

# Bonding ability of 1,1'-bis(diphenylthiophosphoryl)ferrocene (dptpf) and its selenium analogue towards copper(I). Crystal structure of [Cu(dptpf)]BF<sub>4</sub>

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The phosphine chalcogenides Fe[η-C<sub>5</sub>H<sub>4</sub>P(E)Ph<sub>2</sub>]<sub>2</sub> (L) [E = nothing (dppf), S (dptpf) or Se (dpspf)] reacted readily with [Cu(MeCN)<sub>4</sub>]X (X = BF<sub>4</sub>, PF<sub>6</sub> or ClO<sub>4</sub>) in CH<sub>2</sub>Cl<sub>2</sub> to give quantitatively the monomeric two-co-ordinated complexes [CuL]BF<sub>4</sub> (E = S **1** or Se **2**) or polynuclear three-co-ordinated derivatives analysing as [CuL<sub>1.5</sub>]X (E = S **3** or Se **4**), depending on the ligand to copper molar ratio. The complexes have been characterized by multinuclear NMR spectroscopy. Complexes **3** and **4** reversibly dissociate in solution, as was evident from the concentration- and temperature-dependent NMR spectra. The low-temperature <sup>1</sup>H, <sup>31</sup>P-{<sup>1</sup>H} and <sup>19</sup>F NMR spectra are interpreted in terms of a tetranuclear structure in which each copper atom is trigonally bonded by bridging L ligands and one anion molecule is trapped inside the tetrahedral Cu<sub>4</sub> cage. Single-crystal X-ray structure determinations were performed for the two diphosphine chalcogenides and complex **1**. The structure of **1** shows a slightly distorted linear two-co-ordination geometry around the copper atom with an S(1)-Cu-S(2) angle of 171.5(2)°. The Cu-S bond distances [2.144(5) and 2.140(5) Å] and the Cu-S-P angles [100.8(2) and 105.5(2)] point towards a substantially sp<sup>3</sup> hybridization of the sulfur atoms. In the ferrocene moiety the cyclopentadienyl rings are virtually parallel (dihedral angle between the two planes 6.5°) and staggered by 16.1°.

1,1'-Bis(diphenylphosphino)ferrocene (dppf) was synthesized 25 years ago,<sup>1</sup> but its amazing co-ordination chemistry has been widely appreciated in the last decade.<sup>2</sup> It embodies two relevant features: (i) the strong bonding ability of the PPh<sub>2</sub> ligating sites and (ii) an uncommon length coupled with an impressive geometric flexibility due to the organometallic 'ball-joint'. This last feature is extensively presented and discussed in ref. 2, and is likely to play a role in the catalytic ability of various dppf-based metalloorganic catalysts.<sup>3</sup>

We have been interested in the co-ordination chemistry of dppf since 1985<sup>4</sup> and have more recently started to evaluate the possibility of utilizing its 'magic' backbone to obtaining longer and potentially even more flexible dppf-based compounds of general formula Fe[η-C<sub>5</sub>H<sub>4</sub>P(E)Ph<sub>2</sub>]<sub>2</sub> (E = O, S or Se). We were successful in obtaining the E = O compound<sup>4g</sup> in 1991 (X-ray-authenticated in 1993),<sup>5</sup> which turned out to be capable of the unexpected stabilization of Cu<sup>I</sup> inside a fully hard (O<sub>4</sub>) chromophore.<sup>6</sup> Quite recently the bonding ability of the E = S derivative (dptpf) towards Au<sup>I</sup> and Ag<sup>I</sup> has been illustrated by Laguna and co-workers,<sup>7</sup> and their results prompted us to report the crystal structures of dptpf and dpspf (E = Se) and on their bonding ability towards Cu<sup>I</sup>. In addition to the monomeric complexes [CuL]BF<sub>4</sub>, copper(I) forms, at variance with the relevant congeners, polynuclear compounds analysing as [CuL<sub>1.5</sub>]X {L = Fe[η-C<sub>5</sub>H<sub>4</sub>P(E)Ph<sub>2</sub>]<sub>2</sub>; X = BF<sub>4</sub>, PF<sub>6</sub> or ClO<sub>4</sub>}, depending on the molar ratio of the reactants.

## Experimental

### General procedures and materials

All reactions and manipulations of solutions were performed under a nitrogen atmosphere. Anhydrous dichloromethane

and 1,2-dichloroethane (Fluka), dppf and tetrakis(acetonitrile)copper(I) hexafluorophosphate (Aldrich) were used without purification. Tetrakis(acetonitrile)copper(I) tetrafluoroborate and perchlorate were prepared as previously reported.<sup>4f</sup> The compound dptpf was prepared by the literature procedure.<sup>1</sup> The compound dpspf was prepared by the action of an excess of black selenium powder (1.3 g, 16.5 mmol) on the diphosphine (4.0 g, 7.2 mmol) in refluxing chloroform (25 cm<sup>3</sup>) for 3 h, after which the excess of selenium was filtered off. Addition of methanol (50 cm<sup>3</sup>) to the filtrate afforded a yellow precipitate, which was filtered off, washed with methanol and dried under vacuum. Yield 4.9 g, 95% (Found: C, 57.1; H, 3.95. Calc. for C<sub>34</sub>H<sub>28</sub>FeP<sub>2</sub>Se<sub>2</sub>: C, 57.35; H, 3.95%). IR: 573 cm<sup>-1</sup> (P-Se). NMR (CDCl<sub>3</sub>, 300 K): <sup>1</sup>H, δ 7.8–7.4 (m, 10 H, Ph), 4.69 (q, J<sub>HH</sub> ca. 2, 2 H, C<sub>5</sub>H<sub>4</sub>), 4.32 (q, J<sub>HH</sub> ca. 2, 2 H, C<sub>5</sub>H<sub>4</sub>); <sup>31</sup>P-{<sup>1</sup>H}, δ 30.93 (J<sub>PSe</sub> = 737 Hz). All other reagents and starting materials were of reagent-grade quality used as supplied.

### Physical measurements

Proton (89.55), <sup>31</sup>P-{<sup>1</sup>H} (36.23) and <sup>19</sup>F (84.25 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<sub>4</sub>, external H<sub>3</sub>PO<sub>4</sub> (85% w/w) and external CFCl<sub>3</sub>, respectively. Infrared spectra were recorded as Nujol mulls on KBr plates using a Nicolet 5SXC-FTIR spectrometer, electrospray mass spectra on a LCQ Finnigan spectrometer.

### Preparation of copper(I) complexes

**[Cu(dptpf)]BF<sub>4</sub> 1.** To a solution of dptpf (0.940 g, 1.52 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) was added [Cu(MeCN)<sub>4</sub>]BF<sub>4</sub> (0.478 g, 1.52 mmol) and the mixture stirred at room tem-

perature in an inert atmosphere. After 1 h the volatiles were vacuum-evaporated and the residue dissolved in  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ). Addition of pentane (25  $\text{cm}^3$ ) resulted in a yellow precipitate which was filtered off and dried under vacuum. The yield was essentially quantitative (Found: C, 52.8; H, 3.6; S, 8.25. Calc. for  $\text{C}_{34}\text{H}_{28}\text{BCuF}_4\text{FeP}_2\text{S}_2$ : C, 53.1; H, 3.65; S, 8.35%). Mass spectrum:  $m/z$  681 (1 -  $\text{BF}_4^-$ , 100%). IR:  $635\text{ cm}^{-1}$  (P=S) ( $\Delta\nu = -20\text{ cm}^{-1}$  with respect to unco-ordinated dptpf. Molar conductivity in nitromethane (1.00  $\text{mmol dm}^{-3}$ ):  $\Lambda_M = 78.5\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ . NMR ( $\text{CDCl}_3$ , 300 K):  $^1\text{H}$ ,  $\delta$  7.8–7.6 (m, 10 H, Ph), 4.74 (m, 2 H,  $\text{C}_5\text{H}_4$ ) and 4.40 (m, 2 H,  $\text{C}_5\text{H}_4$ ); a resonance due to small amounts of clathrated  $\text{CH}_2\text{Cl}_2$  was also detectable;  $^{31}\text{P}$ - $\{^1\text{H}\}$ ,  $\delta$  45.63 (s). Solutions of complex **1** are sensitive to moisture and reactive towards co-ordinating solvents, yielding some **3a**.

**[Cu(dpspf)BF<sub>4</sub>]**2****. To a solution of dpspf (0.912 g, 1.28 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (20  $\text{cm}^3$ ) was added  $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$  (0.403 g, 1.28 mmol) and the mixture was stirred at room temperature under a nitrogen atmosphere. After 1 h the volatiles were vacuum-evaporated and the residue dissolved in 1,2-dichloroethane (20  $\text{cm}^3$ ). The resulting solution was refluxed for a few minutes, and then evaporated to dryness *in vacuo* at 70 °C. This treatment with dichloroethane and the subsequent drying were repeated three times. At the end addition of pentane (25  $\text{cm}^3$ ) to the residue dissolved in  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ) afforded a yellow precipitate which was filtered off and dried under vacuum. The yield was essentially quantitative. The solid product invariably contained  $\text{CH}_2\text{Cl}_2$  of crystallization, as determined by  $^1\text{H}$  NMR spectroscopy and confirmed by elemental analysis (Found: C, 46.5; H, 3.25. Calc. for  $\text{C}_{34.25}\text{H}_{28.5}\text{BCl}_{0.5}\text{CuF}_4\text{FeP}_2\text{Se}_2$ : C, 46.55; H, 3.25%). Mass spectrum:  $m/z$  775 (2 -  $\text{BF}_4^-$ , 100%). IR:  $563\text{ cm}^{-1}$  (P=Se) ( $\Delta\nu = -10\text{ cm}^{-1}$  with respect to unco-ordinated dpspf). NMR ( $\text{CDCl}_3$ , 300 K):  $^1\text{H}$ ,  $\delta$  7.8–7.6 (m, 10 H, Ph), 4.74 (m, 2 H,  $\text{C}_5\text{H}_4$ ) and 4.35 (m, 2 H,  $\text{C}_5\text{H}_4$ );  $^{31}\text{P}$ - $\{^1\text{H}\}$ ,  $\delta$  33.01 (s with  $^{77}\text{Se}$  satellites,  $^1J_{\text{PSe}} 582$  and  $^3J_{\text{PSe}} 12$  Hz). Solutions of complex **2** are exceedingly sensitive to moisture and reactive towards co-ordinating solvents, yielding some **4a**.

**[Cu<sub>2</sub>(dptpf)<sub>3</sub>(BF<sub>4</sub>)<sub>2</sub>]**3a****. Complex **3a** was obtained upon treating a  $\text{CH}_2\text{Cl}_2$  solution (15  $\text{cm}^3$ ) of dptpf (1.57 g, 2.54 mmol) with  $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$  (0.400 g, 1.27 mmol) with stirring. After 1 h the clear orange solution was evaporated to dryness under vacuum. Redissolution in the minimum volume of  $\text{CH}_2\text{Cl}_2$ , followed by gradual addition of an excess of  $\text{CHCl}_3$  gave a yellow solid, which was filtered off, washed with  $\text{CHCl}_3$  and dried under vacuum. The solid product invariably contained entrapped  $\text{CHCl}_3$  molecules, as suggested by thermal and elemental analyses. Most of the clathrate solvent could be removed by heating *in vacuo* at 75 °C for 48 h to give pure complex **3a**. Yield: 1.23 g (90%) (Found: C, 56.3; H, 3.9; Cu, 5.8; Fe, 7.7; S, 8.8. Calc. for  $\text{C}_{102}\text{H}_{84}\text{B}_2\text{Cu}_2\text{F}_8\text{Fe}_3\text{P}_6\text{S}_6$ : C, 56.8; H, 3.95; Cu, 5.9; Fe, 7.8; S, 8.9%). IR:  $634\text{ cm}^{-1}$  (P=S) ( $\Delta\nu = -21\text{ cm}^{-1}$  with respect to unco-ordinated dptpf). NMR ( $\text{CD}_2\text{Cl}_2$ , 233 K):  $^1\text{H}$ ,  $\delta$  7.8–7.6 (m, 10 H, Ph), 5.76 (s, 1 H,  $\text{C}_5\text{H}_4$ ), 5.18 (s, 1 H,  $\text{C}_5\text{H}_4$ ), 4.96 (s, 1 H,  $\text{C}_5\text{H}_4$ ) and 3.17 (s, 1 H,  $\text{C}_5\text{H}_4$ );  $^{31}\text{P}$ - $\{^1\text{H}\}$ ,  $\delta$  41.02 (s);  $^{19}\text{F}$ ,  $\delta$  -145.7 and -148.7 (br s with relative intensity 1:3,  $\text{BF}_4^-$ ).

**[Cu<sub>2</sub>(dptpf)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub>]**3b****. A similar procedure was adopted to that for the tetrafluoroborate complex using  $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$  (0.496 g, 1.33 mmol) and dptpf (1.64 g, 2.65 mmol) as the substrates in  $\text{CH}_2\text{Cl}_2$ . Yield: 1.33 g (88%) (Found: C, 53.55; H, 3.7; S, 8.5. Calc. for  $\text{C}_{102}\text{H}_{84}\text{Cu}_2\text{F}_{12}\text{Fe}_3\text{P}_6\text{S}_6$ : C, 53.9; H, 3.7; S, 8.45%). IR:  $634\text{ cm}^{-1}$  (P=S). NMR ( $\text{CD}_2\text{Cl}_2$ , 233 K):  $^1\text{H}$ ,  $\delta$  7.8–7.6 (m, 10 H, Ph), 5.60 (s, 1 H,  $\text{C}_5\text{H}_4$ ), 5.34 (s, 1 H,  $\text{C}_5\text{H}_4$ ), 4.89 (s, 1 H,  $\text{C}_5\text{H}_4$ ) and 3.05 (s, 1 H,  $\text{C}_5\text{H}_4$ );  $^{31}\text{P}$ - $\{^1\text{H}\}$ ,  $\delta$  41.10 (s, dptpf), -143.9 and -144.4 (spt with relative intensity 1:3,  $^1J_{\text{PF}} 710$  and 712, respectively,  $\text{PF}_6^-$ );  $^{19}\text{F}$ ,  $\delta$  -70.5 and -73.5 (d with

relative intensity 1:3,  $^1J_{\text{PF}} 710$  and 712 Hz, respectively,  $\text{PF}_6^-$ ).

**[Cu<sub>2</sub>(dptpf)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub>]**3c****. A similar procedure, except for the final heating stage, was adopted using  $[\text{Cu}(\text{MeCN})_4]\text{ClO}_4$  (0.154 g, 0.47 mmol) and dptpf (0.581 g, 0.94 mmol) as the substrates in  $\text{CH}_2\text{Cl}_2$ . The solid contained *ca.* one molecule of entrapped chloroform per copper atom, as determined by elemental analysis. Yield: 0.49 g (86%) (Found: C, 52.1; H, 3.65; S, 8.15. Calc. for  $\text{C}_{104}\text{H}_{86}\text{Cl}_3\text{Cu}_2\text{Fe}_3\text{O}_8\text{P}_6\text{S}_6$ : C, 51.6; H, 3.6; S, 7.95%). IR:  $633\text{ cm}^{-1}$  (P=S). NMR ( $\text{CD}_2\text{Cl}_2$ , 233 K):  $^1\text{H}$ ,  $\delta$  7.6–7.0 (m, 10 H, Ph), 5.71 (s, 1 H,  $\text{C}_5\text{H}_4$ ), 5.36 (s, 1 H,  $\text{C}_5\text{H}_4$ ), 4.92 (s, 1 H,  $\text{C}_5\text{H}_4$ ) and 3.10 (s, 1 H,  $\text{C}_5\text{H}_4$ );  $^{31}\text{P}$ - $\{^1\text{H}\}$ ,  $\delta$  41.05 (s).

**[Cu<sub>2</sub>(dpspf)<sub>3</sub>(BF<sub>4</sub>)<sub>2</sub>]**4a****. To a dichloromethane (15  $\text{cm}^3$ ) solution of dpspf (0.915 g, 1.28 mmol) was added  $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$  (0.202 g, 0.64 mmol). The mixture was stirred for 1 h and then the solution was evaporated to dryness under vacuum. Redissolution in the minimum volume of  $\text{CH}_2\text{Cl}_2$ , followed by gradual addition of an excess of  $\text{CHCl}_3$ , gave complex **4a** as a yellow solid, which was filtered off, washed with  $\text{CHCl}_3$  and dried under vacuum at 75 °C for 48 h. Yield: 0.70 g (90%) (Found: C, 50.6; H, 3.4; Cu, 5.4; Fe, 7.0. Calc. for  $\text{C}_{102}\text{H}_{84}\text{B}_2\text{Cu}_2\text{F}_8\text{Fe}_3\text{P}_6\text{Se}_6$ : C, 50.25; H, 3.45; Cu, 5.2; Fe, 6.85%). IR:  $562\text{ cm}^{-1}$  (P=Se) ( $\Delta\nu = -11\text{ cm}^{-1}$  with respect to unco-ordinated dpspf). NMR ( $\text{CD}_2\text{Cl}_2$ , 233 K):  $^1\text{H}$ ,  $\delta$  7.8–7.6 (m, 10 H, Ph), 5.72 (s, 1 H,  $\text{C}_5\text{H}_4$ ), 5.32 (s, 1 H,  $\text{C}_5\text{H}_4$ ), 5.11 (s, 1 H,  $\text{C}_5\text{H}_4$ ) and 3.23 (s, 1 H,  $\text{C}_5\text{H}_4$ );  $^{31}\text{P}$ - $\{^1\text{H}\}$ ,  $\delta$  28.16 (s with  $^{77}\text{Se}$  satellites,  $^1J_{\text{PSe}} 645$  and  $^4J_{\text{PP}} 3$  Hz);  $^{19}\text{F}$  (84.25 MHz),  $\delta$  -145.7 and -148.7 (br s with relative intensity 1:3,  $\text{BF}_4^-$ ).

**[Cu<sub>2</sub>(dpspf)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub>]**4b****. A similar procedure was adopted using  $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$  (0.295 g, 0.79 mmol) and dpspf (1.14 g, 1.60 mmol) as the substrates in  $\text{CH}_2\text{Cl}_2$ . Yield: 0.94 g (93%) (Found: C, 47.85; H, 3.3. Calc. for  $\text{C}_{102}\text{H}_{84}\text{Cu}_2\text{F}_{12}\text{Fe}_3\text{P}_6\text{Se}_6$ : C, 47.8; H, 3.3%). IR:  $562\text{ cm}^{-1}$  (P=Se). NMR ( $\text{CD}_2\text{Cl}_2$ , 233 K):  $^1\text{H}$ ,  $\delta$  7.8–7.6 (m, 10 H, Ph), 5.65 (s, 1 H,  $\text{C}_5\text{H}_4$ ), 5.39 (s, 1 H,  $\text{C}_5\text{H}_4$ ), 5.12 (s, 1 H,  $\text{C}_5\text{H}_4$ ) and 3.20 (s, 1 H,  $\text{C}_5\text{H}_4$ );  $^{31}\text{P}$ - $\{^1\text{H}\}$ ,  $\delta$  28.01 (s with  $^{77}\text{Se}$  satellites,  $^1J_{\text{PSe}} 647$  and  $^4J_{\text{PP}} 3$ , dptpf), -143.9 and -144.4 (spt with relative intensity 1:3,  $^1J_{\text{PF}} 710$  and 712 Hz, respectively,  $\text{PF}_6^-$ );  $^{19}\text{F}$ ,  $\delta$  -69.48 and -73.85 (d with relative intensity 1:3,  $^1J_{\text{PF}} 710$  and 712 Hz, respectively,  $\text{PF}_6^-$ ).

**[Cu<sub>2</sub>(dpspf)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub>]**4c****. A similar procedure was adopted using  $[\text{Cu}(\text{MeCN})_4]\text{ClO}_4$  (0.105 g, 0.32 mmol) and dpspf (0.456 g, 0.64 mmol) as the starting materials in  $\text{CH}_2\text{Cl}_2$ . The solid contained *ca.* one molecule of entrapped chloroform per copper atom, as determined by elemental analysis. Yield: 0.39 g (90%) (Found: C, 45.9; H, 3.15. Calc. for  $\text{C}_{104}\text{H}_{86}\text{Cl}_3\text{Cu}_2\text{Fe}_3\text{O}_8\text{P}_6\text{Se}_6$ : C, 46.2; H, 3.20%). IR:  $561\text{ cm}^{-1}$  (P=Se). NMR ( $\text{CD}_2\text{Cl}_2$ , 233 K):  $^1\text{H}$ ,  $\delta$  7.8–7.6 (m, 10 H, Ph), 5.72 (s, 1 H,  $\text{C}_5\text{H}_4$ ), 5.44 (s, 1 H,  $\text{C}_5\text{H}_4$ ), 5.11 (s, 1 H,  $\text{C}_5\text{H}_4$ ) and 3.32 (s, 1 H,  $\text{C}_5\text{H}_4$ );  $^{31}\text{P}$ - $\{^1\text{H}\}$ ,  $\delta$  28.13 (s with  $^{77}\text{Se}$  satellites,  $^1J_{\text{PSe}} 647$  and  $^4J_{\text{PP}} 3$  Hz).

**CAUTION:** perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared and handled with great care; particular caution must be exercised when they are dried under vacuum.

### Crystallography

The compounds dptpf and dpspf were recrystallized from hot butanol and  $\text{CH}_2\text{Cl}_2$ -MeOH (by layering) respectively to yield crystals suitable for X-ray diffraction measurements. The diselenide crystallizes as a dichloromethane monosolvate. Single crystals of complex **1**, analysing as  $[\text{Cu}(\text{dptpf})]\text{BF}_4 \cdot \text{CH}_2\text{Cl}_2$ , were grown by slow diffusion of pentane into the sample solution in  $\text{CH}_2\text{Cl}_2$  at -30 °C. Details of the crystal data, intensity measurements and data processing for the three structures are summarized in Table 1. Cell parameters were

**Table 1** Structure determination summary\*

	dtpf	dpspf·CH <sub>2</sub> Cl <sub>2</sub>	[Cu(dtpf)]BF <sub>4</sub> ·CH <sub>2</sub> Cl <sub>2</sub>
Empirical formula	C <sub>34</sub> H <sub>28</sub> FeP <sub>2</sub> S <sub>2</sub>	C <sub>35</sub> H <sub>30</sub> Cl <sub>2</sub> FeP <sub>2</sub> Se <sub>2</sub>	C <sub>35</sub> H <sub>30</sub> BCl <sub>2</sub> CuF <sub>4</sub> FeP <sub>2</sub> S <sub>2</sub>
<i>M</i>	618.5	797.3	853.8
Colour, habit	Yellow needles	Yellow irregularly shaped prisms	Transparent orange parallelepipeds
Crystal size/mm	0.1 × 0.1 × 0.4	0.1 × 0.12 × 0.18	0.2 × 0.3 × 0.15
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>Cc</i> (no. 9)	<i>C2/c</i> (no. 15)	<i>Pna2</i> <sub>1</sub> (no. 33)
<i>a</i> /Å	24.438(2)	13.769(7)	26.387(9)
<i>b</i> /Å	11.036(1)	10.938(8)	12.286(5)
<i>c</i> /Å	12.025(1)	22.491	11.055(3)
β/°	113.0(1)	101.96(4)	
<i>U</i> /Å <sup>3</sup>	2986(2)	3314(1)	3581(2)
<i>D<sub>c</sub></i> /Mg m <sup>-3</sup> ( <i>Z</i> = 4)	1.375	1.598	1.583
μ/mm <sup>-1</sup>	0.53	1.47	1.40
<i>F</i> (000)	1272	1592	1728
Diffractometer	Philips PW 1100	Siemens R3m/V	Siemens R3m/V
2θ Range/°	6.4–50.0	4.5–45.0	4.0–50.0
Scan speed	Variable; 1° per 20–80 s	Variable; 4.4–14.6° min <sup>-1</sup>	Variable; 3.3–14.6° min <sup>-1</sup>
Index ranges	–29 ≤ <i>h</i> ≤ 26; –3 ≤ <i>k</i> ≤ 13; 0 ≤ <i>l</i> ≤ 14	0 ≤ <i>h</i> ≤ 11; 0 ≤ <i>k</i> ≤ 11; –24 ≤ <i>l</i> ≤ 23	0 ≤ <i>h</i> ≤ 32; 0 ≤ <i>k</i> ≤ 14; 0 ≤ <i>l</i> ≤ 13
Reflections collected	3017	1492	3598
Independent reflections	2633	1308	3358
Observed reflections	14594 [ <i>F</i> > 9σ( <i>F</i> )]	683 [ <i>F</i> > 3σ( <i>F</i> )]	2610 [ <i>F</i> > 4σ( <i>F</i> )]
Weighting scheme, <i>w</i> <sup>-1</sup>	σ <sup>2</sup> ( <i>F</i> ) + 0.002( <i>F</i> ) <sup>2</sup>	Unit	σ <sup>2</sup> ( <i>F</i> ) + 0.004( <i>F</i> ) <sup>2</sup>
No. parameters refined	156	104	303
Largest difference peak/e Å <sup>-3</sup>	0.48	0.63	0.66
Data-to-parameter ratio	10:1	7:1	8.6:1
Final <i>R</i> , <i>R'</i> (observed)	0.042, 0.047	0.058, 0.064	0.059, 0.069
Goodness of fit	1.31	1.92	1.18

\* Details in common: 294 K; Mo-*K*α radiation (λ = 0.710 73 Å); highly oriented graphite-crystal monochromator; θ–2θ scans; two standard reflections every 100; no absorption correction; heavy-atom methods; refinement by full-matrix least squares minimizing Σw(|*F<sub>o</sub>*| – |*F<sub>c</sub>*|)<sup>2</sup>; riding model used for H atoms with common variable *U*.

determined from 25 high-angle data (2θ > 22°). To ensure an acceptable observation:variable ratio and to achieve convergence, for dtpf the phenyl rings were refined as rigid bodies with C–C and C–H distances fixed at 1.395 and 1.08 Å, respectively, for dpspf·CH<sub>2</sub>Cl<sub>2</sub> only the heavy atoms were refined anisotropically, while for 1·CH<sub>2</sub>Cl<sub>2</sub> the carbon atoms far from the inner core were treated isotropically. Difference maps, calculated after the refinement, were essentially featureless, apart from some disorder in the CH<sub>2</sub>Cl<sub>2</sub> of 1. Selected bond distances and angles for the two diphosphines and complex 1 are given in Tables 2 and 3, respectively.

The SHELXTL PLUS package of computer programs was employed for the solution and refinement of the structures.<sup>8</sup>

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/364.

## Results and Discussion

An ORTEP drawing of dpspf showing the atom-labelling scheme is depicted in Fig. 1(a). As expected, the molecular structures of the sulfur and selenium derivatives appear to be virtually identical to that of the oxygen analogue,<sup>5</sup> except for the chalcogen–phosphorus distance. The present structures are superimposable [Fig. 1(b)], the weighted root-mean-square deviation, derived from the BMFIT program,<sup>9</sup> being only 0.10 Å, when the fitting is performed using all the non-hydrogen atoms. As a general comment, the molecules are centrosymmetric with the inversion centre at the iron atom and thus the asymmetric unit consists of a half-molecule. The cyclopentadienyl rings are consequently parallel and staggered, with a transoid overall arrangement of the P(E)Ph<sub>2</sub> units. The bond distances and angles are consistent with those found in similar compounds; in particular, the average C–P–Se angle is

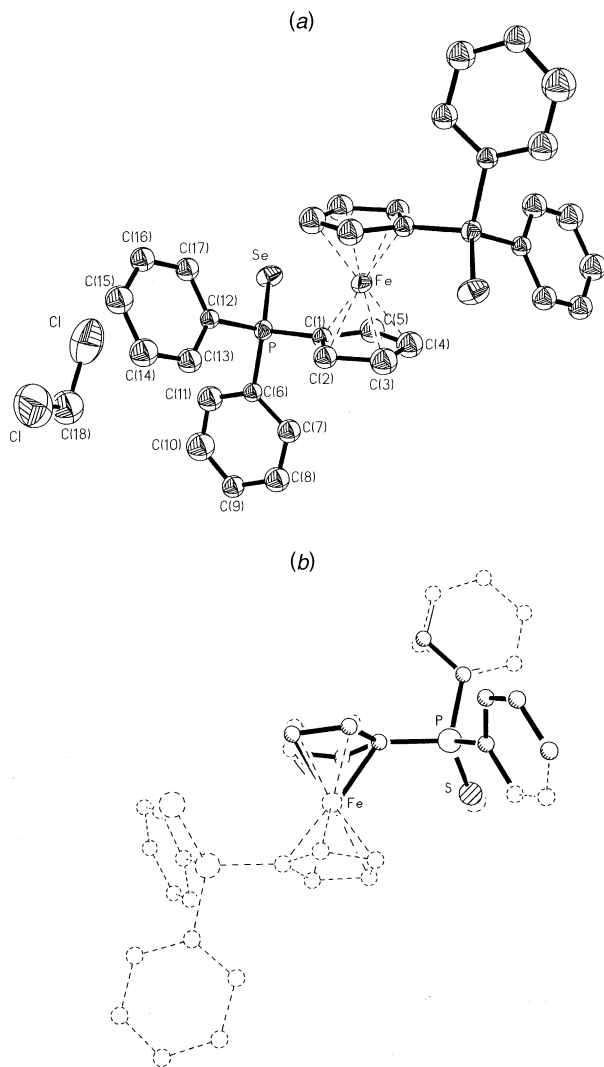
**Table 2** Selected bond distances (Å) and angles (°) for dtpf and dpspf·CH<sub>2</sub>Cl<sub>2</sub>

	dtpf (E = S)	dpspf·CH <sub>2</sub> Cl <sub>2</sub> (E = Se)
P–E	1.944(3)	2.103(6)
P–C(1)	1.794(4)	1.82(2)
P–C(12)	1.815(4)	1.79(2)
P–C(6)	1.825(3)	1.80(2)
Fe–C(1)	2.045(3)	2.00(2)
Fe–C(2)	2.056(5)	2.06(2)
Fe–C(3)	2.049(5)	2.06(2)
Fe–C(4)	2.059(6)	2.05(2)
Fe–C(5)	2.050(5)	2.06(2)
C(1)–P–C(6)	105.5(3)	103.6(8)
C(6)–P–C(12)	104.8(3)	104.2(9)
C(1)–P–C(12)	106.8(3)	107.2(9)
C(1)–P–E	113.0(3)	113.9(7)
C(12)–P–E	113.9(3)	113.6(7)
C(6)–P–E	112.1(2)	113.5(7)
P–C(1)–C(5)	123.6(4)	123(1)
P–C(1)–C(2)	128.3(5)	125(1)

113.7(7)° and the P–Se bond length is 2.103(6) Å, similar to the mean (113.0° and 2.110 Å, respectively) found in the literature.<sup>10</sup> There are no close contacts between neighbouring atoms and for Se atom the shortest interaction (3.53 Å) involves a symmetrically related Se (at –*x*, *y*,  $\frac{1}{2}$  – *z*).

The reaction of dtpf or dpspf with equimolar amounts of [Cu(MeCN)<sub>4</sub>]BF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> at room temperature leads readily to the quantitative displacement of the co-ordinated MeCN molecules to give the cationic complexes [Cu(dtpf)]BF<sub>4</sub> 1 or [Cu(dpspf)]BF<sub>4</sub> 2, respectively. The mass spectra of these complexes show the cationic peaks at *m/z* = 681 (1) and 775 (2).

The <sup>1</sup>H NMR spectra of complexes 1 and 2 display the usual pair of pseudo-quartets typical of two sets of C<sub>5</sub>H<sub>4</sub> protons (H<sub>α</sub>, H<sub>β</sub>) arranged in a symmetric environment. The <sup>31</sup>P spectra show a single phosphorus resonance, downfield shifted by 4.91



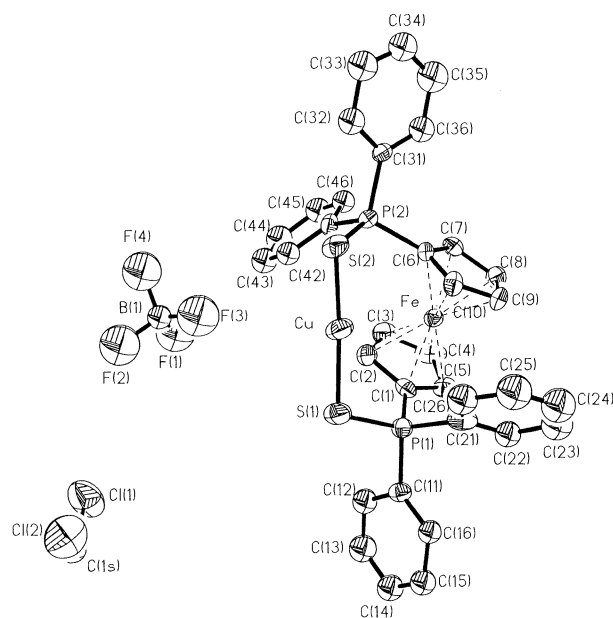
**Fig. 1** (a) An ORTEP representation of  $\text{dpspf}\cdot\text{CH}_2\text{Cl}_2$  showing the atom numbering scheme; atom contours are drawn at 40% probability and hydrogen atoms are omitted for clarity. (b) Superimposition of the structures of  $\text{dptpf}$  (—) and  $\text{dpspf}\cdot\text{CH}_2\text{Cl}_2$  (---)

and 2.08 ppm with respect to the unco-ordinated diphosphine ( $\delta$  40.72 and 30.93 in  $\text{CDCl}_3$ ) for complex **1** and **2**, respectively. For the latter complex the main resonance is symmetrically flanked by satellites due to  $^{77}\text{Se}\text{--}^{31}\text{P}$  coupling ( $^1J_{\text{PSe}} = 582$  and  $^3J_{\text{PSe}} = 12$  Hz), which appear as sharp singlets with the expected relative intensities. Upon cooling, the  $\text{C}_5\text{H}_4$  proton multiplets at higher field gradually change to very broad signals, becoming virtually undetectable at  $-65^\circ\text{C}$ , while the resonances at lower field (likewise those of the phenyl rings) appear only to lose their multiplet feature. Conversely, the phosphorus resonances remain unchanged throughout the temperature range shown.

The crystal structure of complex **1** has been established by X-ray diffraction. The compound crystallizes as a dichloromethane monosolvate. The ORTEP drawing of complex  $\mathbf{1}\cdot\text{CH}_2\text{Cl}_2$  is shown in Fig. 2. Pertinent bond lengths and angles are listed in Table 3. The structure shows a linear two-coordination geometry around the copper atom, with a slight deviation from the ideal  $180^\circ$  because of the  $\text{S}(1)\text{--Cu--S}(2)$  angle of  $171.5(2)^\circ$  imposed by the ligand bite. This value can be compared with those of  $176.83(5)$  and  $176.43(12)\text{--}178.26(11)^\circ$  reported for the isostructural derivatives of  $\text{Ag}^{\text{I}}$  and  $\text{Au}^{\text{I}}$ .<sup>7</sup> The  $\text{Cu--S}$  bond distances [ $2.144(5)$  and  $2.140(5)$  Å] and the  $\text{Cu--S--P}$  angles [ $100.8(2)$  and  $105.5(2)^\circ$ ] fall in the range observed for related compounds.<sup>11</sup> These values point towards a substantially  $\text{sp}^3$  hybridization of the sulfur atoms. The  $\text{BF}_4^-$  ion does not interact with the metal centre, the shortest  $\text{F}\cdots\text{Cu}$  distance

**Table 3** Selected bond distances (Å) and angles ( $^\circ$ ) for  $[\text{Cu}(\text{dptpf})]\text{BF}_4\cdot\text{CH}_2\text{Cl}_2$

$\text{Cu--S}(1)$	2.144(5)	$\text{P}(1)\text{--C}(1)$	1.78(1)
$\text{Cu--S}(2)$	2.140(5)	$\text{P}(2)\text{--C}(6)$	1.80(1)
$\text{S}(1)\text{--P}(1)$	1.985(5)	$\text{Fe--C}_{\text{mean}}$	2.04(1)
$\text{S}(2)\text{--P}(2)$	2.001(4)	$\text{Fe}\cdots\text{Cu}$	3.685
$\text{S}(1)\text{--Cu--S}(2)$	171.5(2)	$\text{P}(1)\text{--C}(1)\text{--C}(5)$	126.9(9)
$\text{Cu--S}(1)\text{--P}(1)$	100.8(2)	$\text{P}(2)\text{--C}(6)\text{--C}(7)$	126.7(8)
$\text{Cu--S}(2)\text{--P}(2)$	105.5(2)	$\text{P}(2)\text{--C}(6)\text{--C}(10)$	123.5(8)
$\text{S}(1)\text{--P}(1)\text{--C}(1)$	112.0(4)	$\text{Fe--C}(1)\text{--P}(1)$	128.0(6)
$\text{S}(2)\text{--P}(2)\text{--C}(6)$	111.3(4)	$\text{Fe--C}(6)\text{--P}(2)$	128.8(6)
$\text{P}(1)\text{--C}(1)\text{--C}(2)$	124.4(9)		



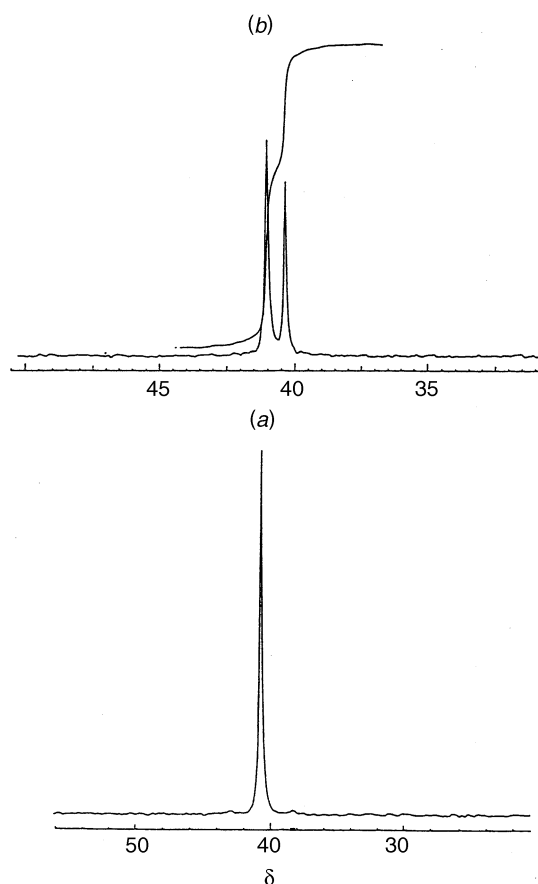
**Fig. 2** An ORTEP diagram of complex  $\mathbf{1}\cdot\text{CH}_2\text{Cl}_2$  with atom contours shown at 40% probability

being  $3.759$  Å, comparable with the  $\text{Fe}\cdots\text{Cu}$  separation ( $3.685$  Å). Copper complexation of the thiophosphoryl ligand causes a slight lengthening of the  $\text{P--S}$  bond, consistent with the lower  $\text{P=S}$  stretching frequency observed in the IR spectrum. The angles  $\text{S--P--C}$  are not significantly different from those found in free  $\text{dptpf}$ . In the ferrocene moiety the cyclopentadienyl rings are virtually parallel (the dihedral angle between the two planes is  $6.5^\circ$ ) and staggered by  $16.1^\circ$  [torsion angle between the two planes is  $6.5^\circ$ ] and staggered by  $16.1^\circ$  [torsion angle  $\text{C}(1)\text{--Cp--Cp--C}(7)$ ].

Complexes **1** and **2** appear to be highly reactive towards an excess of  $\text{dptpf}$  or  $\text{dpspf}$ , being converted into products analysing as  $[\text{Cu}(\text{dptpf})_{1.5}]\text{BF}_4$  **3a** or  $[\text{Cu}(\text{dpspf})_{1.5}]\text{BF}_4$  **4a**, respectively. Many attempts to obtain suitable crystals for X-ray analysis failed. In this context, substitution of either  $\text{PF}_6^-$  or  $\text{ClO}_4^-$  for  $\text{BF}_4^-$  was similarly unsuccessful. Consequently, complexes **3** and **4** were characterized by means of careful  $^{31}\text{P}$  and  $^1\text{H}$  NMR analyses, and spectra are shown in Figs. 3–5.

The spectra appear to be temperature and concentration dependent. Thus, for a  $1.30 \times 10^{-2}$  mol  $\text{dm}^{-3}$  nitromethane solution of complex **3a** only one sharp resonance at  $\delta$  40.35 is observed in the  $^{31}\text{P}$  NMR spectrum at  $-25^\circ\text{C}$ , while two signals at  $\delta$  41.02 and 40.35 are apparent at  $27^\circ\text{C}$  (Fig. 3). At this temperature the resonance at  $\delta$  40.35 loses intensity upon dilution without any change in the chemical shift, whereas the other one moves slightly to lower field and increases concomitantly in intensity.

The  $^1\text{H}$  NMR spectra display a similar temperature-dependent behaviour, but offer far more information (Fig. 4).



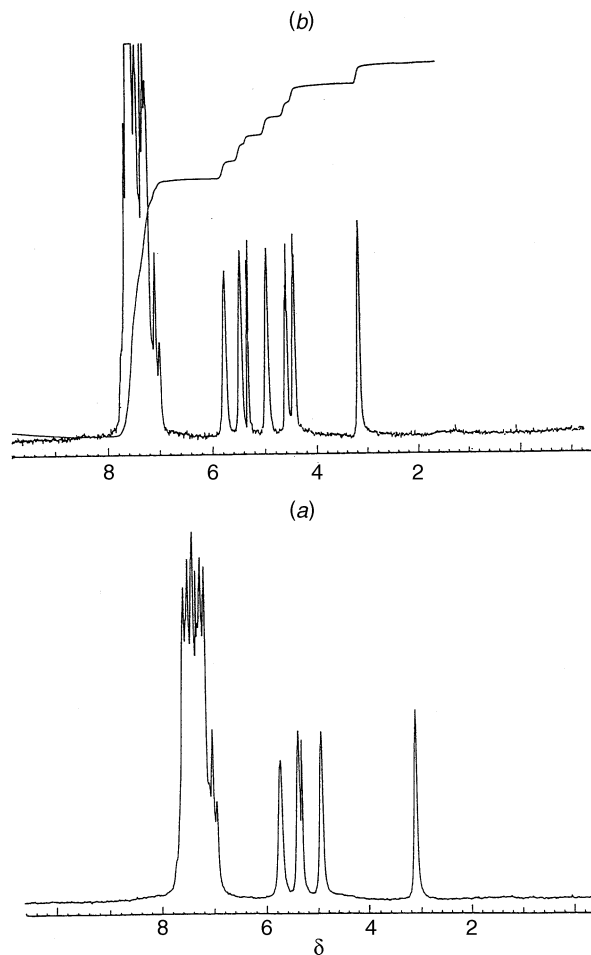
**Fig. 3** The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra of complex **3a** in  $\text{CD}_3\text{NO}_2$  ( $1.3 \times 10^{-2} \text{ mol dm}^{-3}$ ) at (a)  $-25$  and (b)  $27$  °C

At low temperature ( $-30$  °C), solutions of complex **3a** show four fairly broad, equally intense singlets, attributable to the  $\text{C}_5\text{H}_4$  protons. On raising the temperature this set of resonances loses intensity in favour of two new  $\text{C}_5\text{H}_4$  signals the chemical shifts of which are concentration and temperature dependent, and reminiscent of those observed for free and *trans*-chelated (e.g. **1**) dptpf.<sup>7</sup> Finally, all these  $\text{C}_5\text{H}_4$  proton peaks integrate correctly with respect to the phenylphosphine ones.

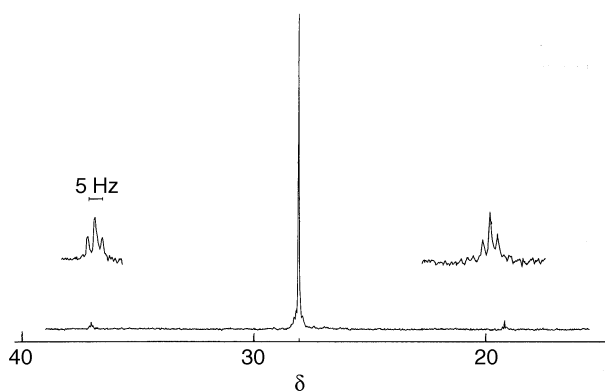
All these observations clearly indicate that complex **3a** in solution reversibly dissociates, the extent of the equilibrium markedly depending on the concentration and temperature. Cyclovoltammetric measurements carried out in 1,2-dichloroethane point unambiguously to the presence in the equilibrium mixture of free dptpf.<sup>12</sup> Moreover, mass spectral analysis for complex **3a** reveals  $[\text{Cu}(\text{dptpf})]^+$  [ $m/z = 681$  (100%)] as the only copper-containing species in  $\text{CH}_2\text{Cl}_2$ . The fragments, namely  $[\text{Cu}(\text{dptpf})]^+$  and dptpf, appear to be in a rapid chemical exchange on the NMR timescale.

As far as the molecular complexity of the associated species is concerned,  $^{31}\text{P}$  NMR measurements on the strictly related selenium derivative **4a**, while confirming the chemical equivalence of the dpspf ligands, provide very strong support, thanks to the effect of the  $^{77}\text{Se}\text{-}^{31}\text{P}$  coupling, to aggregates  $[\{\text{Cu}_2(\text{dpspf})_3(\text{BF}_4)_2\}_n]$  in which each Cu is co-ordinated to three chalcogen donor atoms. The  $^{31}\text{P}$  spectrum in  $\text{CD}_2\text{Cl}_2$  at  $-60$  °C consists in this case of one major signal at  $\delta$  28.19, due to the phosphorus atoms bonded to magnetically inactive Se nuclei, and of a doublet of triplets ( $^1J_{\text{SPe}} = 643$ ,  $^4J_{\text{PP}} = 2.9$  Hz) stemming from the phosphorus nucleus bonded to  $^{77}\text{Se}$  (7.6% natural abundance,  $I = \frac{1}{2}$ ) and interacting with the two indistinguishable phosphorus atoms belonging to a  $\text{Cu}(\text{SeP})_3$  atom set (Fig. 5).

On raising the temperature the resonance at  $\delta$  28.19 loses intensity in favour of a new signal at lower field symmetrically



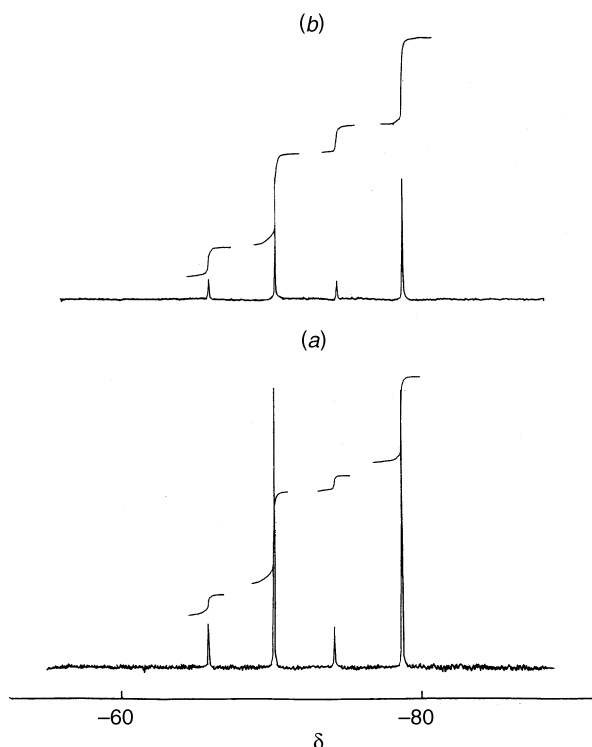
**Fig. 4** Proton NMR spectra of complex **3a** in  $\text{CD}_2\text{Cl}_2$  (saturated solution at room temperature) at (a)  $-30$  and (b)  $27$  °C



**Fig. 5** The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum of complex **4a** in  $\text{CD}_2\text{Cl}_2$  at  $-60$  °C

flanked by  $^{77}\text{Se}$  satellites, the chemical shift of which is concentration and temperature dependent. Moreover, the  $^1\text{H}$  NMR pattern is reminiscent of that exhibited by complex **3a**, in that the same temperature dependence is observed for the cyclopentadienyl protons. The similarity of **3a** and **4a** in their NMR spectra is suggestive of a similar dissociation process in solution, which is confirmed by detection of unco-ordinated dpspf in cyclovoltammetric tests on **4a** in dichloroethane.<sup>12</sup>

We believe that the single phosphorus resonance coupled with the presence of a set of four equally intense  $\text{C}_5\text{H}_4$  signals observed under conditions (lower temperatures or more concentrated solutions) in which the molecular structure is likely to be that of the solid state are the key features of a polynuclear derivative. In this species all the phosphorus atoms have to be

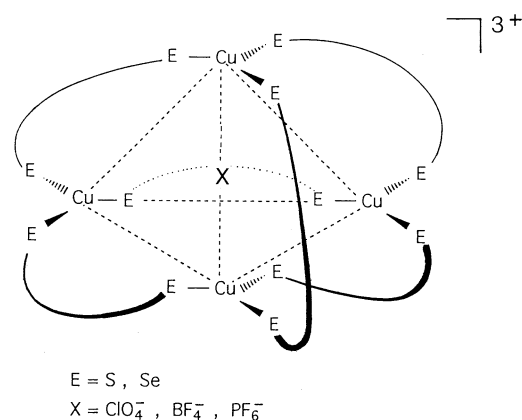


**Fig. 6** The  $^{19}\text{F}$  NMR spectra of complex **4b** in  $\text{CD}_2\text{Cl}_2$  at (a) 27 and (b)  $-40^\circ\text{C}$

chemically equivalent and the four hydrogens of the  $\text{C}_5\text{H}_4$  rings are all chemically non-equivalent. Consequently, in complexes **3a** and **4a**, unlike **1** and **2**, all ligand molecules are co-ordinated in a bridging fashion. This binding mode of the dptpf and dpspf ligands accounts also for the splitting of the two usual  $\text{C}_5\text{H}_4$  ( $\text{H}_a$ ,  $\text{H}_b$ ) resonances into four signals. A similar phenomenology, in terms of both multiplicity and chemical shifts, has been recently described by Hor and co-workers<sup>13</sup> for the complex  $[\text{Re}_2(\mu\text{-OMe})_2(\text{CO})_6(\mu\text{-dppf})]$  and attributed to the blockage of the mutual position of the  $\text{C}_5\text{H}_4$  rings in the dppf bridging ligand as a consequence of the presence of two auxiliary bridging methoxide groups.

As to the structure and molecular complexity of three-coordinate complexes **3** and **4**, additional information stems from a thorough  $^{19}\text{F}$  NMR analysis on the  $\text{BF}_4^-$  (**3a**, **4a**) and  $\text{PF}_6^-$  (**3b**, **4b**) salts. The  $^{31}\text{P}$  spectra for both **3b** and **4b** displayed a pair of septuplets, with a chemical shift difference of *ca.* 0.6 ppm (see Experimental section), for the  $\text{PF}_6^-$  moiety the relative intensities of which were concentration and temperature dependent, thus suggesting two different  $\text{PF}_6^-$  environments. This is confirmed by the  $^{19}\text{F}$  NMR spectra of these complexes, since two doublets in a ratio dependent on the temperature and concentration are observed. Thus, in a  $2.30 \times 10^{-2}$  mol  $\text{dm}^{-3}$   $\text{CD}_2\text{Cl}_2$  solution of **3b** two sharp doublets centred at  $\delta -69.3$  ( $^1J_{\text{PF}} = 714$ ) and  $-74.3$  (711 Hz) in a ratio of *ca.* 1 : 6 appear in the  $^{19}\text{F}$  NMR spectrum at  $27^\circ\text{C}$  [Fig. 6(a)]. The higher-field resonance is assigned to the innocent  $\text{PF}_6^-$  ion by comparison with the  $^{19}\text{F}$  spectrum of  $\text{NBu}_4^+\text{PF}_6^-$  under identical conditions ( $\delta_{\text{F}} -73.5$ ,  $^1J_{\text{PF}} = 711$  Hz). On lowering the temperature the integral ratio between the signals does not remain constant, but gradually decreases to attain a value of *ca.* 1 : 3 at  $-40^\circ\text{C}$  [Fig. 6(b)]. No further change is observed in the spectrum upon cooling to  $-90^\circ\text{C}$ .

It must be stressed that at these temperatures the  $^{31}\text{P}$  NMR spectrum of the solution displays a single dptpf resonance, which is consistent with the presence of only one copper-containing species. A similar pattern is exhibited by the tetrafluoroborate complexes: two sets of  $^{19}\text{F}$  resonances, separated by 3.4 ppm, with the expected isotopic ( $^{10}\text{B}$  and  $^{11}\text{B}$ ) pattern, in a temperature- and concentration-dependent ratio but



**Fig. 7** Schematic line drawing of the proposed structure for complex **3** or **4**

approaching the value of *ca.* 3:1 at lower temperatures, in accord with the presence of two chemically non-equivalent  $\text{BF}_4^-$  groups.

A closer inspection of the  $^1\text{H}$  and  $^{31}\text{P}$  chemical shifts for the complexes  $[\{\text{Cu}_2\text{L}_3\text{X}_2\}_n]$   $\{\text{L} = \text{Fe}[\eta\text{-C}_5\text{H}_4\text{P}(\text{E})\text{Ph}_2]_2; \text{X} = \text{BF}_4^-, \text{PF}_6^- \text{ or } \text{ClO}_4^-\}$ ; see Experimental section, measured under conditions whereby the integrity of the polynuclear species is maintained, shows small but significant differences as a function of the different anion. For instance,  $\delta(^{31}\text{P})$  41.016 ( $\text{BF}_4^-$ ), 41.097 ( $\text{PF}_6^-$ ) and 41.049 ( $\text{ClO}_4^-$ ) for the dptpf derivatives, and 28.160 ( $\text{BF}_4^-$ ), 28.006 ( $\text{PF}_6^-$ ) and 28.127 ( $\text{ClO}_4^-$ ) for the dpspf ones. These differences are not attributable to concentration and/or temperature effects as both the  $\delta$  41.016 and 41.097 resonances are observed in the  $^{31}\text{P}$  spectra in the course of experiments where either some  $\text{NBu}_4^+\text{PF}_6^-$  is added to a  $\text{CD}_2\text{Cl}_2$  solution of complex **3a** or  $\text{NBu}_4^+\text{BF}_4^-$  to **3b**. The formation *in situ* and the coexistence of the new species are documented by the corresponding  $^{19}\text{F}$  NMR spectra. Identical behaviour is shown by dpspf derivatives **4a** and **4b**. In this connection,  $\text{ClO}_4^-$  appears to be far more efficient in displacing either  $\text{BF}_4^-$  or  $\text{PF}_6^-$  as stoichiometric amounts of  $\text{NBu}_4^+\text{ClO}_4^-$  are enough for the quantitative conversion of **3a**, **3b** or **4a**, **4b** into **3c** or **4c**. More polar solvents, such as nitromethane, do not substantially modify the low-temperature  $^{19}\text{F}$  NMR pattern.

All the NMR observations point convincingly to a strong interaction of the anion, mostly for  $\text{ClO}_4^-$ , with the cationic moiety in the complex molecule. A firm covalent bond to the metal centre can be ruled out owing to the lack of any magnetic interaction among the fluorine nuclei in the extra resonance of the fluorinated anion.<sup>14</sup> Thus, the NMR behaviour has simply to be accommodated on the basis of either ion association or 'spinning anion co-ordination' inside the pocket of the cationic framework.<sup>14</sup> Moreover, since only one anion of every four present seems to be involved in the interaction with the copper ions, we tentatively suggest the structure depicted in Fig. 7, consisting of a  $\text{Cu}_4$  tetrahedron with each copper atom trigonally bonded by bridging diposphine ligands and one anion molecule trapped in the  $\text{Cu}_4$  cage to reduce the  $4+$  charge. Such a tetranuclear complex is possibly entropically permitted at higher sample concentrations and at lower temperatures. On the other hand, tetrameric  $\text{Cu}_4^+$  complexes with a variety of ligands are very common and a tetrahedral set of  $\text{Cu}^+$  atoms represents the favoured feature for these compounds.

In conclusion, it appears that the co-ordination mode of the dptpf and dpspf ligands towards  $\text{Cu}^+$  spans from symmetrical bridging to *trans*-chelating modes. This last rare mode, which was previously reported for silver and gold,<sup>7,15</sup> allows a linear arrangement of the metal and chalcogen donor atoms, and precludes further co-ordination of a third ligating group (see below). We here anticipate that complex **1**, upon reaction with dppf, will be readily converted into a mixture of **3a** and the

novel dimeric complex  $\{[Cu(dppf)]_2(\mu-dptpf)[BF_4]_2\}^{12}$  despite the well known bridging ability of dppf.<sup>2</sup> This structural preference, over the obvious alternative with the dppf in the bridging mode and dptpf in the chelating one, may be clear evidence of dptpf in its favoured bridging ligation state. This feature of the chalcogenophosphoryl ligand is not shown by the oxygen analogue, which was found to bind to Cu<sup>I</sup> in the chelate fashion.<sup>5,6</sup> This different ligating behaviour is unlikely to be merely attributed to the well known difference in the dative bonding features of the heavier phosphine chalcogenides to that for the phosphine oxides.<sup>11,16</sup> Indeed, the mono-oxo-, -thio and -seleno derivatives are all found to bind to tetrahedral Cu<sup>I</sup> in the chelating fashion.<sup>4,12</sup> Therefore, a subtle balance of steric and electronic factors seems, as yet, to be responsible for the variety of geometries seen to occur in these copper(I) complexes.

## Acknowledgements

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