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Square $[Pd_4(\mu\text{-}CN)_4(C_6F_5)_4(PEt_3)_4]\cdot 2C_6H_5CH_3$

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Key indicators

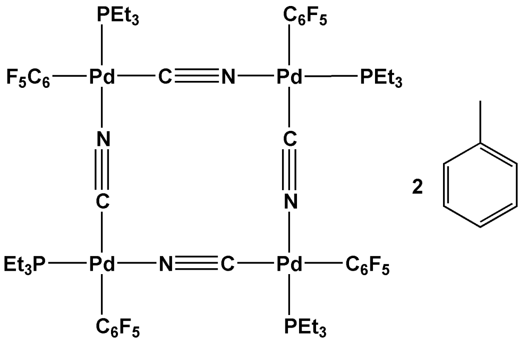
Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.025
wR factor = 0.061
Data-to-parameter ratio = 19.4

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

The tetrameric title complex in the crystal of its toluene disolvate, *i.e.* tetra-μ-cyano-tetrakis[(pentafluorophenyl)(triethylphosphine)palladium(II)] toluene disolvate, $[Pd_4(\mu\text{-}CN)_4(C_6F_5)_4(PEt_3)_4]\cdot 2C_7H_8$, occupies a special position on a crystallographic inversion centre and contains a square arrangement of four square-planar palladium centres.

Comment

The construction of cyclic nanostructures using coordination chemistry is a topic of growing interest (Olenyuk *et al.*, 1998; Fujita, 1998; Navarro & Lippert, 1999). One of the most popular patterns is that of a molecular square where transition metal building blocks affording coordination sites at 90° are linked by bidentate ligands defining bonds at 180°. The latter are usually neutral symmetric *N*-donor ligands such as 4,4′-bipyridyl, 1,4-dicyanobenzene, 4,4′-dicyano-1,1′-diphenyl, linear bis(pyridyl)porphyrins and the like (Stang *et al.*, 1995, 1997; Fujita *et al.*, 1994; Wu *et al.*, 1998).



(I)

The two simplest bridging ligands making two linear bonds are C_2^{2-} and CN^-. While their short length does not afford a square hole useful to host anything inside, they both offer excellent electronic communication and might be used to constitute tetrametallic knots in a more sophisticated network containing other ligands. The CN^- bridge seems to offer two potential advantages over an acetylenic bridge. Firstly, N—*M* bond formation is easily reversible, thus allowing rearrangements in solution towards favourable structures; this ability is usually needed for the self-assembly of nanostructures and cannot be easily achieved with the irreversible formation of acetylide–*M* bonds. Secondly, when coordinated to building blocks with different ligands, the asymmetric CN^- should be able, in principle, to discriminate between different *trans* ligands according to their different *trans* influences.

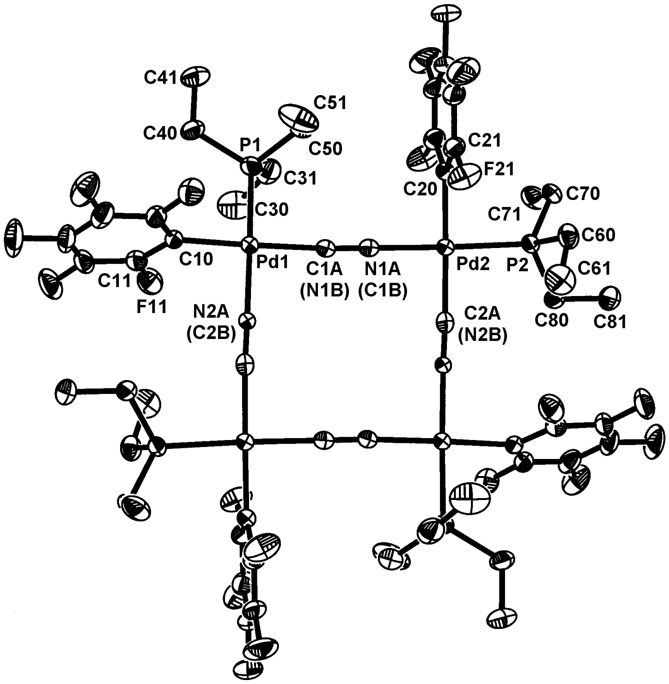


Figure 1
The molecular structure of the tetrameric Pd complex in the crystal of the title compound showing 50% probability displacement ellipsoids. The H atoms have been omitted for clarity. The second component atoms of the disordered part of the structure are shown in parentheses.

Different structural patterns based on CN^- bridges can be found in the structures of metallic cyanide complexes, ranging from chain structures (*e.g.* AgCN) to three-dimensional frameworks, *e.g.* Prussian Blue (Wells, 1984). The structures of $[Rh_4(\mu\text{-}CN)_4(C_2B_{10}H_{11})_4(PPh_3)_4]$ (Kalb *et al.*, 1982), $[Ti_4(\mu\text{-}CN)_4(C_5H_5)_8]$ (Schinnerling & Thewalt, 1992) and $[Cu_4(\mu\text{-}CN)_4(tmtch)_4]$ (tmtch = $SC_{10}H_6$, 3,3,6,6-tetramethyl-1-thiacycloheptyne; Olbrich *et al.*, 1993), have been determined. They are all folded to a greater or lesser extent towards a butterfly geometry, due to the lack of 90° bond angles at the metal. The structure of a box-shaped framework formed from squares of $[\{RhCl(C_5Me_5)\}_2\{Co(C_5H_5)(CN)\}_2(\mu\text{-}CN)_4]$ has also been reported (Klausmeyer *et al.*, 1998). Surprisingly, the only structural determination of a complex with a metal ideally suited to produce 90° bond angles is that of $[Au_4(\mu\text{-}CN)_4(n\text{–}C_3H_7)_8]$ (Phillips & Powell, 1939); this molecule was structurally characterized as early as 1939, and the precision of the data is severely limited by the technology available at that time.

Some time ago, one of the authors reported a number of tetrameric and polymeric Pd complexes containing bridging cyano ligands. Vapour-pressure-based molecular-weight determinations on solutions of some of them suggested a tetranuclear structure $[Pd_4(\mu\text{-}CN)_4R_4L_4]$ ($R = C_6F_5$, C_6Cl_5; L = PEt_3, PPh_3, $AsPh_3$), but this proposal could not be supported by a single-crystal structure determination. Now we have succeeded in crystallizing and solving the structure of the compound with $R = C_6F_5$ and $L = PEt_3$.

As anticipated, the structure contains a square array of palladium centres linked by bridging cyanide ligands (Fig. 1). This perfectly flat arrangement allows the molecule to sit on an inversion centre: any deviation towards a tetrahedral arrangement of Pd atoms would break this symmetry. The asymmetric unit also contains a molecule of toluene solvent.

As mentioned in the Experimental section, disorder is observed in the positions of the C and N atoms of the bridging cyanide ligands. The ^1H and ^{19}F NMR spectra show that a complicated mixture of isomers is present in solution. Solid-state IR shows a single sharp absorption at 2176 cm^{-1} supporting a model with a symmetric arrangement of cyanide ligands and the 'square' having virtual fourfold symmetry.

Experimental

The title compound was prepared as reported in the literature (Usón *et al.*, 1983). Colourless single crystals were grown on cooling a toluene solution of the complex at 253 K for several weeks.

Crystal data

$[Pd_4(CN)_4(C_6F_5)_4(C_6H_{15}P)_4]\cdot 2C_7H_8$
$M_r = 1854.79$
Monoclinic, $P2_1/c$
$a = 11.8845$ (10) Å
$b = 14.8554$ (18) Å
$c = 21.652$ (3) Å
$\beta = 97.372$ (9)°
$V = 3791.0$ (8) Å^3
$Z = 2$
$D_x = 1.625$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 441 reflections
$\theta = 2$–25°
$\mu = 1.11$ mm^{-1}
$T = 173$ (2) K
Block, colourless
0.3 × 0.3 × 0.3 mm

Data collection

CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.695$, $T_{max} = 0.801$
38 987 measured reflections
8699 independent reflections
6789 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 27.5°$
$h = -15 \rightarrow 15$
$k = -19 \rightarrow 19$
$l = -27 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.061$
$S = 0.97$
8699 reflections
449 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0336P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.01$ e Å^{-3}
$\Delta\rho_{min} = -0.75$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd1—C1*A*	2.036 (2)	Pd2—N1*A*	2.046 (2)
Pd1—N2*A*	2.0554 (19)	Pd2—P2	2.2795 (6)
Pd1—P1	2.2490 (7)	Pd2—C20	2.039 (2)
Pd1—C10	2.028 (2)	C1*A*—N1*A*	1.147 (3)
Pd2—C2*A*	2.028 (2)	C2*A*—N2*A*^{i}	1.145 (3)
C1*A*—Pd1—N2*A*	92.09 (8)	C2*A*—Pd2—C20	175.01 (9)
C1*A*—Pd1—P1	87.65 (6)	N1*A*—Pd2—P2	178.10 (6)
N2*A*—Pd1—P1	174.08 (6)	C20—Pd2—N1*A*	89.25 (8)
C10—Pd1—C1*A*	176.64 (9)	C20—Pd2—P2	88.85 (6)
C10—Pd1—N2*A*	88.73 (8)	N1*A*—C1*A*—Pd1	173.6 (2)
C10—Pd1—P1	91.87 (6)	N2*A*^{i}—C2*A*—Pd2	171.7 (2)
C2*A*—Pd2—N1*A*	89.51 (8)	C1*A*—N1*A*—Pd2	176.7 (2)
C2*A*—Pd2—P2	92.39 (6)	C2*A*^{i}—N2*A*—Pd1	170.9 (2)

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

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Disorder is observed in the positions of the C and N atoms of the bridging cyanide ligands. The eventual strategy adopted to model this was to fix the occupancy of each atomic position with a C:N ratio of 1:1 and to constrain the coordinates and displacement parameters of the C and N atoms at each position to be equivalent. This constrains the Pd—N and Pd—C distances to be equivalent and these distances should thus be treated with caution. All H atoms were constrained to ideal geometries. Methyl H atoms were positioned with a rotating group refinement and isotropic displacement parameters 1.5 times that of their carrier C atom. All other H atoms were assigned isotropic displacement parameters 1.2 times that of their carrier C atom. The highest residual electron-density peak (1.01 e Å^{-3}) is found 0.84 Å from P1. All other residual electron-density peaks have values less than 1 e Å^{-3}.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXTL* (Bruker, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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