

## A Cyclohexa-1,4-diene Complex of Palladium(I) Acetate

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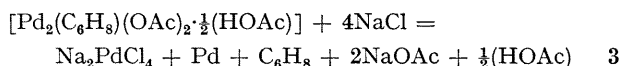
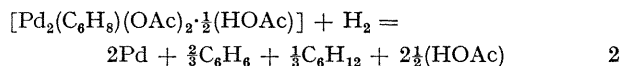
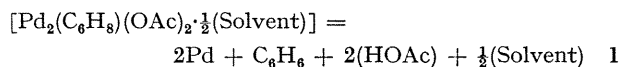
*Summary* In the course of the palladium(II) catalysed autoxidation of cyclohexa-1,4-diene a palladium(I) complex,  $[\text{Pd}_2(\text{C}_6\text{H}_8)(\text{OAc})_2 \cdot \frac{1}{2}(\text{HOAc})]$ , is formed as a by-product; the stoichiometry has been confirmed by analysis and by thermal decomposition, disproportionation and hydrogenation reactions.

of *d*-electrons are probably of considerable importance in homogeneous catalysis. Reaction schemes involving intermediate oxidation states of palladium have been proposed<sup>1-3</sup> and a few complexes have been isolated.<sup>4-6</sup>

Recently<sup>7</sup> it was shown that palladium acetate catalyses the  $\text{O}_2$ -oxidation of cyclohexa-1,4-diene in acetic acid into benzene and cyclohex-4-ene-1,3-diol diacetate. At low catalyst concentrations the acetic acid solution becomes red

COMPLEXES of the platinum metals having an odd number

and remains homogeneous but when diene, 0.32M, and Pd(OAc)<sub>2</sub>, 0.1M, are used red needles commence to crystallise after a reaction time of about 1 h. The crystals are a by-product, cyclohexa-1,4-dienediacetatodipalladium, having 0.5 mol of acetic acid of crystallisation. The acetic acid solvate, [Pd<sub>2</sub>(C<sub>6</sub>H<sub>8</sub>)(OAc)<sub>2</sub>·½(HOAc)], (I), gives satisfactory elemental analyses but since it is thermally unstable and cannot be recrystallised it has been characterised chemically and spectroscopically. The complex (I) is very soluble in dichloromethane† but the solution rapidly precipitates a second solvate, [Pd<sub>2</sub>(C<sub>6</sub>H<sub>8</sub>)(OAc)<sub>2</sub>·½(CH<sub>2</sub>Cl<sub>2</sub>)] (II), leaving ½ mol of acetic acid in the solvent. The i.r. absorptions at 1240 and 1720 cm<sup>-1</sup> caused by acetic acid in (I) are replaced in (II) by one at 725 cm<sup>-1</sup> caused by dichloromethane. The complexes (I) and (II) decompose slowly on pumping at 25° and 10<sup>-6</sup> mmHg pressure. Thermal decomposition was studied *in vacuo* and became vigorous above 70°. Complex (I) gives palladium metal, benzene, and acetic acid in the ratio 2:1:2.5 while (II) gives palladium metal, benzene, acetic acid, and dichloromethane in the ratio 2:1:2:0.5 (Equation 1). The pyrolysis residue was pure



palladium metal and contained no hydride. The mass spectrum of (I) obtained with a direct insertion probe also showed only peaks with the correct relative abundances for acetic acid and benzene and fragments from other possible products such as esters were absent. The complex (I) was readily reduced in dioxan solution by an excess of hydrogen at *ca.* 150 mmHg pressure (Equation 2). Presumably the hydrogenation reaction first liberates cyclohexa-1,4-diene which then undergoes disproportionation to benzene and cyclohexane (2:1) on the palladium metal surface. The palladium precipitate was slightly hydrided. Recovery of all excess hydrogen including that from pyrolysis of the palladium hydride showed the absorption of 0.92 mol of H<sub>2</sub> per mol of complex (I). The presence of cyclohexa-1,4-diene in the complex (I) was confirmed by its recovery from the disproportionation reaction with aqueous sodium chloride (Equation 3). Unfortunately some of the complex decomposes to benzene and palladium metal under these conditions since only about 30% (instead of 50%) of the palladium was recovered from the aqueous solution of Na<sub>2</sub>PdCl<sub>4</sub>. The presence of co-ordinated olefin in the complex was also confirmed by the observation of a broad singlet at  $\tau$  4.89 in the n.m.r. spectrum (an acetic acid solution of cyclohexa-1,4-diene has a multiplet at  $\tau$  4.33). The complex (I) is diamagnetic and presumably has a palladium-palladium bond and bridging acetate groups. The C-O stretching vibrations in the i.r. (1535 and 1385 cm<sup>-1</sup>) have a low separation possibly indicative of a symmetrically bound acetate ligand.<sup>8</sup>

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† All reactions and manipulations were carried out in a greaseless vacuum line which allowed quantitative transfer of volatile products and any solvent into sample tubes for n.m.r. and g.l.c. analysis of yields.

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