

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (2)

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	B _{eq}
Pt(1)	0	0	0	1.96 (1)
Cl(1)	0.2563 (3)	0.0228 (2)	0.1491 (3)	3.82 (5)
S(1)	0.1400 (3)	-0.0297 (2)	-0.2270 (2)	2.86 (4)
C(1)	0.3077 (9)	-0.1367 (7)	-0.1855 (10)	3.9 (2)
C(2)	0.2128 (13)	-0.2371 (7)	-0.1270 (10)	4.4 (2)
C(3)	0.0483 (11)	-0.2442 (6)	-0.2345 (11)	3.7 (2)
C(4)	0.0508 (9)	-0.1458 (6)	-0.3523 (9)	3.0 (2)
C(5)	0.1873 (11)	-0.1635 (7)	-0.4675 (10)	4.0 (2)
C(6)	0.3542 (12)	-0.1572 (9)	-0.3607 (13)	5.4 (3)

Table 4. Selected geometric parameters (Å, °) for (2)

Pt(1)—Cl(1)	2.300 (2)	Pt(1)—S(1)	2.286 (2)
S(1)—C(1)	1.841 (8)	S(1)—C(4)	1.819 (7)
Cl(1)—Pt(1)—Cl(1 ¹)	180.0	C(1)—S(1)—C(4)	80.4 (3)
Cl(1)—Pt(1)—S(1)	89.25 (8)	S(1)—Pt(1)—S(1 ¹)	180.0
Pt(1)—S(1)—C(1)	110.3 (3)	Pt(1)—S(1)—C(4)	112.9 (2)

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

The structures were solved by the heavy-atom method and refined by full-matrix least-squares calculations with non-H atoms anisotropic. Allowance was made for anomalous dispersion (Ibers & Hamilton, 1964).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988) for (1) and *Enraf-Nonius CAD-4 Diffractometer Controlling Software* (Schagen, Straver, van Meurs & Williams, 1988) for (2). Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Structure solution: *DIRDIF PATTY* (Beurskens *et al.*, 1992). Structure refinement: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Preparation of material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1033). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[M(CNMe)₄](PF₆)₂ (M = Pt, Pd)

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Abstract

The compounds tetrakis(methyl isocyanide)platinum bis(hexafluorophosphate), [Pt(CNMe)₄](PF₆)₂, and tetrakis(methyl isocyanide)palladium bis(hexafluorophosphate), [Pd(CNMe)₄](PF₆)₂, are isostructural; both crystallize with a tetragonal unit cell with a simple ionic packing arrangement related to that of NaCl.

Comment

No simple salts of tetrakis(methyl isocyanide)-transition metal complexes have been structurally characterized, apart from [Cu(CNMe)₄]BF₄, in which the Cu atom has a tetrahedral arrangement of CNMe ligands (Spek, 1982). The structures of [M(CNMe)₄](PF₆)₂ [M = Pt (1) and Pd (2)] were determined to allow a comparison of the cation geometry with that previously found in complex salts of general formula [M(CNMe)₄][M'(mnt)₂]_n {mnt = [S₂C₂(CN)₂]²⁻; M, M' = Pt, Pd; n = 1 or 2} (Connelly, Crossley, Orpen & Salter, 1992). Both compounds (1) and (2) crystallize in the tetragonal space group *P4/mbm* and have essentially identical structures.

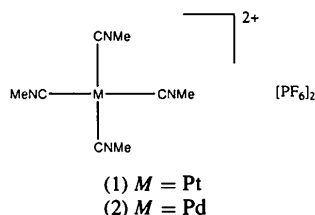


Fig. 1 shows a perspective view of (2); the same numbering scheme was used for (1). The contents of one unit cell of (2) are illustrated in Fig. 2, in which the H atoms have been omitted for clarity.

In each structure, as a consequence of the crystallographic symmetry, the four CNMe ligands are crystallographically equivalent and the cations (excepting the H atoms) are planar, having site symmetry mmm . The dimensions of the $[M(\text{CNMe})_4]^{2+}$ cations are similar (bond lengths within 3σ) to those in the complex salts referred to above (Connelly, Crossley, Orpen & Salter, 1992). The CNMe ligands are almost linear, with $M-C-N = 179.0(7)$ for (1) and $178.0(4)^\circ$ for (2), and $C-N-Me = 176.7(8)$ for (1) and $178.0(5)^\circ$ for (2). There are two distinct $(\text{PF}_6)^-$ groups per structure, with site symmetries $4/m$ and mmm for P(1) and P(2), respectively. As a result, the $F-P(1)-F$ angles are exactly 90 or 180° .

In both structures, the ions are arranged such that the metal atoms occupy positions $(0, \frac{1}{2}, 0)$ and $(\frac{1}{2}, 0,$

$0)$ (Wyckoff site d), the C and N atoms lie on mirror planes (Wyckoff site k), and a P atom, P(1), of one of the $(\text{PF}_6)^-$ groups is found at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ (Wyckoff site a), *i.e.* the $(x, y, 0)$ plane contains a layer of alternate cations and anions. In between this plane and its equivalent $(x, y, 1)$ plane, is a layer containing the second type of $(\text{PF}_6)^-$ group, with the P atoms [P(2)] at positions $(0, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, 0, \frac{1}{2})$ (Wyckoff site c), but with the $(0, 0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ sites (Wyckoff site b) unoccupied. This structure is based, therefore, on the NaCl arrangement, but with cations absent from each alternate layer along the z axis. This appears to be a new type of crystal packing for AB_2 -type salts (Wells, 1975). The vacant b sites have short contacts with four F atoms [all to F(3) 3.181 Å]. As expected, there are no significant metal-metal interactions and no linear stacked structure, in contrast to those found for salts of $[M(\text{CNMe})_4]^{2+}$ with complex planar anions (Connelly, Crossley, Orpen & Salter, 1992). The closest inter-metal distances are equal to $(a/2^{1/2})$, *i.e.* Pt-Pt = 6.713 Å for (1) and Pd-Pd = 6.671 Å for (2). Within the $(x, y, 0)$ planes, the anions and cations are linked by four weak $M \cdots F(2)$ contacts of 3.421 in (1) and 3.385 Å in (2). The $M \cdots F$ contacts for the other PF_6 anion are weaker [4.085 in (1) and 4.128 Å in (2)]. The latter PF_6 shows the larger displacement parameters in both (1) and (2).

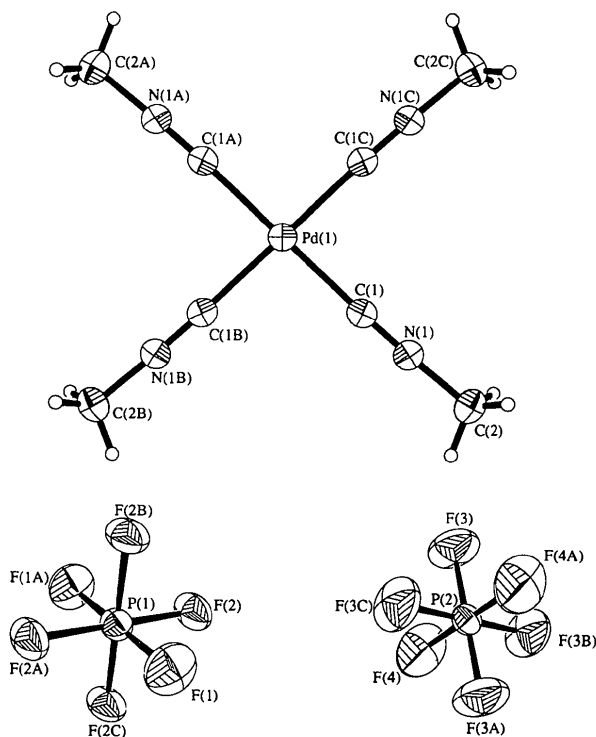


Fig. 1. The structure of $[\text{Pd}(\text{CNMe})_4](\text{PF}_6)_2$, (2). Ellipsoids are drawn to enclose 30% probability density. Atoms with suffixes A, B or C are symmetry related to unsuffixed atoms (see text).

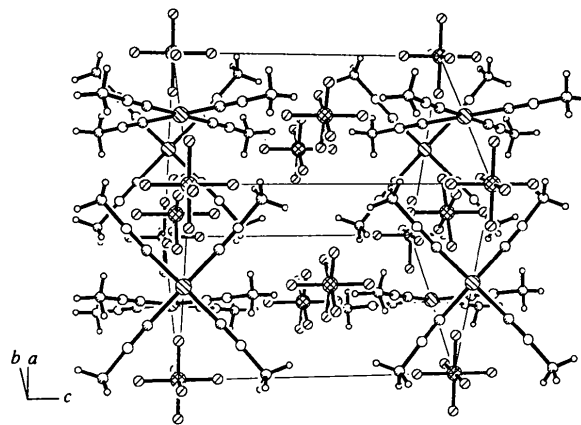


Fig. 2. A view of the unit-cell contents of $[\text{Pd}(\text{CNMe})_4](\text{PF}_6)_2$, (2). H atoms are omitted for clarity.

Experimental

Colourless block-shaped crystals of (1) and (2) were grown by diffusion of diethyl ether into solutions of the complexes in acetonitrile.

Compound (1)

Crystal data

$[\text{Pt}(\text{C}_2\text{H}_3\text{N})_4](\text{PF}_6)_2$
 $M_r = 649.2$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$

Tetragonal
P4/mbm
a = 9.494 (1) Å
c = 11.203 (2) Å
V = 1009.8 (3) Å³
Z = 2
D_x = 2.135 Mg m⁻³

Cell parameters from 36 reflections
 $\theta = 5\text{--}15^\circ$
 $\mu = 7.213 \text{ mm}^{-1}$
T = 293 K
 Regular block
 0.35 × 0.3 × 0.3 mm
 Colourless

Tetragonal
P4/mbm
a = 9.434 (2) Å
c = 11.270 (3) Å
V = 1003.0 (4) Å³
Z = 2
D_x = 1.856 Mg m⁻³

Cell parameters from 21 reflections
 $\theta = 5\text{--}15^\circ$
 $\mu = 1.17 \text{ mm}^{-1}$
T = 293 K
 Regular block
 0.65 × 0.45 × 0.45 mm
 Colourless

Data collection

Siemens *P3m* diffractometer
 $\omega/2\theta$ scans
 Absorption correction:
 empirical [azimuthal ($\equiv\psi$) scan]
T_{min} = 0.187, *T_{max}* = 0.276
 1474 measured reflections
 670 independent reflections
 454 observed reflections
 [*I* > 2σ(*I*)]

R_{int} = 0.0432
 $\theta_{\text{max}} = 27.5^\circ$
 $h = 0 \rightarrow 12$
 $k = 0 \rightarrow 12$
 $l = 0 \rightarrow 14$
 3 standard reflections monitored every 50 reflections
 intensity decay: 2%

Data collection

Siemens *P3m* diffractometer
 $\omega/2\theta$ scans
 Absorption correction:
 empirical [azimuthal ($\equiv\psi$) scan]
T_{min} = 0.385, *T_{max}* = 0.455
 1138 measured reflections
 510 independent reflections
 424 observed reflections
 [*I* > 2σ(*I*)]

R_{int} = 0.0144
 $\theta_{\text{max}} = 25^\circ$
 $h = 0 \rightarrow 11$
 $k = 0 \rightarrow 11$
 $l = 0 \rightarrow 13$
 3 standard reflections monitored every 50 reflections
 intensity decay: 1%

Refinement

Refinement on *F*
R = 0.0287
wR = 0.0339
S = 1.20
 454 reflections
 46 parameters
 H atoms riding with C—
 H = 0.96 Å and *U*(H) = 0.08 Å²

$w = 1/[\sigma_c^2(F) + 0.0005F^2]$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.53 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -1.27 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Refinement

Refinement on *F*
R = 0.0289
wR = 0.0466
S = 1.817
 424 reflections
 46 parameters
 H atoms riding with C—
 H = 0.96 Å and *U*(H) = 0.08 Å²

$w = 1/[\sigma_c^2(F) + 0.0005F^2]$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.54 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.46 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (1)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Pt(1)	0	-1/2	0	0.042 (1)
P(1)	0	0	0	0.053 (1)
P(2)	1/2	0	1/2	0.055 (1)
F(1)	0	0	0.1421 (9)	0.114 (3)
F(2)	-0.0777 (7)	-0.1481 (6)	0	0.087 (3)
F(3)	0.5030 (7)	-0.1648 (10)	1/2	0.162 (6)
F(4)	1/2	0	0.3645 (10)	0.226 (10)
N(1)	0.1678 (5)	<i>x</i> - 1/2	0.1896 (6)	0.055 (2)
C(1)	0.1072 (6)	<i>x</i> - 1/2	0.1227 (7)	0.047 (2)
C(2)	0.2508 (6)	<i>x</i> - 1/2	0.2711 (10)	0.088 (4)

Table 2. Selected geometric parameters (Å, °) for (1)

Pt(1)—C(1)	1.990 (8)	P(2)—F(4)	1.518 (11)
P(1)—F(1)	1.592 (11)	N(1)—C(1)	1.107 (10)
P(1)—F(2)	1.588 (6)	N(1)—C(2)	1.440 (12)
P(2)—F(3)	1.565 (10)		
C(1)—Pt(1)—C(1 ⁱ)	92.7 (4)	F(3)—P(2)—F(3 ⁱⁱ)	92.1 (5)
C(1)—N(1)—C(2)	176.7 (8)	Pt(1)—C(1)—N(1)	179.0 (7)

Symmetry code: (i) $-\frac{1}{2} - y, -\frac{1}{2} - x, z$; (ii) $\frac{1}{2} + y, x - \frac{1}{2}, 1 - z$.

Compound (2)

Crystal data

[Pd(C₂H₃N)₄](PF₆)₂
M_r = 560.5

Mo *K*α radiation
 $\lambda = 0.71073 \text{ Å}$

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Pd(1)	0	-1/2	0	0.043 (1)
P(1)	0	0	0	0.054 (1)
P(2)	1/2	0	1/2	0.054 (1)
F(1)	0	0	0.1397 (5)	0.108 (2)
F(2)	-0.0761 (3)	-0.1494 (3)	0	0.082 (1)
F(3)	0.5043 (5)	-0.1639 (6)	1/2	0.150 (3)
F(4)	1/2	0	0.3662 (6)	0.193 (5)
N(1)	0.1688 (3)	<i>x</i> - 1/2	0.1887 (3)	0.060 (1)
C(1)	0.1067 (3)	<i>x</i> - 1/2	0.1223 (4)	0.050 (1)
C(2)	0.2515 (4)	<i>x</i> - 1/2	0.2710 (7)	0.087 (2)

Table 4. Selected geometric parameters (Å, °) for (2)

Pd(1)—C(1)	1.981 (4)	P(2)—F(4)	1.507 (6)
P(1)—F(1)	1.574 (6)	N(1)—C(1)	1.117 (6)
P(1)—F(2)	1.582 (3)	N(1)—C(2)	1.441 (8)
P(2)—F(3)	1.546 (5)		
C(1)—Pd(1)—C(1 ⁱ)	91.8 (3)	F(3)—P(2)—F(3 ⁱⁱ)	93.0 (4)
C(1)—N(1)—C(2)	178.0 (5)	Pd(1)—C(1)—N(1)	178.0 (4)

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

Computations were performed using the *SHELXTL-Plus* package (Sheldrick, 1990).

We thank the SERC for financial support.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: MU1154). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-Chloromethylbis(triphenylarsine)platinum(II)

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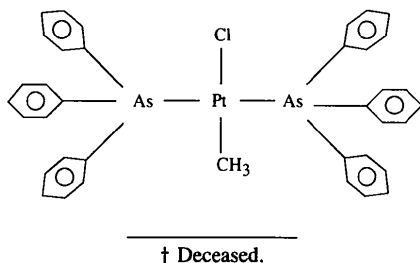
(Received 24 October 1994; accepted 13 December 1994)

Abstract

The title compound, *trans*-chloromethylbis(triphenylarsine)platinum(II), *trans*-[PtCl(CH₃)(C₁₈H₁₅As)₂], is isomorphous and isostructural with one of the two known crystalline forms of the corresponding triphenylphosphine analogue.

Comment

trans-Bis(triphenylarsine)chloromethylplatinum(II), (I), is one of the few bis(AsX₃)–platinum(II) complexes (where X is alkyl or aryl) isolated to date. It is isomorphous and isostructural with the analogous bis(triphenylphosphine) complex described by Bardi & Piazzesi (1981). However, a second crystalline form of the bis(triphenylphosphine) complex has recently been shown to exist (Otto, Roodt & Leipoldt, 1995).



The *trans* influence of the methyl group is marginally less pronounced in (I) than it is in the bis(PPh₃) complex; Pt–Cl bond distances of 2.431 (3) and 2.415 (5) Å found in the above mentioned studies of the bis(PPh₃) complex may be compared with the slightly shorter distance of 2.410 (2) Å obtained from this study. This is in agreement with the electronic influence PPh₃ > AsPh₃ (Cheeseman, Odell & Raethel, 1968). The Pt–Cl bond is shorter than that of 2.437 (2) Å found in *trans*-[PtClMe(AsMe₃)₂(η²-F₃CC₂CF₃)] (Davies, Puddephatt & Payne, 1972). The larger steric demand of the methyl group (C1) compared with that of the chloro ligand is illustrated both by the As1–Pt–As2 angle [176.30 (3)°], which deviates significantly from 180°, and by the C11–As1–Pt and C41–As2–Pt angles, which are *ca* 10° greater than the ideal tetrahedral angle of 109.5°.

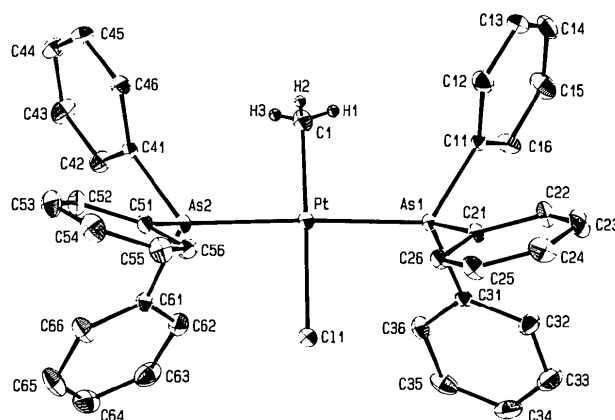


Fig. 1. ORTEP (Johnson, 1976) view of the title structure showing the atom-numbering scheme and 30% displacement ellipsoids. The phenyl H atoms are omitted for clarity.

Experimental

The title complex was prepared by the addition of an excess of [As(C₆H₅)₃] (1.0 g, 3.3 mmol) in acetone (20 ml) to *trans*-[PtCl(CH₃){S(CH₃)₂}₂] (500 mg, 1.35 mmol) (Scott & Puddephatt, 1983) in acetone (10 ml). The solution was stirred for 30 min at room temperature. Filtration and recrystallization from benzene gave the desired product (1.05 g, yield >90%). ¹H NMR (CDCl₃): δ(CH₃) 0.07 p.p.m., ²J(PtH) 78 Hz. IR (KBr): ν(Pt–Cl) 324 cm⁻¹. The density *D_m* was measured by flotation in NaI/H₂O

Crystal data

[PtCl(CH₃)(C₁₈H₁₅As)₂]
M_r = 858.01
 Monoclinic
*P*2₁/*n*
a = 11.749 (1) Å
b = 23.342 (2) Å
c = 12.644 (2) Å
 β = 111.32 (1)°

Mo Kα radiation
 λ = 0.71073 Å
 Cell parameters from 25
 reflections
 θ = 17–20°
 μ = 6.484 mm⁻¹
T = 293 (2) K
 Diamond shape