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Photochemical reactions of palladium(0) and platinum(0) phosphine complexes

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Contents

Abstract

Photochemical reactions of the binuclear palladium(0) complex [$Pd_2(dppm)_3$] with organic halides yield palladium(I) dihalogeno complexes with irradiation of visible light. Photooxidation of alcohols was observed for ethanol and 2-propanol with the palladium complex. Photophysical and quenching properties of a chiral [$Pt(BINAP)_2$] complex (BINAP = *RR*- or *SS*-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) were studied. The emitting MLCT excited state has a long lifetime. Photochemical reactions of [$Pt(BINAP)_2$] with organic halides cause halogen abstraction. Atom and electron transfer may be candidates for the initial stage of the photoreaction. The mechanism of the photoreaction is discussed with the quenching data. © 1998 Elsevier Science S.A.

Keywords: Palladium complex; Platinum complex; Photochemistry

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1. Introduction

The photophysics and photochemistry of d^{10} metal complexes have been widely studied. In particular, the photochemical reaction of dinuclear d^{10}–d^{10} systems are

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attractive because of the long lifetime of their emitting-states upon irradiation with visible light [1–3]. Pd^0–Pd^0, Au^1–Au^1 dinuclear complexes bridged by diphosphines are examples of this category. In 1985, Caspar reported the photophysics and photochemistry of $[Pd_2(dppm)_3]$ [dppm = methylenebis(diphenylphosphine)] and some mononuclear Pd^0–phosphine complexes. He reported that the dinuclear complex shows a comparatively long lifetime of the emitting state and that the complex showed interesting photochemical reactions, e.g. two-center photo-oxidative addition with dichloromethane gives the Pd^{II} dimer of the A-frame structure. These results stimulated us to do further research on the photochemistry of the low-valent palladium and platinum complexes. The chemistry of diphosphine complexes has been extensively studied, but many interesting findings were observed in our study. In this report, we present the recent results of the photophysics and photochemistry of: (1) the phosphine-bridged dinuclear palladium(0) complexes; and (2) the mononuclear $Pt(BINAP)_2$ complex.

2. Experimental

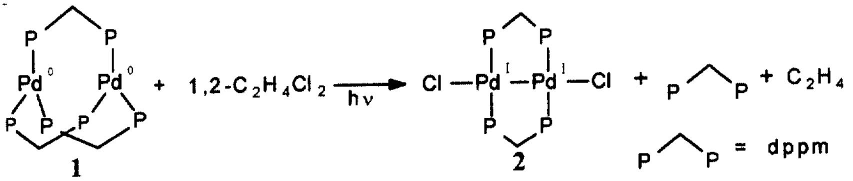
The preparation of the $[Pd_2(dppm)_3]$ and $[Pt(BINAP)_2]$ complexes was according to published methods [4,5]. Other complexes of their analogues were prepared by similar methods. The solvents used in the photochemical and photophysical studies were distilled under argon before use. The solutions of the complexes were further deoxygenated by freeze–pump–thaw cycles before the photophysical measurements. A high-pressure mercury lamp (250 W) equipped with a glass filter was used for the photochemical reaction. For the decay measurements, an N_2 laser (200 kW) was used for excitation of the samples, and monochromator-output of the emission was directed into a photomultiplier tube. The output-signal was analysed using a digital oscilloscope (1 GS/s).

3. Results and discussion

3.1. Phosphine-bridged dinuclear palladium complexes

3.1.1. Photochemical reactions between $[Pd_2(dppm)_3]$ and alkyl halides

The $[Pd_2(dppm)_3]$ complex has a visible absorption band of moderate intensity, which is assigned to a d→p transition, both of the orbitals are split by metal–metal interactions. Moreover, it shows photoluminescence in solution at room temperature [1,2]. We have found that visible light irradiation ($\lambda > 410$ nm) of the 1,2-dichloroethane solution of the palladium complex, $[Pd_2(dppm)_3]$ (**1**), gave a Pd^I complex, $[Pd_2Cl_2(dppm)_2]$ (**2**), and a stoichiometric amount of ethylene [6]. The quantum yield of the photochemical reaction is high (ca. 0.6) compared with a similar reaction of the binuclear iridium complex [7] in which the evolution of ethylene was also reported. This high quantum yield may be related to the long lifetime (6 μs) of the excited state of the palladium complex in solution. Similarly, the photochemical reaction of **1** with 1,2-dichlorohexane produces cyclohexene.



(1)

The changes in the absorption spectra during the above reaction upon irradiation are shown in Fig. 1. The fast decrease with a slight blue shift of the 440 nm band is responsible for reaction (1). Complex **2** shows an absorption maximum at 410 nm. Further irradiation by visible light after the initial reaction caused a decrease in the 410 nm band. When the reaction mixture was kept in the dark after the irradiation, the intensity of the absorption band recovered. Again, irradiation caused a decrease in the absorption band. These reversible changes in the absorption bands by ON–OFF cycling of the irradiation of light can be repeated at least three times. The ^{31}P-NMR spectrum of the photo-irradiated solution of **2** clearly shows a new signal at −1.7 ppm in addition to the −3.4 ppm signal. The latter signal is assigned to complex **2**. Many attempts to isolate the products of the second-step reaction have not yet been successful.

Photochemical reactions of **1** with alkyl bromide were also studied. Changes in the absorption spectra of complex **1** upon irradiation by visible light were very complicated, but the initial step was found to be halogen atom transfer to give $[Pd_2Br_2(dppm)_2]$. The rates of the initial reaction depend on the bromoalkanes used, but they are accelerated by photo-irradiation. The reaction rate for the initial step

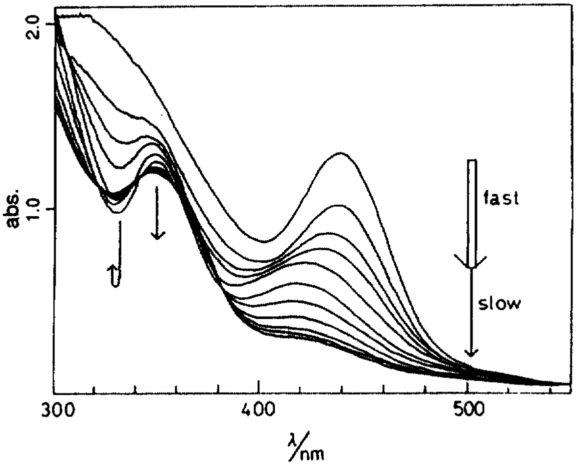


Fig. 1. The changes in the absorption spectra of complex **1** in 1,2-dichloroethane upon irradiation of visible light (λ>410 nm). Two-step reactions were observed.

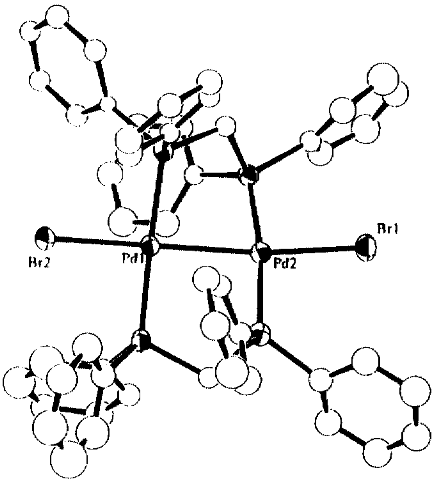


Fig. 2. The molecular structure of $[Pd_2Br_2(dppm)_2]$.

in bromopentane is very slow in the dark, but the reaction was complete within minutes with irradiation of the 10^{-3} M solution of the complex. The dinuclear Pd(I) complex was isolated during the photo-irradiation of the solution of $[Pd_2(dppm)_3]$ in bromobutane during the initial stage, and mononuclear $[PdBr_2(dppm)]$ was identified in the final stage of the photochemical reaction. The crystal structure of the dinuclear complex (Fig. 2) was found to be identical with the previously reported Pd(I) complex, $[Pd_2Br_2(dppm)_2]$ [8]. With the production of the Pd(I) complex, small amounts of corresponding alkanes (C_nH_{2n+2}) and alkenes (C_nH_{2n}) are produced during the initial reaction with alkyl bromide ($C_nH_{2n+1}Br$).

3.1.2. Photophysical properties of [$Pd_2(dmpm)_3$] [dmpm = methylenebis(dimethylphosphine)]

Many interesting photochemical reactions are reported for the alkyl phosphine complexes compared with the aryl phosphines, so that new photochemical features are anticipated in the methyl analogue of the dppm complexes. The dmpm complex was successfully prepared and characterized by X-ray analysis. The structure was found to be similar to that of the dppm complex. But, the Pd–Pd distance [3.021(2) Å] was slightly longer than the dppm complex. The photophysical properties of the complex were similar to the corresponding dppm complex. However, some differences were observed between the two complexes. The absorption band observed in the visible region shows some blue shift (30 nm) compared with the dppm complex (Fig. 3). EHMO calculations based on the model structures suggest that both the electronic effect of the methyl group instead of the aryl group and the geometric effect of the longer Pd–Pd distance affect the narrow band gap of the dmpm complex. The complex also emits luminescence but the intensity of the luminescence is weak, and the lifetime of the emitting state is very short (0.6 μs) compared with the dppm complex.

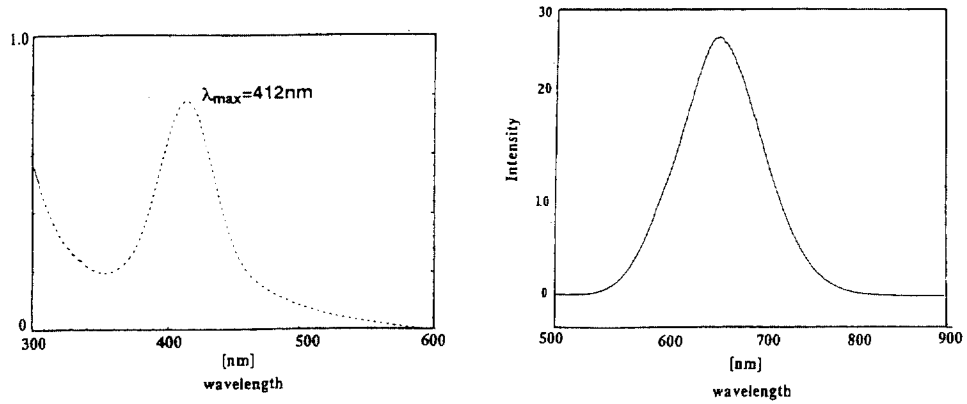


Fig. 3. Absorption (left) and luminescence (right) spectra of [$Pd_2(dmpm)_3$] in benzene.

3.2. *Photophysical and photochemical properties of [Pt(BINAP)$_2$] [5] (Fig. 4)*

The electronic absorption spectrum of [$Pt(BINAP)_2$] (Fig. 5) shows an intense band in the visible region ($\lambda_{max} = 530$ nm, $\epsilon = 14000$ M^{-1} cm^{-1}), although mononuclear platinum(0)–phosphine complexes are usually known to show no visible bands in their absorption spectra. An X-ray crystal structure analysis of the complex revealed that the complex has a distorted tetrahedral geometry. EHMO calculations, performed on the basis of the crystal structure of [$Pt(BINAP)_2$], revealed that the HOMO (b_2 representation in D_2 group symmetry) is mainly made up of d orbitals of the Pt atom, whereas the LUMO (b_1) has a great similarity to the LUMO of the ligand, BINAP, although there is a small contribution of a d orbital by the Pt atom. Therefore, the lowest energy transition was assigned as an MLCT transition, and the π^* orbitals on the chelate part (P-C-C-C-C-P) of the BINAP ligand largely contributes to the MLCT excited states. The complex also showed relatively intense red luminescence even in solution. The lifetime of the excited MLCT state was comparatively long (1.5 μs). The quantum yield of the luminescence ($\Phi = 0.024$,

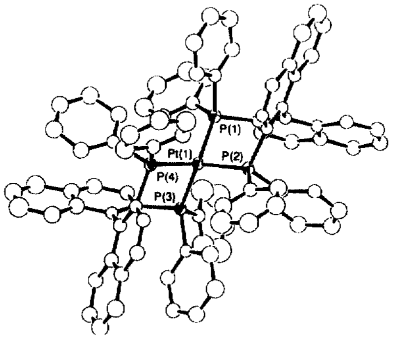


Fig. 4. An ORTEP drawing of [Pt((*S*)-BINAP)$_2$].

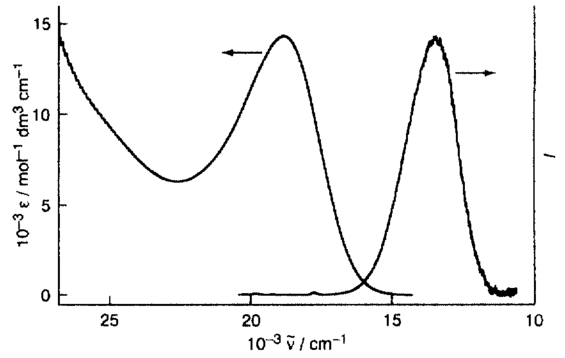


Fig. 5. Absorption (left) and luminescence spectra of $[Pt(BINAP)_2]$ in C_6H_6 ($\lambda_{exc}=480$ nm)

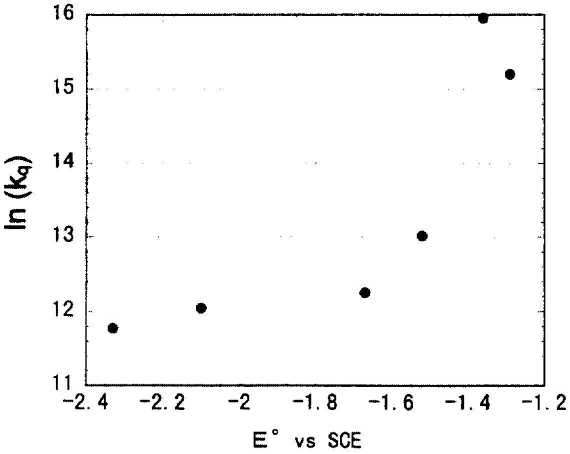


Fig. 6. A ln k_q vs E° plot for the quenching of the luminescence of $[Pt(BINAP)_2]$ by alkyl halides.

$\lambda_{exc}=480$ nm) was comparable to that of tris(2,2′-bipyridine)ruthenium(II). A platinum complex $[Pt(tol\text{-}BINAP)^2]$ where tol-BINAP is a dimethyl derivative of BINAP, 2,2′-bis(di-*p*-tolylphosphono)-1,1′-binaphthyl, was prepared and the photophysical properties were also examined. The absorption and emission spectra of the tol-BINAP complex were similar to the BINAP complex, but the intensity of the luminescence was weak compared to the BINAP complex, and the decay time was found to be short (0.33 μs). Therefore, the BINAP complex was exclusively examined in the photochemical study.

Irradiation of chloroalkane solutions of the $[Pt(BINAP)_2]$ by visible light caused a decrease in the 530 nm absorption band. The isolated product was $[PtCl_2(BINAP)]$. The intensity of the luminescence of $[Pt(BINAP)_2]$ was quenched by many alkyl halides. Linear Stern–Volmer relationships were observed for all the quenching results using the decay data. Bimolecular quenching constants were calculated from the Stern–Volmer plots. The logarithm of the quenching constants were plotted versus the reduction potential of the alkyl halides as shown in Fig. 6. For the alkyl halides with $E^\circ > -1.6$ V, the RT ln k_q vs E° plot obeyed a linear relationship with a slope of 1/2. This implies that the initial step of the photochemical reaction can be described by an electron transfer model in this region. However, a direct atom transfer mechanism might be operating for the alkyl halides with $E^\circ < -1.6$ V.

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