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Bonding ability of 1,1′-bis(diphenylthiophosphoryl)ferrocene (dptpf) and its selenium analogue towards copper(I). Crystal structure of [Cu(dptpf)]BF_4

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The phosphine chalcogenides Fe[η-$C_5H_4P(E)Ph_2]_2$ (L) [E = nothing (dppf), S (dptpf) or Se (dpspf)] reacted readily with [Cu(MeCN)$_4$]X (X = BF_4, PF_6 or ClO_4) in CH_2Cl_2 to give quantitatively the monomeric two-co-ordinated complexes [CuL]BF_4 (E = S **1** or Se **2**) or polynuclear three-co-ordinated derivatives analysing as [CuL$_{1.5}$]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 ^1H, ^{31}P-{^1H} and ^{19}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^I_4 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^3 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,[1] but its amazing co-ordination chemistry has been widely appreciated in the last decade.[2] It embodies two relevant features: (*i*) the strong bonding ability of the PPh_2 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.[3]

We have been interested in the co-ordination chemistry of dppf since 1985[4] 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-$C_5H_4P(E)Ph_2]_2$ (E = O, S or Se). We were successful in obtaining the E = O compound[4g] in 1991 (X-ray-authenticated in 1993),[5] which turned out to be capable of the unexpected stabilization of Cu^I inside a fully hard (O_4) chromophore.[6] Quite recently the bonding ability of the E = S derivative (dptpf) towards Au^I and Ag^I has been illustrated by Laguna and co-workers,[7] and their results prompted us to report the crystal structures of dptpf and dpspf (E = Se) and on their bonding ability towards Cu^I. In addition to the monomeric complexes [CuL]BF_4, copper(I) forms, at variance with the relevant congeners, polynuclear compounds analysing as [CuL$_{1.5}$]X {L = Fe[η-$C_5H_4P(E)Ph_2]_2$; X = BF_4, PF_6 or ClO_4}, 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.[4f] The compound dptpf was prepared by the literature procedure.[1] 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^3) for 3 h, after which the excess of selenium was filtered off. Addition of methanol (50 cm^3) 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 $C_{34}H_{28}FeP_2Se_2$: C, 57.35; H, 3.95%). IR: 573 cm^{-1} (P=Se). NMR ($CDCl_3$, 300 K): ^1H, δ 7.8–7.4 (m, 10 H, Ph), 4.69 (q, J_{HH} *ca.* 2, 2 H, C_5H_4), 4.32 (q, J_{HH} *ca.* 2, 2 H, C_5H_4); ^{31}P-{^1H}, δ 30.93 ($^1J_{PSe}$ = 737 Hz). All other reagents and starting materials were of reagent-grade quality used as supplied.

Physical measurements

Proton (89.55), ^{31}P-{^1H} (36.23) and ^{19}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 $SiMe_4$, external H_3PO_4 (85% w/w) and external $CFCl_3$, 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_4 1. To a solution of dptpf (0.940 g, 1.52 mmol) in anhydrous CH_2Cl_2 (20 cm^3) was added [Cu(MeCN)$_4$]BF_4 (0.478 g, 1.52 mmol) and the mixture stirred at room temperature in an inert atmosphere. After 1 h the volatiles were vacuum-evaporated and the residue dissolved in CH_2Cl_2 (10 cm^3). Addition of pentane (25 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 $C_{34}H_{28}BCuF_4FeP_2S_2$: C, 53.1; H, 3.65; S, 8.35%). Mass spectrum: *m*/*z* 681 (**1** − BF_4, 100%). IR: 635 cm^{-1} (P=S) ($\Delta\nu = -20$ cm^{-1} with respect to unco-ordinated dptpf. Molar conductivity in nitromethane (1.00 mmol dm^{-3}): $\Lambda_M = 78.5\ \Omega^{-1}$ cm^2 mol^{-1}. NMR ($CDCl_3$, 300 K): ^{1}H, δ 7.8–7.6 (m, 10 H, Ph), 4.74 (m, 2 H, C_5H_4) and 4.40 (m, 2 H, C_5H_4); a resonance due to small amounts of clathrated CH_2Cl_2 was also detectable; ^{31}P-{^{1}H}, δ 45.63 (s). Solutions of complex **1** are sensitive to moisture and reactive towards co-ordinating solvents, yielding some **3a**.

[Cu(dpspf)]BF$_4$ 2. To a solution of dpspf (0.912 g, 1.28 mmol) in anhydrous CH_2Cl_2 (20 cm^3) was added $[Cu(MeCN)_4]BF_4$ (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 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 cm^3) to the residue dissolved in CH_2Cl_2 (10 cm^3) afforded a yellow precipitate which was filtered off and dried under vacuum. The yield was essentially quantitative. The solid product invariably contained CH_2Cl_2 of crystallization, as determined by ^{1}H NMR spectroscopy and confirmed by elemental analysis (Found: C, 46.5; H, 3.25. Calc. for $C_{34.25}H_{28.5}BCl_{0.5}CuF_4FeP_2Se_2$: C, 46.55; H, 3.25%). Mass spectrum: *m*/*z* 775 (**2** − BF_4, 100%). IR: 563 cm^{-1} (P=Se) ($\Delta\nu = -10$ cm^{-1} with respect to unco-ordinated dpspf). NMR ($CDCl_3$, 300 K): ^{1}H, δ 7.8–7.6 (m, 10 H, Ph), 4.74 (m, 2 H, C_5H_4) and 4.35 (m, 2 H, C_5H_4); ^{31}P-{^{1}H}, δ 33.01 (s with ^{77}Se satellites, $^1J_{PSe}$ 582 and $^3J_{PSe}$ 12 Hz). Solutions of complex **2** are exceedingly sensitive to moisture and reactive towards co-ordinating solvents, yielding some **4a**.

[{Cu$_2$(dptpf)$_3$(BF$_4$)$_2$}$_n$] 3a. Complex **3a** was obtained upon treating a CH_2Cl_2 solution (15 cm^3) of dptpf (1.57 g, 2.54 mmol) with $[Cu(MeCN)_4]BF_4$ (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 CH_2Cl_2, followed by gradual addition of an excess of $CHCl_3$ gave a yellow solid, which was filtered off, washed with $CHCl_3$ and dried under vacuum. The solid product invariably contained entrapped $CHCl_3$ 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 $C_{102}H_{84}B_2Cu_2F_8Fe_3P_6S_6$: C, 56.8; H, 3.95; Cu, 5.9; Fe, 7.8; S, 8.9%). IR: 634 cm^{-1} (P=S) ($\Delta\nu = -21$ cm^{-1} with respect to unco-ordinated dptpf). NMR (CD_2Cl_2, 233 K): ^{1}H, δ 7.8–7.6 (m, 10 H, Ph), 5.76 (s, 1 H, C_5H_4), 5.18 (s, 1 H, C_5H_4), 4.96 (s, 1 H, C_5H_4) and 3.17 (s, 1 H, C_5H_4); ^{31}P-{^{1}H}, δ 41.02 (s); ^{19}F, δ −145.7 and −148.7 (br s with relative intensity 1:3, BF_4^-).

[{Cu$_2$(dptpf)$_3$(PF$_6$)$_2$}$_n$] 3b. A similar procedure was adopted to that for the tetrafluoroborato complex using $[Cu(MeCN)_4]PF_6$ (0.496 g, 1.33 mmol) and dptpf (1.64 g, 2.65 mmol) as the substrates in CH_2Cl_2. Yield: 1.33 g (88%) (Found: C, 53.55; H, 3.7; S, 8.5. Calc. for $C_{102}H_{84}Cu_2F_{12}Fe_3P_8S_6$: C, 53.9; H, 3.7; S, 8.45%). IR: 634 cm^{-1} (P=S). NMR (CD_2Cl_2, 233 K): ^{1}H, δ 7.8–7.6 (m, 10 H, Ph), 5.60 (s, 1 H, C_5H_4), 5.34 (s, 1 H, C_5H_4), 4.89 (s, 1 H, C_5H_4) and 3.05 (s, 1 H, C_5H_4); ^{31}P-{^{1}H}, δ 41.10 (s,. dptpf), −143.9 and −144.4 (spt with relative intensity 1:3, $^1J_{PF}$ 710 and 712, respectively, PF_6^-); ^{19}F, δ −70.5 and −73.5 (d with relative intensity 1:3, $^1J_{PF}$ 710 and 712 Hz, respectively, PF_6^-).

[{Cu$_2$(dptpf)$_3$(ClO$_4$)$_2$}$_n$] 3c. A similar procedure, except for the final heating stage, was adopted using $[Cu(MeCN)_4]ClO_4$ (0.154 g, 0.47 mmol) and dptpf (0.581 g, 0.94 mmol) as the substrates in CH_2Cl_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 $C_{104}H_{86}Cl_8Cu_2Fe_3O_8P_6S_6$: C, 51.6; H, 3.6; S, 7.95%). IR: 633 cm^{-1} (P=S). NMR (CD_2Cl_2, 233 K): ^{1}H, δ 7.6–7.0 (m, 10 H, Ph), 5.71 (s, 1 H, C_5H_4), 5.36 (s, 1 H, C_5H_4), 4.92 (s, 1 H, C_5H_4) and 3.10 (s, 1 H, C_5H_4); ^{31}P-{^{1}H}, δ 41.05 (s).

[{Cu$_2$(dpspf)$_3$(BF$_4$)$_2$}$_n$] 4a. To a dichloromethane (15 cm^3) solution of dpspf (0.915 g, 1.28 mmol) was added $[Cu(MeCN)_4]BF_4$ (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 CH_2Cl_2, followed by gradual addition of an excess of $CHCl_3$, gave complex **4a** as a yellow solid, which was filtered off, washed with $CHCl_3$ 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 $C_{102}H_{84}B_2Cu_2F_8Fe_3P_6Se_6$: C, 50.25; H, 3.45; Cu, 5.2; Fe, 6.85%). IR: 562 cm^{-1} (P=Se) ($\Delta\nu = -11$ cm^{-1} with respect to unco-ordinated dpspf). NMR (CD_2Cl_2, 233 K): ^{1}H, δ 7.8–7.6 (m, 10 H, Ph), 5.72 (s, 1 H, C_5H_4), 5.32 (s, 1 H, C_5H_4), 5.11 (s, 1 H, C_5H_4) and 3.23 (s, 1 H, C_5H_4); ^{31}P-{^{1}H}, δ 28.16 (s with ^{77}Se satellites, $^1J_{PSe}$ 645 and $^4J_{PP}$ 3 Hz); ^{19}F (84.25 MHz), δ −145.7 and −148.7 (br s with relative intensity 1:3, BF_4^-).

[{Cu$_2$(dpspf)$_3$(PF$_6$)$_2$}$_n$] 4b. A similar procedure was adopted using $[Cu(MeCN)_4]PF_6$ (0.295 g, 0.79 mmol) and dpspf (1.14 g, 1.60 mmol) as the substrates in CH_2Cl_2. Yield: 0.94 g (93%) (Found: C, 47.85; H, 3.3. Calc. for $C_{102}H_{84}Cu_2F_{12}Fe_3P_8Se_6$: C, 47.8; H, 3.3%). IR: 562 cm^{-1} (P=Se). NMR (CD_2Cl_2, 233 K): ^{1}H, δ 7.8–7.6 (m, 10 H, Ph), 5.65 (s, 1 H, C_5H_4), 5.39 (s, 1 H, C_5H_4), 5.12 (s, 1 H, C_5H_4) and 3.20 (s, 1 H, C_5H_4); ^{31}P-{^{1}H}, δ 28.01 (s with ^{77}Se satellites, $^1J_{PSe}$ 647 and $^4J_{PP}$ 3, dptpf), −143.9 and −144.4 (spt with relative intensity 1:3, $^1J_{PF}$ 710 and 712 Hz, respectively, PF_6^-); ^{19}F, δ −69.48 and −73.85 (d with relative intensity 1:3, $^1J_{PF}$ 710 and 712 Hz, respectively, PF_6^-).

[{Cu$_2$(dpspf)$_3$(ClO$_4$)$_2$}$_n$] 4c. A similar procedure was adopted using $[Cu(MeCN)_4]ClO_4$ (0.105 g, 0.32 mmol) and dpspf (0.456 g, 0.64 mmol) as the starting materials in CH_2Cl_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 $C_{104}H_{86}Cl_8Cu_2Fe_3O_8P_6Se_6$: C, 46.2; H, 3.20%). IR: 561 cm^{-1} (P=Se). NMR (CD_2Cl_2, 233 K): ^{1}H, δ 7.8–7.6 (m, 10 H, Ph), 5.72 (s, 1 H, C_5H_4), 5.44 (s, 1 H, C_5H_4), 5.11 (s, 1 H, C_5H_4) and 3.32 (s, 1 H, C_5H_4); ^{31}P-{^{1}H}, δ 28.13 (s with ^{77}Se satellites, $^1J_{PSe}$ 647 and $^4J_{PP}$ 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 CH_2Cl_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 $[Cu(dptpf)]BF_4\cdot CH_2Cl_2$, were grown by slow diffusion of pentane into the sample solution in CH_2Cl_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*

	dptpf	dpspf·CH_2Cl_2	[Cu(dptpf)]BF_4·CH_2Cl_2
Empirical formula	$C_{34}H_{28}FeP_2S_2$	$C_{35}H_{30}Cl_2FeP_2Se_2$	$C_{35}H_{30}BCl_2CuF_4FeP_2S_2$
M	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	*Cc* (no. 9)	*C*2/*c* (no. 15)	$Pna2_1$ (no. 33)
a/Å	24.438(2)	13.769(7)	26.387(9)
b/Å	11.036(1)	10.938(8)	12.286(5)
c/Å	12.025(1)	22.491	11.055(3)
β/°	113.0(1)	101.96(4)	
U/Å^3	2986(2)	3314(1)	3581(2)
D_c/Mg m^{-3} ($Z = 4$)	1.375	1.598	1.583
μ/mm^{-1}	0.53	1.47	1.40
F(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
Span speed	Variable; 1° per 20–80 s	Variable; 4.4–14.6° min^{-1}	Variable; 3.3–14.6° min^{-1}
Index ranges	$-29 \leqslant h \leqslant 26$; $-3 \leqslant k \leqslant 13$; $0 \leqslant l \leqslant 14$	$0 \leqslant h \leqslant 11$; $0 \leqslant k \leqslant 11$; $-24 \leqslant l \leqslant 23$	$0 \leqslant h \leqslant 32$; $0 \leqslant k \leqslant 14$; $0 \leqslant l \leqslant 13$
Reflections collected	3017	1492	3598
Independent reflections	2633	1308	3358
Observed reflections	14594 [$F > 9\sigma(F)$]	683 [$F > 3\sigma(F)$]	2610 [$F > 4\sigma(F)$]
Weighting scheme, w^{-1}	$\sigma^2(F) + 0.002(F)^2$	Unit	$\sigma^2(F) + 0.004(F)^2$
No. parameters refined	156	104	303
Largest difference peak/e Å^{-3}	0.48	0.63	0.66
Data-to-parameter ratio	10:1	7:1	8.6:1
Final *R*,*R′* (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-Kα 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 $\Sigma w(|F_o| - |F_c|)^2$; 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 dptpf 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_2Cl_2 only the heavy atoms were refined anisotropically, while for **1**·CH_2Cl_2 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_2Cl_2 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.[8]

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.

Table 2 Selected bond distances (Å) and angles (°) for dptpf and dpspf·CH_2Cl_2

	dptpf (E = S)	dpspf·CH_2Cl_2 (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)

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,[5] 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,[9] 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_2 units. The bond distances and angles are consistent with those found in similar compounds; in particular, the average C–P–Se angle is 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.[10] 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 dptpf or dpspf with equimolar amounts of $[Cu(MeCN)_4]BF_4$ in CH_2Cl_2 at room temperature leads readily to the quantitative displacement of the co-ordinated MeCN molecules to give the cationic complexes [Cu(dptpf)]BF_4 **1** or [Cu(dpspf)]BF_4 **2**, respectively. The mass spectra of these complexes show the cationic peaks at $m/z = 681$ (**1**) and 775 (**2**).

The ^1H NMR spectra of complexes **1** and **2** display the usual pair of pseudo-quartets typical of two sets of C_5H_4 protons (H_α, H_β) arranged in a symmetric environment. The ^{31}P spectra show a single phosphorus resonance, downfield shifted by 4.91

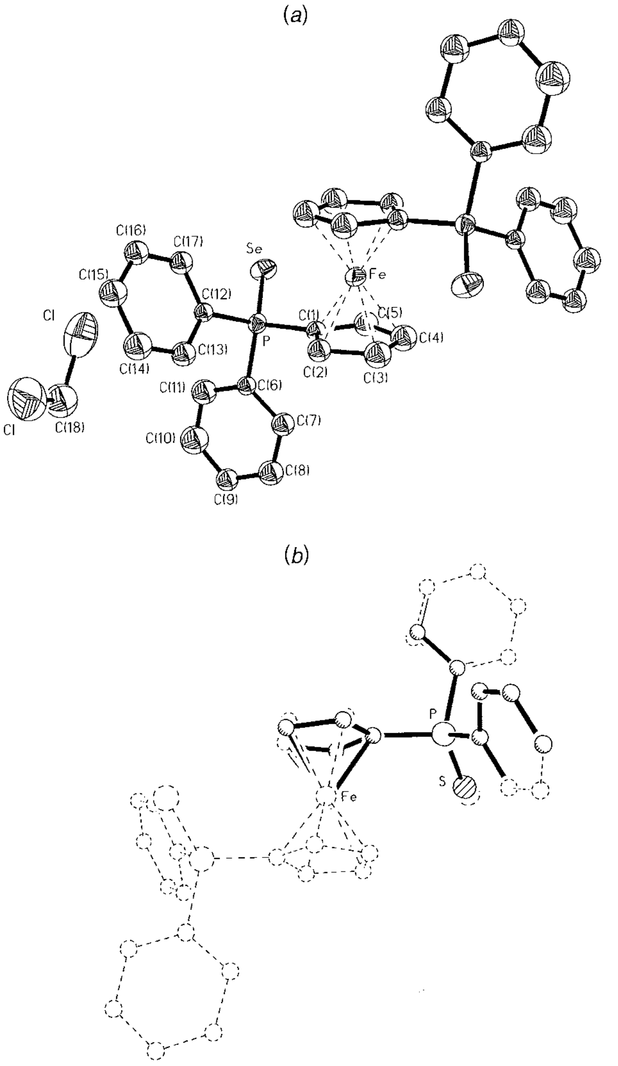

Fig. 1 (*a*) An ORTEP representation of dpspf·CH_2Cl_2 showing the atom numbering scheme; atom contours are drawn at 40% probability and hydrogen atoms are omitted for clarity. (*b*) Superimposition of the structures of dptpf (——) and dpspf·CH_2Cl_2 (- - - -)

and 2.08 ppm with respect to the unco-ordinated diphosphine (δ 40.72 and 30.93 in $CDCl_3$) for complex **1** and **2**, respectively. For the latter complex the main resonance is symmetrically flanked by satellites due to ^{77}Se–^{31}P coupling ($^1J_{PSe} = 582$ and $^3J_{PSe}$ 12 Hz), which appear as sharp singlets with the expected relative intensities. Upon cooling, the C_5H_4 proton multiplets at higher field gradually change to very broad signals, becoming virtually undetectable at −65 °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 **1**·CH_2Cl_2 is shown in Fig. 2. Pertinent bond lengths and angles are listed in Table 3. The structure shows a linear two-co-ordination geometry around the copper atom, with a slight deviation from the ideal 180° because of the S(1)–Cu–S(2) angle of 171.5(2)° imposed by the ligand bite. This value can be compared with those of 176.83(5) and 176.43(12)–178.26(11)° reported for the isostructural derivatives of Ag^I and Au^I.[7] 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)°] fall in the range observed for related compounds.[11] These values point towards a substantially sp^3 hybridization of the sulfur atoms. The BF_4^- ion does not interact with the metal centre, the shortest F···Cu distance being 3.759 Å, comparable with the Fe···Cu separation (3.685 Å). Copper complexation of the thiophosphoryl ligand causes a slight lengthening of the P–S bond, 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 free dptpf. In the ferrocene moiety the cyclopentadienyl rings are virtually parallel (the dihedral angle between the two planes is 6.5°) and staggered by 16.1° [torsion angle between the two planes is 6.5°] and staggered by 16.1° [torsion angle C(1)–Cp–Cp–C(7)].

Table 3 Selected bond distances (Å) and angles (°) for [Cu(dptpf)]BF_4·CH_2Cl_2

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

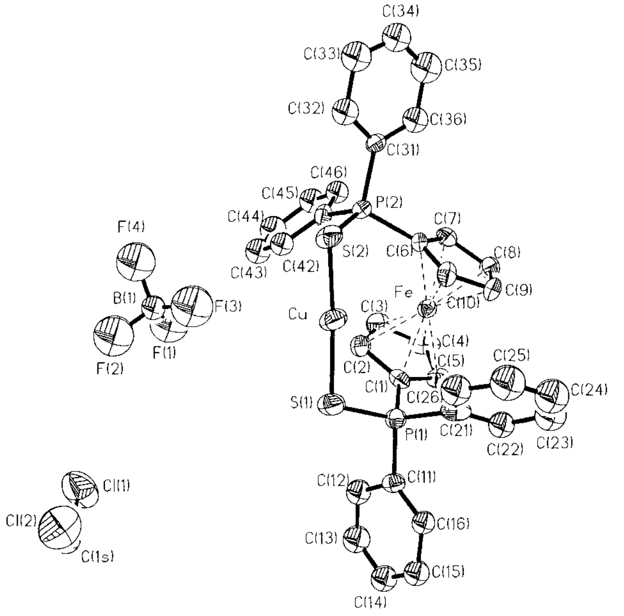

Fig. 2 An ORTEP diagram of complex **1**·CH_2Cl_2 with atom contours shown at 40% probability

Complexes **1** and **2** appear to be highly reactive towards an excess of dptpf or dpspf, being converted into products analysing as [Cu(dptpf)$_{1.5}$]BF_4 **3a** or [Cu(dpspf)$_{1.5}$]BF_4 **4a**, respectively. Many attempts to obtain suitable crystals for X-ray analysis failed. In this context, substitution of either PF_6^- or ClO_4^- for BF_4^- was similarly unsuccessful. Consequently, complexes **3** and **4** were characterized by means of careful ^{31}P and ^1H NMR analyses, and spectra are shown in Figs. 3–5.

The spectra appear to be temperature and concentration dependent. Thus, for a 1.30×10^{-2} mol dm^{-3} nitromethane solution of complex **3a** only one sharp resonance at δ 40.35 is observed in the ^{31}P NMR spectrum at −25 °C, while two signals at δ 41.02 and 40.35 are apparent at 27 °C (Fig. 3). At this temperature the resonance at δ 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 ^1H NMR spectra display a similar temperature-dependent behaviour, but offer far more information (Fig. 4).

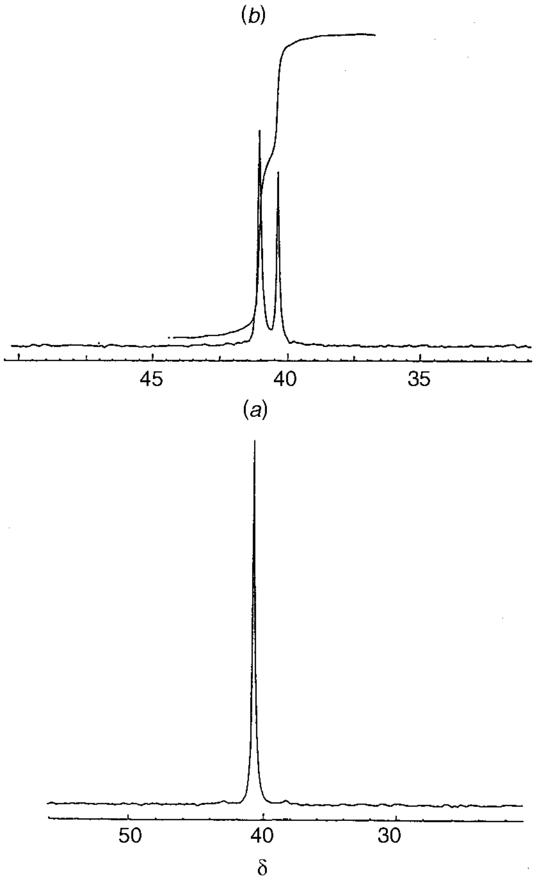

Fig. 3 The ^{31}P-{^1H} NMR spectra of complex **3a** in CD_3NO_2 (1.3×10^{-2} mol dm^{-3}) at (*a*) −25 and (*b*) 27 °C

At low temperature (−30 °C), solutions of complex **3a** show four fairly broad, equally intense singlets, attributable to the C_5H_4 protons. On raising the temperature this set of resonances loses intensity in favour of two new C_5H_4 signals the chemical shifts of which are concentration and temperature dependent, and reminescent of those observed for free and *trans*-chelated (*e.g.* **1**) dptpf.[7] Finally, all these C_5H_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.[12] Moreover, mass spectral analysis for complex **3a** reveals $[Cu(dptpf)]^+$ [*m*/*z* = 681 (100%)] as the only copper-containing species in CH_2Cl_2. The fragments, namely $[Cu(dptpf)]^+$ 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}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}Se–^{31}P coupling, to aggregates $[\{Cu_2(dpspf)_3(BF_4)_2\}_n]$ in which each Cu is co-ordinated to three chalcogen donor atoms. The ^{31}P spectrum in CD_2Cl_2 at −60 °C consists in this case of one major signal at δ 28.19, due to the phosphorus atoms bonded to magnetically inactive Se nuclei, and of a doublet of triplets ($^1J_{SPe} = 643$, $^4J_{PP} = 2.9$ Hz) stemming from the phosphorus nucleus bonded to ^{77}Se (7.6% natural abundance, $I = \frac{1}{2}$) and interacting with the two indistinguishable phosphorus atoms belonging to a $Cu(SeP)_3$ atom set (Fig. 5).

On raising the temperature the resonance at δ 28.19 loses intensity in favour of a new signal at lower field symmetrically flanked by ^{77}Se satellites, the chemical shift of which is concentration and temperature dependent. Moreover, the ^1H NMR pattern is reminescent 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.[12]

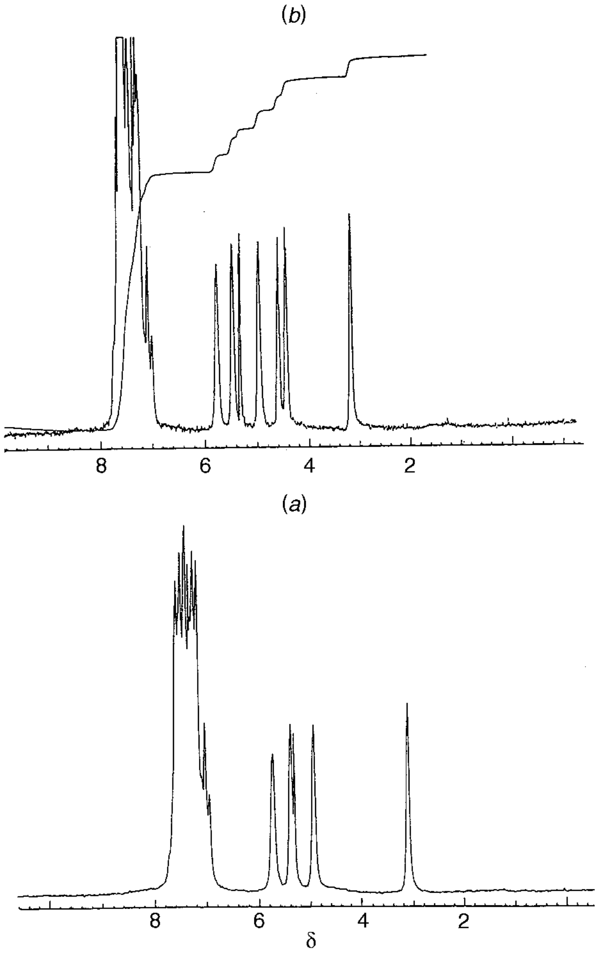

Fig. 4 Proton NMR spectra of complex **3a** in CD_2Cl_2 (saturated solution at room temperature) at (*a*) −30 and (*b*) 27 °C

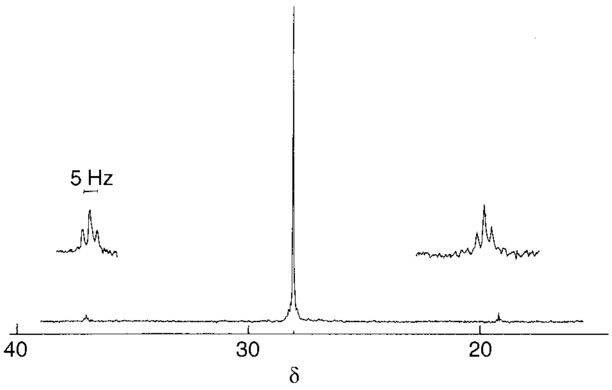

Fig. 5 The ^{31}P-{^1H} NMR spectrum of complex **4a** in CD_2Cl_2 at −60 °C

We believe that the single phosphorus resonance coupled with the presence of a set of four equally intense C_5H_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

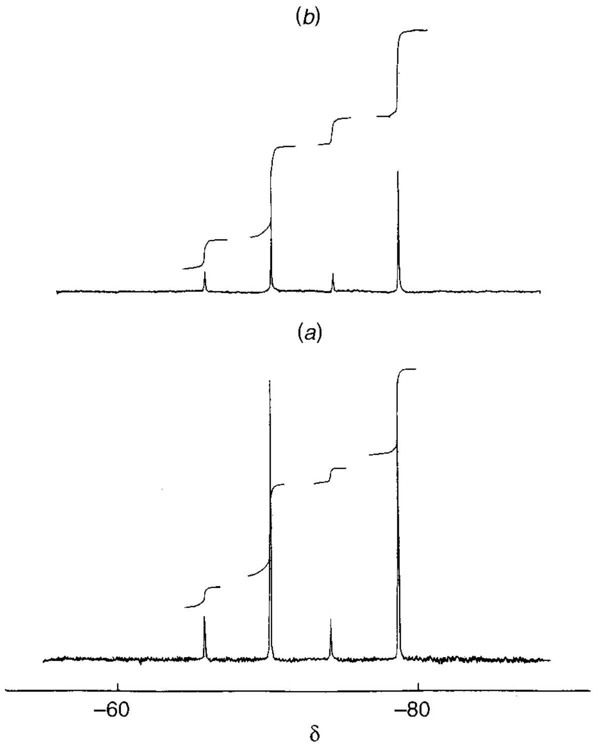

Fig. 6 The ^{19}F NMR spectra of complex **4b** in CD_2Cl_2 at (*a*) 27 and (*b*) −40 °C

chemically equivalent and the four hydrogens of the C_5H_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 C_5H_4 (H_α, H_β) resonances into four signals. A similar phenomenology, in terms of both multiplicity and chemical shifts, has been recently described by Hor and co-workers[13] for the complex $[Re_2(\mu\text{-}OMe)_2(CO)_6(\mu\text{-dppf})]$ and attributed to the blockage of the mutual position of the C_5H_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-co-ordinate complexes **3** and **4**, additional information stems from a thorough ^{19}F NMR analysis on the BF_4^- (**3a**, **4a**) and PF_6^- (**3b**, **4b**) salts. The ^{31}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 PF_6 moiety the relative intensities of which were concentration and temperature dependent, thus suggesting two different PF_6 environments. This is confirmed by the ^{19}F NMR spectra of these complexes, since two doublets in a ratio dependent on the temperature and concentration are observed. Thus, in a 2.30×10^{-2} mol dm^{-3} CD_2Cl_2 solution of **3b** two sharp doublets centred at δ −69.3 ($^1J_{PF} = 714$) and −74.3 (711 Hz) in a ratio of *ca.* 1:6 appear in the ^{19}F NMR spectrum at 27 °C [Fig. 6(*a*)]. The higher-field resonance is assigned to the innocent PF_6^- ion by comparison with the ^{19}F spectrum of $NBu^n{}_4{}^+PF_6^-$ under identical conditions (δ_F −73.5, $^1J_{PF} = 711$ 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 °C [Fig. 6(*b*)]. No further change is observed in the spectrum upon cooling to −90 °C.

It must be stressed that at these temperatures the ^{31}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 tetrafluoroborato complexes: two sets of ^{19}F resonances, separated by 3.4 ppm, with the expected isotopic (^{10}B and ^{11}B) pattern, in a temperature- and concentration-dependent ratio but approaching the value of *ca.* 3:1 at lower temperatures, in accord with the presence of two chemically non-equivalent BF_4 groups.

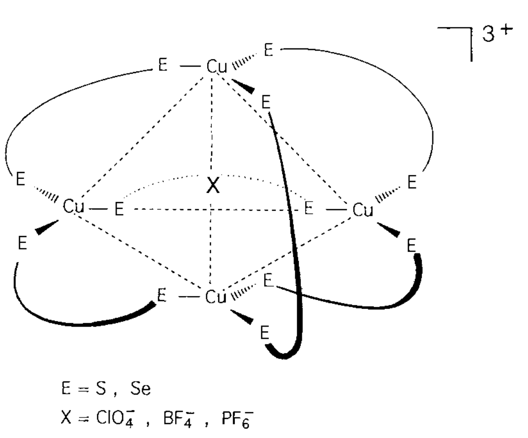

Fig. 7 Schematic line drawing of the proposed structure for complex **3** or **4**

A closer inspection of the ^1H and ^{31}P chemical shifts for the complexes $[\{Cu_2L_3X_2\}_n]$ $\{L = Fe[\eta\text{-}C_5H_4P(E)Ph_2]_2;\ X = BF_4, PF_6$ or 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, δ(^{31}P) 41.016 (BF_4), 41.097 (PF_6) and 41.049 (ClO_4) for the dptpf derivatives, and 28.160 (BF_4), 28.006 (PF_6) and 28.127 (ClO_4) for the dpspf ones. These differences are not attributable to concentration and/or temperature effects as both the δ 41.016 and 41.097 resonances are observed in the ^{31}P spectra in the course of experiments where either some $NBu^n{}_4{}^+PF_6^-$ is added to a CD_2Cl_2 solution of complex **3a** or $NBu^n{}_4{}^+BF_4^-$ to **3b**. The formation *in situ* and the coexistence of the new species are documented by the corresponding ^{19}F NMR spectra. Identical behaviour is shown by dpspf derivatives **4a** and **4b**. In this connection, ClO_4^- appears to be far more efficient in displacing either BF_4^- or PF_6^- as stoichiometric amounts of $NBu^n{}_4{}^+ClO_4^-$ 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}F NMR pattern.

All the NMR observations point convincingly to a strong interaction of the anion, mostly for 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.[14] 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.[14] 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 Cu_4 tetrahedron with each copper atom trigonally bonded by bridging diphosphine ligands and one anion molecule trapped in the 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 $Cu^I{}_4$ complexes with a variety of ligands are very common and a tetrahedral set of Cu^I atoms represents the favoured feature for these compounds.

In conclusion, it appears that the co-ordination mode of the dptpf and dpspf ligands towards Cu^I spans from symmetrical bridging to *trans*-chelating modes. This last rare mode, which was previously reported for silver and gold,[7,15] 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 $[\{Cu(dppf)\}_2(\mu\text{-}dptpf)][BF_4]_2$,[12] despite the well known bridging ability of dppf.[2] 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^I in the chelate fashion.[5,6] 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.[11b,16] Indeed, the mono-oxo-, -thio and -seleno derivatives are all found to bind to tetrahedral Cu^I in the chelating fashion.[4i,12] 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.

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