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Carbonatobis(triethylphosphine)platinum(II)

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Abstract. $[Pt(C_6H_{15}P)_2(CO_3)]$, $M_r = 491{\cdot}42$, monoclinic, $P2_1/n$, $a = 12{\cdot}653\,(2)$, $b = 11{\cdot}576\,(2)$, $c = 12{\cdot}733\,(2)$ Å, $\beta = 105{\cdot}72\,(1)°$, $V = 1795\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}82$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 80{\cdot}7$ cm^{-1}, $F(000) = 960$, $T = 294\,(1)$ K, $R = 0{\cdot}028$ for 2814 unique reflections with $F^2 > 3\sigma(F^2)$ of 3698 total unique data. Principal bond lengths (Å) and angles (°) are: Pt—P 2·241 (2), 2·225 (1); Pt—O 2·061 (4), 2·076 (4); O—C 1·310 (7), 1·326 (7); C=O 1·223 (6); P—Pt—P 99·49 (5); P—Pt—O 101·3 (1), 95·5 (1); O—Pt—O 63·8 (2); O—C—O 112·2 (4).

Introduction. In 1983 it was reported (Robertson & Tucker, 1983) that attempts to crystallize *trans*-$[PtH_2(P^iPr_3)_2]$ from 2-methoxyethanol in air led to formation of $[Pt(CO_3)(P^iPr_3)_2]$ (1), whose structure was determined by single-crystal X-ray diffraction methods. Prior to this it had been shown (Cariati, Mason, Robertson & Ugo, 1967, and references therein) that attempts to prepare $[PtH_2(PPh_3)_2]$ led to formation of $[Pt(CO_3)(PPh_3)_2]$ (2), whose structure had similarly been determined by X-ray diffraction methods. Reports of the structural characterization of these two carbonate complexes are the only ones extant for members of the $[Pt(CO_3)L_2]$ family.

Recently we have attempted to grow crystals of the complex *trans*-$[PtH(CH_2CN)(PEt_3)_2]$, prepared in a fashion directly analogous to the known PPh_3 complex (Ros, Michelin, Bataillard & Roulet, 1977), for characterization by X-ray and neutron diffraction analyses. Repeated crystallization of an authentic sample of *trans*-$[PtH(CH_2CN)(PEt_3)_2]$ (see *Experimental*) from acetonitrile/heptane led to the formation of colorless square-plate crystals which were shown to be the title compound (3) whose structure we report here.

Experimental. The complex *trans*-$[PtH(CH_2CN)(PEt_3)_2]$ was prepared in a fashion directly analogous to that used in the synthesis of the known PPh_3 complex (Ros *et al.*, 1977). Thus, *trans*-$[PtHCl(PEt_3)_2]$ (66·2 mg) was treated with NaH (8 mg, Alfa, 50% oil dispersion) in acetonitrile solution (30 ml) under a nitrogen atmosphere. Removal of the solution under vacuum and spectroscopic examination showed quantitative formation of *trans*-$[PtH(CH_2CN)(PEt_3)_2]$.

Table 1. *Positional parameters with e.s.d.'s in parentheses*

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

	x	y	z	B_{eq}(Å^2)
Pt	0·84121 (2)	0·19269 (2)	0·59000 (2)	2·557 (4)
P1	0·7414 (1)	0·3512 (1)	0·5959 (1)	2·94 (3)
P2	0·8011 (1)	0·1682 (1)	0·4102 (1)	3·00 (3)
O1	0·9456 (3)	0·0530 (3)	0·6279 (3)	3·38 (8)
O2	0·9120 (4)	0·1629 (4)	0·7549 (3)	3·80 (9)
O3	1·0337 (4)	0·0172 (4)	0·8017 (4)	4·5 (1)
C1	0·5951 (5)	0·3401 (5)	0·5523 (5)	3·6 (1)
C2	0·5490 (6)	0·2314 (7)	0·5890 (7)	6·4 (2)
C3	0·7747 (5)	0·4774 (5)	0·5260 (5)	4·0 (1)
C4	0·7191 (6)	0·5883 (5)	0·5423 (6)	5·4 (2)
C5	0·7679 (6)	0·3949 (6)	0·7380 (5)	4·5 (1)
C6	0·8861 (7)	0·4334 (7)	0·7927 (6)	6·1 (2)
C7	0·7982 (6)	0·0134 (5)	0·3853 (5)	4·3 (1)
C8	0·7101 (7)	−0·0483 (6)	0·4242 (7)	6·5 (2)
C9	0·9056 (7)	0·2204 (7)	0·3497 (6)	7·4 (2)
C10*A*	0·950 (1)	0·330 (1)	0·370 (1)	5·1 (3)
C10*B*	1·005 (1)	0·241 (2)	0·402 (1)	7·1 (4)
C11	0·6743 (6)	0·2231 (6)	0·3209 (6)	4·9 (2)
C12*A*	0·6481 (8)	0·1848 (8)	0·2032 (7)	2·4 (2)
C12*B*	0·664 (1)	0·313 (2)	0·400 (2)	8·8 (6)
C13	0·9670 (5)	0·0727 (5)	0·7328 (4)	3·1 (1)

Table 2. *Distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Pt—P1	2·241 (2)	P2—C9	1·807 (9)
Pt—P2	2·225 (1)	P2—C11	1·812 (7)
Pt—O1	2·061 (4)	O1—C13	1·310 (7)
Pt—O2	2·076 (4)	O2—C13	1·326 (7)
P1—C1	1·788 (6)	O3—C13	1·223 (6)
P1—C3	1·818 (6)	C1—C2	1·51 (1)
P1—C5	1·821 (7)	C3—C4	1·505 (9)
P2—C7	1·819 (6)	C5—C6	1·53 (1)
		C7—C8	1·52 (1)

P1—Pt—P2	99·49 (5)	Pt—P2—C9	114·1 (2)
P1—Pt—O1	165·1 (1)	Pt—P2—C11	121·2 (3)
P1—Pt—O2	101·3 (1)	C7—P2—C9	103·7 (4)
P2—Pt—O1	95·5 (1)	C7—P2—C11	105·3 (3)
P2—Pt—O2	159·2 (1)	C9—P2—C11	104·0 (4)
O1—Pt—O2	63·8 (2)	Pt—O1—C13	92·5 (3)
Pt—P1—C1	118·5 (2)	Pt—O2—C13	91·4 (3)
Pt—P1—C3	115·7 (2)	P1—C1—C2	114·7 (4)
Pt—P1—C5	107·9 (2)	P1—C3—C4	116·0 (5)
C1—P1—C3	105·4 (3)	P1—C5—C6	115·2 (6)
C1—P1—C5	103·0 (3)	P2—C7—C8	112·9 (5)
C3—P1—C5	105·1 (3)	O1—C13—O2	112·2 (4)
Pt—P2—C7	107·1 (2)	O1—C13—O3	123·5 (5)
		O2—C13—O3	124·2 (5)

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^{31}P NMR (C_6D_6 solution; chemical shift relative to external 85% phosphoric acid): $\delta = 18{\cdot}8$ p.p.m., ^1J(Pt,P) = 2737 Hz; ^1H NMR (C_6D_6 solution, chemical shift relative to internal tetramethylsilane, hydride region only): $\delta = -8{\cdot}7$ p.p.m.; ^1J(Pt,H) = 808 Hz; ^2J(P,H) = 18 Hz; ^3J(H,H) = 3 Hz. An authentic sample of *trans*-[PtH(CH_2CN)(PEt_3)$_2$] was dissolved in heptane/acetonitrile (1:2 *v*/*v*) and slowly evaporated by passing a gentle stream of nitrogen over the solution for one week. Colorless square-plate crystals suitable for X-ray analysis were obtained and shown to be [Pt(CO_3)(PEt_3)$_2$]. Crystal $0{\cdot}35 \times 0{\cdot}35 \times 0{\cdot}20$ mm; Enraf–Nonius CAD-4 computer-controlled κ-axis diffractometer, graphite monochromator; cell dimensions from 25 reflections, $24 < 2\theta < 28°$; ω–2θ scan type; relative transmission coefficients, range 0·402–0·999; max. $2\theta = 52°$; h −1 to 15, k −1 to 14, l −15 to 15; three standard reflections, average decay 9·3%, intensities adjusted accordingly; 4628 data, 3698 unique, 884 unobserved, $R_{\rm int} = 0{\cdot}020$; structure solved by Patterson and Fourier methods; refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 4F_o^2/\sigma^2(F_o)^2$, 190 parameters; H atoms refined as riding atoms with fixed isotropic thermal parameters, anisotropic thermal parameters for non-H atoms; final $R = 0{\cdot}028$, $wR = 0{\cdot}037$; maximum shift to e.s.d. = 0·66; max. and min. of ΔF synthesis 1·01 and −0·86 e Å^{-3}; e.s.d. of observations of unit weight = 1·33, atomic scattering factors for neutral Pt, P, O, C, and spherically bonded H atoms from *International Tables for X-ray Crystallography* (1974); anomalous-dispersion effects were included in F_c (Ibers & Hamilton, 1964); values of f' and f'' from *International Tables for X-ray Crystallography* (1974); computer programs *SDP*/VAX (Frenz, 1978).

The C atoms C10 and C12 were found to be disordered and therefore were refined as atomic positions C10*A*, C10*B* and C12*A*, C12*B* respectively with *A* and *B* having occupancies of 0·5 C atoms each. C10*B* and C12*B* have been excluded from Fig. 1 for clarity.

Discussion. Final atomic coordinates for non-H atoms are listed in Table 1 and principal bond lengths and angles are listed in Table 2.* The atom-numbering scheme is shown in Fig. 1.

The geometry about the Pt center in (3) is distorted square planar. The Pt—P bond lengths in (3) [2·241 (2), 2·225 (1) Å] are comparable to those of the PPh_3 analog (2) (mean = 2·244 Å) but are shorter than the two equivalent bond lengths measured for the P^iPr_3 complex (1) [2·2626 (7) Å]. Using Tolman's electronic and steric parameters (Tolman, 1977) for comparative purposes shows that P^iPr_3 and PEt_3 are electronically very similar ($\nu = 2059{\cdot}2$ and $2061{\cdot}7$ cm^{-1} respectively) but sterically very different ($\theta = 160$ and 132° respectively) implying that the increased Pt—P bond length in (1) compared with (3) is a result of steric crowding of the more bulky P^iPr_3 ligand. It is less meaningful to compare (2) and (3) since the PPh_3 ligand differs from the PEt_3 ligand both electronically and sterically ($\nu = 2068{\cdot}9$ cm^{-1} and $\theta = 145°$ for PPh_3). The equivalent Pt—O bond lengths in (1) [2·060 (2) Å] are similar to the mean Pt—O bond length in (2) (2·060 Å) and to the Pt—O bond lengths found for (3) [2·061 (4), 2·076 (4) Å]. While the O—Pt—O angles in (1) [64·2 (1)°], (2) [63·4 (4)°] and (3) [63·8 (2)°] are very similar, differences are apparent in the P—Pt—P angles [(1), 108·04 (4); (2), 98·6 (2); (3), 99·49 (5)°], no doubt a result of the higher steric bulk of the P^iPr_3 ligand in (1) compared to the less demanding PPh_3 and PEt_3 ligands in (2) and (3) respectively.

The geometry of the carbonato ligand in (3) is unexceptional and the bond lengths and angles associated with this ligand are comparable with those of the carbonato group in (1). Similarly, the bond lengths and angles of the PEt_3 ligands of (3) are comparable to those found in other triethylphosphine Pt^{II} complexes (Hartley, 1973, and references therein).

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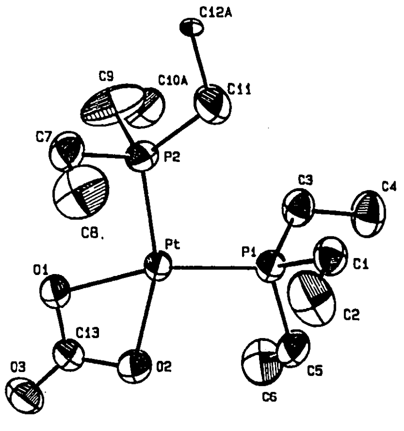

Fig. 1. *ORTEP* (Johnson, 1965) drawing showing the atom-numbering scheme and 50% probability ellipsoids: C10*A* and C12*A* each represent one of two sites with assumed occupancy of 0·5.

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* Lists of structure factors, anisotropic thermal parameters, calculated hydrogen positions, distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43954 (48 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure de Complexe Tétrathiafulvalène–Diméthyl-6,7 Tetracyano-11,11,12,12 Naphtoquinodiméthane-1,4 (TTF–DMTCNNQ)

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Abstract. 2,2′-Bi-1,3-dithiolylidene–6,7-dimethyl-1,4-naphthalenediylidenebis(malononitrile), $C_{18}H_{10}N_4.C_6H_4S_4$, $M_r = 626{\cdot}73$, triclinic, $P\bar{1}$, $a = 10{\cdot}499$ (4), $b = 7{\cdot}239$ (4), $c = 16{\cdot}879$ (5) Å, $\alpha = 86{\cdot}08$ (4), $\beta = 112{\cdot}26$ (3), $\gamma = 107{\cdot}15$ (3)°, $V = 1133$ (1) Å^3, $Z = 4$, $D_m = 3{\cdot}69$ (2), $D_x = 3{\cdot}675$ Mg m^{-3}, $\lambda(\text{Cu } K\bar{\alpha}) = 1{\cdot}5418$ Å, $\mu = 3{\cdot}853$ mm^{-1}, $F(000) = 500$, $T = 298$ K, final $R = 0{\cdot}065$ for 2826 observed reflections. The bond lengths and angles of TTF agree with those of the uncomplexed molecule, but the molecule has a boat conformation and not the chair of the free molecule. DMTCNNQ has similar bond lengths to the uncomplexed non-methylated molecule (TCNNQ), indicating there is no charge transfer with TTF. DMTCNNQ has a less-marked boat conformation than TCNNQ with the $C(CN)_2$ groups twisted around the methylene bonds. Intra- and intermolecular interactions and the alternate donor–acceptor structure in the packing explain the zero conductivity of this compound.

Introduction. Depuis les résultats de Kistenmacher, Phillips & Cowan (1974) sur le complexe TTF–TCNQ, de nombreux travaux ont été effectués sur cette famille de '*métaux organiques*'. Dans le cadre d'une étude des relations structure–conductivité nous avons été amené à synthétiser ce complexe du tétrathiafulvalène (TTF) et du diméthyl-6,7 tétracyano-11,11,12,12 naphtoquinodiméthane-1,4 (DMTCNNQ).

Partie expérimentale. Complexe obtenu par précipitation lente d'une solution de chloroforme contenant du TTF et du DMTCNNQ, recristallisé dans le chloroforme. Cristal en forme d'aiguille parallélépipédique de couleur rouge 0,70 × 0,22 × 0,05 mm, D_m mesurée par flottaison. Diffractomètre Enraf–Nonius CAD-3, balayage θ–2θ. Paramètres de la maille obtenus à partir de 20 réflexions avec $14 \leq \theta \leq 58°$. 3353 réflexions indépendantes mesurées ($\theta \leq 60°$; $\sin\theta/\lambda \leq 0{,}561$ Å^{-1}), 2828 observées [$I > 2{,}5\sigma(I)$], 525 inobservées, h −11–11, k −8–8, l 0–18. Pas de correction d'absorption. Réflexion de référence 3,6,$\overline{10}$ mesurée toute les 60 réflexions, pas de variation significative (3%). Structure déterminée par les méthodes directes (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) et affinée par moindres carrés avec matrice complete (*SHELX*76; Sheldrick, 1976), quantité minimisée $\sum(|F_o| - |F_c|)^2$ sans pondération. Hydrogènes déterminés par synthèse Fourier différence exception faite de H(2) et H(613) placés en position théorique. Affinement anisotrope pour les atomes lourds, pas d'affinement pour les atomes d'hydrogène. Valeurs finales de $R = 0{,}065$; $wR = 0{,}065$; $w = 1$; $(\Delta/\sigma)_{\max}$ du dernier affinement $= 0{,}77$. Pour le dernier calcul de synthèse Fourier différence $(\Delta\rho)_{\max} = 0{,}54$, $(\Delta\rho)_{\min} =$

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