Deprotonation Reactions by Transition-metal Peroxo-complexes. Synthesis of Aroylhydrazido- and Aroylhydroxylamido-complexes of Palladium and Platinum and the Crystal and Molecular Structures of [Pt-(PPh3)2{NHNC(O)C6H4NO2-p}] and [Pt(PPh3)2{ONC(O)C6H5}] †

By **Pier Luigi Bellon**,* **Sergio Cenini**,* **Francesco Demartin**, **Mario Manassero**, **Maddalena Pizzotti**, and **Francesca Porta**, Istituto di Chimica Generale and C.N.R. Center, Via Venezian 21, 20133 Milano, Italy

By treating [M(PPh3)2(O2)] (M = Pd or Pt) with C6H5C(O)NHOH, C6H5C(NH)NHOH, and p-RC6H4C(O)NHNH2 in ethanol, the complexes [M(PPh3)2{ONC(O)C6H5}], [Pt(PPh3)2{ONC(NH)C6H5}], and [Pt(PPh3)2{NHNC(O)-C6H4R-p}] (R = H, CH3, or NO2) respectively have been obtained. The reactions of [Pt(PPh3)2(O2)] with RNHNH2 (R = H or C6H5) lead only to the zerovalent complex, [Pt(PPh3)3], while by treating [Pt(PPh3)2(O2)] with C6H5NHOH the known complex [Pt(PPh3)2(C6H5NO)] is obtained. Reactions of the aroylhydrazido-platinum complexes with molecular oxygen and mineral acids are also reported. The structure of the two title complexes has been determined by X-ray diffraction. The compound [Pt(PPh3)2{ONC(O)C6H5}] is orthorhombic and crystallizes in space group $Pna2_1$ with a = 17.365(6), b = 11.218(7), and c = 18.431(8) Å, whereas the disordered [Pt(PPh3)2{NHNC(O)C6H4NO2-p}] is monoclinic and crystallizes in space group $P2_1/m$ with a = 15.829(6), b = 12.269(5), c = 11.833(5) Å, and β = 93.51(3)°. Both structures have been solved by Patterson and Fourier methods, and refined to R 0.031 and 0.062 for 2 057 and 2 119 independent reflections, respectively. Both compounds, in the solid state, are essentially square-planar complexes of Pt^{II}. The differences between the two structures, which display different packing efficiency, are mainly due to the conformations of the phosphine groups, which are imposed by the chelating ligands.
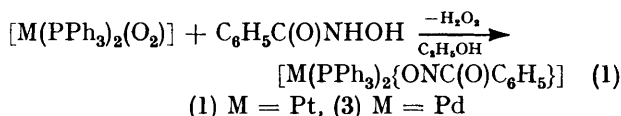
We have recently shown that [Pt(PPh3)2(O2)] can readily deprotonate *ortho*-phenylenediamine, to give the diamido-derivative, [Pt(PPh3)2{C6H4(NH)2-o}].[1] This reaction failed when it was attempted with monoamines, thus, only the formation of a five-membered metallo-cycle allowed the formation of a characterizable product. We report here on related reactions where the transition-metal peroxo-complexes, [M(PPh3)2(O2)] (M = Pd or Pt), deprotonate aroylhydroxylamine and aroylhydrazine to give the aroylhydroxylamido- and aroylhydrazido-derivatives, [M(PPh3)2{ONC(O)C6H5}] and [Pt(PPh3)2-{NHNC(O)C6H4R-p}].

The trapping of aroylhydroxylamido- and aroyl-hydrazido-ligands on a ML2 co-ordinating centre (M = Pd or Pt; L = PPh3) can in principle yield two kinds of complexes, a or b, depending upon the formal oxidation state of the metal in the final product. When, for in-

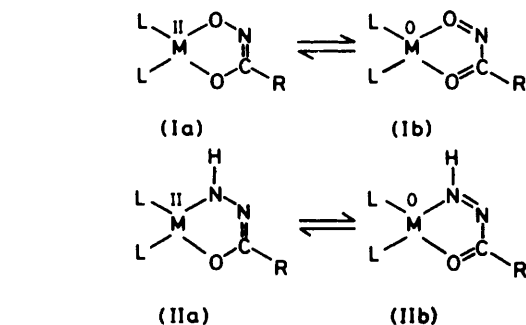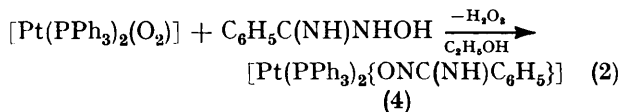(Ia)   (Ib)

(IIa)   (IIb)

stance, an aroylhydrazide is chelated to the metal atom, the result is either a square-planar aroylhydrazido-complex (IIa) or the tetrahedral derivative (IIb) having the aroyldiazene as ligand. It cannot be ruled out *a priori*

† [*para*-Nitrobenzoylhydrazido(2−)-*NO*]bis(triphenylphos-phine)platinum and [benzoylhydroxylamido(2−)-*OO′*]bis(tri-phenylphosphine)platinum respectively.

that there exists a resonance between formulae (a) and (b), which implies a distortion of the complexes toward an intermediate geometry. This point is interesting since the reduction of diazene could occur *via* an electron transfer from the metal atom. Conversely, C-nitroso-aroyl intermediates have been postulated as transient species in the oxidative cleavage of phenylhydroxamic acids [2] (or aroylhydroxylamines), and they have been involved in an organic reaction with the appropriate reagent.[3] The synthesis of these aroylhydroxylamido- and aroylhydrazido-complexes of platinum and palladium, and the X-ray structures of two of them, [Pt-(PPh3)2{ONC(O)C6H5}] (1) and [Pt(PPh3)2{NHNC(O)-C6H4NO2-p}] (2), are part of our investigations into the dehydrogenation of amines and related derivatives by transition-metal oxo-[4] and peroxo-[1,4] compounds.

RESULTS AND DISCUSSION

Synthesis of Aroylhydroxylamido- and Aroylhydrazido-derivatives.—Treatment of [M(PPh3)2(O2)] (M = Pd or Pt) with C6H5C(O)NHOH in ethanol at room temperature and under a nitrogen atmosphere gives the complexes [M(PPh3)2{ONC(O)C6H5}] [see equation (1) and Table 1]. No reaction was observed between [Pt(PPh3)3]

$$[M(PPh_3)_2(O_2)] + C_6H_5C(O)NHOH \xrightarrow[C_2H_5OH]{-H_2O_2}$$
$$[M(PPh_3)_2\{ONC(O)C_6H_5\}] \quad (1)$$
$$(1) \text{ M} = \text{Pt}, (3) \text{ M} = \text{Pd}$$

and C6H5C(O)NHOH in an ethanol–benzene (1 : 1) homogeneous solution, emphasizing the role of the peroxo-group in this reaction. An analogous reaction has been observed with C6H5(NH)NHOH [equation (2)]. The

$$[Pt(PPh_3)_2(O_2)] + C_6H_5C(NH)NHOH \xrightarrow[C_2H_5OH]{-H_2O_2}$$
$$[Pt(PPh_3)_2\{ONC(NH)C_6H_5\}] \quad (2)$$
$$(4)$$

general character of this reaction, where two protons from two adjacent atoms of the aroyl reagent are displaced by the peroxo-group to give a five-membered metallocycle, has been confirmed with the aroylhydrazines [equation (3)]. With hydrazine and phenyl-

$$[Pt(PPh_3)_2(O_2)] + p\text{-}RC_6H_4C(O)NHNH_2 \xrightarrow[C_2H_5OH]{-H_2O_2}$$

$$[Pt(PPh_3)_2\{NHNC(O)C_6H_4R\text{-}p\}] \quad (3)$$

(2) R = NO$_2$, (5) R = H, (6) R = CH$_3$
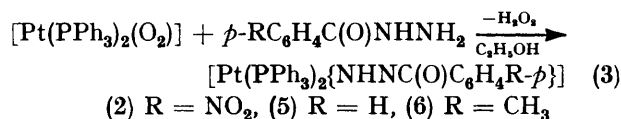
hydrazine, only [Pt(PPh$_3$)$_3$] which is insoluble in ethanol was isolated from this reaction. Presumably the intermediate diazene formed, RN=NH (R = H or C$_6$H$_5$), is not able to stabilize a zerovalent complex such as [Pt-(PPh$_3$)$_2$(RN=NH)].[5] However, even from the reaction of [Pt(PPh$_3$)$_2$(O$_2$)] with C$_6$H$_5$NHOH in ethanol we were unable to obtain a characterizable product from the clear

states employed here, it is more likely that hydrogen peroxide is formed,[9] particularly in view of the acidic character of reagents such as C$_6$H$_5$C(O)NHOH. Iodometric titrations of the mother-liquor from the reaction which leads to (1) have indicated less than the required amount of hydrogen peroxide (70% with respect to the starting platinum peroxo-complex). However reaction (1), which can be conducted with a 1 : 1 ratio of the reactants, gives compound (1) in *ca.* 70—75% yields, which supports the formation of hydrogen peroxide.

In order to clarify the extent of contributions of formulae (a) and (b) to the description of the bonding between platinum and these ligands a single-crystal X-ray diffraction study was carried out on compounds (1), [Pt(PPh$_3$)$_2$\{ONC(O)C$_6$H$_5$\}], and (2), [Pt(PPh$_3$)$_2$\{NHNC-(O)C$_6$H$_4$NO$_2$-p\}].

Description and Discussion of the Structures of Com-

TABLE 1

Analytical data

		M.p.		Analysis (%) [a]		
	Complex	(θ_c/°C)	Colour	C	H	N
(1)	[Pt(PPh$_3$)$_2$\{ONC(O)C$_6$H$_5$\}]·0.5C$_2$H$_5$OH [b]	302	Yellow	60.2	4.3	1.6
				(60.1)	(4.3)	(1.6)
(2)	[Pt(PPh$_3$)$_2$\{NHNC(O)C$_6$H$_4$NO$_2$-p\}]	233	Violet	57.1	3.8	4.6
				(57.4)	(3.9)	(4.7)
(3)	[Pd(PPh$_3$)$_2$\{ONC(O)C$_6$H$_5$\}]	205	Pale brown	66.5	4.6	1.8
				(67.4)	(4.6)	(1.8)
(4)	[Pt(PPh$_3$)$_2$\{ONC(NH)C$_6$H$_5$\}]	310	Pale yellow	60.8	4.5	3.1
				(60.4)	(4.2)	(3.3)
(5)	[Pt(PPh$_3$)$_2$\{NHNC(O)C$_6$H$_5$\}]·C$_2$H$_5$OH [b,c]	207	Orange	59.2	4.5	2.9
				(60.0)	(4.7)	(3.1)
(6)	[Pt(PPh$_3$)$_2$\{NHNC(O)C$_6$H$_4$Me-p\}]	147	Orange	61.7	4.9	3.0
				(60.8)	(4.4)	(3.2)
(7)	[Pt(PPh$_3$)$_2$\{NH$_2$NHC(O)C$_6$H$_5$\}][BF$_4$]$_2$·C$_2$H$_5$OH [b,d]	196	White	49.8	3.9	2.5
				(50.2)	(4.1)	(2.6)
(8)	[Pt(PPh$_3$)$_2$\{N$_2$H$_2$C(O)C$_6$H$_5$\}][BF$_4$] [e]	>240	White	54.7	3.6	2.9
				(54.8)	(3.9)	(3.0)

[a] Calculated values are given in parentheses. [b] The presence of ethanol was confirmed by ^{1}H n.m.r. spectroscopy. [c] By crystallisation from CHCl$_3$–n-hexane the complex with clathrated chloroform was obtained. [d] Λ_M = 32.0 S cm^2 mol^{-1} in nitrobenzene. [e] Λ_M = 24 S cm^2 mol^{-1} in nitrobenzene.

solution thus formed, while in a suspension of n-hexane–ethanol, the yellow known complex [Pt(PPh$_3$)$_2$(C$_6$H$_5$-NO)][6] could be isolated.

When reaction (3) is attempted (R = H) with the palladium peroxo-complex, a transient violet colour is observed. However, a pale brown product is finally obtained (the platinum aroylhydrazido-complexes are orange or violet), the elemental analyses of which show a very low nitrogen content. Admittedly, the resonance formula (IIa) is the one which stabilises this type of complex and being platinum(o), a better π donor than palladium(o),[5] one can understand why the palladium aroylhydrazido-complexes are not stable. This implies that the aroylhydroxylamido- is a better π acceptor than the aroylhydrazido-ligand.

Recently the reactions of *cis*-molybdenum(vi) dioxo-[7] and of oxoperoxomolybdenum(vi)[8] derivatives with hydroxylamines have been reported. These reactions lead to molybdo-oxaziridines, compounds having η^2 bonding of the RNO group, and water.[8] With the peroxo-complexes of transition metals in low oxidation

plexes (1) *and* (2).—The crystal structures of (1) and (2) consist of the discrete molecular units shown in Figures 1 and 2 respectively; the packing efficiencies are different in the two species as can be appreciated by comparing the densities [D_c = 1.57 for (1) and 1.30 g cm^{-3} for (2)].

Due to the difficulty in obtaining suitable crystals, different p-substituted aroylhydrazido-complexes have been prepared and crystallized by diffusion; we finally got good crystals of the p-nitro-derivative (2) by diffusion at 0 °C of n-pentane into a solution of the complex in a xylene–n-pentane (4 : 1) mixture. Unfortunately the crystal structure which builds up in these conditions is highly disordered (see Experimental section) and so the molecular parameters are determined with less accuracy than for compound (1).

The difficulty in obtaining good crystals of (2) is encountered for several derivatives; the difference in the packing efficiency between (1) and (2) does not, therefore, necessarily arise from the presence of the p-nitro group in (2) but rather from the conformations of the triphenylphosphine groups, which are different in the two
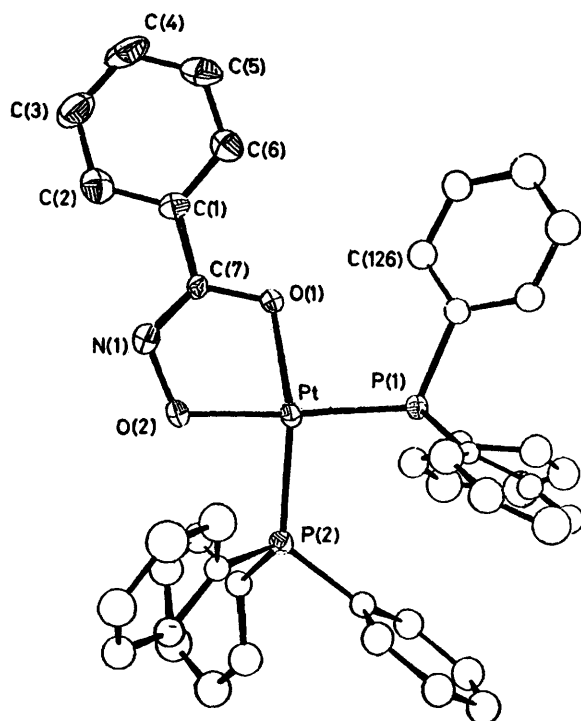
FIGURE 1 A molecular unit in the crystal structure of
[Pt(PPh₃)₂{ONC(O)C₆H₅}]

structures. In (1), the O(1) atom seems to interact with
the phenyl carbon atom C(126) *via* an electrostatic inter-
action O ⋯ H–C. Since the angle at the hydrogen atom
in its postulated position is 120°, the observed distance
O(1) ⋯ C(126), 2.940(14) Å, must be close to the sum of
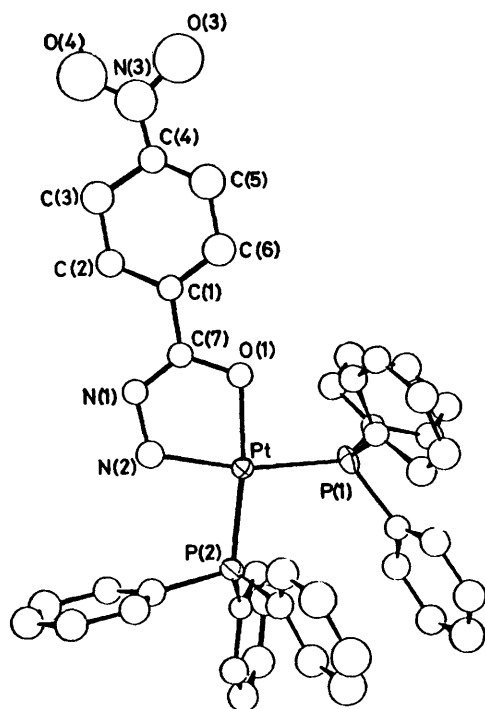
FIGURE 2 A molecular unit in the disordered crystal
structure of [Pt(PPh₃)₂{NHNC(O)C₆H₄NO₂-*p*}]

the van der Waals radii $r_O + r_O$ (3.20 Å), likewise the
distance O ⋯ H (computed) is similar to the expected
van der Waals contact (2.24 compared with 2.60 Å).
This interaction is similar to that described in the
structure of [IrI₂(CO)(CO₂Me)(bipy)] (bipy = 2,2′-bi-
pyridyl) (see discussion in ref. 10) and is interpreted in
terms of the slight acidic character of an *ortho*-hydrogen
atom and the relatively high charge on atom O(1). In
compound (1) the overall conformation of the phosphine
ligand to which C(126) belongs is dictated by this inter-
action and by the interaction with the second phosphine,
placed in a *cis* position, which does not exhibit a potenti-
ally similar interaction with O(2).

The situation changes in compound (2), probably
because of the steric hindrance of the N(2)–H group
which substitutes O(2),* as can be seen by comparing the
P(2)–Pt–O(2),N(2) angles and this induces a change in
the conformations of both ligands. A comparison of
the two structures shows that the geometries of the two
mutually *cis* triphenylphosphine groups are tightly inter-
locked because of the ' quasi graphite-like ' stacking of
two phenyl rings,[11] one from each phosphine, which lie
almost parallel at a distance of 3.4 Å. This is true, of
course, for other bis(triphenylphosphine) complexes such

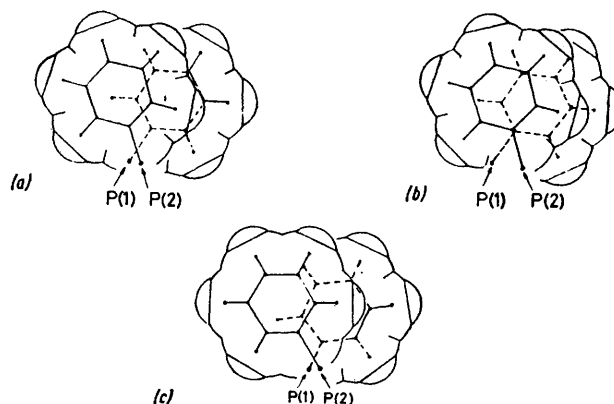FIGURE 3 Stacking of phenyl rings in three *cis*-[Pt(PPh₃)₂]
complexes: (*a*) [Pt(PPh₃)₂{ONC(O)C₆H₅}]; (*b*) [Pt(PPh₃)₂-
{NHNC(O)C₆H₄NO₂-*p*}]; (*c*) [Pt(PPh₃)₂{C₆H₅C(O)N₂C(O)-
C₆H₅}] from data of ref. 12

as the analogue of (2), [Pt(PPh₃)₂{PhC(O)N₂C(O)Ph}],
(2′), described by Ittel and Ibers.[12] The arrangements
of the phenyl ring pairs in the three complexes are
shown in Figure 3.

In Table 2 the most relevant bonding parameters in
the two crystals (derived from the atomic parameters of
Tables 3 and 4) are compared. The two molecules are
square-planar complexes of Pt^II in which the isoelec-
tronic ligands forming the five-membered metallocycle
are present as aroylhydroxylamido- and aroylhydrazido-
dianions in (1) and (2) respectively; clearly the resonance
equilibria between forms (a) and (b) lie essentially to the
left. In compound (1) the metallocycle lies on the same

* The hydrogen atom bonded to N(2) has not been detected
in the final difference synthesis of (2). Its presence is inferred
from the i.r. spectral data (see below).

plane at the P–Pt–P moiety whereas in compound (2) it forms an angle of 5°. The situation, which is shown in Figure 4, may be due to electronic factors as well as to intra- and inter-molecular interactions.*

TABLE 2

Selected intramolecular distances (Å) and angles (°) in [Pt(PPh₃)₂{ONC(O)C₆H₅}] (1) and [Pt(PPh₃)₂{NHNC-(O)C₆H₄NO₂-p}] (2)

	(1)	(2)
Pt–P(1)	2.248(4)	2.302(10)
Pt–P(2)	2.248(4)	2.229(6)
Pt–O(1)	2.013(10)	2.024(15)
Pt–O(2),N(2)	2.005(12)	2.001(20)
P(1) · · · P(2)	3.388(5)	3.488(29)
O(1) · · · O(2),N(2)	2.590(15)	2.586(27)
P(1) · · · O(1)	3.162(11)	2.985(22)
P(2) · · · O(2),N(2)	2.911(13)	3.062(21)
O(1)–C(7)	1.351(26)	1.345(27)
N(1)–O(2),N(2)	1.417(25)	1.389(28)
N(1)–C(7)	1.281(27)	1.268(29)
P(1)–C(111)	1.828(10)	1.810(16)
P(1)–C(121)	1.834(9)	1.792(36)
P(1)–C(131)	1.820(10)	1.836(31)
P(2)–C(211)	1.832(10)	1.791(31)
P(2)–C(221)	1.833(11)	1.832(18)
P(2)–C(231)	1.835(13)	1.830(17)
C(7)–C(1)	1.46(3)	1.46(3)
C(1)–C(2)	1.41(2)	1.39(3)
C(2)–C(3)	1.38(3)	1.44(4)
C(3)–C(4)	1.36(3)	1.44(4)
C(4)–C(5)	1.36(3)	1.37(4)
C(5)–C(6)	1.38(3)	1.47(5)
C(6)–C(1)	1.41(2)	1.34(4)
C(4)–N(3)		1.31(5)
N(3)–O(3)		1.25(5)
N(3)–O(4)		1.30(6)
P(1)–Pt–P(2)	97.8(1)	100.7(8)
P(1)–Pt–O(1)	95.7(3)	87.0(9)
P(1)–Pt–O(2),N(2)	175.9(3)	166.3(11)
P(2)–Pt–O(2),N(2)	86.2(3)	92.6(6)
P(2)–Pt–O(1)	166.1(3)	172.1(5)
O(1)–Pt–O(2),N(2)	80.3(4)	79.9(7)
Pt–O(1)–C(7)	109.9(13)	110.2(13)
Pt–O(2), N(2)–N(1)	113.0(12)	112.2(13)
O(1)–C(7)–N(1)	123.7(22)	121.8(20)
C(7)–N(1)–O(2),N(2)	112.9(19)	115.9(19)
Pt–P(1)–C(111)	114.7(5)	105.2(8)
Pt–P(1)–C(121)	117.4(4)	114.4(13)
Pt–P(1)–C(131)	111.7(5)	120.3(18)
Pt–P(2)–C(211)	108.1(4)	122.2(10)
Pt–P(2)–C(221)	122.8(4)	111.6(6)
Pt–P(2)–C(231)	113.8(4)	115.0(6)
C(111)–P(1)–C(121)	97.7(5)	123.0(19)
C(111)–P(1)–C(131)	111.3(6)	90.7(13)
C(121)–P(1)–C(131)	102.7(6)	102.1(8)
C(211)–P(2)–C(221)	103.0(6)	103.5(11)
C(211)–P(2)–C(231)	104.6(6)	111.2(10)
C(221)–P(2)–C(231)	102.6(5)	102.3(8)
O(1)–C(7)–C(1)	116.6(20)	117.3(19)
N(1)–C(7)–C(1)	119.2(21)	120.9(20)
C(1)–C(2)–C(3)	120.0(17)	123.0(25)
C(2)–C(3)–C(4)	122.1(20)	115.0(26)
C(3)–C(4)–C(5)	118.0(21)	121.7(30)
C(4)–C(5)–C(6)	123.0(19)	122.4(33)
C(5)–C(6)–C(1)	118.8(17)	119.2(28)
C(6)–C(1)–C(2)	118.0(14)	118.7(24)
C(5)–C(4)–N(3)		128.2(33)
C(3)–C(4)–N(3)		110.1(28)
O(3)–N(3)–O(4)		111.5(38)

The N(1)–C(7) distances of both complexes are equivalent and compare well with the value found in (2'): 1.281(27) and 1.268(29) vs. 1.286(10) Å. These inter-

* A Table of 'best planes' is available, for both structures, upon request to the authors.

actions correspond to a typical double bond as required by formulae of type (a). The distances N(1)–O(2) in (1) and N(1)–N(2) in (2) are also equivalent; their mean, 1.40 Å, and the value found in (2'), 1.401(9) Å, are shorter
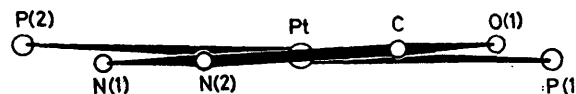

FIGURE 4 The 5° twist between the P–Pt–P plane and the plane of the metallocycle in [Pt(PPh₃)₂{NHNC(O)C₆H₄NO₂-p}]

than those found in hydrazine and hydroxylamine [1.453(5) and 1.47(3) Å; see ref. 13]. The shortening indicates that a certain amount of electron density is

TABLE 3

Positional parameters (× 10⁴) in [Pt(PPh₃)₂{ONC(O)-C₆H₅}]

Atom	x	y	z
Pt	2 022(0)	910(0)	2 500
P(1)	1 616(2)	2 295(3)	1 705(2)
P(2)	1 269(2)	1 439(3)	3 438(2)
O(1)	2 834(6)	213(9)	1 846(5)
O(2)	2 443(6)	355(11)	3 157(6)
N(1)	3 041(12)	−1 030(16)	2 834(14)
C(7)	3 182(14)	−715(19)	2 179(14)
C(1)	3 819(8)	−1 282(13)	1 787(8)
C(2)	4 223(10)	−2 236(16)	2 100(9)
C(3)	4 829(12)	−2 751(19)	1 733(13)
C(4)	5 032(12)	−2 404(21)	1 053(12)
C(5)	4 650(11)	−1 462(20)	753(10)
C(6)	4 055(8)	−879(18)	1 099(8)
C(111)	616(5)	2 127(12)	1 414(6)
C(112)	255(6)	2 968(9)	975(6)
C(113)	−477(6)	2 746(10)	702(6)
C(114)	−850(5)	1 682(12)	868(6)
C(115)	−490(6)	840(9)	1 308(6)
C(116)	243(6)	1 063(10)	1 580(6)
C(121)	2 061(6)	2 299(9)	803(4)
C(122)	2 116(6)	3 367(7)	421(5)
C(123)	2 387(6)	3 369(7)	−289(5)
C(124)	2 603(6)	2 304(9)	−618(4)
C(125)	2 549(6)	1 236(7)	−236(5)
C(126)	2 278(6)	1 234(7)	474(5)
C(131)	1 805(6)	3 799(7)	2 030(8)
C(132)	1 274(4)	4 728(9)	2 057(7)
C(133)	1 499(5)	5 846(8)	2 307(7)
C(134)	2 255(6)	6 035(7)	2 530(8)
C(135)	2 785(4)	5 107(9)	2 504(7)
C(136)	2 560(5)	3 988(8)	2 254(7)
C(211)	1 885(6)	1 645(14)	4 235(5)
C(212)	1 626(5)	1 354(13)	4 928(6)
C(213)	2 103(6)	1 530(9)	5 525(4)
C(214)	2 839(6)	1 997(14)	5 430(5)
C(215)	3 097(5)	2 288(13)	4 737(6)
C(216)	2 620(6)	2 112(9)	4 140(4)
C(221)	677(6)	2 792(8)	3 434(6)
C(222)	925(4)	3 806(9)	3 802(5)
C(223)	458(6)	4 814(7)	3 827(5)
C(224)	−255(6)	4 808(8)	3 485(6)
C(225)	−503(4)	3 794(9)	3 117(5)
C(226)	−36(6)	2 786(7)	3 092(5)
C(231)	578(7)	285(10)	3 708(6)
C(232)	−51(7)	567(8)	4 143(6)
C(233)	−565(5)	−320(11)	4 351(6)
C(234)	−450(7)	−1 491(10)	4 125(6)
C(235)	179(7)	−1 773(8)	3 690(6)
C(236)	693(5)	−885(11)	3 482(6)

delocalized on the two bonds and, in this respect, some contribution from formula (b) seems evident. The bond C(7)–O(1) is 1.351(26) in (1) and 1.345(27) Å in (2); the corresponding interaction found in (2'), 1.318(10) Å, is

not statistically different; however, it might represent a different electronic interaction for this complex in which, mainly because of the crowded chelating ligand, a significant deviation from planarity has been observed. The Pt–O,N bonds in (1) and (2) have lengths statistically indistinguishable in both cases; the mean statif of the four values is 2.011 Å; the bonds, however, have different properties as can be seen by comparing the lengths of the Pt–P interactions *trans* to them. In (1), where the

TABLE 4

Positional parameters ($\times$ 10^4) in
[Pt(PPh$_3$)$_2$\{NHNC(O)C$_6$H$_4$NO$_2$-p\}]

Atom	x	y	z
Pt	1 787(0)	2 972(0)	−1 844(0)
P(1)	2 848(2)	2 535(31)	−504(4)
P(2)	1 392(3)	4 595(4)	−1 214(4)
O(1)	2 056(9)	1 555(11)	−2 621(13)
O(3)	1 472(20)	−2 500	−7 060(27)
O(4)	2 608(27)	−2 898(32)	−6 122(32)
N(1)	927(11)	2 065(14)	−3 795(17)
N(2)	880(12)	2 973(15)	−3 100(18)
N(3)	1 947(23)	−2 266(39)	−6 207(29)
C(7)	1 515(14)	1 394(17)	−3 526(19)
C(1)	1 634(14)	418(18)	−4 202(19)
C(2)	1 111(17)	201(22)	−5 163(23)
C(3)	1 228(21)	−722(26)	−5 886(27)
C(4)	1 915(17)	−1 437(22)	−5 520(24)
C(5)	2 388(24)	−1 239(31)	−4 636(32)
C(6)	2 258(20)	−284(26)	−3 909(27)
C(111)	3 824(8)	2 747(18)	−1 195(12)
C(112)	3 985(9)	2 205(14)	−2 205(13)
C(113)	4 740(8)	2 396(13)	−2 716(10)
C(114)	5 333(8)	3 130(18)	−2 217(12)
C(115)	5 172(9)	3 671(14)	−1 207(13)
C(116)	4 417(8)	3 480(13)	−696(10)
C(121)	2 646(18)	1 340(12)	306(14)
C(122)	2 118(11)	552(13)	−208(10)
C(123)	1 971(12)	−418(14)	352(14)
C(124)	2 351(18)	−601(12)	1 428(14)
C(125)	2 878(11)	186(13)	1 944(10)
C(126)	3 025(13)	1 157(14)	1 383(14)
C(131)	3 182(13)	3 520(14)	602(13)
C(132)	2 639(10)	3 706(16)	1 463(15)
C(133)	2 853(10)	4 465(14)	2 302(13)
C(134)	3 610(13)	5 038(14)	2 280(13)
C(135)	4 154(10)	4 853(16)	1 420(15)
C(136)	3 940(10)	4 093(14)	581(13)
C(211)	2 270(18)	5 504(28)	−978(18)
C(212)	2 859(17)	5 500(16)	−1 805(15)
C(213)	3 545(11)	6 210(23)	−1 723(15)
C(214)	3 642(18)	6 924(28)	−812(18)
C(215)	3 054(17)	6 928(16)	14(15)
C(216)	2 368(11)	6 218(23)	−67(15)
C(221)	702(10)	5 310(16)	−2 270(14)
C(222)	995(8)	6 101(16)	−2 987(16)
C(223)	431(11)	6 591(12)	−3 777(14)
C(224)	−424(10)	6 290(16)	−3 850(14)
C(225)	−717(8)	5 499(16)	−3 133(16)
C(226)	−154(11)	5 010(12)	−2 343(14)
C(231)	743(10)	4 552(15)	11(12)
C(232)	581(11)	3 546(11)	495(14)
C(233)	112(11)	3 494(11)	1 450(14)
C(234)	−195(10)	4 447(15)	1 920(12)
C(235)	−33(11)	5 453(11)	1 436(14)
C(236)	435(11)	5 506(11)	482(14)

two phosphine ligands are *trans* to two oxygen atoms, the Pt–P distances are equal [2.248(4) Å] whereas in (2) the bond *trans* to Pt–N(2) is significantly longer than that *trans* to Pt–O(1): 2.302(10) *vs.* 2.229(6) Å. We can formulate the hypothesis that a hydrazido-ligand, like a diazenato-ligand, possesses a *trans* labilizing effect which

is not observed for the corresponding conjugated species hydrazine and diazene (see ref. 14 for discussions on the *trans* effect of these groups). This point is to be confirmed by further work; the effect is barely noticeable in the structure of (2'), highly distorted, and possessing an aroyl moiety bonded to N(2).

The phosphine groups are regular in both compounds. The angle at the co-ordinating centre, P(1)–Pt–P(2), of *ca.* 100° is dictated by the phenyl ring interactions shown in Figure 3. As expected, the mean angles Pt–P–C and C–P–C, involving ring carbon atoms bonded to phosphorus, are enlarged and contracted respectively by *ca.* 5° with respect to the tetrahedral angle, in both compounds.

Spectral Data and Reactivity of Aroylhydroxylamido- and Aroylhydrazido-derivatives.—The absorptions observed in the i.r. spectra of compounds (1)—(6) (Table 5)

TABLE 5

Infrared (cm^{-1}, in Nujol) spectral data

Complex	ν(NH)	ν(C=N)	ν(CO)	ν(N–O)
(1)		1 550	1 330 [a]	920
(2) [b, c]	3 370	[d]	[d]	
(3)		1 550	1 325	920
(4) [e]	3 360	1 580		915
(5)	3 380	1 560	1 325 [a]	
(6) [f, g]	3 380	1 560	1 320	
(7) [h]	3 180—3 240		1 635	
(8)	3 200—3 280		1 350,	
	[3 180 (sh)]		1 540,	
			1 580,	
			1 610	

[a] A band was observed at 1 050 cm^{-1} attributable to ν(C–O) of the clathrated ethanol; this band was absent when (5) was crystallized from chloroform. [b] $\delta(p$-NO$_2$) = 850—860 cm^{-1}. [c] ν(NO$_2$) = 1 515 and 1 305 cm^{-1}. [d] Covered by the broad absorptions of the nitro-group. [e] τ(NH) = 5.95 in CDCl$_3$. [f] $\delta(p$-CH$_3$) = 835 cm^{-1}. [g] τ(Me) = 7.82 in CDCl$_3$. [h] A broad band was also observed at 3 500 cm^{-1}.

are in complete agreement with the X-ray structures discussed above. In particular, for compounds (1) and (3) the 3 100—3 600 cm^{-1} region contains no absorption bands, confirming that a complete dehydrogenation of the hydroxylamino-group has taken place. On the other hand, for compounds (2), (5), and (6) the vibration associated with the N–H group was clearly observed at *ca.* 3 380 cm^{-1}.

While the aroylhydroxylamido-complex (1) is stable in solution in the presence of molecular oxygen, the aroylhydrazido-complexes (2), (5), and (6) react rapidly with dioxygen, giving products which give rise to i.r. spectral bands at *ca.* 1 630 and 1 335 cm^{-1} attributable to a unidentate carboxylato-ligand.[15] From the reaction conducted on (5) (R = H), a substance which did not contain nitrogen and whose i.r. spectrum was comparable to that of [Pt(PPh$_3$)$_2$(O$_2$CPh)$_2$] obtained from [Pt(PPh$_3$)$_3$] and PhCOOH was separated from the other by-products. This reaction corresponds to the expected rearrangement of the aroyldiazene, PhC(O)N=NH, with loss of nitrogen and oxidation of benzaldehyde to benzoic acid. The oxidation of the aldehyde to the acid is known to be catalysed by [Pt(PPh$_3$)$_2$(O$_2$)].[16,17]

Compound (5) reacted readily with tetrafluoroboric

acid, with double protonation of the chelating ligand [equation (4)]. When compound (5) was treated with hydrochloric acid, only cis-[PtCl₂(PPh₃)₂] and the salt of benzoylhydrazine, deduced by comparison with authentic samples, were obtained. The white complex (7) gives rise to a band at 1 635 cm⁻¹ in its i.r. spectrum, attributable to the carbonyl group co-ordinated to the metal

(7)
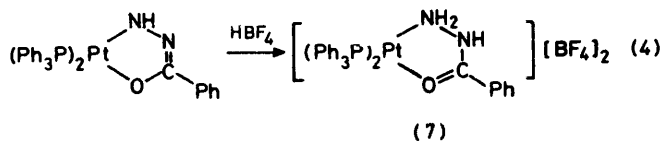
[ν(C=O) = 1 660 cm⁻¹ in the free ligand], bands in the 3 100—3 250 cm⁻¹ region due to the NH groups (Table 5), and the expected absorptions due to the BF₄⁻ anion.

Compound (7) undergoes a deprotonation reaction with Na[HCO₃], to give a complex of composition [Pt(PPh₃)₂-{N₂H₂C(O)C₆H₅}][BF₄] (8). On the basis of the i.r. spectrum only, which shows several bands in the 1 300—1 600 cm⁻¹ region, it is not possible to decide unambiguously what the true structure is; in any case, the compound should have a carbonyl group involved in co-ordination since no bands are observed between 1 610 and 1 700 cm⁻¹.

When compound (8) was treated with K[OH] an orange product having an i.r. spectrum comparable to that of (5) was obtained.

Even compound (3) reacts with tetrafluoroboric acid, but the product did not give satisfactory elemental analyses. This material, when treated with Na[HCO₃], gave back the starting complex (3).

These reactions have confirmed that co-ordination of an amino-group to platinum(II) makes the N–H acidic enough to be deprotonated by a base.[1]

EXPERIMENTAL

All reactions (and work-up of reaction mixtures) were carried out under an atmosphere of pure nitrogen, unless stated otherwise, with magnetic stirring. Solvents were dried and purified. Starting palladium and platinum phosphine complexes were prepared as described in the literature.[18,19] Infrared spectra were recorded on a Perkin-Elmer 457 instrument and a Beckmann IR 4210 spectrophotometer. Hydrogen-1 n.m.r. spectra were recorded on a Varian NV-14 spectrometer with SiMe₄ as internal standard. Conductivity data were obtained with a Philips PR9500 instrument. Melting points were determined on a Leitz Heiztischmikroskop. Elemental analyses were carried out in the analytical laboratory of Milan University. The aroylhydrazidoplatinum complexes decompose in a few hours when exposed to air, even in the solid state, so they were stored under nitrogen.

[Pt(PPh₃)₂{ONC(O)C₆H₅}]·0.5C₂H₅OH (1) (solvated).—To solid [Pt(PPh₃)₂(O₂)] (0.3 g) and C₆H₅(O)NHOH (0.166 g), ethanol (10 cm³) was added. After 4 h the yellow precipitate was filtered off, washed with a little ethanol and diethyl ether, and dried in vacuo (43% yield).

In another experiment the suspension was evaporated to ca. half the volume and the yellow precipitate was filtered off (75% yield). The same results were obtained by con-

ducting the reaction with equimolar amounts of [Pt(PPh₃)₂-(O₂)] (0.3 g) and C₆H₅C(O)NHOH (0.06 g). However when the solvent was in part evaporated, the product was less pure. By crystallization from chloroform–n-hexane, analytically pure (1) was obtained. Pale yellow crystals of the complex free of solvent and suitable for the X-ray structure determination were obtained from CHCl₃–n-hexane (2 : 1), under nitrogen.

[Pt(PPh₃)₂{NHNC(O)C₆H₄NO₂-p}] (2).—To a solution of [Pt(PPh₃)₂(O₂)] (0.057 g) in ethanol (3 cm³), a solution of p-NO₂C₆H₄C(O)NHNH₂ (0.029 g) in ethanol (2 cm³) was added. A clear violet solution was obtained. After 2.5 h a violet precipitate was filtered off, washed with a little ethanol and n-hexane, and dried in vacuo (89% yield). Crystals of the complex suitable for the X-ray structure determination were obtained as described in the text.

[Pd(PPh₃)₂{ONC(O)C₆H₅}] (3).—To solid [Pd(PPh₃)₂(O₂)] (0.4 g) and C₆H₅C(O)NHOH (0.165 g), ethanol (15 cm³) was added. After 4 h the pale brown precipitate was filtered off and washed with a little ethanol. It was crystallized from CHCl₃–diethyl ether and dried in vacuo (60% yield).

[Pt(PPh₃)₂{ONC(NH)C₆H₅}] (4).—To solid [Pt(PPh₃)₂-(O₂)] (0.2 g) and C₆H₅C(NH)NHOH (0.108 g), ethanol (8 cm³) was added. After 24 h a small quantity of a pale yellow precipitate was filtered off, washed with a little ethanol and n-hexane, and dried in vacuo.

[Pt(PPh₃)₂{NHNC(O)C₆H₅}]·C₂H₅OH (5) (solvated).—To a solution of [Pt(PPh₃)₂(O₂)] (0.5 g) in ethanol (10 cm³), solid C₆H₅C(O)NHNH₂ (0.156 g) was added. After a few minutes the orange complex began to precipitate. After 3 h the orange precipitate was filtered off, washed with a little ethanol and n-hexane, and dried in vacuo (57% yield).

[Pt(PPh₃)₂{NHNC(O)C₆H₄CH₃-p}] (6).—This compound was prepared as described for (5) by using [Pt(PPh₃)₂(O₂)] (0.3 g), p-CH₃C₆H₄C(O)NHNH₂ (0.12 g), and ethanol (7.5 cm³) and by filtering off the orange complex after 4.5 h (54% yield).

[Pt(PPh₃)₂{NH₂NHC(O)C₆H₅}][BF₄]₂·C₂H₅OH (7) (solvated).—To a suspension of (5) (0.1 g) in ethanol (5 cm³), three drops of HBF₄ (40% in water) were added. The solution immediately became colourless. After 1 h the white precipitate was filtered off, washed with a little ethanol and n-hexane, and dried in vacuo (60% yield).

[Pt(PPh₃)₂{N₂H₂C(O)C₆H₅}][BF₄] (8).—To a suspension of (7) (0.177 g) in diethyl ether (10 cm³), Na[HCO₃] (0.03 g) in water was added. Gas evolution was noted. After 5 h the white precipitate was filtered off, washed repeatedly with water, diethyl ether, and n-hexane, and dried in vacuo. By treating (8) in ethanol with K[OH], dissolved in water, an orange insoluble product having an i.r. spectrum similar to that of (5) was obtained.

Reaction of (5) with HCl.—To ethanol (20 cm³) saturated with gaseous HCl, compound (5) (50 mg) was added. A white precipitate was immediately formed. After 1 h it was filtered off and washed with ethanol and diethyl ether. It was shown to be cis-[PtCl₂(PPh₃)₂] by its i.r. spectrum. The mother-liquor of the reaction was evaporated to dryness, and the residue was shown to be the salt of benzoylhydrazine, by comparison of its i.r. spectrum with that of an authentic sample obtained from C₆H₅C(O)NHNH₂ and gaseous HCl in ethanol.

Reaction of (5) with O₂.—A solution of (5) (0.17 g) in acetone (7 cm³) was kept in an atmosphere of pure oxygen for 2 h. The starting orange solution became brown. It was evaporated to a small volume. By adding n-hexane, an

oily material precipitated, which was solidified by using diethyl ether. This material was crystallized several times from $CHCl_3$–diethyl ether.

A complex having an i.r. spectrum similar to that of this material and analysing for $[Pt(PPh_3)_2(O_2CC_6H_5)_2]\cdot CHCl_3$, was obtained by treating $[Pt(PPh_3)_3]$ (0.2 g) with PhCOOH (0.1 g) in benzene (5 cm³). The initial yellow-orange solution became slowly yellow. After 40 h it was evaporated to a small volume. By adding diethyl ether and scratching a pale brown material was obtained. It was crystallized from chloroform–diethyl ether, m.p. = 229 °C {Found: C, 57.4; H, 4.1. $[Pt(PPh_3)_2(O_2CC_6H_5)_2]\cdot CHCl_3$ requires C, 56.7; H, 3.8%}. The tendency to clathrate the chlorinated solvent was confirmed for a sample crystallized from CH_2Cl_2–diethyl ether; its ¹H n.m.r. spectrum in $CDCl_3$ clearly showed a peak at τ 4.25, which was still present after a prolonged drying under vacuum of the crystallized product.

It is noteworthy that a solution of (5) in acetone kept under nitrogen is stable both to sunlight and to heating at reflux for a short time. On the other hand, when (1) was left in acetone in an atmosphere of pure oxygen no sign of decomposition was observed after 5 h.

Reaction of $[Pt(PPh_3)_2(O_2)]$ *with* $RNHNH_2$ (R = H or C_6H_5).—To $[Pt(PPh_3)_2(O_2)]$ (0.4 g) in ethanol (30 cm³), eight drops of phenylhydrazine were added. The yellow solution turned orange and after *ca.* 15 min the yellow-orange product began to precipitate. After 4 h it was filtered off under nitrogen and washed with diethyl ether. Its elemental analyses (Found: C, 64.7; H, 4.6; N, 0.0%) and i.r. spectrum confirmed the formulation of this product as $[Pt(PPh_3)_3]$. The same behaviour was observed by using a solution of NH_2NH_2 in water instead of $C_6H_5NHNH_2$.

Reaction of $[Pt(PPh_3)_2(O_2)]$ *with* C_6H_5NHOH.—To $[Pt(PPh_3)_2(O_2)]$ (0.2 g) suspended in n-hexane (10 cm³), C_6H_5-NHOH (0.05 g) and ethanol (30 drops) were added. After 15 h the yellow-green powder was filtered off, washed with a little diethyl ether, and dried *in vacuo*. The product did not show an absorption due to the peroxo-group in its i.r. spectrum, while a new band was observed at 970 cm⁻¹ in Nujol {lit.,⁶ ν(N–O) = 973 cm⁻¹ for $[Pt(PPh_3)_2(C_6H_5NO)]$}. No other significant bands besides those due to triphenylphosphine were observed in the i.r. spectrum.

Crystal Data.—Compound (1). $C_{43}H_{35}NO_2P_2Pt$, M 854.80, Orthorhombic, space group $Pna2_1$ (C_{2v}^9, no. 33), $a =$ 17.365(6), $b = 11.218(7)$, $c = 18.431(8)$ Å, $U = 3 590$ Å³, $D_c = 1.57$, $D_m = 1.58$ g cm⁻³ (by flotation), $Z = 4$, $F(000)$ = 1 560, μ(Mo-K_α) = 42.4 cm⁻¹.

Compound (2). $C_{43}H_{35}N_3O_3P_2Pt$, M 898.80, Monoclinic, space group $P2_1/m$ (C_{2h}^2, no. 11), disordered, $a = 15.829(6)$, $b = 12.269(5)$, $c = 11.833(5)$ Å, β = 93.51(3)°, $U = 2 293$ Å³, $D_c = 1.30$, $D_m = 1.34$ g cm⁻³, $Z = 2$, $F(000) = 824$, μ(Mo-K_α) = 33.8 cm⁻¹.

The cell parameters have been obtained, in both cases, from least-squares refinement of 25 high-angle reflections (graphite-monochromated radiation Mo-K_α; λ = 0.710 73 Å).

Determination and Refinement of the Structures.—Intensities for both samples were collected on our BASIC diffractometer,* θ in the range 3—25°. The sets of observations used in the solutions and in the refinement of the structures were limited to independent reflections having

* The BASIC automatic diffractometer was assembled by one of us (P. L. B.) from a Siemens four-circle goniometer and a Hewlett–Packard 2100 A minicomputer. All of its programmes are written in the Dartmouth College ' Basic ' language.

$\sigma(I)/I \leqslant 0.3$, which were corrected for Lorentz-polarization and absorption effects [2 057 observations for (1) and 2 119 for (2)].

The solution of the structure of compound (1) by conventional Patterson and Fourier methods was absolutely straightforward. The Patterson map of (2) had a vector, 1.15 Å long, on the unique axis, having about half the weight of the origin peak. A parallel image was reproduced by a satellite peak at 1.15 Å from the Pt–Pt peak of the Harker section, the weight ratio between the satellite and the Harker peak being again 1 : 2. Although the interpretation of lighter peaks allowed a PtP_2 moiety to be correctly defined, any attempt to refine the model in space group $P2_1$, disregarding the strongest Patterson peaks, invariably failed. All problems were finally overcome by interpreting those peaks in terms of two ' half ' Pt atoms belonging to enantiomeric molecules related by a statistical mirror. The assumption of this disordered model and the use of rigid-body techniques (see below) led to a nearly straightforward refinement in space group $P2_1/m$.†

For both structures the refinements have been carried out by full-matrix least squares, with the phenyl rings of phosphine ligands constrained to D_{6h} symmetry (C–C 1.392 Å). In compound (2) the carbon atoms of the triphenylphosphine ligand have been treated isotropically; all the remaining atoms were assigned anisotropic temperature factors.

In (2), owing to the disorder in the refined model, only Pt and P atoms were treated anisotropically. The contributions of all the hydrogen atoms, apart from H–N(2) in (2), in their postulated positions were included in the computations. Atomic scattering factors given in refs. 20 and 21 were used in structure-factor and least-squares computations. Corrections for real and imaginary dispersion of Pt and P species were included as specified in ref. 22.

The least-squares matrix of compound (2) was almost singular in correspondence with the y co-ordinate of atom O(3); since the co-ordinate was very nearly at −0.25, the atom was fixed on the mirror plane. The weighting scheme adopted for both structures was of the type $1/w = A + B$-$F_0 + CF_0^2$ with the following coefficients: 17.0, −0.14, and 6.3 × 10⁻⁴ for (1) and 17.9, −0.83, and 1.44 × 10⁻² for (2).

The final reliability indices were $R = 0.031$ and $R' = 0.035$ for (1); 0.062 and 0.087 respectively for (2) {$R' = [\Sigma w(F_0 - k|F_c|)^2/wF_0^2]^{\frac{1}{2}}$}. Tables 3 and 4 list the final co-ordinates of all non-hydrogen atoms in compounds (1) and (2) respectively. Thermal parameters and observed and calculated structure factors are listed in Supplementary Publication No. SUP 22852 (19 pp.).‡

The final difference-Fourier syntheses show signals of 0.2 e in (1), associated with the position of the metal atom. Signals of 0.4 e in the corresponding positions are noticeable in (2), together with signals of 1.5—2 e in the vicinity of the chelating ligand. Although no coherent interpretation is possible for these peaks, we might conclude that some very disordered molecules of solvent are trapped in the structure; this explains the difference between the computed and observed densities of this species.

† The hypothesis of a crystal in which the relative abundances of the two enantiomers are significantly different from 50% has been rejected on the basis of both the relative weights of the Patterson peaks and the results of a least-squares refinement, in the polar space group, of the occupancy numbers of the two PtP_2 moieties, which converged to relative abundances 49 and 51%.

‡ For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

All computations were done on a Univac 1108 Computer. The programs used for Fourier analysis, least-squares, and molecular-geometry computations belong to our own library; Johnson's ORTEP program was used in preparing Figures 1 and 2.

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