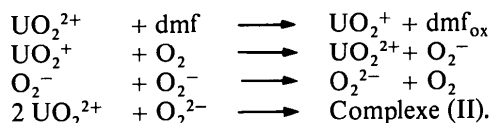


L'empilement des dimères est montré sur la Fig. 2: celui-ci est tel que des plans de bipyramides hexagonales se trouvent séparés par des plans de molécules de dmf.

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(C₆H₄FN)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-

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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^\alpha,C^1*)-(triphenylphosphine)dirhenium(I), $[\text{Re}_2\{\text{P}(\text{C}_6\text{H}_5)_2(\text{C}_7\text{H}_3\text{O})\}(\text{CO})_7\{\text{P}(\text{C}_6\text{H}_5)_3\}]$

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Abstract. $(\text{C}_6\text{H}_5)_2\text{P}\{\overbrace{[\text{C}_6\text{H}_3(\text{CO})\text{Re}(\text{CO})_4]}^{\text{}}\}\|\text{Re}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]$, $M_r = 1119.05$, 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, $\text{Mo } K\alpha$, $\lambda = 0.71069$ 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 $\text{C}_{44}\text{H}_{28}\text{O}_8\text{P}_2\text{Re}_2$ 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 $\text{Re}_2(\text{CO})_8[\text{P}(\text{C}_6\text{H}_5)_3]_2$ in the presence of Ga_2I_3 leads to the previously unknown heterocyclic title compound, which can exist in several isomeric molecular formulas. ¹H NMR and IR spectroscopic measurements of $\text{C}_{44}\text{H}_{28}\text{O}_8\text{P}_2\text{Re}_2$ 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 $\text{Re}_2(\text{CO})_8[\text{P}(\text{C}_6\text{H}_5)_3]_2$ in the presence of Ga_2I_3 at 423 K. $\omega/2\theta$ scan, scan width 1.45° , Enraf–Nonius CAD-4 diffractometer, graphite-monochromated $\text{Mo } K\alpha$, crystal size $0.1 \times 0.1 \times 0.4$ mm, lattice parameters refined from 25 reflections $5 \leq \theta \leq 10^\circ$; 4 standard reflections recorded every 680 reflections showed only random deviations; $1 \leq \theta \leq 22^\circ$,