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Photoreactions of Palladium Phosphine Complex with Chloroalkane. Production of Ethylene with 1,2-Dichloroethane and Novel Photochromic Behavior

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Photoirradiation on [Pd$^{0}_{2}$(dppm)$_3$] (dppm = bis(diphenylphosphino)methane) in 1,2-dichloroethane solution with visible light yields [Pd$^{I}_{2}$Cl$_2$(dppm)$_2$] (**2**) and ethylene quantitatively. Irradiation of **2** in various solutions shows interesting photochromic behavior.

There has been considerable interest in the photochemistry of binuclear metal complexes.[1)] However, relatively little studies have been reported on the photochemistry of d^{10}-d^{10} metal complexes[2)] in comparison with d^{8}-d^{8} metal systems. Caspar reported that the photoreaction of [Pd$^{0}_{2}$(dppm)$_3$] (**1**) in dichloromethane quantitatively yields an A-frame-structure complex, μ-CH$_2$-[Pd$^{II}_{2}$Cl$_2$(CH$_2$)(dppm)$_2$], under irradiation of visible light.[3)] We report here the reaction of **1** with 1,2-dichloroethane to give Pd^{I} complex, **2**, and an equimolar amount of ethylene. Further irradiation shows interesting photochromic behavior.

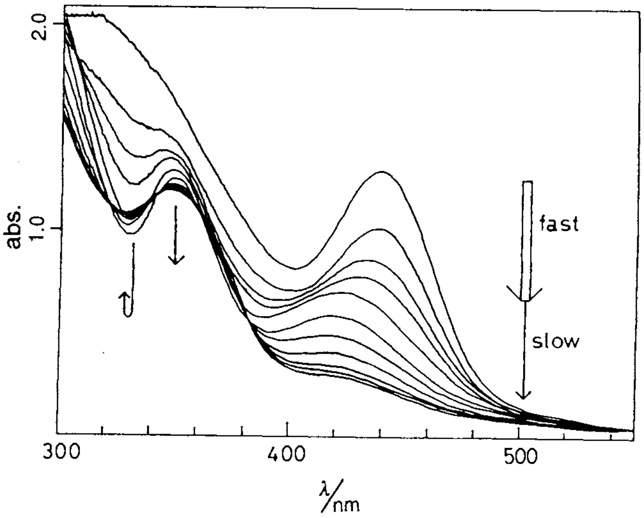
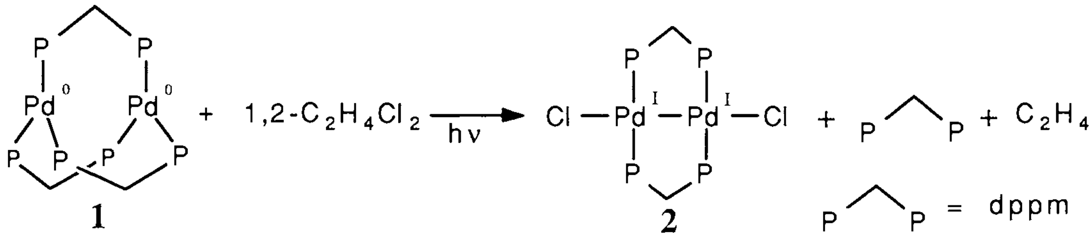


Fig. 1. Absorption spectral changes of [Pd$_2$(dppm)$_3$] in 1,2-dichloroethane (4 × 10^{-4} M) with irradiation of visible ($\lambda > 410$ nm) light. Irradiation times are 0, 10, 20, 40, 60, 370, 970, 1570, 2770, 3370 and 3970 s.

The electronic spectrum of **1** has a band in the visible region located at 440 nm, which is ascribed as a $d\delta^* \rightarrow p\sigma$ transition.3,4) The intensity of the band simply decreased when a dichloro-methane solution of **1** was irradiated with visible light (250-W high-pressure mercury lamp filtered to give $\lambda > 410$ nm). However, in 1,2-dichloroethane solution, more complicated changes of the spectra were observed upon irradiation with the same light as shown in Fig. 1. First, the 440 nm peak was moved to 410 nm with decrease of the intensity and a new band located at 350 nm appeared. In the second step, the intensity of the 410 nm peak decreased more slowly and that of the 350 nm peak also decreased slightly. In the absence of light, absorption changes correspond to the first step of the photoreaction were observed, but the reaction was much more slower than the photoreaction.5)

GC-Mass spectrometry revealed that ethylene is formed in the photoreaction mixture. The amount of ethylene is equivalent with that of the starting binuclear Pd^0 complex, **1**. The ethylene production finished at the end of the first step of the photoreaction. The Pd^{I} binuclear complex **2** was separated in high yield from the mixture after the first-step photoreaction using alumina column chromatography. The identification of **2** was confirmed by elemental analysis, UV-VIS absorption,6) and ^{31}P-NMR data.7) During the first-step photoreaction, no ^{31}P-NMR spectral peaks except those ascribed to **1**, **2**, and free dppm were observed.8) Thus, it is concluded that the photoreaction of **1** with 1,2-dichloroethane gives **2**, dppm, and ethylene quantitatively as shown in the scheme.



1 **2**

Similar photoreactions involving ethylene production had already been reported for some d^8-d^8 binuclear metal systems.1a, 9) This paper gives the first examples for d^{10}-d^{10} metal system. The quantum yield of the first-step reaction is very high ($\Phi \cong 0.6$) compared with the binuclear d^8-d^8 Ir-cyclooctadiene-pyrazolyl system ($\Phi = 0.05$).9) The high quantum yield may be due to a long lifetime ($\tau = 6$ ms)4) of the excited triplet state of **1**. The lifetime of the Ir complex is much shorter ($\tau = 250$ ns)1b) than that of **1**. As shown in this study, the product **2** obtained by the photoreaction of **1** in 1,2-dichloroethane is different from that obtained in dichloromethane. In either case, oxidative addition of C-Cl bond to the palladium center may be the first-stage of the reaction. It is supposed that the thermodynamically stable methylene-bridged A-frame complex is formed in the case of the reaction with dichloroethane, and β-elimination is ready to occur for the reaction with 1,2-dichloroethane. It should be noted that the reaction of chloroalkane with metal complexes, which is generally very slow compared with bromo- and iodo- derivatives, is smoothly caused by irradiation of visible light.[10)]

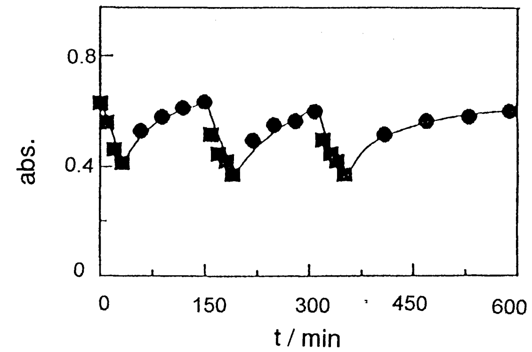


Fig. 2. The changes of intensity of the absorption band (410 nm) with ON-OFF cycles of irradiation for the second-step reaction of [$Pd_2(dppm)_3$] in 1,2-dichloroethane. The squares and circles denote the data during irradiation and in dark, respectively.

In the second step of the reaction, photochromic behavior was observed. After the first-step photoreaction, further irradiation of the 1,2-dichloroethane solution with visible light caused slow decrease of the 410 nm band assigned to **2**. When the reaction mixture was kept in dark after the irradiation, the intensity of the absorption band recovered. Again, irradiation caused the decrease of the absorption bands. These reversible changes of the absorption bands by ON-OFF of the irradiation of the light can be repeated at least three times (Fig. 2). Same photochromic behavior was observed when the solution of **2** was directly irradiated with visible light. The reversible photoreactions occur not only in 1,2-dichloroethane solution of **2** but also in other chloroalkane solvents such as dichloromethane or 1,1-dichloroethane. The absorption spectral changes of the back reaction show clear isosbestic points at 320, 343, 358 and 380 nm as shown in Fig. 3. Although reversibility is not so good, photochromism also occurs in THF solution of **2**. The absorption change of the back reaction is found to obey first-order kinetics in all solvents mentioned above. ^{31}P-NMR spectrum of photoirradiated solution of **2** showed two peaks (-3.4 ppm and -1.7 ppm) clearly. When the spectrum was measured again after the solution was kept in dark for 12 h, only a peak of -3.4 ppm which was assigned to complex **2** was detected. The results show that the P atoms of the photoreaction product from **2** may be all equivalent.

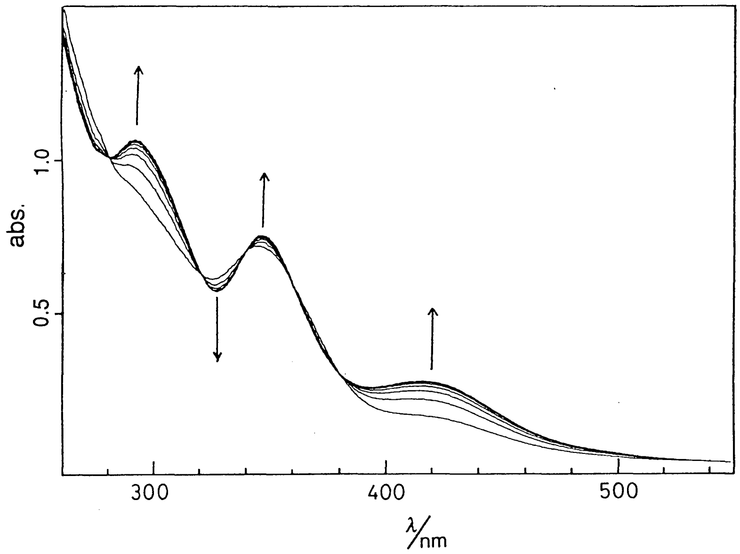


Fig. 3. Absorption spectral changes of the solution after the irradiation of **2** in dichloromethane (10^{-4} M) in dark place. Spectra were recorded at every 30 min.

It is known that photolysis on Pd(I) binuclear complexes causes homolysis of Pd-Pd bond.11) For the photoreaction of **2**, the homolysis of the binuclear complex and generation of mononuclear species are unlikely, because the rate of the back-reaction is little affected by the concentration of Pd complex. Recently, Pd-X bond scissions of bridged binuclear Pd(I) complex upon irradiation of light were suggested.12) Pd-X bond scission is also doubtful for this system because of the reversibility of the reaction, so that we propose that rearrangements of **2** occur to form a symmetric binuclear complex such as that containing bridged chlorine atoms. Unfortunately, many attempts to isolate the products of the second-step reaction have not been successful yet, so that we cannot give certain information for the structure of the photo product. Further studies for the characterization of the photochromic reaction are in progress.

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5) It requires 1 hour to complete the thermal reaction for the 2×10^{-4} M solution of **1**. On the other hand, the reaction finished within 60 s under the irradiation of the light.

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10) Besides the palladium complex, photoreactions of corresponding platinum(0) complex involving C-Cl bond cleavage were also observed.

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