# metal-organic papers

# Tris(triphenylphosphine)copper(I) hexafluorophosphate

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**Key indicators**

Single-crystal X-ray study

$T$ = 295 K

Mean $\sigma$(C–C) = 0.007 Å

$R$ factor = 0.053

$wR$ factor = 0.163

Data-to-parameter ratio = 14.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $[Cu(C_{18}H_{15}P)_3](PF_6)$, crystallizes as an ionic salt with no coordination between the $[(PPh_3)_3Cu]^+$ cation and the $[PF_6]^-$ anion. The three-coordinate Cu atoms lie in a distorted trigonal-planar environment.

## Comment

The structure of the title compound, (I), has been determined as part of an investigation into the structural properties of the adducts formed between the tris(triphenylphosphine)-copper(I) cation and monovalent anions. The structure determination of (I) shows the complex to consist of discrete $[(PPh_3)_3Cu]^+$ cations and $[PF_6]^-$ anions, with the shortest $Cu\cdots F$ distance being 4.44 (2) Å (Fig. 1 and Table 1).



(I)
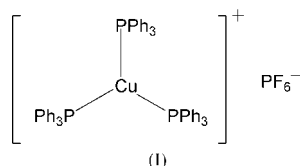
The packing arrangement of the cations and anions is illustrated in Fig. 2. In the cation, steric congestion by the phenyl rings of the PPh$_3$ ligands results in a distorted trigonal-planar environment for Cu, with P—Cu—P angles of 125.20 (4), 120.01 (4) and 113.28 (4)°, and a mean value of 120 (6)°. The Cu atom lies less than 0.2 Å out of the plane of the three P atoms. The Cu—P bond lengths of 2.277 (1), 2.286 (1) and 2.301 (1) Å [mean 2.288 (12) Å] are similar to those reported for the two other known ionic $[(PPh_3)_3Cu]X$ salts with unco-ordinated anions: $X$ = FeCl$_4$ (Saturnino & Arif, 1993) with Cu—P bond lengths of 2.303 (2), 2.294 (2) and 2.288 (2) Å [mean 2.295 (8) Å]; and $X$ = V(CO)$_6$ (Doyle et al., 1985) with Cu—P bond lengths of 2.293 (1), 2.297 (1) and 2.296 (1) Å [mean 2.295 (2) Å]. These Cu—P bond lengths are shorter than those reported for four-coordinate complexes in which the anion is coordinated to the Cu atom. For example, with $X$ = ClO$_4$ (Dyason et al., 1986), the Cu—P bond lengths are 2.314 (5), 2.313 (7) and 2.317 (8) Å [mean 2.315 (2) Å], with $X$ = NO$_3$ (Dyason et al., 1986), the Cu—P bond lengths are 2.312 (2), 2.321 (2) and 2.338 (2) Å [mean 2.324 (13) Å], and with $X$ = Cl (Gill et al., 1976), the Cu—P bond lengths are 2.348 (2), 2.351 (2) and 2.355 (2) Å [mean 2.351 (3) Å].

## Experimental

$[Cu(PPh_3)_3(CH_3CN)]PF_6\cdot CH_3CN$ (0.25 g), prepared by crystallization from an acetonitrile solution of a 3:1 stoichiometric ratio of PPh$_3$ and $[Cu(CH_3CN)_4]PF_6$ as described for the synthesis of the analogous perchlorate complex (Barron et al., 1985), was suspended
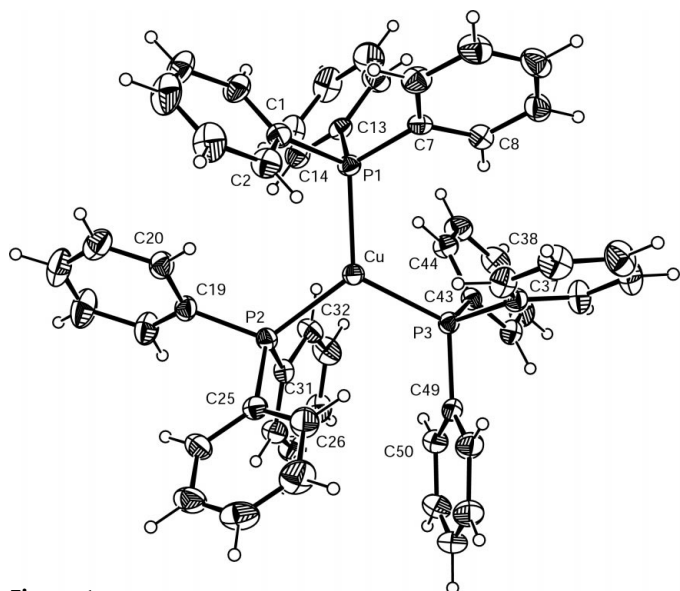
**Figure 1**
ORTEP-3 (Farrugia, 1997) plot, showing the atomic numbering scheme for the cation of (I). Displacement ellipsoids are drawn at the 30% probability level for non-H atoms.
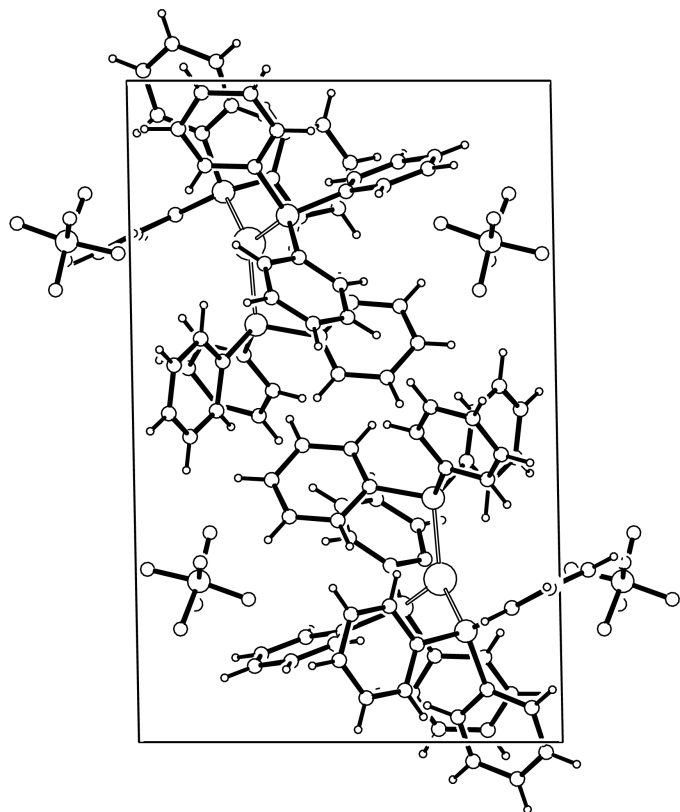


**Figure 2**
Unit-cell diagram for (I), projected down the *a* axis. The *b* axis is horizontal and the *c* axis is vertical.

in ethanol (20 ml). The resultant mixture was gently boiled for 30 min giving a clear solution. The hot solution was filtered and left to stand overnight, yielding crystalline hexagonal plates of (I) (m.p. 502–506 K). Analysis found: C 65.2, H 4.7%; calculated for $C_{54}H_{45}CuF_6P_4$: C 65.2, H 4.6%.

*Crystal data*

| | |
|---|---|
| $[Cu(C_{18}H_{15}P)_3](PF_6)$ | $Z = 2$ |
| $M_r = 995.33$ | $D_x = 1.371$ Mg m$^{-3}$ |
| Triclinic, $P\bar{1}$ | MoK$\alpha$ radiation |
| $a = 11.057$ (2) Å | Cell parameters from 25 |
| $b = 12.1900$ (18) Å | reflections |
| $c = 18.790$ (3) Å | $\theta = 12.8$–$15.3°$ |
| $\alpha = 88.4$ (8)° | $\mu = 0.65$ mm$^{-1}$ |
| $\beta = 100.633$ (15)° | $T = 295$ K |
| $\gamma = 104.349$ (13)° | Plate, colorless |
| $V = 2411.0$ (10) Å$^3$ | $0.30 \times 0.20 \times 0.15$ mm |

*Data collection*

| | |
|---|---|
| Rigaku AFC-7R diffractometer | $\theta_{max} = 25.0°$ |
| $\omega$–$2\theta$ scans | $h = -13 \rightarrow 6$ |
| Absorption correction: none | $k = -14 \rightarrow 14$ |
| 9918 measured reflections | $l = -21 \rightarrow 22$ |
| 8479 independent reflections | 3 standard reflections |
| 6045 reflections with $I > 2\sigma(I)$ | every 150 reflections |
| $R_{int} = 0.042$ | intensity decay: 1.2% |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0874P)^2$ |
| $R[F^2 > 2\sigma F^2] = 0.053$ | $+ 1.8564P]$ |
| $wR(F^2) = 0.163$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.02$ | $(\Delta/\sigma)_{max} = 0.002$ |
| 8479 reflections | $\Delta\rho_{max} = 0.72$ e Å$^{-3}$ |
| 587 parameters | $\Delta\rho_{min} = -0.56$ e Å$^{-3}$ |
| H-atom parameters constrained | |

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cu—P1 | 2.2773 (11) | P2—C19 | 1.824 (4) |
| Cu—P2 | 2.2865 (11) | P2—C25 | 1.818 (4) |
| Cu—P3 | 2.3009 (12) | P2—C31 | 1.824 (4) |
| P1—C1 | 1.819 (4) | P3—C37 | 1.820 (4) |
| P1—C7 | 1.821 (4) | P3—C43 | 1.820 (4) |
| P1—C13 | 1.822 (4) | P3—C49 | 1.826 (4) |
| | | | |
| P1—Cu—P2 | 125.2 (8) | C43—P3—C49 | 105.3 (8) |
| P1—Cu—P3 | 120.0 (8) | P1—C1—C2 | 117.6 (9) |
| P2—Cu—P3 | 113.3 (8) | P1—C1—C6 | 122.9 (9) |
| Cu—P1—C1 | 114.1 (8) | P1—C7—C8 | 119.0 (8) |
| Cu—P1—C7 | 117.5 (8) | P1—C7—C12 | 123.0 (9) |
| Cu—P1—C13 | 110.1 (8) | P1—C13—C14 | 117.9 (9) |
| C1—P1—C7 | 104.5 (8) | P1—C13—C18 | 123.8 (9) |
| C1—P1—C13 | 104.9 (8) | P2—C19—C20 | 118.3 (9) |
| C7—P1—C13 | 104.7 (8) | P2—C19—C24 | 122.7 (9) |
| Cu—P2—C19 | 122.8 (8) | P2—C25—C26 | 118.0 (9) |
| Cu—P2—C25 | 115.9 (8) | P2—C25—C30 | 123.3 (9) |
| Cu—P2—C31 | 103.7 (8) | P2—C31—C32 | 116.2 (9) |
| C19—P2—C25 | 102.0 (8) | P2—C31—C36 | 125.5 (9) |
| C19—P2—C31 | 104.0 (8) | P3—C37—C38 | 118.6 (9) |
| C25—P2—C31 | 107.1 (8) | P3—C37—C42 | 123.0 (9) |
| Cu—P3—C37 | 112.2 (8) | P3—C43—C44 | 118.0 (9) |
| Cu—P3—C43 | 110.4 (8) | P3—C43—C48 | 123.8 (8) |
| Cu—P3—C49 | 118.2 (8) | P3—C49—C50 | 121.0 (9) |
| C37—P3—C43 | 106.2 (8) | P3—C49—C54 | 120.0 (9) |
| C37—P3—C49 | 103.6 (8) | | |

H atoms were constrained as riding atoms, fixed to their parent C atoms at a C—H distance of 0.95 Å. $U_{iso}$(H) values were set to $1.2U_{eq}$ of the parent atom.

Data collection: *MSC/AFC-7 Diffractometer Control for Windows* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC-7 Diffractometer Control for Windows*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997–2001); program(s) used to solve structure: *TEXSAN for Windows*; program(s) used to refine structure: *TEXSAN for Windows* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP-3*

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