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Preliminary communication

A *cis*-OXYPALLADIUM ADDUCT OF CYCLOOCTADIENE: DIRECT SYNTHESIS AND ISOLATION FROM A PHOTOLYTIC REACTION

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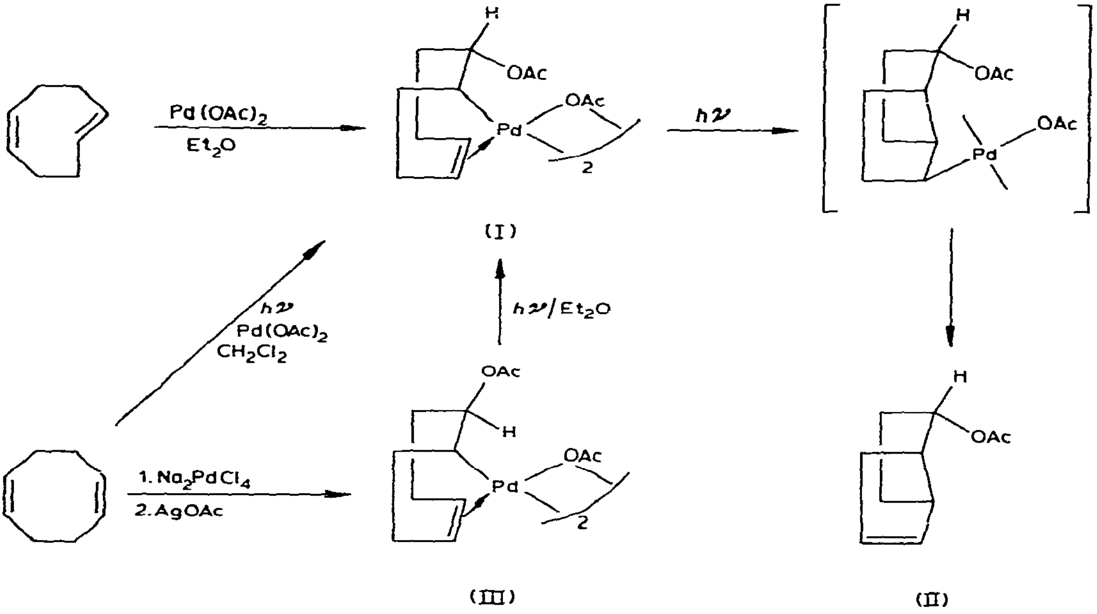
Summary

A *cis*-oxypalladium adduct of an olefin, di-μ-acetatobis(*cis*-2-acetoxycyclooct-5-enyl)dipalladium(II), I, was prepared from *cis,trans*-cycloocta-1,5-diene, and was isolated from photolysis of *cis,cis*-cyclooctadiene in the presence of $Pd(OAc)_2$ or from photolysis of the *trans*- adduct.

The stereochemistry of oxypalladation has been extensively studied and has been found to be *trans* [1]. The only evidences to the contrary are the kinetic studies of ethylene oxidation [2] and a suggested mechanism proposed by us some years ago [3]. We reported that the photolysis of the acetoxypalladium ad-



duct of cyclooctadiene, di-μ-acetatobis(2-acetoxycyclooct-5-enyl)dipalladium(II), yielded *exo*-6-acetoxybicyclo[3.3.0]oct-2-ene, II, 4-cyclooctenone, and palladium metal [3]. The ester product was all *exo*, no *endo*. This *exo* product was rationalized as the result of photolysis of a *cis*-acetoxypalladium adduct I. In the light of subsequent work [1], the adduct that was photolyzed must be the *trans*-oxypalladium adduct, III.

We have now synthesized the *cis*-acetoxy adduct I by *trans*-oxypalladation of *cis,trans*-cycloocta-1,5-diene. A pentane solution of the diene, prepared by the method of Deyrup or Whitesides [4], was stirred in ether solution with an excess of $Pd(OAc)_2$ for one hour. The solvent was evaporated, and the yellow solid which remained was recrystallized from methylene chloride (60% yield based on the estimate of diene). Under these conditions the *cis,cis*-diene does not react. Elemental analysis was satisfactory, and the complex decomposes at 138°C, somewhat higher than the known *trans*-acetoxy adduct III which decomposes at 120°C [5]. The ^{1}H NMR spectrum of the *cis*-adduct differs significantly from that of the *trans*-adduct [5]. The vinyl protons and the proton at the 2-position of the *cis*-adduct give broad signals at δ 5.5 ppm (m, 2 protons) and 6.2 ppm (m, 1 proton), respectively, compared to 5.4 and 5.8 ppm for the *trans*-adduct. Singlets for the ionic and ester acetate protons are nearly the same: 1.91 and 2.03 vs. 1.93 and 2.03 ppm. The other nine protons give a very broad absorption, δ 3.8—1.0 ppm for the *cis*-adduct and 3.2—1.0 ppm for the *trans*-adduct. This *cis*-adduct I upon photolysis in ether under nitrogen using a 200 W Hanovia mercury vapor lamp at room temperature for three days gave a 90% yield of *exo*-ester II and a 10% yield of cyclooctenone. Palladium metal was recovered in 95% yield.

Irradiation of *cis,cis*-cyclooctadiene in methylene chloride with $Pd(OAc)_2$ in stirred suspension with the same lamp for three hours yielded the same *cis* complex I after a work-up which consisted of filtering off $Pd(OAc)_2$, evaporating the solvent, washing the residue with pentane, and recrystallizing from ether (23% yield based on Pd).

It has been possible to isolate the *cis*-adduct I from the photolysis of the *trans*-adduct (1.6 mmol) in ether (200 ml) with toluene (5 ml) as a sensitizer (200 W Hanovia lamp, 2.2 h reaction time). After filtering off the palladium and removing the solvent, the residue was washed with pentane and recrystallized from ether to give I in 30% yield.

The above results indicate that the *exo*-ester II does derive from a *cis*-adduct I, but also this *cis*-adduct is itself a photoproduct of the *trans*-adduct III and is not a product of *cis*-oxypalladation as we suggested 13 years ago [3].

References

1 P.M. Henry, Adv. Organometal. Chem., 13 (1975) 363; P.M. Maitlis, The Organic Chemistry of Palladium, Vol. I, Academic Press, New York, 1971, pp. 74—78; J.K. Stille and D.E. James, J. Organometal. Chem., 108 (1976) 401; J.K. Stille and R. Divakaruni, ibid., 169 (1979) 239; M. Tetsuro and H. Kurosawa, J. Chem. Soc., Chem. Commun., (1977) 610; J.E. Bäckvall, B. Åkermark and S.O. Ljunggren, J. Amer. Chem. Soc., 101 (1979) 2411, and citations therein.

2 P.M. Henry, J. Amer. Chem. Soc., 86 (1964) 3246; 88 (1966) 1595; L.I. Moiseev, O.G. Levanda, and M.N. Vargaftig, ibid., 96 (1974) 1003.

3 C.B. Anderson and B.J. Burreson, Chem. Ind. (London), (1967) 620.

4 J.A. Deyrup and M.F. Betkouski, J. Org. Chem., 40 (1975) 284; G.M. Whitesides, G.L. Goe and A.C. Cope, J. Amer. Chem. Soc., 91 (1969) 2608.

5 C.B. Anderson and B.J. Burreson, J. Organometal. Chem., 7 (1967) 181.