metal-organic compounds

(η^2-Tetracyanoethene)bis(triphenyl-phosphine-κP)palladium–dichloromethane (1/0.7)

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The title compound, [Pd(C$_6$N$_4$)(C$_{18}$H$_{15}$P)$_2$]·0.7CH$_2$Cl$_2$, shows a planar coordination geometry around the metal atom that is an almost perfect isosceles triangle if the tetracyanoethene (tcne) ligand is deemed to occupy a single coordination site. The framework of the tcne ligand shows small distortions due to intramolecular steric contacts between the C≡N groups and phenyl rings of the triphenylphosphine ligands.

Comment

Tetracyanoethene (tcne) is a highly electron-deficient alkene that has found use both as a ligand in transition-metal chemistry (Kaim & Moscherosch, 1994) and as an electron acceptor in intermolecular charge-transfer complexes (Schneider & Mohammad-Ali, 1996). It can coordinate to metal atoms or ions through its *N*-donors (σ-coordination) or through its C=C double bond (π-coordination) and, particularly when π-bound, is one of the strongest π-acceptor ligands known (Kaim & Moscherosch, 1994). One of the first π-coordinated tcne complexes to be synthesized was [Pd-(PPh$_3$)$_2$(tcne)] (Fitton & McKeon, 1968), although this was not crystallographically characterized at the time. We now report the structure analysis of the 0.7-solvate of [Pd(PPh$_3$)$_2$-(tcne)], (I).
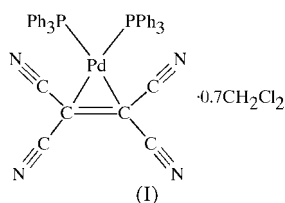
The asymmetric unit of (I) contains one (η^2-tetracyanoethene)bis(triphenylphosphine)palladium molecule in a general position (Fig. 1) and a CH$_2$Cl$_2$ molecule disordered over two orientations whose occupancies sum to 0.70. The tcne ligand is π-bound to the Pd atom, as expected. The two

Pd—P bond lengths in (I) are equal within standard uncertainties, while the three angles P12—Pd1—P31 [108.12 (2)°], P12—Pd1—*X* [125.6 (3)°] and P31—Pd1—*X* [126.3 (3)°], where *X* is the centre of the C2=C3 bond, sum to exactly 360°, confirming the planarity at the Pd centre. Hence, the Pd centre can be thought of as having a coordination geometry which, if the tcne ligand is deemed to occupy one coordination site, corresponds to an almost perfect isosceles triangle. However, the tcne ligand is twisted slightly out of this trigonal plane, the dihedral angle between the Pd1/P12/P31 and Pd1/C2/C3 planes being 6.3 (2)°. This distortion is also reflected in the C—C—Pd angles involving the four cyano groups of the tcne moiety, in that the C6—C2—Pd1 angle is 6.4 (3)° wider than C4—C2—Pd1, and C8—C3—Pd1 is 5.9 (3)° wider than C10—C3—Pd1. These distortions might be attributed to intramolecular steric contacts between the cyano groups and the faces of the phenyl substituents in the molecule, as illustrated by the following distances: C4···C13 = 3.468 (4), N5···C18 = 3.471 (4), N7···C30 = 3.449 (4), C8···C38 = 3.382 (4) and C10···C39 = 3.315 (4) Å. Since the radius of a C atom participating in a π-bond is 1.70 Å (Pauling, 1960), these distances place the cyano groups and their adjacent phenyl rings within the sum of the relevant van der Waals radii. There are also some close intermolecular N···C distances that might similarly influence the geometry of the tcne ligand, notably N7···C21^i = 3.434 (4), N9···C40^{ii} = 3.436 (4), N9···C46^{iii} = 3.243 (4) and N11···C22^{iv} = 3.408 (4) Å [symmetry codes: (i) $-1 + x, y, -1 + z$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $1 + x, y, 1 + z$]. Related distortions of the tcne framework are also present in other Pd–tcne complexes containing aryl-phosphine co-ligands (Kranenburg *et al.*, 1997; Mashima *et al.*, 1998).

The degree of charge transfer from the Pd atom to the tcne ligand in (I) is evident in two parameters (Kaim & Moscher-
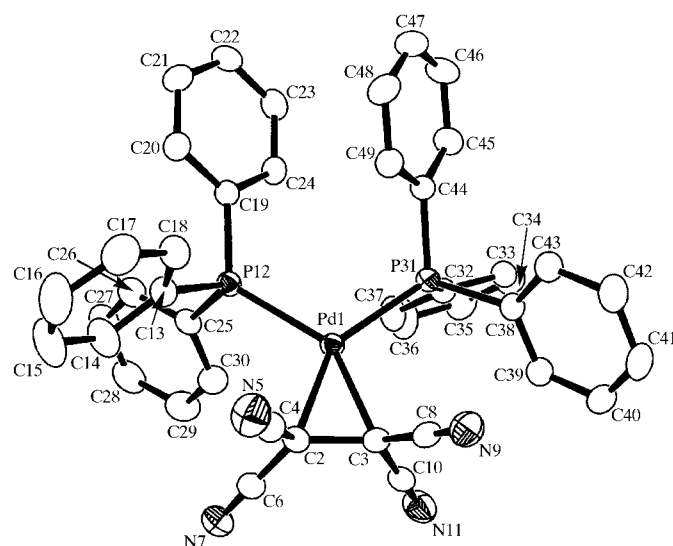

Figure 1
The molecular structure of the [Pd(PPh$_3$)$_2$(tcne)] molecule in (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

osch, 1994). First, the C2=C3 bond length of 1.488 (4) Å is substantially longer than in uncoordinated tcne [1.328 (5) and 1.344 (3) Å in the monoclinic (Chaplot *et al.*, 1991) and cubic (Little *et al.*, 1971) phases of this compound, respectively]. Second, the coordinated alkene C atoms in (I) are significantly pyramidalized. This is evidenced both by the C—C—C bond angles at the tcne ligand, which lie between 115.3 (2) and 118.0 (2)°, compared to 120° in free tcne, and by the dihedral angle of 56.34 (16)° between the least-squares planes formed by the two C(CN)$_2$ fragments (C2/C4/C6/N5/N7 and C3/C8/C10/N9/N11) of the tcne ligand. This angle is 0° in the unco-ordinated alkene. Both these parameters are within the ranges previously observed in other Pd–tcne complexes (Zagorod-nikov *et al.*, 1989; Tsubouchi *et al.*, 1994; Kranenburg *et al.*, 1997; Mashima *et al.*, 1998; van Belzen *et al.*, 1998; Canovese *et al.*, 2000) and indicate partial rehybridization of the alkene C=C bond caused by substantial Pd→tcne back-donation into the tcne π* orbitals.

The molecular structure of (I) is visually indistinguishable from that of its Pt analogue [Pt(PPh$_3$)$_2$(tcne)] (Bombieri *et al.*, 1970), and the metal–carbon distances in the two compounds are not signifcantly different. However, the Pd—P bonds in (I) are 0.039 (9)–0.041 (8) Å longer than those in the Pt compound, presumably reflecting the improved back-bonding between the phosphine ligands and the Pt 5*d* orbitals, as opposed to the Pd 4*d* orbitals. The low precision of the structure analysis of the Pt complex prevents any more detailed comparison of the two compounds.

There are two intermolecular N···H contacts of *ca* 2.5 Å in (I), which are within the sum of the van der Waals radii of H (1.2 Å) and N (1.5 Å) (Pauling, 1960) and so could correspond to weak C—H···N interactions (Table 2). There are no other noteworthy intermolecular interactions in the lattice.

Experimental

Complex (I) was prepared from Pd(PPh$_3$)$_4$ and tcne, following the literature method of Fitton & McKeon (1968). The crystal used for this study was grown from CH$_2$Cl$_2$/pentane (1:3).

Crystal data

[Pd(C$_6$N$_4$)(C$_{18}$H$_{15}$P)$_2$]·0.7CH$_2$Cl$_2$
$M_r = 818.49$
Monoclinic, $P2_1/c$
$a = 10.3363 (1)$ Å
$b = 37.2805 (4)$ Å
$c = 10.8142 (1)$ Å
$\beta = 111.1463 (7)°$
$V = 3886.57 (7)$ Å^3
$Z = 4$
$D_x = 1.399$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 29 108 reflections
$\theta = 2.7–27.5°$
$\mu = 0.69$ mm^{-1}
$T = 150 (2)$ K
Plate, yellow–orange
$0.50 \times 0.40 \times 0.13$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
Area-detector scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.724$, $T_{max} = 0.916$
29 108 measured reflections
8877 independent reflections

7450 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 27.5°$
$h = -13 \rightarrow 12$
$k = -48 \rightarrow 48$
$l = -13 \rightarrow 14$

Table 1
Selected geometric parameters (Å, °).

Pd1—C2	2.123 (3)	Pd1—P12	2.3304 (7)
Pd1—C3	2.099 (3)	Pd1—P31	2.3279 (7)
C2—Pd1—C3	41.26 (10)	C3—Pd1—P12	146.19 (8)
C2—Pd1—P12	105.18 (8)	C3—Pd1—P31	105.64 (7)
C2—Pd1—P31	146.60 (8)	P12—Pd1—P31	108.12 (2)

Table 2
Weak intermolecular C—H···N interactions (Å, °) in the structure of (I).

C—H···N	C—H	H···N	C···N	C—H···N	H···N≡C
C23^v—H23^v···N5	0.95	2.54	3.400 (4)	151	150
C40^{vi}—H40^{vi}···N9	0.95	2.49	3.436 (4)	178	106

Symmetry codes: (v) $1 + x, y, z$; (vi) $x, \frac{1}{2} - y, -\frac{1}{2} + z$.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0582P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.039$	$+ 3.3475P]$
$wR(F^2) = 0.110$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
8877 reflections	$\Delta\rho_{max} = 0.75$ e Å^{-3}
482 parameters	$\Delta\rho_{min} = -0.80$ e Å^{-3}
H-atom parameters constrained	

Following an initial refinement, high displacement parameters for the dichloromethane Cl atoms indicated disorder in the solvent. Two orientations were refined [C50A/Cl5A/Cl5B (occupany 0.5) and C50B/Cl5C/Cl5D (occupany 0.2)], giving a total solvent occupany of 0.7. The C—Cl distances were restrained to 1.75 (2) Å, and the Cl—C—Cl angle restrained to be tetrahedral by restraining the Cl···Cl distances within a given disorder component to be 2.86 (2) Å. All non-H atoms, except those of the minor solvent component, were refined anisotropically, and all H atoms were placed in calculated positions and refined using a riding model. The fixed C—H distances used were 0.95 Å for C*sp*^{2}—H and 0.99 Å for C*sp*^{3}—H. For all H atoms, U_{iso}(H) values were set to 1.2U_{eq}(C).

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: local program.

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