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Cairns *et al.*, 1977]. The facile synthesis of the complex [Pd(CH₂CN)₂(PPh₃)₂] from [PdCl₂(PPh₃)₂] and LiCH₂CN provides access to a range of aggregation and degradation products, including a ligand-free [Pd(CH₂CN)₂] complex (Pracejus *et al.*, 1976). One anomalous result was observed in a study into the formation of platinum dicarboxylate complexes. The reaction of [Pt(CO₃)(PPh₃)₂] with PhC≡CCO₂H was found to produce the bis(phenylalkynyl) complex *cis*-[Pt(C≡CPh)₂(PPh₃)₂] by loss of CO₂ from both the carbonate and carboxylate groups (Burrows *et al.*, 1997).

The platinum centre of (I) shows the expected four-coordinate square-planar environment, with the phosphine ligands in a *cis* arrangement. The P1—Pt—P2 bond angle is slightly more obtuse [98.09(6)°] than perfect square-planar coordination, while the C2—Pt—C4 and C4—Pt—P2 bond angles have closed up [85.3(3) and 85.6(2)°, respectively]. The remaining bond angle (C2—Pt—P1) is near ideal at 90.9(2)°. Steric considerations clearly give rise to these distortions from regular geometry. The Pt—C bond lengths [2.104(7) and 2.138(7) Å for Pt—C2 and Pt—C4, respectively] are comparable with, if fractionally longer than, those in the related [Pt(CH₂Cl)₂L₂] complexes [L₂ = bis(diphenylphosphino)methane (dppm) or (2*S*,4*S*)-Ph₂CHMeCH₂CHMePPh₂ (*S,S*-skewphos)] [2.069(8)–2.109(10) Å; Alcock *et al.*, 1990; Bergamini *et al.*, 1993].

The interesting feature of complex (I) is the orientation of the cyanomethyl ligands. The ligands have

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cis-Bis(cyanomethyl)bis(triphenylphosphine)platinum(II)–dichloromethane (1/0.6)

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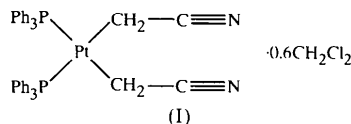
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Abstract

The cyanomethyl ligands of the title complex, *cis*-[Pt(CH₂CN)₂(PPh₃)₂].0.6CH₂Cl₂, adopt a *syn* geometry. The Pt—C bond lengths have an average value of 2.121(17) Å, and the C—Pt—C bond angle is 85.3(3)°.

Comment

Silver(I) oxide promotes the synthesis of a wide range of novel metallacycles (Henderson *et al.*, 1994; Dinger & Henderson, 1998). While attempting to synthesize metallalactone complexes using cyanoacetic acid and *cis*-[PtCl₂(PPh₃)₂], we observed instead a novel decarboxylation reaction giving the title compound, (I).



The structure of only one other bis(cyanomethyl) complex, [Ir(CH₂CN)₂(CO)₂][(Ph₃P)₂N], has been reported (Porta *et al.*, 1990). Reactions of platinum(II) hydroxo complexes with CH₃CN, some in the presence of silver(I) oxide, gave *cis*-[Pt(CH₂CN)(X)L₂] complexes [X = cyclohexene, OH, Cl or CH₃, and L₂ = Ph₂PCH₂CH₂PPh₂ (dpppe); Arnold & Bennett, 1980;

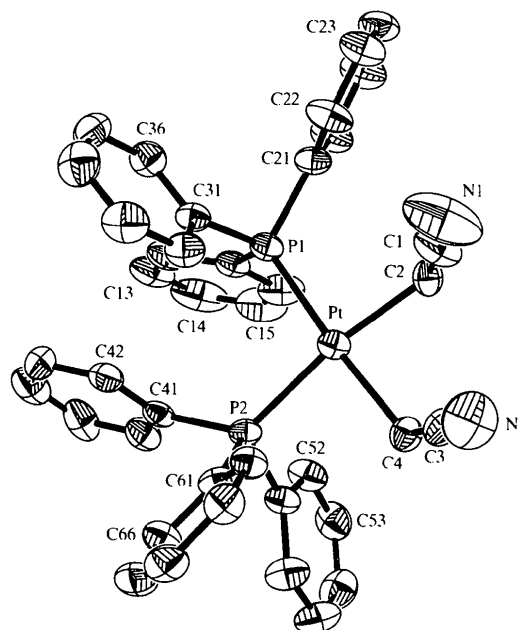


Fig. 1. The molecular structure of complex (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

adopted a *syn* arrangement, with both cyanomethyl ligands oriented in the same direction. The only other reported bis(cyanomethyl) complex, $[\text{Ir}(\text{CH}_2\text{CN})_2(\text{CO})_2][(\text{Ph}_3\text{P})_2\text{N}]$, has the ligands oriented almost perpendicular to each other (Porta *et al.*, 1990). A lack of steric interference from the *cis*-carbonyl ligands would allow this, but an *anti* conformation should be preferable on steric grounds. The cyanomethyl ligands do not completely eclipse each other: the C2—C1—C3—C4 dihedral angle is $-20.6(7)^\circ$. The related $[\text{Pt}(\text{CH}_2\text{Cl})_2\text{L}_2]$ complexes ($\text{L}_2 = \text{dppm}$ or *S,S*-skewphos) display quite different geometries for the orientation of the chloromethyl ligands. The chloromethyl ligands of $[\text{Pt}(\text{CH}_2\text{Cl})_2(\text{dppm})]$ are oriented so that the Cl atoms lie in the plane of the Pt coordination sphere (Alcock *et al.*, 1990), while the chloromethyl ligands of $[\text{Pt}(\text{CH}_2\text{Cl})_2(\text{S,S-skewphos})]$ are oriented approximately perpendicular to one another (Bergamini *et al.*, 1993).

The dichloromethane molecule of crystallization could not be determined accurately as it appears to be disordered about the inversion centre of the unit cell. Although diethyl ether and dichloromethane were used in the crystallization process, NMR analysis of the crystals indicates that some dichloromethane is present.

Experimental

A stirred mixture of *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ (0.058 g, 0.073 mmol), cyanoacetic acid (0.14 g, 0.390 mmol) and silver(I) oxide (0.164 g, excess) was refluxed in dichloromethane (20 ml) for 3 h under nitrogen. Silver salts were removed by filtration in air and the remaining solvent was removed under vacuum (0.052 g, 85%). Yellow crystals were obtained from dichloromethane/diethyl ether by vapour diffusion. ^{31}P NMR: δ (p.p.m.) 23.53 [$J(\text{Pt}-\text{P}) = 2376 \text{ Hz}$]; ^{13}C NMR: δ (p.p.m.) 136.5–124.0 (*m*, Ph), 110.6 (*s*, $\text{C}\equiv\text{N}$), 53.52 (*s*, CH_2); ^1H NMR: δ (p.p.m.) 7.85–6.85 (*m*, Ph), 3.65 (*s*, CH_2).

Crystal data

$[\text{Pt}(\text{C}_2\text{H}_2\text{N})_2(\text{C}_{18}\text{H}_{15}\text{P})_2] \cdot 0.6\text{CH}_2\text{Cl}_2$	Mo $K\alpha$ radiation
$M_r = 850.71$	$\lambda = 0.71073 \text{ \AA}$
Triclinic	Cell parameters from 8192 reflections
$P\bar{1}$	$\theta = 2.08\text{--}26.00^\circ$
$a = 10.2264(2) \text{ \AA}$	$\mu = 4.038 \text{ mm}^{-1}$
$b = 10.3606(1) \text{ \AA}$	$T = 203(2) \text{ K}$
$c = 18.0965(3) \text{ \AA}$	Tablet
$\alpha = 87.360(1)^\circ$	$0.25 \times 0.21 \times 0.06 \text{ mm}$
$\beta = 81.604(1)^\circ$	Yellow
$\gamma = 74.839(1)^\circ$	
$V = 1830.72(5) \text{ \AA}^3$	
$Z = 2$	
$D_x = 1.549 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Siemens SMART CCD area-detector diffractometer	5644 reflections with $I > 2\sigma(I)$
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Multi-scan	$R_{\text{int}} = 0.049$
Absorption correction: empirical (Blessing, 1995)	$\theta_{\text{max}} = 26^\circ$
$T_{\text{min}} = 0.439$, $T_{\text{max}} = 0.837$	$h = -12 \rightarrow 12$
13 799 measured reflections	$k = -12 \rightarrow 12$
7070 independent reflections	$l = 0 \rightarrow 22$
	Intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.047$	$\Delta\rho_{\text{max}} = 2.93 \text{ e \AA}^{-3}$
$wR(F^2) = 0.113$	$\Delta\rho_{\text{min}} = -1.70 \text{ e \AA}^{-3}$
$S = 0.968$	Extinction correction: none
7070 reflections	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
406 parameters	
H atoms riding	
$w = 1/[\sigma^2(F_o^2) + (0.0571P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Selected geometric parameters (\AA , $^\circ$)

Pt—C2	2.104(7)	N1—C1	1.136(10)
Pt—C4	2.138(7)	C1—C2	1.413(10)
Pt—P1	2.2953(18)	N2—C3	1.150(10)
Pt—P2	2.3161(18)	C3—C4	1.433(10)
C2—Pt—C4	85.3(3)	P1—Pt—P2	98.09(6)
C2—Pt—P1	90.9(2)	N1—C1—C2	176.7(12)
C4—Pt—P1	175.7(2)	C1—C2—Pt	112.1(5)
C2—Pt—P2	170.8(2)	N2—C3—C4	178.0(9)
C4—Pt—P2	85.6(2)	C3—C4—Pt	111.8(5)

The *SQUEEZE* function of the *PLATON* program (Spek, 1998) was applied to the data. This indicated that a 50-electron 206 \AA^3 void existed, which would be consistent with a diffuse disordered dichloromethane of crystallization. NMR analysis of a selection of the crystals showed that dichloromethane was present. The structure was refined on the corrected data. The final difference map showed a feature of 2.93 e \AA^{-3} lying 1.05 \AA from the Pt atom.

Data collection: *SMART* (Siemens, 1994a). Cell refinement: *SAINTE* (Siemens, 1994a). Data reduction: *SAINTE*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *SHELXTL* (Siemens, 1994b). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1536). Services for accessing these data are described at the back of the journal.

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cis-Bis(phenoxyacetato-*O*)bis(triphenylphosphine-*P*)platinum(II) dichloromethane solvate

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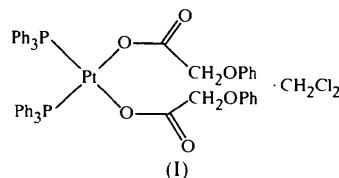
Abstract

The title complex, [Pt(C₈H₇O₃)₂(C₁₈H₁₅P)₂].CH₂Cl₂, has carboxylate ligands bonded in a monodentate manner.

Comment

We have been investigating silver(I) oxide-mediated reactions of carboxylic acids with platinum group metal halide complexes as a route to four-membered-ring metallalactone complexes of type *L*₂*M*{CHRC(O)O}. The product is dependent on the nature of the carboxylic acid; PhSO₂CH₂CO₂H gives the platinalactone complex [Pt{CH(SO₂Ph)C(O)O}(PPh₃)₂], whereas NCCH₂-CO₂H gives the bis(cyanomethyl) complex *cis*-[Pt(CH₂-CN)₂(PPh₃)₂], which has been characterized by X-ray crystallography (Henderson & Oliver, 1999). This paper describes the structure of the product formed in the

case of phenoxyacetic acid, *i.e.* *cis*-[Pt(O₂CCH₂OPh)₂(PPh₃)₂].CH₂Cl₂, (I).



Carboxylate ligands predominantly adopt a chelating or a bridging mode (Oldham, 1987), and when two carboxylate ligands are in a *cis* conformation, they tend to be of the latter type, often bridging several metal centres. Tan *et al.* (1996) isolated and characterized several short-chain platinum(II) carboxylic acid derivatives, which adopted a monodentate bonding mode. The title complex also demonstrates this monodentate bonding mode. One notable difference between the previously reported crystal structures of *cis*-carboxylatoplatinum(II) complexes and that presented here is the ancillary ligands. In the reported crystal structures of the complexes *cis*-[Pt(O₂CR)₂L₂] [*R* = Me or Ph, L₂ = Fe(C₅H₄PPh₂)₂ (dppf); *R* = CF₃, L₂ = Ph₂PCH₂PPh₂ (dppm)], chelating phosphines were employed, forcing a *cis* arrangement of the acetate ligands (Tan *et al.*, 1996).

The coordination around the platinum centre of *cis*-[Pt(O₂CCH₂OPh)₂(PPh₃)₂] is a distorted square plane as a result of the steric bulk of the triphenylphosphine and phenoxyacetate ligands. Thus, the P1—Pt—P2 angle [98.00 (6)°] is more obtuse than the O1—Pt—P1 angle [85.54 (15)°]. The remaining two bond angles are closer to ideal [O11—Pt—O1 87.75 (19) and O11—Pt—P2 89.93 (14)°]. The phenoxyacetate ligands are distorted out of the plane around the Pt atom. The O1 atom lies 0.433 (6) Å above the plane defined by atoms P1, P2 and Pt, while O11 is 0.178 (5) Å below this plane. This distortion is also reflected in the bond angles of the atoms *trans* to the O atoms [167.53 (16) and 170.64 (14)° for O1—Pt—P2 and O11—Pt—P1, respectively] with respect to an ideal value of 180°. The Pt—O bond lengths [2.082 (5) and 2.056 (4) Å for Pt—O1 and Pt—O11, respectively] are within the ranges of the platinum(II) carboxylate complexes described previously, *i.e.* *cis*-[Pt(O₂CR)₂L₂] [*R* = Me or Ph, L₂ = dppf; *R* = CF₃, L₂ = dppm; 2.034 (6)–2.089 (6) Å; Tan *et al.*, 1996]. The Pt—P bond lengths are not unusual.

The geometry of the carboxylate ligands with respect to one another is an *anti* arrangement of the carbonyl ligands [O2—C1—C11—O12 177.9 (6)°]. This geometry has been observed in the other reported *cis*-acetatoplatinum(II) complexes (Tan *et al.*, 1996). The O1—C1 bond distance is 1.177 (9) Å, fractionally shorter than that of O2—C1 [1.225 (9) Å], where O1 is the oxygen coordinated to the platinum. The other coordinating oxygen (O11) shows more single-bond charac-