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# Bis($\mu$-tricyanomethanido)tetrakis(triphenylphosphine)-dicopper(I)

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**Key indicators**

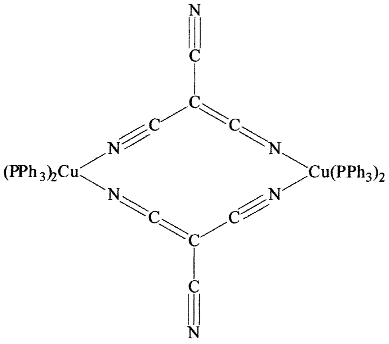
Single-crystal X-ray study
*T* = 213 K
Mean $\sigma$(C–C) = 0.006 Å
*R* factor = 0.052
*wR* factor = 0.152
Data-to-parameter ratio = 14.1

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

Colourless crystals of the title compound, $[Cu_2(C_4N_3)_2(C_{18}H_{15}P)_4]$, were obtained by the reaction of $CuC(CN)_3$ with excess of molten $PPh_3$. The crystal structure contains centrosymmetric dimeric units bridged by two $C(CN)_3$ ligands. The Cu atoms have a distorted tetrahedral coordination.

## Comment

The pseudohalide tricyanomethanide $C(CN)_3^-$ is well known as a versatile ligand in coordination compounds. With four available lone electron pairs, its coordination modes vary from unidentate terminal to bi- or tridentate bridging ligand (Golub *et al.*, 1986). Continuing our structural studies on the coordination behaviour of pseudohalides in the system $M(PPh_3)_nX$, $M$ = Cu(I), Ag(I) or Au(I), we present here the crystal and molecular structure of $[Cu(PPh_3)_2\{C(CN)_3\}]_2$. So far, $[Au(PPh_3)_2\{C(CN)_3\}]$ is the only structurally characterized example involving tricyanomethanide within the above-mentioned system (Baukova *et al.* 1989; Wang & Wang, 1993).



(I)

The crystal structure of the title compound is built up of centrosymmetric dimeric molecules, in which two Cu atoms are asymmetrically bridged end-to-end by two $C(CN)_3$ ligands, forming a twelve-membered non-planar ring. The distorted tetrahedral coordination at the Cu atoms is completed by two triphenylphosphine ligands, showing wide P—Cu—P and small N—Cu—N angles of 124.87 (3)° and 95.92 (12)°, respectively. The Cu—N distances are 2.027 (3) and 2.090 (3) Å. The corresponding Cu—N—C bond angles are 159.6 (3) and 151.7 (3) Å. The $C(CN)_3$ ligand does not differ significantly from the ideal planar $D_{3h}$ geometry of non-coordinated tricyanomethanide. The largest deviation from the mean plane is observed for C1 [0.0718 (36) Å]. The bond length C(13)—N(13) of the non-coordinated cyano group is slightly shorter [1.131 (5) Å] compared to the coordinated cyano groups C(12)—N(12) [1.144 (4) Å] and C(11)—N(11)

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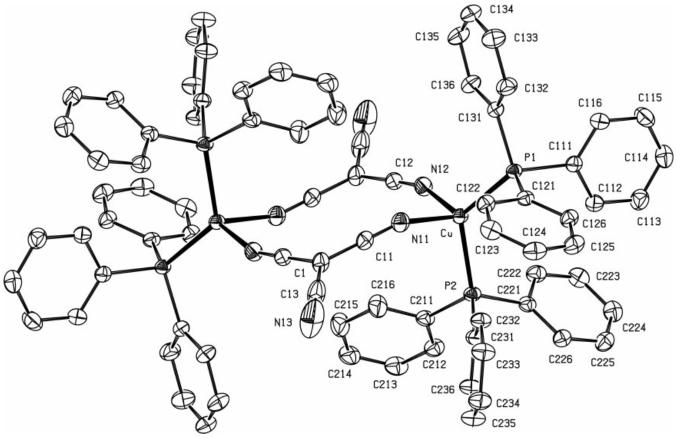

**Figure 1**
A view of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

[1.152 (4) Å]. The C—N distances in non-coordinated tricyanomethanide lie within the range 1.131–1.139 Å (Potočňák *et al.*, 1997, 1998). Selected bond lengths and angles are given in Table 1. Similar end-to-end bridged structures were found for $[Ag(PPh_3)_2N(CN)_2]_2$ (Bessler *et al.*, 2000) and $[Cu(PPh_3)_2N_3]_2$ (Ziolo *et al.*, 1971).

## Experimental

$KC(CN)_3$ was prepared according to Trofimenko *et al.* (1962). $CuC(CN)_3$ was obtained from $KC(CN)_3$, $CuSO_4$ and $NaHSO_3$ in $H_2O$ solution as a microcrystalline precipitate. $[Cu(PPh_3)_2C(CN)_3]_2$ was synthesized by the reaction of $CuC(CN)_3$ in molten $PPh_3$ at 373 K. The excess $PPh_3$ was removed with *n*-hexane and the residue was submitted to continuous extraction with $CH_2Cl_2$, from which the title compound was obtained in high yield as colourless crystal plates, m.p. 498 K. Elem. anal. (calc. for $C_{40}H_{20}CuN_3P_2$/found) C = 70.84/70.63, rn>H = 4.46/4.15 N = 6.20/6.15%.

### Crystal data

$C_{80}H_{60}Cu_2N_6P_4$
$M_r = 1356.30$
Triclinic, $P\bar{1}$
$a = 12.113$ (3) Å
$b = 12.8530$ (16) Å
$c = 13.0084$ (14) Å
$\alpha = 85.113$ (11)°
$\beta = 69.290$ (12)°
$\gamma = 66.945$ (13)°
$V = 1739.7$ (5) Å$^3$

$Z = 1$
$D_x = 1.295$ Mg m$^{-3}$
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 29.9$–50.2°
$\mu = 2.00$ mm$^{-1}$
$T = 213$ (2) K
Block, colourless
0.50 × 0.20 × 0.10 mm

### Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega$ scans
Absorption correction: $\psi$ scan (Spek, 1997)
$T_{\min} = 0.634$, $T_{\max} = 0.817$
6696 measured reflections
5840 independent reflections
5634 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.077$
$\theta_{\max} = 65.0°$
$h = -1 \rightarrow 14$
$k = -14 \rightarrow 15$
$l = -14 \rightarrow 15$
3 standard reflections every 400 reflections intensity decay: 2.2%

### Refinement

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.152$
$S = 1.10$
5840 reflections
415 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0797P)^2 + 2.1459P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.64$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.87$ e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| Cu—N12 | 2.027 (3) | C11—C1 | 1.404 (5) |
| Cu—N11 | 2.090 (3) | C1—C13 | 1.402 (5) |
| Cu—P1 | 2.2607 (8) | C1—C12$^{\rm i}$ | 1.402 (4) |
| Cu—P2 | 2.2916 (9) | C12—N12 | 1.144 (4) |
| N11—C11 | 1.152 (4) | C13—N13 | 1.131 (5) |
| | | | |
| N12—Cu—N11 | 95.92 (12) | N11—C11—C1 | 176.8 (3) |
| N12—Cu—P1 | 119.59 (9) | C13—C1—C12$^{\rm i}$ | 121.1 (3) |
| N11—Cu—P1 | 105.21 (8) | C13—C1—C11 | 121.3 (3) |
| N12—Cu—P2 | 103.34 (9) | C12$^{\rm i}$—C1—C11 | 117.2 (3) |
| N11—Cu—P2 | 102.77 (9) | N12—C12—C1$^{\rm i}$ | 176.9 (3) |
| P1—Cu—P2 | 124.87 (3) | C12—N12—Cu | 159.6 (3) |
| C11—N11—Cu | 151.7 (3) | N13—C13—C1 | 178.7 (5) |

Symmetry code: (i) $1 - x, 2 - y, 2 - z$.

The terminal N13 atom exhibits greater displacement parameters due to its thermal movements. No improvement of the structure factors model can be achieved by splitting it into two positions. The H atoms were placed in calculated positions (C—H = 0.94 Å) and allowed to ride with isotropic displacement parameters 20% larger than those of the attached C atom.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1997), *ORTEP*3 for Windows (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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