Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

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Key indicators

Single-crystal X-ray study T = 295 KMean $\sigma(\text{C-C}) = 0.007 \text{ Å}$ R factor = 0.053 wR factor = 0.163Data-to-parameter ratio = 14.4

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

Tris(triphenylphosphine)copper(I) hexafluoro-phosphate

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.

Received 14 May 2003 Accepted 19 May 2003 Online 31 May 2003

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).

$$\begin{bmatrix} & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & \\ & & \\$$

The packing arrangement of the cations and anions is illustrated in Fig. 2. In the cation, steric congestion by the phenyl rings of the PPh3 ligands results in a distorted trigonal-planar environment for Cu, with P-Cu-P angles of 125.20 (4), 120.01 (4) and $113.28 (4)^{\circ}$, and a mean value of $120 (6)^{\circ}$. 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 [(PPh₃)₃Cu]X salts with uncoordinated anions: $X = \text{FeCl}_4$ (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) A]. 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 = ClO₄ (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 = NO₃ (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(PPh₃)₃(CH₃CN)]PF₆·CH₃CN (0.25 g), prepared by crystallization from an acetonitrile solution of a 3:1 stoichiometric ratio of PPh₃ and [Cu(CH₃CN)₄]PF₆ as described for the synthesis of the analogous perchlorate complex (Barron *et al.*, 1985), was suspended

DOI: 10.1107/S1600536803010973

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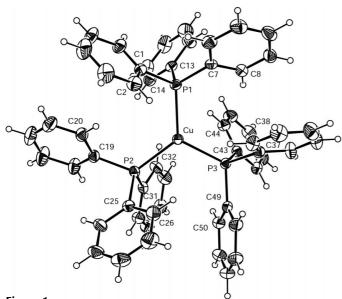


Figure 1ORTEP-3 (Farrugia, 1997) plot, showing the atomic numbering scheme for the cation of (I). Displacement ellipsoids are drawn at the 30% probability level for non-H atoms.

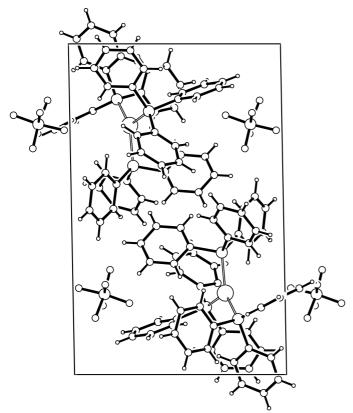


Figure 2 Unit-cell diagram for (I), projected down the a axis. The b axis is horizontal and the c axis is vertical.

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
$M_r = 995.33$	$D_x = 1.371 \text{ Mg m}^{-3}$
Triclinic, $P\overline{1}$	MoKa radiation
a = 11.057 (2) Å	Cell parameters from 25
b = 12.1900 (18) Å	reflections
c = 18.790 (3) Å	$\theta = 12.8 15.3^{\circ}$
$\alpha = 88.4 (8)^{\circ}$	$\mu = 0.65 \text{ mm}^{-1}$
$\beta = 100.633 (15)^{\circ}$	T = 295 K
$\gamma = 104.349 (13)^{\circ}$	Plate, colorless
$V = 2411.0 (10) \text{ Å}^3$	$0.30 \times 0.20 \times 0.15 \text{ mm}$

Data collection

Rigaku AFC-7R diffractometer	$\theta_{\rm max} = 25.0^{\circ}$
ω –2 θ 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
$R_{\rm int} = 0.042$	intensity decay: 1.2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0874P)^2]$
	$W = 1/[O(\Gamma_O) + (0.08/4P)]$
$R[F^2 > 2\sigma F^2] = 0.053$	+ 1.8564 <i>P</i>]
$wR(F^2) = 0.163$	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.02	$(\Delta/\sigma)_{\text{max}} = 0.002$
8479 reflections	$\Delta \rho_{\text{max}} = 0.72 \text{ e Å}^{-3}$
587 parameters	$\Delta \rho_{\min} = -0.56 \text{ e Å}^{-3}$
H-atom parameters constrained	

 Table 1

 Selected geometric parameters (\mathring{A} , $^{\circ}$).

	•		
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 (8)
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. $U_{\rm iso}({\rm H})$ values were set to $1.2U_{\rm eq}$ 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 SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3

metal-organic papers

(Farrugia, 1997) and *PLATON* (Spek, 2001); software used to prepare material for publication: *TEXSAN for Windows* and *PLATON*.

We acknowledge financial support of this work by Griffith University and the Australian Institute of Nuclear Science and Engineering (AINSE) for funding of AINSE project AINGRA03055.

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