-3}); *Z*	1.436; 2	1.509; 2	1.391; 4
μ (mm^{-1})	11.3	22.3	18.4
F(000)	1094	1148	3056
Data collection			
2*θ* range (°)	4.0–45.0	4.5–44.0	4.5–40.0
Index ranges	$0\le h\le 10$ $-15\le k\le 15$ $-18\le l\le 18$	$0\le h\le 10$ $-15\le k\le 15$ $-18\le l\le 18$	$0\le h\le 14$ $0\le k\le 1$ $0\le l\le 19$
No. independent reflections	6522	6261	3608
No. observed reflections [$I>2\sigma(I)$]	4092	3505	2198
Solution and refinement			
No. parameters refined	513	488	269
Final *R* [b], *wR*2 [c] indices (obs. data)	0.057, 0.159	0.073, 0.192	0.071, 0.170
Goodness of fit [d]	1.34	1.29	1.26
Largest difference peak (e Å^{-3})	0.77	0.98	0.69

[a] Details in common: Nicolet Siemens R3m/V diffractometer; 294 K; Mo Kα radiation (λ = 0.71073 Å); highly oriented graphite-crystal monochromator; *ω*–2*θ* scan mode; variable scan speed 4.51–14.65° min^{-1} in *ω*; scan range (*ω*) 0.65° + Kα separation; two standard reflections every 150.

[b] $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[c] $wR2=[\Sigma[w(|F_o|^2-|F_c|^2)^2]/\Sigma[w(|F_o|^2)^2]]^{1/2}$.

[d] $GOF=[\Sigma[w(|F_o|^2-|F_c|^2)^2]/(n-p)]^{1/2}$.

Table 2
Selected interatomic distances (Å) and angles (°) for $[\{Cu(dppf)\}_2(\mu\text{-}dppfS_2)](BF_4)_2\cdot CHCl_3$ (**1a**) and $[\{Cu(dppf)\}_2(\mu\text{-}dppfS_2)](BF_4)_2\cdot CHBr_3$ (**1b**)

1a		**1b**
2.269(2)	Cu–P(1)	2.277(3)
2.229(2)	Cu–P(2)	2.228(3)
2.235(2)	Cu–S(1)	2.231(4)
1.990(3)	S(1)–P(3)	1.995(4)
1.804(8)	P(1)–C(1)	1.79(1)
1.806(8)	P(2)–C(6)	1.76(1)
1.767(8)	P(3)–C(11)	1.79(1)
116.0(1)	P(1)–Cu–P(2)	115.5(1)
104.2(1)	P(1)–Cu–S(1)	104.4(1)
138.3(1)	P(2)–Cu–S(1)	138.8(1)
113.2(3)	Cu–P(1)–C(1)	114.1(4)
109.6(3)	Cu–P(2)–C(6)	111.0(4)
117.8(1)	Cu–S(1)–P(3)	117.5(2)
112.7(3)	S(1)–P(3)–C(11)	113.3(4)

Table 3
Selected bond distances (Å) and angles (°) for $[Cu(dppfSe)_2]BF_4\cdot C_6H_5Me$, **2**$\cdot C_6H_5Me$

Cu–Se(1)	2.675(5)	Se(1)–Cu–Se(2)	103.4(2)
Cu–Se(2)	2.475(4)	Se(1)–Cu–P(2)	111.5(2)
Cu–P(2)	2.271(8)	Se(1)–Cu–P(4)	96.1(2)
Cu–P(4)	2.262(8)	Se(2)–Cu–P(2)	105.5(2)
Se(1)–P(1)	2.132(8)	Se(2)–Cu–P(4)	116.8(2)
Se(2)–P(3)	2.143(8)	P(2)–Cu–P(4)	121.9(3)
P(1)–C(1)	1.82(3)	Cu–Se(1)–P(1)	132.9(2)
P(2)–C(6)	1.82(3)	Cu–Se(2)–P(3)	124.5(2)
P(3)–C(11)	1.78(3)	Se(1)–P(1)–C(1)	113(1)
P(4)–C(16)	1.89(3)	Se(2)–P(3)–C(11)	111(1)

the *trans*-chelate complex $[Cu(dppfS_2)]^+$ [1], but it compares well with the average Cu–S bond length of 2.28 Å in five copper(I)-phosphinechalcogenide complexes [11]. Moreover, the Cu–S–P(3) angle exhibits a value (117.8(1)–117.5(2)°) slightly larger than those adopted by the thio-

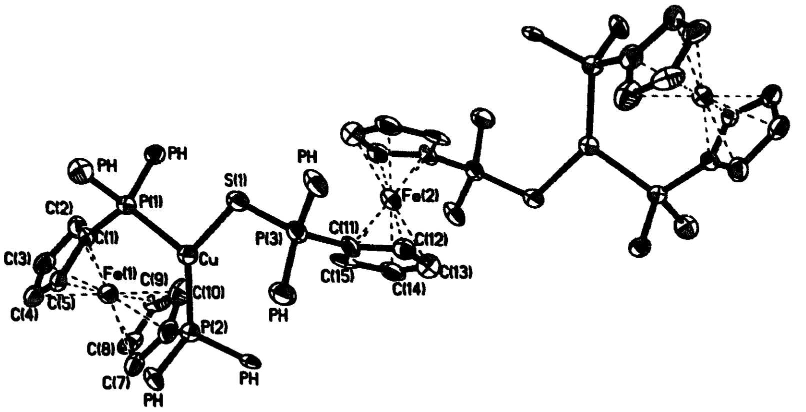

Fig. 1. ORTEP view of complex **1**. Tetrafluoroborate counteranion and solvent molecules have been omitted for clarity, and phenyl rings are designated as PH. The thermal ellipsoids are drawn at 40% probability.

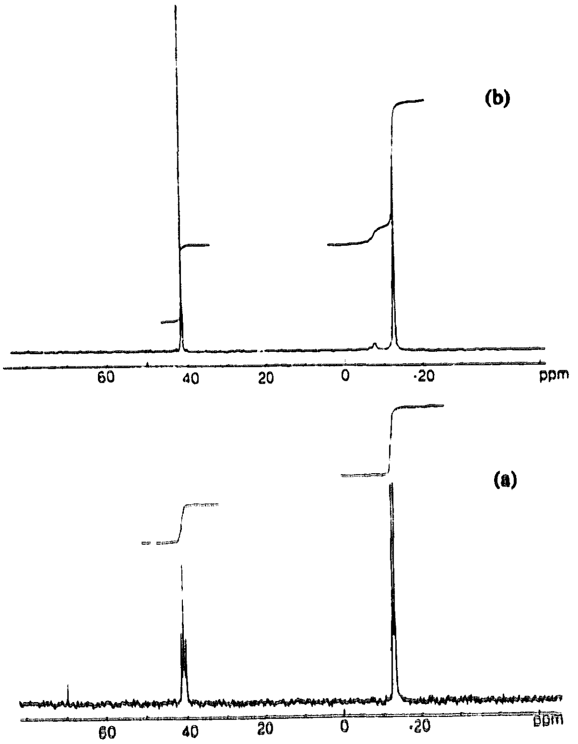

Fig. 2. $^{31}P\{^{1}H\}$ NMR spectra of **1**: (a) at −90°C in 3:1 $CDCl_3/CH_2Cl_2$ solvent mixture; (b) at 27°C in $CDCl_3$.

phosphorylic system ranging typically 115–98° [3]. Copper complexation of the thiophosphoryl ligand causes a slight lengthening of the P–S bond (1.990(3)–1.995(4) versus 1.944(3) Å) [1], consistent with the lower P=S stretching frequency observed in the IR spectrum. The angles S–P–C are not significantly different from those found in uncoordinated $dppfS_2$ [1]. In the ferrocene moieties the cyclopentadienyl rings exhibit perfect staggered conformation and are rigorously parallel with the phosphorus atoms being exactly 180° opposed as required by the inversion site symmetry in bridging $dppfS_2$. Conversely, in the chelating dppf molecule the cyclopentadienyl rings are partially staggered and inclined by 0.4° to each other with the phosphorus atoms being 44.4° apart.

The structure of complex **1** appears to be maintained in solution at low temperature, as shown by ^{31}P NMR spectroscopy in chlorinated solvents. As expected, the spectra show two different phosphorus environments, and two sets of resonances, a perfectly resolved triplet ($^{3}J_{PP}$ 20.8 Hz) and a sharp doublet ($^{3}J_{PP}$ 20.8 Hz) centred at δ 40.78 and −13.00, respectively, in a ratio of about 1:2 are apparent at −90°C (Fig. 2(a)). The lower field signal is clearly attributable to coordinated $dppfS_2$ and the higher field signal has to be attributed to coordinated dppf (for uncoordinated $dppfS_2$ and dppf in $CDCl_3$ at 27°C δ 40.72 and −17.19, respectively). Raising the temperature causes a marked change of the ^{31}P NMR pattern in that the signals shift to higher frequencies converting into sharp singlets (δ 41.63 and −12.24 at 27°C), and a new broad resonance at $\delta \sim -7.6$ emerges at ambient temperature (Fig. 2(b)). The temperature-dependent NMR pattern is indicative of a chemical exchange process, recognizable in the partial dissociation of one of the Cu–S bonds, which would become significant at room temperature on the NMR time scale. A similar observation has previously been made for the isostructural derivative $[\{Cu(dppf)\}_2(\mu\text{-}dppf)](BF_4)_2$ [5]. In this context, the −7.6 ppm extra resonance is reminiscent of that already observed in the ^{31}P spectrum of the homoleptic dppf-bridged complex at room temperature [5] and suggests the presence in the equilibrium mixture of appreciable amounts of $[\{Cu(dppf)\}_2(\mu\text{-}dppf)](BF_4)_2$. As a consequence, some $[Cu_4(\mu\text{-}dppfS_2)_6(BF_4)](BF_4)_3$ derivative [1] in rapid chemical exchange with complex **1** should be formed according to the following overall ligand-exchange reaction:

$$
\begin{aligned}
&6[\{Cu(dppf)\}_2(\mu\text{-}dppfS_2)](BF_4)_2\\
&\rightleftharpoons 4[\{Cu(dppf)\}_2(\mu\text{-}dppf)](BF_4)_2\\
&\quad + [Cu_4(\mu\text{-}dppfS_2)_6(BF_4)](BF_4)_3 \qquad (1)
\end{aligned}
$$

^{31}P NMR control experiments confirm that the addition of $[Cu_4(\mu\text{-}dppfS_2)_6(BF_4)](BF_4)_3$ to a $CDCl_3$ solution of $[\{Cu(dppf)\}_2(\mu\text{-}dppf)](BF_4)_2$ in 1:4 molar ratio at room temperature causes the rapid equilibration of the mixture to the $[\{Cu(dppf)\}_2(\mu\text{-}dppfS_2)](BF_4)_2$ species, thus proving that the equilibrium lies to the left in Eq. (1), favouring complex **1** in $CHCl_3$. Moreover, these findings together with the previous observation that complex **1** can be alternatively generated by reacting $[Cu(dppfS_2)]BF_4$ with dppf [1] demonstrate the extreme substitution lability of these systems in which, however, $dppfS_2$ appears to compete successfully with dppf for adopting the bridging coordination mode, despite the well known bridging ability of dppf [13]. The structural preference for **1** is a clear indication of $dppfS_2$ in its favoured bridging ligation state.

As far as dppf-monoselenide complex **2** is concerned, its unexpected formation under conditions a priori suited for obtaining the dinuclear species analogous to complex **1** arises from the well-known rapid selenium exchange between the phosphorus atoms of diphosphine systems [14]. In fact, diphosphine monoselenides exist only in solution, and in equilibrium with the diphosphine and the diselenide derivative [14]. Control experiments confirm that the chalcogen transfer between $dppfSe_2$ and dppf takes place on the NMR time scale at room temperature and the mixture equilibrates to a 1:2:1 mixture of dppf, dppfSe and $dppfSe_2$. Thus, the ^{31}P NMR spectrum of the mixture in $CDCl_3$ displays a set of equally intense signals at δ −17.19, 30.93 ($^1J_{PSe}$ 737 Hz), −17.66 and 31.33 ($^1J_{PSe}$ 734 Hz), the two latter resonances being attributable to the monoselenium species by comparison with the spectra of dppf and $dppfSe_2$. Now, the isolation of complex **2** in essentially quantitative yield clearly indicates that selenium exchange occurs not only between uncoordinated dppf and its diselenide derivative, but also when these ligands are bonded to copper centres.

The identity of complex **2**, assigned initially on the basis of the NMR data in solution (see below), has been definitely established by an X-ray crystal structure determination. The complex crystallizes with one occluded toluene molecule. The structure of **2** (Fig. 3) reveals that the cationic complex contains monomeric entities in which the coordination geometry around the metal is markedly distorted tetrahedral where the two dppfSe moieties act as chelating ligands with bite angles of 111.5(2) and 116.8(2)°. The remaining Se(1)–Cu–Se(2) and Se(2)–Cu–P(2) angles (103.4(2) and 105.5(2)°) approach the value for tetrahedral geometry, whereas the Se(1)–Cu–P(4) and P(2)–Cu–P(4) angles differ significantly from the ideal value being 96.1(2) and 121.9(3)°. An alternative description involves a trigonal pyramid, in which the copper atom is severely out of the basal plane, defined by the atoms Se(2), P(2) and P(4), by 0.55 Å towards the apical Se(1) atom. In line, a survey of Cu–Se bond distances reveals a lengthening of the Cu–Se(1) distance (2.675(5) Å), while the Cu–Se(2) one (2.475(4) Å) compares well with the mean value of 2.46(1) Å [15]. The average P–Se bond length (2.137(8) Å) is slightly longer than that of the uncoordinated selenophosphorylic ligand (2.103(6) Å) [1], consistent with the lower P=Se stretching frequency observed in the IR spectrum of the complex ($\Delta\nu = \sim 10\ cm^{-1}$). The Cu–Se–P angles appear to be the widest observed to date [3] ranging from 124.5(2) to 132.9(2)° and point towards a substantially sp^2 hybridization of the selenium atom. The cyclopentadienyl rings are all planar (within 0.02 Å) and the two ferrocene moieties exhibit a 'synclinal eclipsed' conformation [13], the torsion angle being 77.4° for Fe(1) and 69.9° for Fe(2), with Cu···Fe(1) and Cu···Fe(2) separations of 4.536 and 4.481 Å, respectively.

The ^{31}P NMR data in solution are consistent with the solid-state highly distorted tetrahedral structure. Thus, the ^{31}P NMR spectrum of complex **2** in $CDCl_3$ at −65°C consists of well-resolved AA'XX' multiplets centred at δ 30.66, flanked by satellites due to ^{77}Se–^{31}P coupling ($^1J_{PSe}$ 710 Hz, and $^3J_{PP}$ 25.6 and 16 Hz), and δ −7.55 ($^3J_{PP}$ 25.6 and 16 Hz), respectively (Fig. 4(a)). As the temperature increases, the higher field resonance gradually loses its multiplet feature, converting into a broad singlet at 27°C, while the multiplet at lower field remains substantially unchanged throughout the temperature range shown (Fig. 4(b)). Interestingly, the ^{77}Se–^{31}P coupling constant appears to be temperature-dependent ranging from 710 Hz at −65°C to 670 Hz at 27°C. This observation points convincingly to the occurrence of confor-

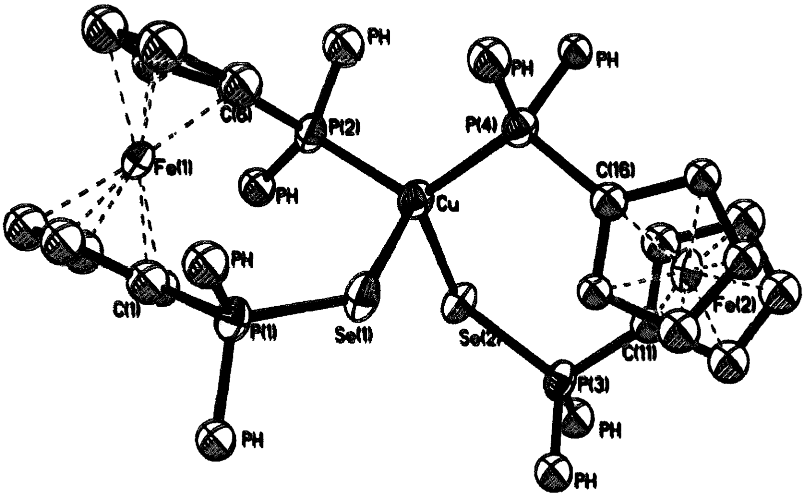

Fig. 3. ORTEP view of complex **2**. Tetrafluoroborate counteranion and solvent molecules have been omitted for clarity, and phenyl rings are designated as PH. The thermal ellipsoids are drawn at 40% probability.

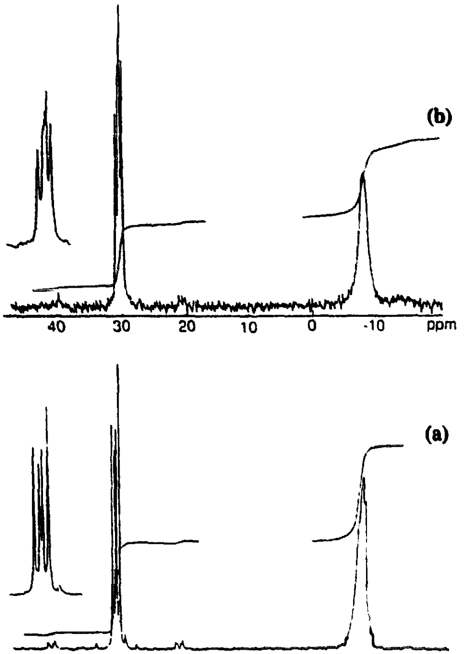

Fig. 4. $^{31}P\{^1H\}$ NMR spectra of 2 in $CDCl_3$: (a) at −65°C; (b) at 27°C.

mational equilibria in solution and provides additional evidence for the assigned structure. Moreover, the decrease in the $^1J_{PSe}$ coupling constant as a result of coordination of the free dppfSe appears to be unusually small and consistent with retention of much P–Se multiple bonding [3], in full agreement with the X-ray structural data.

The ^{31}P NMR pattern of dppf-monosulfide complex 3 is reminiscent of that exhibited by selenium analogue 2 and suggestive of a similar structure. Thus, a poorly resolved double doublet is apparent at δ 40.64 ($^3J_{PP}$ 23 and 16 Hz) and an unresolved doublet of doublets occurs at δ −8.99 in CD_2Cl_2 solution at −90°C. On raising the temperature, the resonance at δ 40.64 moves slightly to higher frequency (δ 40.87 at 300 K) retaining the multiplet feature ($^3J_{PP}$ 18 and 13.5 Hz), whereas the resonance at δ −8.99 changes to a very broad signal downfield-shifted by 0.34 ppm at 27°C. By analogy, a sizable temperature dependence of the $^3J_{PP}$ values is evident.

Diphosphine monooxide complex 4 stands as a rare copper(I) compound to be stabilized by a mixed soft–hard (P_2O_2) coordination sphere and deserves particular attention as it can be compared with the already reported isomer [Cu(dppf)(dppfO$_2$)]BF_4 [2a], as well as with selenium (2) or sulfur (3) analogues featured by a purely soft ligand set. The ^{31}P NMR spectra may be interpreted as an A_2X_2 pattern for two chelated dppfO molecules. In fact, a triplet at δ 33.71 ($^3J_{PP}$ 6 Hz) and a very broad signal at δ −12.2 appear in CD_2Cl_2 solution at ambient temperature (Fig. 5(a)). In agreement with the general trend associated with the coordination of phosphine ligands to a metal centre, both resonances are shifted to higher frequencies when compared with those of free dppfO (δ 28.74, P^V and −17.50, P^{III}, respectively), at variance with the low-frequency shift of the P^{III} resonance previously observed for the closely related complex [Cu(dppf)(dppfO$_2$)]BF_4 [2a]. Upon cooling to −90°C, the signals sharpen and move slightly in the opposite direction (δ 34.15 ($^3J_{PP}$ 6 Hz) and −13.06), but still no evidence is found for the expected triplet in the phosphorus(III) resonance (Fig. 5(b)). Again, no change is here apparent in the $^3J_{PP}$ value throughout the temperature range shown. The striking absence of $^{31}P^{III}$–$^{31}P^V$ coupling in the higher field resonance is likely to arise from coupling to quadrupolar $^{63/65}Cu$ nuclei of the phosphorus atoms directly bonded to the metal centre inside a roughly symmetrical environment. The A_2X_2 spin system exhibited by oxophosphoryl complex 4, at variance with the AA′XX′ one of chalcogen analogues 2 or 3, is interpreted as being due to a low-energy exchange process which equilibrates the phosphine sites in the tetracoordinate species. Similarly facile fluxionality has been noted in the related complex [Cu(dppf)(dppfO$_2$)]BF_4 [2a].

In this connection, it is worthwhile to compare the ^1H NMR pattern of complex 4 with that of uncoordinated dppfO. The ^1H NMR spectrum of the free ligand displays, owing to the chemical inequivalence of the two cyclopentadienyl rings, four multiplets typical of two sets of C_5H_4 protons (H_α, H_β) centred at δ 4.03, 4.22, 4.35 and 4.55, where J_{HH} and/or J_{PH} are ~2 Hz, in $CDCl_3$ solution at 27°C. The 4.55 and 4.03 ppm signals, which are $^1H \leftrightarrow {}^1H$ correlated as indicated by selective $^1H\{^1H\}$ decoupling, are attributed to the protons of the cyclopentadienyl ring bearing the oxophosphoryl unit [16]. Copper complexation causes a dramatic change of the

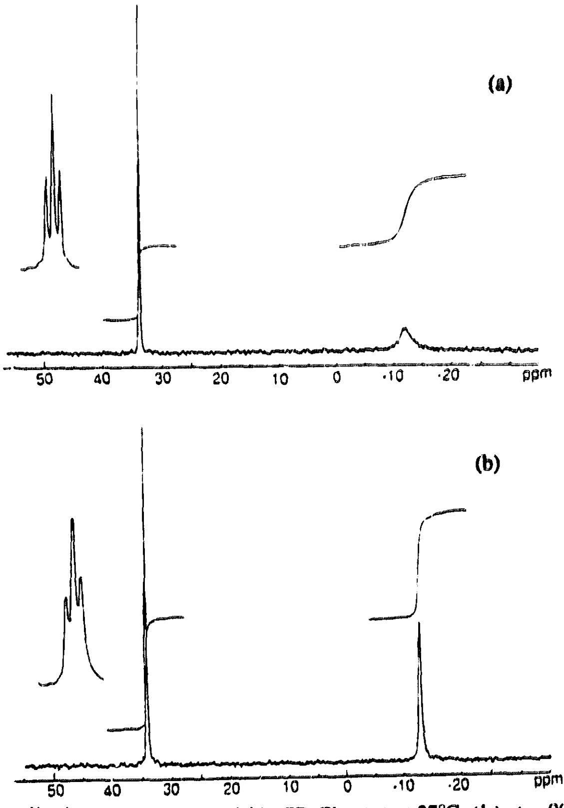

Fig. 5. $^{31}P\{^1H\}$ NMR spectra of 4 in CD_2Cl_2: (a) at 27°C; (b) at −90°C.

NMR pattern, as two broad singlets at δ 4.68 and 4.28 with an approximate intensity ratio of 1:3 are now observed. The dynamic process responsible for the near-equivalence of the cyclopentadienyl protons is probably related to the already suggested rapid inversion at the phosphorus atoms and/or to mutual twisting of the cyclopentadienyl rings in the chelating ligand. Notably, this feature of the oxophosphoryl ligand is not shown by the sulfur analogue, which appears to bind to copper(I) retaining the morphology of its own ^{1}H NMR pattern.

4. Supplementary material

Additional material available from the Crystallographic Data Centre comprises anisotropic thermal parameters, final fractional atomic coordinates, full listings of bond lengths/angles and a table of the structure factors.

References

[1] G. Pilloni, B. Longato, G. Bandoli and B. Corain, J. Chem. Soc., Dalton Trans., (1997) 819.

[2] (a) G. Pilloni, B. Corain, M. Degano, B. Longato and G. Zanotti, J. Chem. Soc., Dalton Trans., (1993) 1777; (b) G. Pilloni, G. Valle, C. Corvaja, B. Longato and B. Corain, Inorg. Chem., 34 (1995) 5910.

[3] See, for example, N. Burford, B.W. Royan and R.E.v.H. Spence, J. Chem. Soc., Dalton Trans., (1990) 2111; N. Burford, Coord. Chem. Rev., 112 (1992) 1; D.G. Gilheany, in F.R. Hartley (ed.), The Chemistry of Organophosphorus Compounds, Vol. 2, Wiley-Interscience, 1992, Ch. 1 and Refs. therein.

[4] See, for example, T.S. Lobana, in F.R. Hartley (ed.), The Chemistry of Organophosphorus Compounds, Vol. 2, Wiley-Interscience, 1992, Ch. 8, and Refs. therein; J.R. Black and W. Levason, J. Chem. Soc., Dalton Trans., (1994) 3225.

[5] G. Pilloni, R. Graziani, B. Longato and B. Corain, Inorg. Chim. Acta, 190 (1991) 165.

[6] G. Pilloni, B. Longato and B. Corain, J. Organomet. Chem., 420 (1991) 57.

[7] J.J. Bishop, A. Davison, M.L. Katcher, D.W. Lichtenberg, R.E. Merrill and J.C. Smart, J. Organomet. Chem., 27 (1971) 241.

[8] S. Ninoreille, R. Broussier, R. Amardeil, M.M. Kubicki and B. Gautheron, Bull. Soc. Chim. Fr., 132 (1995) 128.

[9] (a) G.M. Sheldrick, SHELXTL/PC, Version 5.03, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1994; (b) G.M. Sheldrick, SHELXL-93, program for the refinement of crystal structures, University of Göttingen, Germany, 1993.

[10] C.K. Johnson, ORTEP, Rep. ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

[11] F.H. Allen, J.E. Davies, J.J. Galloy, O. Johnson, O. Kennard, C.F. Macrae, E.M. Mitchell, G.F. Mitchell, J.M. Smith and D.G. Watson, J. Chem. Inf. Comput. Sci., 31 (1991) 187; Cambridge Structural Database (CSD) System, Version 5.12, Oct. 1996.

[12] U. Casellato, R. Graziani and G. Pilloni, J. Crystallogr. Spectrosc. Res., 23 (1993) 571.

[13] K.-S. Gan and T.S.A. Hor, in A. Togni and T. Hayashi (eds.), Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science, VCH, Weinheim, 1995, Ch. 1, and Refs. therein.

[14] D.H. Brown, R.J. Cross and R. Keat, J. Chem. Soc., Dalton Trans., (1980) 871.

[15] (a) J. Kaiser, R. Richter and J. Sieler, Acta Crystallogr., Sect. B, 31 (1975) 260; (b) M. Bonamico and G. Dessy, J. Chem. Soc. A, (1971) 264.

[16] J. Podlaha, P. Štepnička, J. Ludvík and I. Císařová, Organometallics, 15 (1996) 543.