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UNEXPECTED BEHAVIOUR OF ALKOXYCARBONYL LIGANDS

THE CRYSTAL AND MOLECULAR STRUCTURE OF *trans*- BIS(ETHOXYCARBONYL)BIS(TRIPHENYLPHOSPHINE)PLATINUM

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Summary

The crystal and molecular structures of the title compound have been determined from three-dimensional X-ray data collected by counter methods. The crystals are triclinic, space group $P\bar{1}$, with $Z = 1$; cell dimensions: $a = 10.204(8)$, $b = 11.602(8)$, $c = 8.363(7)$Å, $\alpha = 106.04(8)°$, $\beta = 88.04(7)°$, $\gamma = 108.98(7)°$. The structure, determined from 3435 reflections, has been refined by full-matrix least-squares methods down to $R = 0.038$. It consists of discrete centrosymmetric molecules; the Pt atom lies on an inversion centre. Pt—P and Pt—C bonds lengths are 2.302(2) and 2.059(7) Å respectively. Essentially planar Pt—COO moieties are present, which make an angle of 80.8° with the coordination plane.

A *trans* configuration for a complex containing two Pt^{II}—C bonds is unexpected; alkoxycarbonyl ligands therefore show a peculiar behaviour which deserves further investigation.

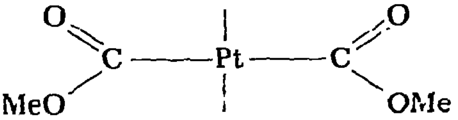
Introduction

The structures of complexes containing alkoxycarbonyl ligands (—COOR) have not been studied thoroughly. They represent a stable model of metallated formic acid, M—COOH, a very labile intermediate involved in the reaction in which a cationic carbonyl complex reacts with OH^- or with H_2O to yield CO_2 and a metal hydrido derivative [1].

An alkoxycarbonyl ligand would be expected to display a large *trans* influence; in $Ir(CO)(COOMe)(dipy)I_2$ (I) the structure of which has been reported [2], there are two statistically equivalent Ir—N bonds, 2.13(2) and 2.15(2) Å long, *trans* to the CO and to the COOMe ligands.

The structure of the title compound II was undertaken as part of a more general investigation of the geometry and ground state effects of alkoxycarbonyl ligands.

Beck, who prepared the first complex containing two such ligands, has assigned the *trans-syn* configuration to $Pt(COOMe)_2(PPh_3)_2$ on the basis of ^{31}P



NMR and dipole moment measurements [3]; this assignment is interesting because a *cis* configuration would be expected for a complex containing two strongly "antisymbiotic" [4] Pt^{II}—C bonds. Because of the lack of an inversion centre in the *trans-syn* isomer a significant deviation from strict planarity could be observed in the molecule. Conversely, the dipole moment reported by Beck (2.49 D) [3] could arise from a *trans-anti* isomer lacking in planarity.

Experimental

Crystal data

$C_{42}H_{40}PtO_4P_2$, mol.wt. = 865.8, prepared as in ref. 3, gives colourless crystals of triclinic habit. The reduced cell dimensions are: a = 10.204(8), b = 11.602(8), c = 8.363(7) Å, α = 106.04(8), β = 88.04(7), γ = 108.98(7)°, U = 898.1 Å^3; space group $P\bar{1}$ (No. 2), D_m 1.60 g cm^{-3} (by flotation), Z = 1, D_c = 1.61, $F(000)$ 432. Cell dimensions determined from precession photographs using Mo-$K\alpha$ radiation (λ = 0.7107 Å).

Structure determination and refinement

The intensities were collected on a Pailred linear equi-inclination diffractometer with Mo-$K\alpha$ radiation, using a graphite single crystal monochromator. The crystal sample, a multifaced polyhedron of approximate dimensions 0.18 × 0.13 × 0.30 mm was mounted along the direction of maximum elongation (c axis). 3435 reflections, belonging to ten different reciprocal lattice layers, from $hk0$ to $hk9$, and having $\sigma(I)/I \leqslant 0.3$, were measured by a stationary counter-moving crystal technique, within the limit angle $2\theta \leqslant 54°$ since no significant reflections were noticed outside this range. No crystal decay was noticed, monitored during the data collection.

The integrated intensities were corrected for Lorentz and polarisation effects, the latter allowing for the presence of the monochromator [5]. Transmission factors (42.4 cm^{-1} for Mo-$K\alpha$) were sampled for each reflection in 8^3 points of the crystal with the method of ref. 6.

The structure was solved by conventional Patterson and Fourier methods. A centrosymmetric model was refined by full-matrix least-squares, the minimized function being $\Sigma w(F_o - k|F_c|)^2$. The three independent C_6 groups were treated as rigid bodies of D_{6h} symmetry (C—C 1.392 Å). The ring carbon atoms were assigned individual thermal factors; all other non-hydrogen atoms were treated anisotropically. In structure factor computations the contribution of all hydrogen atoms were included. Their coordinates, updated after each refine-

TABLE 1 [a]

(i) POSITIONAL AND THERMAL ANISOTROPIC PARAMETERS (10^4) OF NON-GROUP ATOMS

Atom	x	y	z	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Pt	0	0	0	53 (0)	21 (0)	2 (0)	41 (0)	37 (0)	79 (0)
P	−1259 (1)	−1772 (1)	792 (1)	61 (1)	27 (2)	6 (2)	44 (1)	41 (2)	79 (2)
O(1)	2685 (4)	−33 (5)	1156 (5)	87 (5)	76 (9)	−22 (10)	126 (5)	63 (10)	119 (7)
O(2)	1882 (4)	−1382 (4)	−1344 (6)	87 (5)	92 (8)	C (10)	92 (4)	28 (10)	179 (9)
C(1)	1769 (5)	−482 (5)	27 (7)	61 (5)	26 (8)	3 (11)	65 (5)	74 (10)	104 (9)
C(2)	3137 (8)	−1736 (8)	−1487 (11)	101 (8)	127 (14)	47 (18)	120 (8)	70 (18)	218 (16)
C(3)	2820 (11)	−3027 (9)	−1303 (16)	162 (13)	116 (19)	−57 (20)	120 (10)	82 (25)	341 (27)

(ii) POSITIONAL PARAMETERS OF RING CARBON ATOMS DERIVED FROM RIGID GROUP PARAMETERS AND ISOTROPIC THERMAL FACTORS

Atom	x	y	z	B(Å^2)	Atom	x	y	z	B(Å^2)
C (11)	−218 (5)	−2336 (4)	1939 (5)	2.5 (0)	C (24)	−3428 (5)	−5008 (4)	−3856 (4)	4.1 (1)
C (12)	−321 (3)	−3606 (3)	1618 (4)	3.3 (1)	C (25)	−2293 (4)	−3992 (4)	−4009 (4)	4.1 (1)
C (13)	407 (5)	−3971 (2)	2654 (5)	4.3 (1)	C (26)	−1627 (4)	−3028 (4)	−2596 (5)	3.3 (1)
C (14)	1239 (5)	−3067 (4)	4012 (5)	4.4 (1)	C (31)	−2693 (4)	−1670 (6)	2166 (4)	2.4 (0)
C (15)	1341 (3)	−1797 (3)	4332 (4)	3.7 (1)	C (32)	−3850 (4)	−1495 (4)	1568 (3)	3.3 (1)
C (16)	613 (5)	−1431 (2)	3295 (5)	3.1 (1)	C (33)	−4925 (4)	−1378 (5)	2602 (5)	4.0 (1)
C (21)	−2099 (5)	−3082 (4)	−1028 (4)	2.4 (0)	C (34)	−4843 (4)	−1436 (6)	4235 (4)	3.7 (1)
C (22)	−3236 (4)	−4100 (4)	−873 (4)	4.2 (1)	C (35)	−3685 (4)	−1610 (1)	4833 (3)	3.7 (1)
C (23)	−3900 (4)	−5063 (4)	−2288 (5)	1.7 (1)	C (36)	−2611 (4)	−1727 (5)	3798 (5)	3.2 (1)

[a] Numbers in parentheses here and in subsequent tables are the estimated standard deviations on least significant digits; the form of anisotropic temperature factors is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$; in phenyl rings, C($i$1) are bonded to P and are *para* to C(i4).

ment cycle, were generated with the assumptions: (i) C—H 1.08 Å, (ii) C—C—H 120° and 109.5° in phenyl rings and in C_2H_5 group, (iii) ethyl group in the staggered configuration. Including a scale factor, a total of 97 parameters were refined.

In least-squares and structure-factor computations the atomic scattering factors of ref. 7 were used for all but the H atoms; for the latter the scattering factor of ref. 8 was assumed. Real and imaginary part of anomalous dispersion of Ir and P atoms were taken into account [9]. The weight assigned to each observation was $w = (4.8 - 0.14\,F_o + 0.0021 F_o^2)^{-1}$.

The final reliability indices were $R = 0.038$ and R', $[\Sigma\, w(F_o - k|F_c|)^2 / \Sigma w F_o^2]^{1/2}$, 0.046. A final difference synthesis gave no signals exceeding 0.4 e Å^{-3}.

A list of computed and observed structure factors is available on application to the authors; the final atomic coordinates are reported in Table 1.

Computations

All computations were carried out on a Univac 1106 computer; for absorption corrections our programme was used in which the directions of primary and diffracted beams are evaluated as already described [10]; counter data reduction and statistical analysis for weighting schemes were also based upon programmes written in our laboratory. In addition, local versions of entries 7528, 7531, 7532 and 7535 in the 1966 World List of Crystallographic Programs were used for Fourier analyses, structure-factor and least-squares computations.

Description of the structure and discussion

The crystal consists of discrete monomeric molecules of (II) packed as shown in Fig. 1. A thorough examination of the non-bonding intermolecular

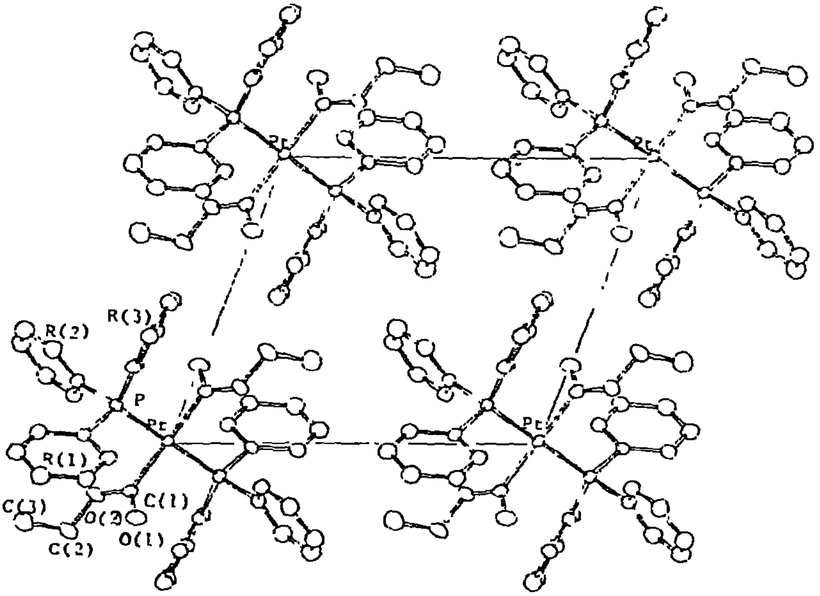


Fig. 1. Unit cell content, in crystals of compound II, projected down the c axis. R(i) stands for ring atoms C(i1)-C(i6).

TABLE 2

DISTANCES (Å) AND ANGLES (°) IN COMPOUND II [a]

Pt—P	2.302(2)	Pt—P—C(11)	113.8(2)	P—Pt—C(1)	90.3(2)
Pt—C(1)	2.059(7)	Pt—P—C(21)	110.5(2)	P—Pt—C(1)'	89.7(2)
Pt · · · O(1)	2.952(5)	Pt—P—C(31)	118.4(3)		
Pt · · · O(2)	2.896(6)	Pt—C(11)—C(14)	173.5(3)		
P · · · C(1)	3.096(6)	P—C(21)—C(24)	177.4(3)		
P · · · C(1)'	3.081(7)	P—C(31)—C(34)	178.2(4)		
P—C(11)	1.828(6)	P—C(11)—C(12)	123.6(3)		
P—C(21)	1.824(3)	P—C(11)—C(16)	116.1(4)		
P—C(31)	1.843(4)	P—C(21)—C(22)	120.9(3)		
		P—C(21)—C(26)	119.0(3)		
		P—C(31)—C(32)	119.2(3)		
		P—C(31)—C(36)	120.8(4)		

[a] C(1)' is obtained from C(1) by inversion

contacts shows that the packing is essentially dictated by a number of H · · · H interactions. The shortest of these is 2.13 Å, with the rest being longer than 2.3 Å. This result shows that the constraint imposed on the symmetry and dimensions of phenyl rings and the assumptions adopted in generating the H atom coordinates are fairly adequate.

The most relevant intramolecular interactions of compound II are listed in Table 2. The *trans-syn* configuration proposed by Beck [3] for $Pt(COOMe)_2(PPh_3)_2$ is not observed here; the platinum atom lies on an inversion centre and so the centrosymmetric molecule possesses a *trans-anti* configuration with an almost ideal square geometry; the mutually *cis* metal—ligand bonds make angles which are not significantly different from 90°.

The crystallographically equivalent Pt—P bonds, 2.302(2)Å long, are comparable with a number of similar interactions observed in *trans*-bis(phosphine) complexes, which are in the range 2.27-2.32 Å [11]. Only in Clark's cation, *trans*-$[Pt(CO)Cl(PEt_3)_2]^+$, were longer interactions found (2.34 and 2.35 Å); the latter are probably due to the competing π accepting ability of the CO group [12].

The Pt—COO moieties are essentially planar: the metal atom is only 0.008 Å out of the plane defined by the COO group. The length of the metal—carbon interactions and a number of structural parameters within the alkoxycarbonyl ligand in compounds I and II are compared in Table 3. Not only is the same metal—carbon distance found but also a characteristic pattern of angular deformation (with respect to an ideal sp^2 hybridisation on the carbon) is observed. For compound I, the relatively large M—C=O angle (126° in both complexes) was explained in term of a non-linear hydrogen bond connecting the oxygen atom to an α-carbon atom of a pyridine ring. This interaction is still a possibility but the results obtained for compound I and II as well as those reported recently for an accurate structural determination on a methoxycarbonyl derivative of a dimethano[14]annulene, $C_{18}H_{20}O_2$, III [13], whose geometry is also reported in Table 3, show that the angular pattern around the carbon atom of an ester remains essentially unperturbed in widely different environments.

The metal—carbon bond lengths of 2.059(7) Å in II are comparable with those usually found in Pt^{II}—C interactions (2.04—2.12 Å; see, e.g. ref. 14). The

TABLE 3

DISTANCES (Å) AND ANGLES (°) WITHIN THE MCOOR MOIETIES IN COMPOUNDS I, II AND III (M = Ir, Pt AND C, RESPECTIVELY)

	I	II	III
M—C(1)	2.05(2)	2.059(7)	1.485(2)
C(1)=O(1)	1.18(2)	1.228(7)	1.199(2)
C(1)—O(2)	1.28(2)	1.351(7)	1.329(2)
C(2)—O(2)	1.48(3)	1.459(11)	1.444(2)
C(2)—C(3)		1.476(16)	
O(1) ··· O(2)	2.23(2)	2.229(6)	2.218(2)
M—C(1)=O(1)	126.6(16)	125.9(5)	126.3(1)
M—C(1)—O(2)	112.8(11)	114.6(4)	111.2(1)
O(1)—C(1)—O(2)	120.6(19)	119.5(6)	122.6(19)
C(1)—O(2)—C(2)	118.3(14)	118.8(5)	117.0(1)
O(2)—C(2)—C(3)		110.1(7)	

symmetry of the complex allows some degree of π interaction to take place in the metal—carbon bonds. The d_{xy} metal orbital overlaps with the antibonding orbitals of the $\rangle$C=O groups; the plane of each M—COO moiety makes an angle of 80.8° with respect to the plane PtC_2P_2 and it is not easy to establish whether or not the rotation of the alkoxycarbonyl ligand around the metal—carbon bond results in a better π overlap (the lobes of the π^* orbital on the carbon are out of the coordination plane). The amount of rotation is anyhow dictated by some non-bonding contacts of the ligand with two neighbouring phenyl rings, as shown in Fig. 2.

The structure of the present compound is important in one respect. It is generally accepted that "alkylation of d^8 transition metals is stereospecific, for not only are the gold(III) exclusively *cis* but also only *cis* dialkylplatinum(II) complexes seem to have been isolated" [15]. Moreover, all the known complexes

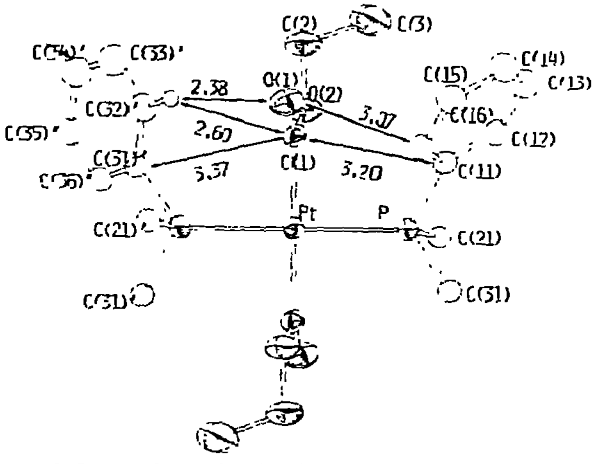


Fig. 2. View of a molecule of compound II, projected onto the coordination plane, four rings are omitted. Relevant non-bonding interactions, indicated by arrows, are given in Å.

of the type $Pt(CO)_2X_2$ [16] and $[M(CO)_2X_2]^-$ (M = Rh, Ir; X = Cl, Br, I) [17] are *cis*.

The reasons for these facts, put forward by Chatt and Heaton [18] and by Tobias [15], have recently been given a compact form by Pearson [4] who points out that two soft ligands in mutually *trans* position will have a destabilising effect on each other when attached to a class *b* metal atom.

The *trans* configuration of compound II is an exception to the above rule. One reason why a *trans* isomer is preferred could be the presence of bulky groups; two triphenylphosphine ligands could, in principle, destabilise the *cis* isomer because of a severe distortion in the P—Pt—P angle. However, since this angle can be as low as 97—98° [19] no major deformations caused by steric hindrance are to be expected in the coordination geometry. The present structure on the other hand could support the view that actually an alkoxycarbonyl group behaves as a relatively hard ligand; this seems not to be the case in the structure of compound I where a *trans* influence comparable to that of CO is observed for the COOMe group (see Introduction).

It is clear from the present results that alkoxycarbonyl ligands show peculiar behaviour and deserve further investigation; it would be particularly interesting, for instance, to collect data on their ground-state effects in d^8 metal complexes of the type *trans*-$M(COOR)X(PPh_3)_2$.

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