

# The Synthesis and Structure of the Two Hexafluorophosphate Salts {Cu[P(C<sub>7</sub>H<sub>7</sub>)<sub>3</sub>](CH<sub>3</sub>CN)<sub>2</sub>]PF<sub>6</sub> and {Cu[P(C<sub>7</sub>H<sub>7</sub>)<sub>3</sub>]<sub>2</sub>]PF<sub>6</sub> Containing the Ligand Tri(1-cyclohepta-2,4,6-trienyl)phosphane

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The reactions of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> (**1**) with one or two equivalents of tri(1-cyclohepta-2,4,6-trienyl)phosphane lead to {Cu[P(C<sub>7</sub>H<sub>7</sub>)<sub>3</sub>](CH<sub>3</sub>CN)<sub>2</sub>]PF<sub>6</sub> (**2**) and {Cu[P(C<sub>7</sub>H<sub>7</sub>)<sub>3</sub>]<sub>2</sub>]PF<sub>6</sub> (**3**), respectively. According to the X-ray structure analyses, the cations in both **2** and **3** contain copper(I) in a pseudo-tetrahedral coordination sphere, in which a P(C<sub>7</sub>H<sub>7</sub>)<sub>3</sub> ligand provides one or two olefinic bonds for weak interaction with the metal.

**Key words:** Copper(I) Complexes, Olefinic Phosphanes, X-Ray

## Introduction

Tetrakis(acetonitrile) copper(I) salts, [Cu(CH<sub>3</sub>CN)<sub>4</sub>]<sup>+</sup>X<sup>−</sup> (X<sup>−</sup> = ClO<sub>4</sub><sup>−</sup>, BF<sub>4</sub><sup>−</sup>, PF<sub>6</sub><sup>−</sup> (**1**)), react readily with group V donor ligands (e.g. PPh<sub>3</sub> or AsPh<sub>3</sub>) to give cationic pseudo-tetrahedral copper(I) compounds. Thus, the perchlorate, [Cu(CH<sub>3</sub>CN)<sub>4</sub>]ClO<sub>4</sub> [1,2], is a suitable educt for the synthesis of the complex [Cu(PPh<sub>3</sub>)<sub>4</sub>]ClO<sub>4</sub> [2–4], in which up to two phosphane ligands may be exchanged to give mixed-ligand derivatives such as [Cu(PPh<sub>3</sub>)<sub>2</sub>(py)<sub>2</sub>]ClO<sub>4</sub> or [Cu(PPh<sub>3</sub>)<sub>2</sub>(bipy)]ClO<sub>4</sub> [4]. Mixed-ligand acetonitrile intermediates, [Cu(PPh<sub>3</sub>)<sub>n</sub>(CH<sub>3</sub>CN)<sub>4−n</sub>]ClO<sub>4</sub> (*n* = 2, 3) have been isolated [3], and dinuclear complexes such as [Cu<sub>2</sub>(μ-dppm)<sub>2</sub>(CH<sub>3</sub>CN)<sub>*m*</sub>](BF<sub>4</sub>)<sub>2</sub> (*m* = 2, 4) containing bridging bis(diphenylphosphinyl)-methane ligands are also known [5]. The crystal structure of the hexafluorophosphate, [Cu(PPh<sub>3</sub>)<sub>4</sub>]PF<sub>6</sub>, has been determined [6].

We have used the olefinic phosphane ligand tri(1-cyclohepta-2,4,6-trienyl)phosphane, P(C<sub>7</sub>H<sub>7</sub>)<sub>3</sub>, in the reaction with [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> (**1**), with the expectation that the unsaturated seven-membered rings might be available for coordination in addition to the phosphorus atom. Earlier results on the reactions of a related olefinic phosphane, *ortho*-allylphenyl-diphenylphosphane, with copper(I) halides had been reported by Bennett *et al.* [7].

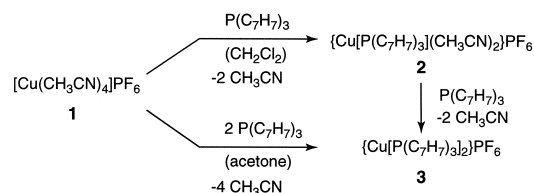
## Results and Discussion

A solution of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> (**1**) in polar solvents such as dichloromethane or acetone reacts with P(C<sub>7</sub>H<sub>7</sub>)<sub>3</sub> under stepwise displacement of the acetonitrile ligands to give **2** and **3**.

The diamagnetic products **2** and **3** are stable in the presence of air and moisture under ambient conditions. The <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra are similar to those of the free phosphane; in particular, only a single type of P(C<sub>7</sub>H<sub>7</sub>)<sub>3</sub> ligand can be observed in the spectra (CDCl<sub>3</sub> solution, room temperature). This suggests non-rigid structures of the cations in solution.

### X-ray crystal structure determinations of **2** and **3**

In both cations, the copper(I) atom can be considered as the center of a distorted tetrahedral coordination sphere (Fig. 1 and 2). Relevant distances and angles are given in Tables 1 and 2.



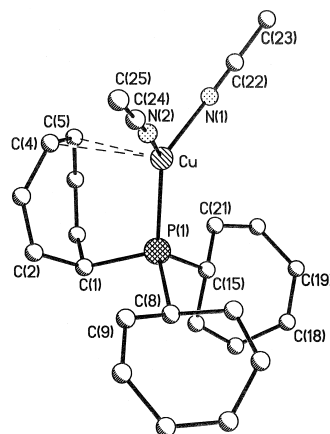


Fig. 1. Structure of the cation  $\{\text{Cu}[\text{P}(\text{C}_7\text{H}_7)_3](\text{CH}_3\text{CN})_2\}^+$  in **2**.

Table 1. Selected atomic distances (pm) and angles ( $^\circ$ ) for the cation in  $\{\text{Cu}[\text{P}(\text{C}_7\text{H}_7)_3](\text{CH}_3\text{CN})_2\}\text{PF}_6$  (**2**).

Cu-N(1)	196.6(4)	N(1)-C(22)	111.7(5)
Cu-N(2)	197.2(4)	N(2)-C(24)	112.0(5)
Cu-P	218.99(11)	C(22)-C(23)	145.3(6)
Cu-C(4)	259.1(4)	C(24)-C(25)	145.2(5)
Cu-C(5)	271.9(4)	P-C(1)	186.2(4)
Cu-Z(C4,C5)	257.1(4)	P-C(8)	184.3(3)
		P-C(15)	183.8(3)
C(1)-C(2)	150.8(6)	C(8)-C(9)	150.9(5)
C(1)-C(7)	151.2(5)	C(8)-C(14)	149.9(5)
C(2)-C(3)	133.6(8)	C(9)-C(10)	132.8(5)
C(3)-C(4)	142.8(8)	C(10)-C(11)	142.4(6)
C(4)-C(5)	133.5(7)	C(11)-C(12)	134.2(6)
C(5)-C(6)	142.8(7)	C(12)-C(13)	143.8(6)
C(6)-C(7)	132.7(6)	C(13)-C(14)	133.5(5)
N(1)-Cu-N(2)	106.76(15)	Cu-P-C(1)	110.56(14)
N(1)-Cu-P	126.23(11)	Cu-P-C(8)	117.92(11)
N(2)-Cu-P	121.47(11)	Cu-P-C(15)	116.97(12)
C(4)-Cu-C(5)	29.0(2)	Cu-N(1)-C(22)	178.0(4)
		Cu-N(2)-C(24)	176.1(4)
C(1)-P-C(8)	103.15(17)		
C(1)-P-C(15)	106.10(18)	N(1)-C(22)-C(23)	179.3(6)
C(8)-P-C(15)	100.56(16)	N(2)-C(24)-C(25)	179.8(6)

Z(C4,C5) is the center of the olefinic double bond C(4)-C(5).

In the solid-state structure of the bis(acetonitrile) complex,  $\{\text{Cu}[\text{P}(\text{C}_7\text{H}_7)_3](\text{CH}_3\text{CN})_2\}\text{PF}_6$  (**2**), the two cycloheptatrienyl substituents (containing C(8) and C(15)) which are attached to phosphorus in an equatorial position, are freely pending. On the contrary, the remaining ring substituent (containing C(1)) approaches the coordination sphere of Cu *via* the olefinic double bond C(4)-C(5), and is therefore axially connected to phosphorus. Although the bond length C(4)-C(5) (133.5(7) pm)

appears not to be widened as a result of  $\pi$ -complexation, the geometrical conditions for the chelate function of the  $\text{P}(\text{C}_7\text{H}_7)_3$  ligand may be deduced from typical angle variations. Thus, the angle Cu-P-C(1) ( $110.56(14)^\circ$ ) involving the axially connected ring substituent is significantly smaller than the corresponding angles Cu-P-C(8) ( $117.92(11)^\circ$ ) and Cu-P-C(15) ( $116.97(12)^\circ$ ) related to the equatorially substituted rings. Furthermore, the angle C(8)-P-C(15) ( $100.56(16)^\circ$ ) at the trigonal-pyramidal phosphane ligand is also smaller than its counterparts involving C(1), *i.e.* C(1)-P-C(8) ( $103.15(17)^\circ$ ) and C(1)-P-C(15) ( $106.10(18)^\circ$ ). The copper atom protrudes by *ca.* 20 pm from the plane N(1)N(2)P towards the olefinic bond C(4)-C(5). The distances Cu-C(4) (259.1(4) pm) and Cu-C(5) (271.9(4) pm) are comparatively long, but significantly shorter than the shortest Cu·····C distances to the free  $\text{C}_7\text{H}_7$  substituents (Cu-C(8) 346.0(5), Cu-C(9) 389.1(5), Cu-C(15) 343.9(5) and Cu-C(21) 367.4(5) pm). In general, the bond lengths between copper(I) and the olefinic carbon atoms of a side-on coordinated ethylene ligand are found in the range of 194–203 pm; examples are the perchlorates  $[\text{Cu}(\text{C}_2\text{H}_4)(\text{L-L})]\text{ClO}_4$  (L-L = di(2-pyridyl)amine (201.9(3) pm) [8], 2,2'-dipyridine (194.3(14)–202.8(11) pm, *av.* 199.2 pm) [9] or ortho-phenanthroline (199.8(13) and 202.2(12) pm) [9]) and the hydro-tris(3,5-dimethyl-1-pyrazolyl)borate complex  $(\text{Tp}^*)\text{Cu}(\text{C}_2\text{H}_4)$  (200.4(6) and 202.3(5) pm) [10]. Somewhat longer Cu-C separations were reported for the norbornene compound  $[\text{Cu}(\text{dien})-(\text{C}_7\text{H}_{10})]\text{BPh}_4$  containing diethylenetriamine (219(1) pm) [11] and for the dimeric chloro-bridged complex with 1-allyl-3,5-dimethylpyrazole as a chelating ligand (212.6(13) and 215.1(11) pm) [12]. In the light of these results, the interaction of Cu(I) with the olefinic double bond C(4)-C(5) in **2**, although indicated by the geometrical arrangement of the  $\text{P}(\text{C}_7\text{H}_7)_3$  ligand, can only be weak. It is remarkable, however, that in all copper(I)-olefin complexes which were investigated so far by X-ray structure analysis, the length of the coordinated double bond is always close to that of the free olefin.

The Cu-P (218.99(11) pm) and the Cu-N distances (196.6(4) and 197.2(4) pm) in **2** may be compared with the corresponding values in the perchlorates  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$  (Cu-N 195(1)–202(1)

pm, av. 199.25 pm) [1] and  $[\text{Cu}(\text{PPh}_3)_2(\text{CH}_3\text{CN})_2]\text{ClO}_4$  (Cu-P 225.7(3) and 227.8(3) pm, Cu-N 202.8(8) and 206.8(8) pm) [3]. The Cu-P bond in **2** is considerably shorter than the Cu-P bond lengths in the – sterically crowded – tetrakis(triphenylphosphane) copper(I) cations which are present in  $[\text{Cu}(\text{PPh}_3)_4]\text{ClO}_4$  (252.4(6) and 260.5(11) pm) [4] and  $[\text{Cu}(\text{PPh}_3)_4]\text{PF}_6$  (246.5(2) and 256.6(2) pm) [6]. The acetonitrile ligands in **2** are linear, as in the tetrahedral tetrakis(acetonitrile) copper(I) cation in  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$  (**1**), and the angle N(1)-Cu-N(2) ( $106.76(15)^\circ$ ) remains close to the tetrahedral angle, cf.  $[\text{Cu}(\text{PPh}_3)_2(\text{CH}_3\text{CN})_2]\text{ClO}_4$  with N-Cu-N  $99.2(3)^\circ$  [3].

In the crystal of the bis(phosphane) complex,  $\{\text{Cu}[\text{P}(\text{C}_7\text{H}_7)_3]_2\}\text{PF}_6$  (**3**), the central copper(I) is coordinated primarily by the two phosphorus atoms which include a P(1)-Cu-P(2) angle of  $137.36(7)^\circ$ . This angle indicates that the coordination number at copper(I) must be higher than 2; related cations containing bulky phosphanes such as tribenzylphosphane ( $\text{PBz}_3$ ) or trimesitylphosphane ( $\text{PMes}_3$ ) possess a strictly linear coordination geometry, as confirmed by X-ray crystallography for  $[\text{Cu}(\text{PBz}_3)_2]\text{X}$  (X =  $\text{PF}_6$  [13],  $\text{CuCl}_2$  [14],  $\text{CuBr}_2$  [15]) and also found for  $[\text{Cu}(\text{PMes}_3)_2]\text{BF}_4$  [16]. With respect to the P-P vector in **3**, the six 1-cyclohepta-2,4,6-trienyl substituents assume a staggered arrangement; the rings containing C(1), C(8) and C(22) are attached to phosphorus in an equatorial position. The staggered conformation

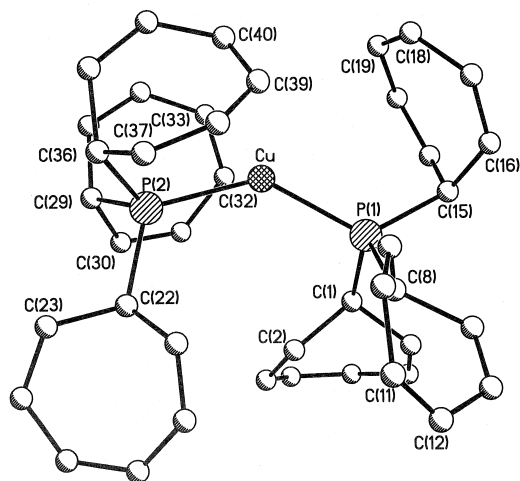


Fig. 2. Structure of the cation  $\{\text{Cu}[\text{P}(\text{C}_7\text{H}_7)_3]_2\}^+$  in **3**.

Table 2. Selected atomic distances (pm) and angles ( $^\circ$ ) for the cation in  $\{\text{Cu}[\text{P}(\text{C}_7\text{H}_7)_3]_2\}\text{PF}_6$  (**3**).

Distances			
Cu-P(1)	224.14(18)	Cu-P(2)	221.55(19)
P(1)-C(1)	184.3(6)	P(2)-C(22)	183.5(6)
P(1)-C(8)	184.3(6)	P(2)-C(29)	184.9(7)
P(1)-C(15)	186.9(6)	P(2)-C(36)	188.1(7)
C(1)-C(2)	148.9(8)	C(22)-C(23)	150.0(8)
C(1)-C(7)	150.6(8)	C(22)-C(28)	148.1(8)
C(2)-C(3)	132.9(8)	C(23)-C(24)	135.2(9)
C(3)-C(4)	141.9(11)	C(24)-C(25)	140.9(12)
C(4)-C(5)	133.3(11)	C(25)-C(26)	132.9(12)
C(5)-C(6)	144.0(12)	C(26)-C(27)	145.5(12)
C(6)-C(7)	134.1(9)	C(27)-C(28)	133.7(9)
C(29)-C(30)	152.1(11)	C(36)-C(37)	149.7(10)
C(29)-C(35)	149.7(9)	C(36)-C(42)	152.2(9)
C(30)-C(31)	135.0(11)	C(37)-C(38)	134.0(10)
C(31)-C(32)	142.9(12)	C(38)-C(39)	143.6(11)
C(32)-C(33)	133.2(11)	C(39)-C(40)	133.7(9)
C(33)-C(34)	137.4(11)	C(40)-C(41)	140.5(10)
C(34)-C(35)	131.0(10)	C(41)-C(42)	133.4(9)
Cu-C(32)	285.7(12)	Cu-C(18)	384.2(12)
Cu-C(33)	297.4(12)	Cu-C(19)	359.0(12)
Cu-C(39)	260.4(12)		
Cu-C(40)	281.0(12)		
Angles			
Cu-P(1)-C(1)	107.4(2)	Cu-P(2)-C(22)	116.4(2)
Cu-P(1)-C(8)	111.66(19)	Cu-P(2)-C(29)	115.6(2)
Cu-P(1)-C(15)	124.2(2)	Cu-P(2)-C(36)	112.2(2)
C(1)-P(1)-C(8)	104.3(3)	C(22)-P(2)-C(29)	100.0(3)
C(1)-P(1)-C(15)	100.9(3)	C(22)-P(2)-C(36)	104.5(3)
C(8)-P(1)-C(15)	106.1(3)	C(29)-P(2)-C(36)	106.8(3)
P(1)-Cu-P(2)	137.36(7)	Z <sup>1</sup> -Cu-Z <sup>2</sup>	108.43(30)
P(1)-Cu-Z <sup>1</sup>	109.5(3)	P(2)-Cu-Z <sup>1</sup>	84.3(3)
P(1)-Cu-Z <sup>2</sup>	122.6(3)	P(2)-Cu-Z <sup>2</sup>	87.8(3)

Z<sup>1</sup> and Z<sup>2</sup> indicate the centers of the double bonds C(32)-C(33) (Z<sup>1</sup>) and C(39)-C(40) (Z<sup>2</sup>).

The Cu-C distances and the angles at Cu involving the double bonds (Z<sup>1</sup> and Z<sup>2</sup>) were calculated; the standard deviations (e.s.d.'s) are assumed to be in the range of those of bond lengths (0.8–1.2 pm) and bond angles ( $0.3^\circ$ ), respectively.

facilitates an additional interaction of Cu with the central double bond of the – axially attached – substituents at P(2) containing C(29) and C(36). Although the two double bonds involved, C(32)-C(33) (133.2(11) pm) and C(39)-C(40) (133.7(9) pm), are again not enlarged significantly as a result of  $\pi$ -complexation, the Cu-C distances to these two double bonds are shorter (260–300 pm) than all other Cu·····C distances (> 300 pm). If the midpoints of the two double bonds C(32)-C(33) (= Z<sup>1</sup>) and C(39)-C(40) (= Z<sup>2</sup>) are defined as ligand centers in addition to P(1) and

P(2) in a distorted tetrahedron ( $Z^1\text{-Cu-Z}^2$  108.4°), the angles between the four “ligands” vary between 84.3 and 137.4° (*cf.* Table 2). The “bite angles” of the formally tridentate  $\text{P}(\text{C}_7\text{H}_7)_3$  chelate ligand containing P(2) in **3** are in the expected range of 84–88°, only marginally smaller than the three “bite angles” of the formally tetradentate ligand in  $\text{RhCl}[\text{P}(\text{C}_7\text{H}_7)_3]$  which are 90° as a consequence of its molecular symmetry  $\text{C}_{3v}$  [17].

## Experimental Section

Standard syntheses for the starting compounds,  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (**1**) [18] and  $\text{P}(\text{C}_7\text{H}_7)_3$  [19], have been described; **1** is commercially available (Strem).

Instrumentation: IR spectra: Perkin-Elmer 983G; NMR spectra: Bruker ARX 250.

### $\{\text{Cu}[\text{P}(\text{C}_7\text{H}_7)_3](\text{CH}_3\text{CN})_2\}\text{PF}_6$ (**2**)

A solution of 0.37 g (0.99 mmol) of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (**1**) in 20 ml of dichloromethane was stirred in the presence of 0.35 g (1.15 mmol) of  $\text{P}(\text{C}_7\text{H}_7)_3$  for 6 h at ambient temperature. The solvent was then evaporated, the residue washed with diethyl ether and recrystallized from  $\text{CH}_2\text{Cl}_2$ . Light-yellow powder, m.p. 145 °C; yield 0.40 g (49.4%).

IR (CsI):  $\nu = 2318$  and  $2286$  ( $\text{C}\equiv\text{N}$ ). –  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 2.24$  (s, 6 H,  $\text{CH}_3\text{CN}$ ), 3.00 (q, 3 H,  $\text{H}^1$ ), 5.26 (q, 6 H,  $\text{H}^{2,7}$ ), 6.22 (m, 6 H,  $\text{H}^{3,6}$ ), 6.63 (s, 6 H,  $\text{H}^{4,5}$ ). –  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 2.8$  ( $\text{CH}_3\text{CN}$ ), 36.0 (d,  $^1J(\text{P,C}) = 19.8$  Hz,  $\text{C}^1$ ), 118.6 (s,  $\text{C}^{2,7}$ ), 128.5 (d,  $^3J(\text{P,C}) = 8.8$  Hz,  $\text{C}^{3,6}$ ), 130.6 (s,  $\text{C}^{4,5}$ ). –  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -21.8$  (s,  $\text{P}(\text{C}_7\text{H}_7)_3$ ),  $-143.1$  (septet,  $^1J(\text{P,F}) = 712$  Hz,  $\text{PF}_6^-$ ).

### $\{\text{Cu}[\text{P}(\text{C}_7\text{H}_7)_3]_2\}\text{PF}_6$ (**3**)

A solution containing 0.30 g (0.80 mmol) of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (**1**) and 0.475 g (1.56 mmol) of  $\text{P}(\text{C}_7\text{H}_7)_3$  in 20 ml of dry acetone was heated under reflux (56 °C) for 2 h. The solvent was removed under vacuum, the residue **3** washed with diethyl ether, then dissolved in THF and the solution filtered through  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated and the product **3** dried in a high vacuum. Yield 0.37 g (45.3%), m.p. 166 °C.

$^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 2.80$  (br, 6 H,  $\text{H}^1$ ), 5.41 (br, 12 H,  $\text{H}^{2,7}$ ), 6.34 (br, 12 H,  $\text{H}^{3,6}$ ), 6.69 (br, 12 H,  $\text{H}^{4,5}$ ). –  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):

$\delta = 35.1$  (d,  $^2J(\text{P,C}) = 21.6$  Hz,  $\text{C}^1$ ), 118.7 ( $\text{C}^{2,7}$ ), 128.2 ( $\text{C}^{3,6}$ ), 129.1 ( $\text{C}^{4,5}$ ). –  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -4.5$  ( $\text{P}(\text{C}_7\text{H}_7)_3$  ligand),  $-143.0$  (septet,  $^1J(\text{P,F}) = 713$  Hz,  $\text{PF}_6^-$ ).

## Crystal structure determinations of **2** and **3**

The intensity data were collected at room temperature. All hydrogen atoms were refined on calculated positions, applying the riding model with fixed isotropic temperature factors. The non-hydrogen atoms were refined with anisotropic temperature factors. The radiation used was  $\text{Mo-K}\alpha$  ( $\lambda = 71.073$  pm) generated by a graphite monochromator.

### $\{\text{Cu}[\text{P}(\text{C}_7\text{H}_7)_3](\text{CH}_3\text{CN})_2\}\text{PF}_6$ (**2**):

Data collection by Siemens P4 diffractometer; the irregular colourless crystal of dimensions  $0.22 \times 0.16 \times 0.14$  mm belonged to the triclinic space group  $P\bar{1}$ ; lattice parameters  $a = 1086.21(9)$ ,  $b = 1153.72(10)$ ,  $c = 1343.40(17)$  pm,  $\alpha = 106.027(7)^\circ$ ,  $\beta = 98.633(7)^\circ$ ,  $\gamma = 117.626(5)^\circ$ ;  $Z = 2$ ,  $\mu = 0.982$   $\text{mm}^{-1}$ ; 4878 reflections collected in the range  $2^\circ$ – $24.99^\circ$  in  $\vartheta$ , 4547 reflections independent, 3125 assigned to be observed ( $I > 2\sigma(I)$ ). Full matrix least squares refinement with 361 parameters, empirical absorption correction (by  $\psi$ -scans), min/max. transmission factors 0.7827/0.9139;  $R_1/wR_2$ -values 0.049/0.105, max./min residual electron density 0.225/– 0.431  $\text{e} \cdot 10^{-6} \text{ pm}^{-3}$ .

### $\{\text{Cu}[\text{P}(\text{C}_7\text{H}_7)_3]_2\}\text{PF}_6$ (**3**):

Data collection by STOE IPDS; the crystal was a yellowish plate of dimensions  $0.28 \times 0.18 \times 0.12$  mm, monoclinic, space group  $P2_1/c$ ; lattice parameters  $a = 1033.7(2)$ ,  $b = 1956.2(4)$ ,  $c = 1935.9(4)$  pm;  $\beta = 93.87(3)^\circ$ ;  $Z = 4$ ,  $\mu = 0.740$   $\text{mm}^{-1}$ ; 30120 reflections collected in the range  $2^\circ$ – $26.2^\circ$  in  $\vartheta$ , 7613 reflections independent, 2441 reflections assigned to be observed ( $I > 2\sigma(I)$ ). Full matrix least squares refinement with 469 parameters,  $R_1/wR_2$ -values 0.058/0.127, numerical absorption correction (crystal shape refined by program HABITUS); max./min residual electron density 0.525/– 0.307  $\text{e} \cdot 10^{-6} \text{ pm}^{-3}$ .

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no CCDC-204 755 (**2**) and CCDC-204 754 (**3**).

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