Synthesis and *X*-Ray Structure of Carbon-bonded Palladium(II) Chelates of Acetic Anhydride and Acetic Acid

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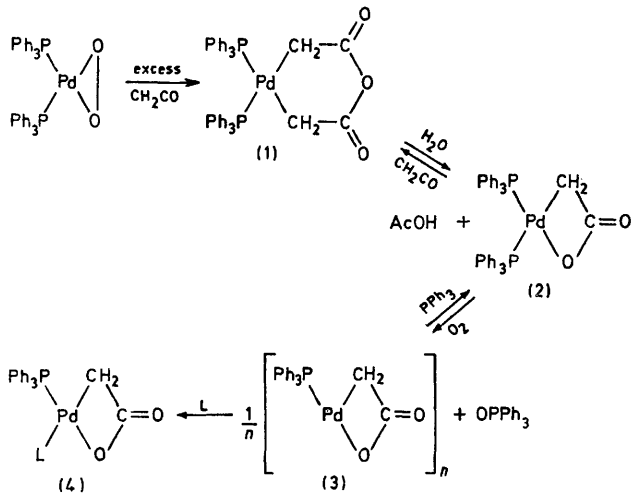
Summary Two types of palladium(II) complex, $Pd(C_4H_4O_3)(PPh_3)_2$ and $Pd(C_2H_2O_2)(PPh_3)(py)$, containing a carbon-bonded chelate ring of acetic anhydride and acetic acid, respectively, have been prepared by reactions of $Pd(O_2)(PPh_3)_2$ with keten, and their molecular structures have been determined by *X*-ray diffraction.

WHEN keten was bubbled into a solution of $Pd(O_2)(PPh_3)_2$ in benzene $Pd(C_4H_4O_3)(PPh_3)_2$ (**1**) was obtained,† m.p. 153° (decomp.). Hydrolysis of (**1**) in THF gave acetic acid and $Pd(C_2H_2O_2)(PPh_3)_2$ (**2**), m.p. 116° (decomp.). Complex (**1**) is obtained when (**2**) is treated with keten in benzene. Complex (**2**) is oxidized on refluxing in THF resulting in

† A satisfactory analysis was obtained.

PPh_3O and $Pd(C_2H_2O_2)(PPh_3)$ (**3**), m.p. 155° (decomp.). Compound (**3**) is transformed into (**2**) or $Pd(C_2H_2O_2)(PPh_3)L$ (**4**) by treatment with PPh_3 or bases such as pyridine, diethylamine, di-n-propylamine, or triphenylarsine.



SCHEME

Complex (**1**) is air-stable and gives acetic anhydride (40%) by thermal decomposition, which is also produced, together with *trans*-$PdCl_2(PPh_3)_2$ by the reaction of (**1**) with dry HCl in CH_2Cl_2. Treatment of (**1**) with aniline in refluxing chloroform gives acetanilide (55%). These results, and the i.r. and n.m.r. data indicate that (**1**) is a carbon-bonded palladium(II) chelate of acetic anhydride (Scheme).

The polymeric nature of (**3**) is presumed on the basis of its insolubility and the large low frequency shift of $\nu(C{=}O)$ (1545 cm^{-1}) indicative of oxygen co-ordination to another Pd atom.

Crystal data:‡ (**1**) orthorhombic, space group $P2_12_12_1$, $a = 16{\cdot}311 \pm 0{\cdot}003$, $b = 20{\cdot}153 \pm 0{\cdot}002$, $c = 10{\cdot}306 \pm 0{\cdot}003$ Å, $D_m = 1{\cdot}41$, $Z = 4$, $D_c = 1{\cdot}43$, Cu-K_α ($\lambda = 1{\cdot}5418$ Å), (**4**), monoclinic, space group $P2_1/c$, $a = 8{\cdot}798 \pm 0{\cdot}007$, $b = 14{\cdot}630 \pm 0{\cdot}012$, $c = 19{\cdot}862 \pm 0{\cdot}008$ Å, $\beta = 101{\cdot}53° \pm 0{\cdot}04°$, $D_m = 1{\cdot}47$, $Z = 4$, $D_c = 1{\cdot}46$.

Intensity data for (**1**) were collected by multiple-film equi-inclination Weissenberg photographs and for (**4**) on a Rigaku on-line, four-circle diffractometer. Totals of 1181 non-zero reflexions for (**1**) and 2811 for (**4**) were measured.

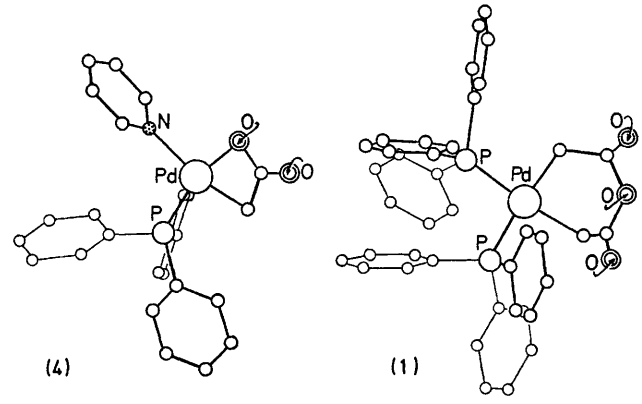


FIGURE. *Molecular structure of* $[Pd(C_2H_2O_2)(PPh_3)(py)]$ (*left*) *and* $[Pd(C_4H_4O_3)(PPh_3)_2]$ (*right*).

During the data collection (**4**) decomposed gradually. Both structures have been solved by the heavy-atom method, and refined by block-diagonal least-squares using isotropic and anisotropic temperature factors for non-hydrogen atoms for (**1**) and (**4**), respectively: $R = 0{\cdot}13$ for (**1**) and 0·09 for (**4**).

The molecular structures are shown in the Figure. The Pd–P distance in (**4**) [2·232(3) Å] is much shorter than those in (**1**) [2·35(2) and 2·36(2) Å].

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‡ (**2**) decomposed on irradiation with *X*-rays.