metal-organic compounds

A novel trinuclear palladium cluster compound: di-μ_3-chloro-tris[chloro-(triphenylphosphine-*P*)palladium] acetone solvate

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The title triangular tripalladium cluster, [Pd$_3$Cl$_5$(C$_{18}$H$_{15}$P)$_3$]$\cdot$C$_3$H$_6$O, (I), has a trigonal-bipyramidal framework of Pd$_3$(μ_3-Cl)$_2$, with the two Cl atoms in apical positions. Each Pd atom in the framework has two additional coordination sites to establish square-planar *cis*-PdL_2(μ_3-Cl)$_2$ geometry. Three P atoms are located on the same side of the plane defined by the Pd$_3$ triangle, which leads to a pseudo-C_{3v} symmetry for the core framework of Pd$_3$(μ_3-Cl)$_2$P$_3$Cl$_3$. The average Pd—Cl distance *trans* to PPh$_3$ is 2.473 (8) Å, which is significantly longer than the average Pd—Cl distance of 2.294 (4) Å for those *trans* to terminal Cl, due to the strong *trans* effect of a P atom compared with a Cl atom. Compound (I) has 49 valence electrons and shows a rhombic electron-spin resonance signal, indicating an $S = \frac{1}{2}$ ground state.

Comment

As far as we know (Allen *et al.*, 1983, 1987), only chalcogen atoms have been reported as μ_3-bridging ligands in compounds [$M_3(\mu_3$-$E)_2(L)_6$]$^{2+}$ [M = Ni, Pd; E = O, S or Se(SiMe$_3$)$_2$; L = P- or S-centred ligands or halogen anions; Ghilardi *et al.*, 1978, 1984, 1985; Carmona *et al.*, 1985; Cecconi *et al.*, 1990; Werner *et al.*, 1980; Cowan *et al.*, 1987; Fenske *et al.*, 1990] with a three-fliers-waterwheel structure. As a chalcogen-bridged system has 48 valence electrons, replacing two bridging ligands from chalcogen to halogen causes the addition of two electrons to the trimetal compound, forming a compound with 50 valence electrons. Trimetal compounds with more than 49 valence electrons are rare. To our knowledge, only those containing electronegative cyclopentadienyl (Cp) ligands in cobalt and nickel systems are known to exist (Michael *et al.*, 1990). In the course of our study of trimetal cluster chemistry (Maekawa *et al.*, 1995*a,b*), we have found a new tripalladium compound with two bridging Cl atoms, [Pd$_3$(μ_3-Cl)$_2$-

(PPh$_3$)$_3$Cl$_3$]$\cdot$(CH$_3$)$_2$CO, (I). The valence-electron count of (I) is 49. We report here the crystal structure and electron-spin resonance (ESR) study of (I).

(I)
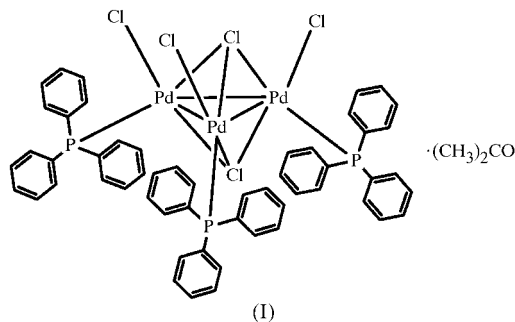
An *ORTEP*II (Johnson, 1976) view of the molecular structure of (I) together with the atom-numbering scheme is shown in Fig. 1. The core framework of Pd$_3$(μ_3-Cl)$_2$P$_3$Cl$_3$ is similar to those of chalcogen-bridged tripalladium compounds, which can be described as three square-planar PdPCl$_3$ moieties having two chloride anions in common. One of two bridging Cl atoms (Cl1) is located *trans* to all P atoms, while the other (Cl2) is located *cis*, which corresponds to a pseudo-C_{3v} symmetry for the core framework. The average Pd—Cl1 distance is 2.473 (8) Å, which is significantly longer than the average Pd—Cl2 distance of 2.294 (4) , due to the strong *trans* effect of a P atom compared to a Cl atom. The average Pd—Cl distance of 2.327 (3) Å for terminal chloride anions falls within two Pd—Cl distances for bridging chloride anions. The average Pd—P distance of 2.22 (1) Å is shorter than those reported for chalcogen-bridged tripalladium compounds [2.248 (7)–2.339 (3) Å]. The Pd$\cdots$Pd distances are 3.0817 (5), 3.0638 (4) and 3.1536 (5) Å for Pd1$\cdots$Pd2, Pd2$\cdots$Pd3 and Pd1$\cdots$Pd3, respectively. These values are similar to those reported for chalcogen-bridged tripalladium compounds [3.011 (2)–3.1814 (4) Å], indicating weak Pd$\cdots$Pd interaction.
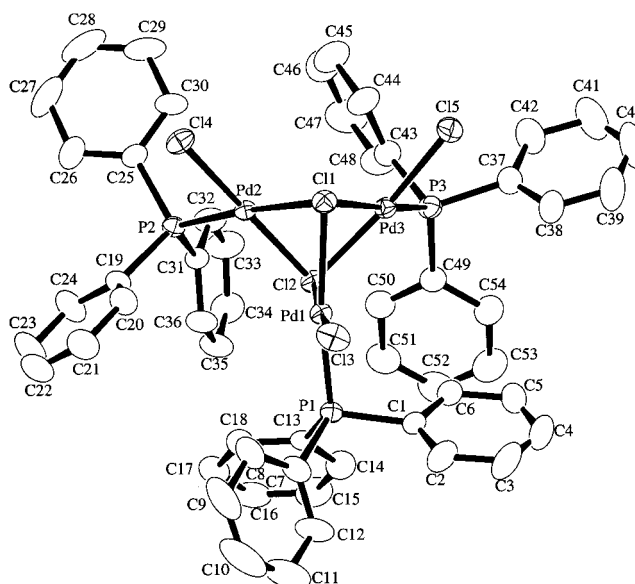
Figure 1
The molecular structure of (I) showing 30% probability displacement ellipsoids. H atoms and the (CH$_3$)$_2$CO solvate have been omitted for clarity.

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In contrast to the chalcogen-bridged trimetal compounds, (I) shows paramagnetic behaviour. The solid-state powder ESR spectrum of (I) measured at room temperature shows a rhombic pattern with $g_1 = 2.144$, $g_2 = 2.044$ and $g_3 = 1.996$. The observation of the ESR signal is consistent with the valence electron count of 49 and $S = \frac{1}{2}$.

Experimental

[Pd(PhCN)$_2$Cl$_2$] (46 mg, 0.12 mmol), PPh$_3$ (31 mg, 0.12 mmol) and rhodanine (27 mg, 0.24 mmol) as reducing agent were stirred in acetone (10 ml) under argon at room temperature. The suspension became clear during stirring. After filtration, the filtrate was transferred to glass tubes and the same amount of n-pentane was added slowly. The glass tubes were sealed and allowed to stand at room temperature. After one week, red crystals of (I) were obtained.

Crystal data

[Pd$_3$Cl$_5$(C$_{18}$H$_{15}$P)$_3$]·C$_3$H$_6$O
$M_r = 1341.42$
Triclinic, $P\bar{1}$
$a = 18.515\,(2)$ Å
$b = 14.295\,(3)$ Å
$c = 10.916\,(1)$ Å
$\alpha = 84.90\,(1)°$
$\beta = 87.874\,(9)°$
$\gamma = 77.04\,(1)°$
$V = 2803.9\,(8)$ Å^3

$Z = 2$
$D_x = 1.589$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 15.1-19.1°$
$\mu = 1.314$ mm^{-1}
$T = 296\,(1)$ K
Plate, red
$0.20 \times 0.20 \times 0.10$ mm

Data collection

Rigaku AFC-7R diffractometer
$\omega-2\theta$ scans
Absorption correction: ψ scan (North et $al.$, 1968)
  $T_{min} = 0.728$, $T_{max} = 0.877$
13 420 measured reflections
12 899 independent reflections
9622 reflections with $I > 2\sigma(I)$

$R_{int} = 0.015$
$\theta_{max} = 27.51°$
$h = -23 \rightarrow 24$
$k = 0 \rightarrow 18$
$l = -14 \rightarrow 14$
3 standard reflections
  every 150 reflections
  intensity decay: 2.4%

Refinement

Refinement on F^2
$R(F) = 0.037$
$wR(F^2) = 0.101$
$S = 1.024$
9622 reflections
625 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.6836P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.005$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ e Å^{-3}
Extinction correction: $SHELXL$97 (Sheldrick, 1997)
Extinction coefficient: 0.0005

The acetone solvate was refined as an idealized molecule.

Data collection: MSC/AFC $Diffractometer$ $Control$ $Software$ (Molecular Structure Corporation, 1993); cell refinement: MSC/AFC $Diffractometer$ $Control$ $Software$; data reduction: $TEXSAN$ (Molecular Structure Corporation & Rigaku Corporation, 1999); program(s) used to solve structure: $PATTY$ in $DIRDIF$92 (Beurskens et $al.$, 1992); program(s) used to refine structure: $TEXSAN$ and $SHELXL$97 (Sheldrick, 1997); molecular graphics: $ORTEP$II (Johnson, 1976); software used to prepare material for publication: $TEXSAN$.

Table 1
Selected geometric parameters (Å, °).

Pd1···Pd2	3.0818 (5)	Pd2—Cl1	2.4735 (9)
Pd1···Pd3	3.1537 (6)	Pd2—Cl2	2.2896 (9)
Pd2···Pd3	3.0639 (4)	Pd2—Cl4	2.328 (1)
Pd1—Cl1	2.462 (1)	Pd2—P2	2.2264 (9)
Pd1—Cl2	2.293 (1)	Pd3—Cl1	2.482 (1)
Pd1—Cl3	2.329 (1)	Pd3—Cl2	2.300 (1)
Pd1—P1	2.220 (1)	Pd3—Cl5	2.323 (1)
Pd2···Pd3	3.0639 (4)	Pd3—P3	2.238 (1)
Cl1—Pd1—Cl2	82.58 (4)	Cl2—Pd2—Cl4	173.96 (4)
Cl1—Pd1—Cl3	92.30 (4)	Cl2—Pd2—P2	95.00 (3)
Cl1—Pd1—P1	171.78 (4)	Cl4—Pd2—P2	89.97 (4)
Cl2—Pd1—Cl3	174.50 (4)	Pd2···Pd3—Cl1	51.68 (2)
Cl2—Pd1—P1	94.69 (4)	Pd2···Pd3—Cl2	47.98 (2)
Cl3—Pd1—P1	90.11 (4)	Pd2···Pd3—Cl5	124.95 (3)
Pd3···Pd2—Cl1	51.94 (3)	Pd2···Pd3—P3	121.54 (3)
Pd3···Pd2—Cl2	48.26 (3)	Cl1—Pd3—Cl2	82.01 (4)
Pd3···Pd2—Cl4	129.93 (3)	Cl1—Pd3—Cl5	90.18 (4)
Pd3···Pd2—P2	128.68 (3)	Cl1—Pd3—P3	172.31 (4)
Cl1—Pd2—Cl2	82.40 (3)	Cl2—Pd3—Cl5	171.95 (4)
Cl1—Pd2—Cl4	92.40 (3)	Cl2—Pd3—P3	95.42 (4)
Cl1—Pd2—P2	175.16 (4)	Cl5—Pd3—P3	92.08 (5)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1241). Services for accessing these data are described at the back of the journal.

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