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Photochemical Behavior of Chlorocarbonylbis(triphenylphosphine)rhodium(I), $ClRh(CO)\mathbf{P}_2$ ($\mathbf{P}$ = PPh_3). Laser Flash Photolysis with Infrared Detection[†]

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Laser flash photolysis of $ClRh(CO)\mathbf{P}_2$ with monitoring infrared region gave definite evidence of photoelimination of CO, rather than **P**. $ClRh\mathbf{P}_2$ generated reacts with the remaining $ClRh(CO)\mathbf{P}_2$ to give a transient binuclear rhodium carbonyl, which regenerates $ClRh(CO)\mathbf{P}_2$ via the reaction with CO.

$ClRh(CO)\mathbf{P}_2$ is known as a catalyst precursor for the photochemical C-H activation,1-4) in which $ClRh\mathbf{P}_2$ formed by the photoelimination of CO is speculated to be a real catalytic species. On the other hand, **P** is thought to be detached photochemically from $ClRh(CO)\mathbf{P}_2$, from the fact that the photochemical decarbonylation of aldehydes does not occur by using $ClRh(CO)\mathbf{P}_2$ although the thermal decarbonylation proceeds easily by using $ClRh\mathbf{P}_3$ which dissociates **P** to give $ClRh\mathbf{P}_2$ in solution.5) The transient UV spectral observation applied to $ClRh(CO)\mathbf{P}_2$ seems not to clear up the ambiguity since the transient spectrum could hardly be assigned to a specific compound.6,7) We herein describe observations at infrared region.

$$ClRh(CO)\mathbf{P}_2 \xrightarrow{h\nu} \begin{cases} ClRh\mathbf{P}_2 + CO & \text{(1a)} \\ & \text{or} \\ ClRh(CO)\mathbf{P} + \mathbf{P} & \text{(1b)} \end{cases}$$

For laser flash photolysis with IR detection, the optical system of an EPI-G2 (HITACHI) infrared spectrometer was used basically with modifying the detector to an MCT element with an amplifier (P3412-01, HAMAMATSU), and the widths of slits were fixed to 1 mm.8-11) Sample solutions were flowed (0.1 ml min^{-1}) through a water-cooled CaF_2 cell

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[†] Dedicated to Professor Emeritus Osamu Simamura of The University of Tokyo on the occasion of his 80th birthday.

(0.5 mm in optical path) by using a pump for HPLC (CCPE-II, TOSOH) so that every laser pulse hit fresh solution. A laser beam (355 nm, the third harmonic of Q-switched Nd:YAG laser, DCR-11, SPECTRA PHYSICS) was overlapped to the IR window (5 mm in diameter) with an angle of 10° to the IR path. Signals from MCT were introduced to a storage scope (TS-8123, IWATSU) and the trace digitized was averaged for 25 shots, at least, at one wavenumber on a microcomputer. Solutions were laser-photolyzed every 20 s with 4-10 mJ of pulse so that artifacts arising from the thermal blooming,12) which were significant when laser power was higher than 20 mJ per pulse, were eliminated.

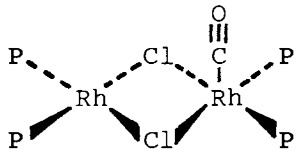
Figure 1 shows typical reaction traces obtained for chloroform solutions of $ClRh(CO)P_2$ (3.0 mmol dm^{-3}) under Ar. At 1980 cm^{-1} where $ClRh(CO)P_2$ has an absorption for carbonyl stretching, a swift bleaching can be seen just after the laser pulse and a slow bleaching follows up to 45 μs, which coincides with a slow increase of absorbance at 2035 cm^{-1}. Points corresponding to just after the laser pulse and 45 μs, indicated by arrows in Fig. 1, were collected with varying wavenumber to compose differential IR spectra (Fig. 2). The spectrum just after the pulse shows a bleaching at 1985 cm^{-1} caused by the photolysis of $ClRh(CO)P_2$, but no new absorption appears in the typical region of metal carbonyls (2150-1850 cm^{-1}).13) This indicates that CO rather than P dissociates photochemically (Reaction 1a). Since the molar absorption coefficient for CO is smaller than those for metal carbonyls by two orders of magnitude, the absorption for free CO can not be observed.

A reaction trace at 1980 cm^{-1} under CO (7.8 mmol dm^{-3}) is shown in Fig. 1, where the recovery of $ClRh(CO)P_2$ can be seen, indicating the reaction of $ClRhP_2$ with CO. The absorption at 2035 cm^{-1} does not appear

$$ClRhP_2 + CO \longrightarrow ClRh(CO)P_2 \qquad (2)$$

in this case. Slow appearance of the 2035 cm^{-1} peak and the additional bleaching at 1980 cm^{-1} under Ar in Figs. 1 and 2 can be explained rationally by the idea that $ClRhP_2$ reacts with the remaining $ClRh(CO)P_2$ to give a binuclear rhodium carbonyl. This is supported by the fact

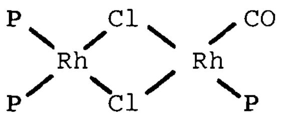
$ClRhP_2 + ClRh(CO)P_2 \longrightarrow$



(3)

1

that bleaching at 45 μs reaches to an amount twice of that just after the laser pulse. The absorption at 2035 cm^{-1} is consistently assigned to an axial carbonyl as shown in **1**.14) An equatorial carbonyl, for example, in $ClRh(CO)P_2$ or Compound 2 shows a carbonyl stretching vibration at a lower wavenumber, 1980 cm^{-1}, owing to effective back donation by the other ligands.15) Transient **1** decayed with a few miliseconds of lifetime and the bleaching at 1980 cm^{-1} recovers simultaneously.



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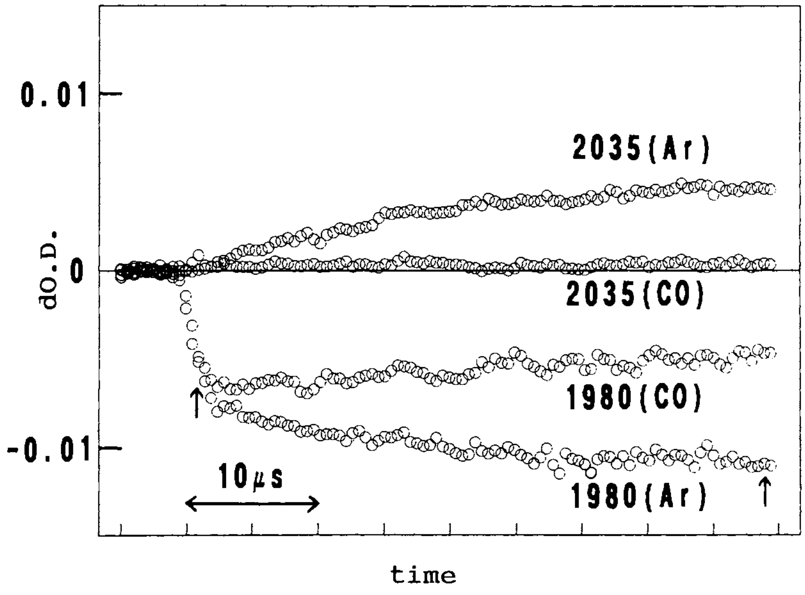

Fig. 1. Typical traces by LFP of $ClRh(CO)P_2$. Wavenumber and atmosphere are shown for each trace.

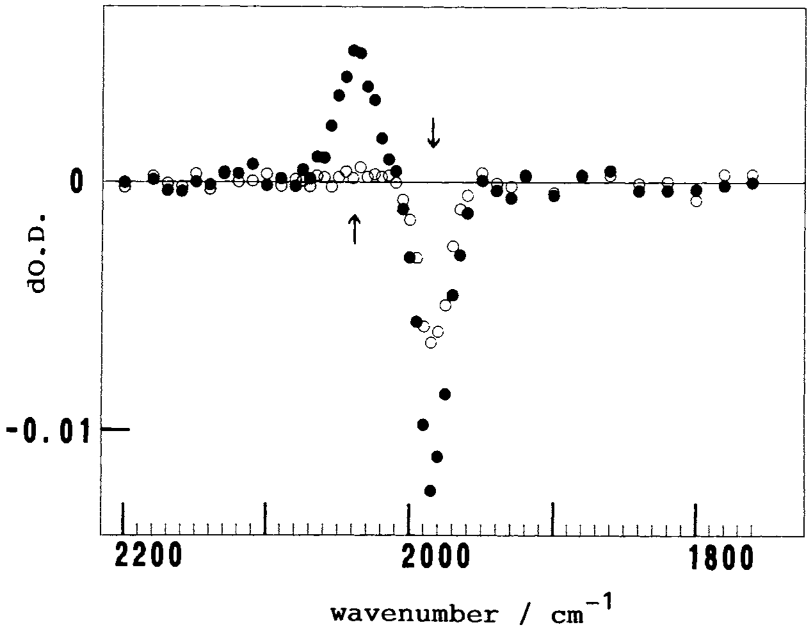

Fig. 2. Time-resolved IR spectra just after the laser pulse (circles) and at 45 μs (solid circles).

Reaction traces under Ar in Fig. 1 were identical with those in the presence of heptanal (15 mmol dm^{-3}), indicating that the coordination of heptanal to ClRh$\mathbf{P}_2$ was far slower than that of ClRh(CO)$\mathbf{P}_2$. Thus, the order of coordination rates to ClRh$\mathbf{P}_2$ is CO $\approx$ ClRh(CO)$\mathbf{P}_2$ >> aldehydes. In the presence of CO and the precursor ClRh(CO)$\mathbf{P}_2$, an aldehyde has no chance to coordinate to ClRh$\mathbf{P}_2$, nor the chance of decarbonylation.

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