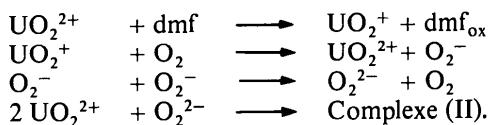


L'empilement des dimères est montré sur la Fig. 2: celui-ci est tel que des plans de bipyramides hexagonales se trouvent séparés par des plans de molécules de dmf.

Les deux structures montrent nettement l'état initial et l'état final d'une réaction d'activation de la molécule d'oxygène. Le composé (II) qui présente un groupe de type peroxy est obtenu à partir de l'oxygène atmosphérique, lequel a donc subi une réduction à 2 électrons. Il est connu par ailleurs qu'en présence de lumière, l'uranyle excité est capable d'oxyder les substrats organiques et en particulier les amides jusqu'à CO et CO₂. En général, en présence d'une source lumineuse intense, l'uranium est réduit à l'état d'uranium(IV); mais si l'on opère à la lumière et en présence d'oxygène, il est probable que la première forme réduite de l'uranyle UO₂⁺ est réoxydée par O₂ en UO₂²⁺ en donnant O₂⁻ dans un premier stade, puis O₂²⁻ par dismutation, ce dernier formant un complexe stable avec l'uranyle. Dans ces conditions on prévoit que le dérivé peroxy ne sera obtenu que pour des conditions de réactions bien particulières où la réoxydation de l'UO₂²⁺ sera plus rapide que la réaction de dismutation conduisant à U^{IV}.

On peut proposer un mécanisme de formation de (II) par les réactions:



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Structure of *trans*-Dichlorobis(*p*-fluoroaniline)palladium(II), [PdCl₂(C₆H₆FN)₂]

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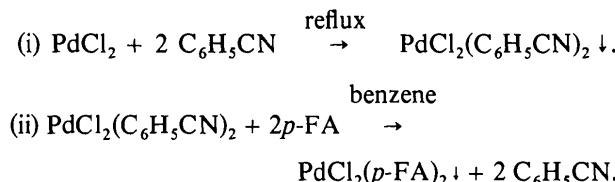
Abstract. $M_r = 399.5$, m.p. = 515 K (dec.), monoclinic, $P2_1/c$, $a = 4.621$ (4), $b = 6.248$ (4), $c = 23.925$ (6) Å, $\beta = 97.22$ (4)°, $V = 685.3$ Å³, $Z = 2$, $D_x = 1.936$, $D_m = 1.922$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 17.39$ cm⁻¹, $F(000) = 392$, room temperature, $R = 0.055$ for 888 observed reflections. Palladium is four-coordinated with *trans* stereochemistry, Pd–Cl = 2.318 (2), Pd–N = 2.052 (7) Å. The symmetry of the benzene ring of *p*-fluoroaniline (*p*-FA) is essentially

C_{2v} (mm). The aniline N atom deviates by 0.011 (7) Å from the least-squares plane of the benzene ring. The minor axis of the thermal ellipsoid of the F atom is collinear with the C–F bond.

Introduction. Palladium and platinum compounds have attracted attention as a consequence of their application in homogeneous and heterogeneous catalysis. The structure, stereochemistry and bonding in these com-

ounds have been an area of considerable research since the discovery of antitumour properties in certain *cis*-platinum complexes. The structure determination of a series of palladium and platinum complexes with substituted anilines and amino-acid ligands using X-ray and spectroscopic techniques, has been taken up in order to study the substituent effects on coordination and the interaction of these ions with biologically significant ligands. Preliminary results of structural studies of bis(4-hydroxy-L-prolinato)palladium(II) trihydrate have been reported elsewhere (Sinh, Padmanabhan, Patel, Ranganathan & Rao, 1982). The title compound is second in the series.

Experimental. The complex was synthesized as follows:



Orange-red crystals of the complex were grown by slow evaporation from dimethylformamide solution. D_m by flotation in CCl_4 and 1,2-dibromoethane. Intensity data (crystal size $0.20 \times 0.22 \times 0.28$ mm) collected with a computer-controlled four-circle diffractometer (indigenously fabricated), Zr-filtered $\text{Mo K}\alpha$ radiation, $\omega-2\theta$ step scan, 1165 unique reflections recorded in range $8 < 2\theta < 55^\circ$, 897 with $I \geq 2.5\sigma(I)$ considered observed; index range $h -6/5, k 0/7, l 0/28$. Corrections applied for Lorentz and polarization effects and for absorption, max. and min. values of absorption corrections 0.735 and 0.697 respectively. Unit-cell parameters obtained from least-squares fit of 2θ values of 25 reflections measured on the diffractometer. Structure solved using heavy-atom method. Structure isotropically and anisotropically refined by least squares based on F values using *SHELX76* (Sheldrick, 1976). In final stages, H atoms fixed at calculated positions with isotropic thermal parameters $U = 0.05 \text{ \AA}^2$. Atomic scattering factors with corrections for dispersion effects from *International Tables for X-ray Crystallography* (1974). In final stages of refinement, nine reflections showing large $(F_o - F_c)/\sigma(F_o)$ due to extinction were excluded. For 888 observed reflections, $R = 0.055$, $wR = 0.069$ with $w = k/[\sigma^2(F_o) + g(F_o)^2]$ where k and g refined to 1.0381 and 0.00226 respectively. $\Delta/\sigma(\text{max.}) = 0.6$; $\Delta\rho$ in final difference map -0.7 to 1.4 e \AA^{-3} . The final positional parameters are given in Table 1.*

Discussion. An *ORTEP* drawing (Johnson, 1971) of the molecule is shown in Fig. 1. Bond distances and angles are listed in Table 2. The central Pd atom is four-coordinated having essentially a square-planar geometry. The two Cl atoms and the aniline N atoms are coordinated to Pd in *trans* configuration. Infrared spectra of the complex and the free ligand recorded as Nujol mulls reveal the stretching (ν_{as} , ν_s) and the in-plane deformation (δ) frequencies to be depressed by 170, 190 and 20 cm^{-1} , respectively, in the complex, as expected, due to coordination. The $\nu^{M-\text{Cl}}$ band at 330 cm^{-1} shows a splitting. Such a splitting is generally attributed to a *cis* configuration of the complex (Kong & Rochon, 1981). However, the present work shows

Table 1. Final positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
Pd	1.0	0.5	0.5	34 (1)
Cl	0.6691 (5)	0.2354 (4)	0.4677 (1)	44 (1)
N	0.8113 (15)	0.7072 (11)	0.4396 (3)	39 (3)
F	1.4334 (15)	0.7632 (12)	0.2584 (3)	86 (4)
C(1)	0.9725 (17)	0.7203 (14)	0.3909 (3)	51 (4)
C(2)	0.9742 (19)	0.5478 (14)	0.3555 (4)	44 (4)
C(3)	1.1325 (20)	0.5636 (17)	0.3098 (4)	58 (4)
C(4)	1.2798 (21)	0.7488 (20)	0.3030 (4)	53 (4)
C(5)	1.2849 (21)	0.9202 (18)	0.3378 (5)	39 (4)
C(6)	1.1287 (18)	0.9077 (15)	0.3838 (4)	37 (3)

$$* U_{\text{eq}} = (U_{11} + U_{22}\sin^2\beta + U_{33} + 2U_{13}\cos\beta)/3(1-\cos^2\beta).$$

Table 2. Bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

Pd—Cl	2.318 (2)	Cl—Pd—N	90.6 (2)
Pd—N	2.052 (7)	Pd—N—C(1)	112.5 (5)
N—C(1)	1.461 (10)	N—C(1)—C(2)	119.4 (8)
C(1)—C(2)	1.371 (12)	N—C(1)—C(6)	117.8 (8)
C(2)—C(3)	1.394 (13)	C(1)—C(2)—C(3)	118.2 (8)
C(3)—C(4)	1.362 (15)	C(2)—C(3)—C(4)	118.2 (9)
C(4)—C(5)	1.355 (16)	C(3)—C(4)—C(5)	124.6 (9)
C(5)—C(6)	1.393 (13)	C(4)—C(5)—C(6)	118.1 (9)
C(6)—C(1)	1.397 (12)	C(5)—C(6)—C(1)	118.0 (9)
C(4)—F	1.356 (10)	C(6)—C(1)—C(2)	122.8 (8)
		C(3)—C(4)—F	118.0 (10)
		C(5)—C(4)—F	117.4 (10)

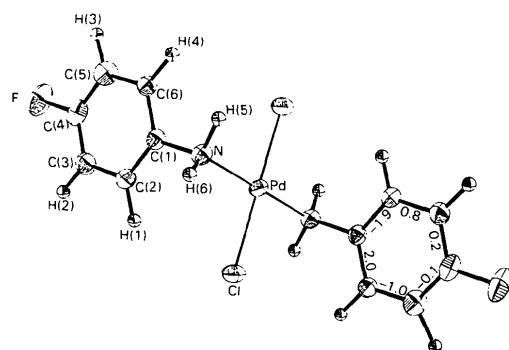


Fig. 1. Perspective view of the molecule. Atom labelling and ring torsion angles ($^\circ$, average e.s.d. 0.2°) are indicated.

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42277 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

that the complex has a *trans* stereochemistry and the observed splitting is, therefore, due to the solid-state correlation effect. We would hence like to emphasize that assignments of configuration solely on the basis of the number of ν^{M-Cl} bands could be erroneous in the absence of X-ray or other confirmatory evidence. The Pd—N and Pd—Cl distances are close to those published in the literature for related complexes (Navarro-Ranninger, Martínez-Carrera & García-Blanco, 1985). The aromatic ring of *p*-FA has C_{2v} (*mm*) symmetry. The deviations of the ring C atoms are hardly significant. However, they suggest a minor deformation of the ring towards a twist-boat model. The ring angles at the C atoms to which the substituents are attached are considerably larger than 120° . These results are in agreement with those in *p*-fluoroaniline hydrochloride (Colapietro, Domenicano, Marciante & Portalone, 1981). The bond distances C(2)—C(3), C(5)—C(6) and C(6)—C(1) are considerably longer than the other three C—C distances of the ring. The deviations of the atoms from planarity are: C(1) —0.010 (8), C(2) 0.006 (6), C(3) 0.001 (6), C(4) —0.004 (7), C(5) 0.000 (6), C(6) 0.007 (7), N 0.011 (7) and F —0.008 (8) Å. The ring torsion angles

are shown in Fig. 1. The least-squares plane of the benzene ring makes an angle of $73.2(9)^\circ$ with the metal coordination plane. The C(4)—F distance 1.36 (1) Å is the same as in *p*-fluoroaniline hydrochloride (Colapietro *et al.*, 1981); the minor axis of the thermal ellipsoid of the F atom is collinear with the C(4)—F bond.

There are no intermolecular contacts less than the van der Waals distance.

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Heptacarbonyl- μ -(2-formyl-3-diphenylphosphinophenylido-*O,P,C^a,C¹*)-(triphenyl-phosphine)dirhenium(I), [Re₂{P(C₆H₅)₂(C₇H₃O)}(CO)₇{P(C₆H₅)₃}]

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Abstract. (C₆H₅)₂P[C₆H₃(CO)Re(CO)₄][Re(CO)₃—P(C₆H₃)₃], $M_r = 1119.05$, monoclinic, $P2_1/n$, $a = 15.265$ (2), $b = 13.506$ (5), $c = 19.869$ (2) Å, $\beta = 93.54(9)^\circ$, $U = 4089$ (2) Å³, $Z = 4$, $D_x = 1.817$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 58.07$ cm⁻¹, $F(000) = 2144$, $T = 294$ (1) K, final $R = 0.064$ for 3629 unique reflexions. The molecular structure of C₄₄H₂₈O₈P₂Re₂ contains two rhenium atoms each with an essentially octahedral arrangement of ligands. One rhenium atom is coordinated to four carbonyl groups while each of the three CO ligands on the other rhenium atom is *trans* to a different atom. The two rhenium atoms are bridged by a quadridentate ligand that is bidentate to each metal atom. The molecule has an extended planar tricyclic ring system that includes two five-membered heterocyclic rings and one homonuclear ring.

Introduction. A complex decomposition process of the substance Re₂(CO)₈[P(C₆H₅)₃]₂ in the presence of Ga₂I₃ leads to the previously unknown heterocyclic title compound, which can exist in several isomeric molecular formulas. ¹H NMR and IR spectroscopic measurements of C₄₄H₂₈O₈P₂Re₂ gave no indication which isomer was present; therefore, the molecular structure has been elucidated.

Experimental. Dark-yellow crystals prepared in a one-pot process with Re₂(CO)₈[P(C₆H₅)₃]₂ in the presence of Ga₂I₃ at 423 K. $\omega/2\theta$ scan, scan width 1.45° , Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$, crystal size 0.1 × 0.1 × 0.4 mm, lattice parameters refined from 25 reflections $5 \leq \theta \leq 10^\circ$; 4 standard reflections recorded every 680 reflections showed only random deviations; $1 \leq \theta \leq 22^\circ$,