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Structure of Transient $Cr(CO)_5(phen)$ Studied by Time-resolved Infrared Spectroscopy

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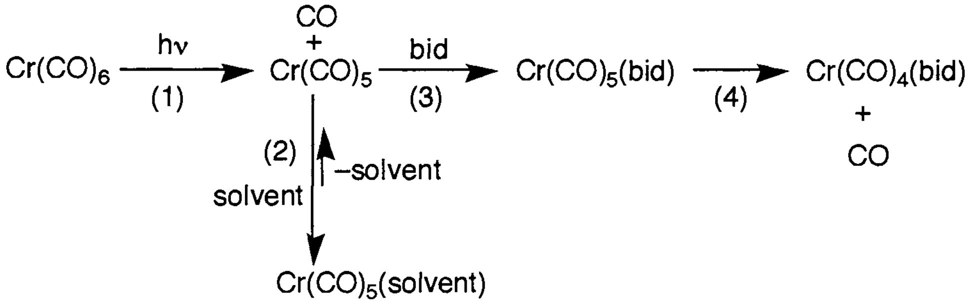
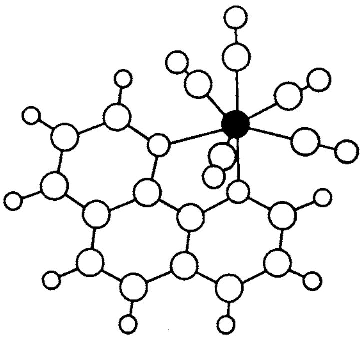
$Cr(CO)_5(phen)$ generated as an intermediate in the photochemical carbonyl substitution of $Cr(CO)_6$ with 1,10-phenanthroline (phen) has been investigated by laser flash photolysis with infrared detection. $Cr(CO)_5(phen)$ was found to have a capped-octahedron type structure; five carbonyls maintained a square-pyramidal geometry and phen coordinated unusually in a monodentate fashion.

Ultraviolet irradiation of a solution of $Cr(CO)_6$ in the presence of bidentate ligand (bid) gives $Cr(CO)_4(bid)$. The reaction proceeds through the following steps; (1) photo-decarbonylation generating coordinatively unsaturated $Cr(CO)_5$, (2) coordination of solvent molecule to give $Cr(CO)_5(solvent)$ and regeneration of $Cr(CO)_5$, (3) coordination of bid, and (4) elimination of another CO.1-5) Even with a ligand as well-suited to bidentate bonding as phen, the coordination (3) did not concert with the extrusion of the second carbonyl (4); $Cr(CO)_5(phen)$ could be observed on visible absorption spectra in microsecond to millisecond time scales.3) The shift of d-d absorption in $Cr(CO)_5(phen)$ and the acceleration which appeared in the steps of coordination (3) and expulsion of CO (4)3,5) suggested significant interaction between the "non-coordinating" nitrogen and the metal. Though a pentagonal bipyramid type or an octahedral-wedge type structure6,7) was supposed for the intermediate,3) it could not be concluded by the transient visible spectra. We wish to report here the results obtained by time-resolved infrared spectroscopy.

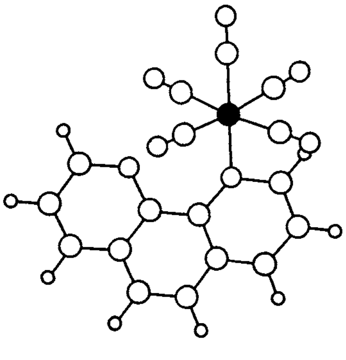


For laser flash photolysis with infrared detection, the optical system of an EPI-G2 (HITACHI) infrared spectrometer was basically used except that an MCT element with an amplifier (P3412-01, HAMAMATSU) was employed as a detector and that the width of slits was fixed to 1 mm.8-11) Sample solutions in a water-cooled CaF_2 cell (0.5 mm in optical path length) were laser-photolyzed every 6 s by the third harmonic (355 nm, 7 ns of pulse width) of a Q-switched Nd:YAG laser (DCR-11, SPECTRA-PHYSICS) with an energy lower than 20 mJ per pulse, and were renewed for every laser pulse by a computer-controlled electric valve. Signals from the MCT were introduced to a digital storage scope (DS-8606, IWATSU) and accumulated for at least 25 shots on a microcomputer. As benzene used in the case of transient visible spectra was not transparent in the region of metal carbonyl stretching, other solvents were tested for pulsed and continuous photolysis. In trichloroethylene as a solvent, the results in benzene$^{3)}$ could be reproduced.

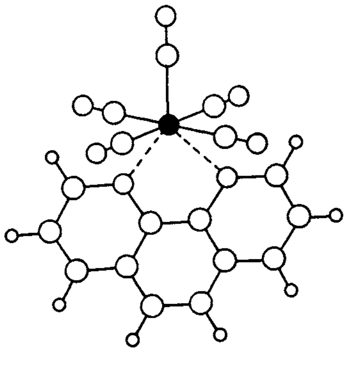
Trichloroethylene solutions of $Cr(CO)_6$ (4.0 mM) and phen (15.0 mM) were deaerated by bubbling argon for 20 min and then subjected to laser flash photolysis. As $Cr(CO)_6$ had only weak absorption at 355 nm, 11% of the pulse energy, i. e., $\approx$ 2 mJ, was estimated to be utilized for excitation. Typical reaction traces at infrared region are shown in Fig. 1. At 1980 cm^{-1} where the starting $Cr(CO)_6$ has an absorption for carbonyl stretching, a swift bleaching takes place and continues throughout the time range, indicating the consumption of $Cr(CO)_6$. An absorption at 1960 cm^{-1} which appeared just after the laser pulse decayed with a pseudo-first order rate constant 4.98×10^3 s^{-1}, which is in good agreement with that for the increase of absorption at 1940 cm^{-1} (4.81×10^3 s^{-1}). Points corresponding to 0, 130, and 370 μs after the laser pulse, indicated by arrows in Fig. 1, were collected with varying wavenumber to compose differential infrared spectra (Fig. 2a). As an isosbestic point can be seen at 1955 cm^{-1}, the species just after the laser pulse clearly changes to the next one. These were found to be consistent with the results obtained in transient visible absorption spectra.$^{3)}$ Namely, the infrared spectral change in Fig. 2a reveals the conversion of $Cr(CO)_5$(trichloroethylene) to $Cr(CO)_5$(phen), which shows three peaks at 2070, 1940, and 1900 cm^{-1} with weak, strong, and medium intensities, respectively. This pattern is characteristic of a square pyramid structure of $M(CO)_5$ fragment. A simulation spectrum shown in Fig. 2b was obtained by applying the Cotton-Kraihanzel approximation and Timney's empirical equation$^{12-14)}$ to a capped-octahedron type$^{15)}$ structure of $Cr(CO)_5$(phen), assuming axial-equatorial bond angle 90.4°, a dipole derivative ratio $\mu_{ax}'/\mu_{eq}' = 1$, and the force constants (Nm^{-1}) $k_{ax} = 1478$, $k_{eq} = 1580$, $k_{ax,eq} = 38$, $k_{eq,eq} = 33$, $k_{trans} = 62$. The observed bands at 2070, 1940, and 1900 cm^{-1} were assigned to the $A_1^{(1)}$ (2070 cm^{-1}), E(1939 cm^{-1}), and $A_1^{(2)}$ (1898 cm^{-1}) fundamentals, respectively. The frequency for the B_1 fundamental which is infrared inactive was calculated as 1975 cm^{-1}.



Pentagonal bipyramid



Capped octahedron



Octahedral wedge

If we assume a pentagonal bipyramid structure for $Cr(CO)_5$(phen), nitrogen atoms of phen cannot occupy two corners of the pentagon because of congestion in the plane. Nitrogen atoms of phen should occupy one of the tops of bipyramid and one corner of the pentagon as shown above. Carbonyls in this geometry are expected to show five bands for the stretching. Therefore, a pentagonal bipyramid is excluded.

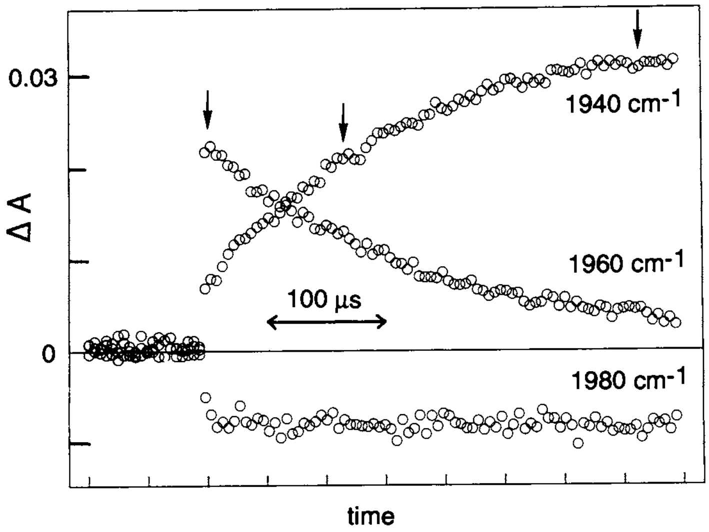


Fig. 1. Typical reaction traces by laser flash photolysis of trichloroethylene solutions of $Cr(CO)_6$ (4.0 mM) and 1,10-phenanthroline (15.0 mM) under argon. A trace at 1980 cm^{-1} was obtained for a 2.0 mM solution of $Cr(CO)_6$. Points indicated by arrows were collected for making time-resolved infrared spectra.

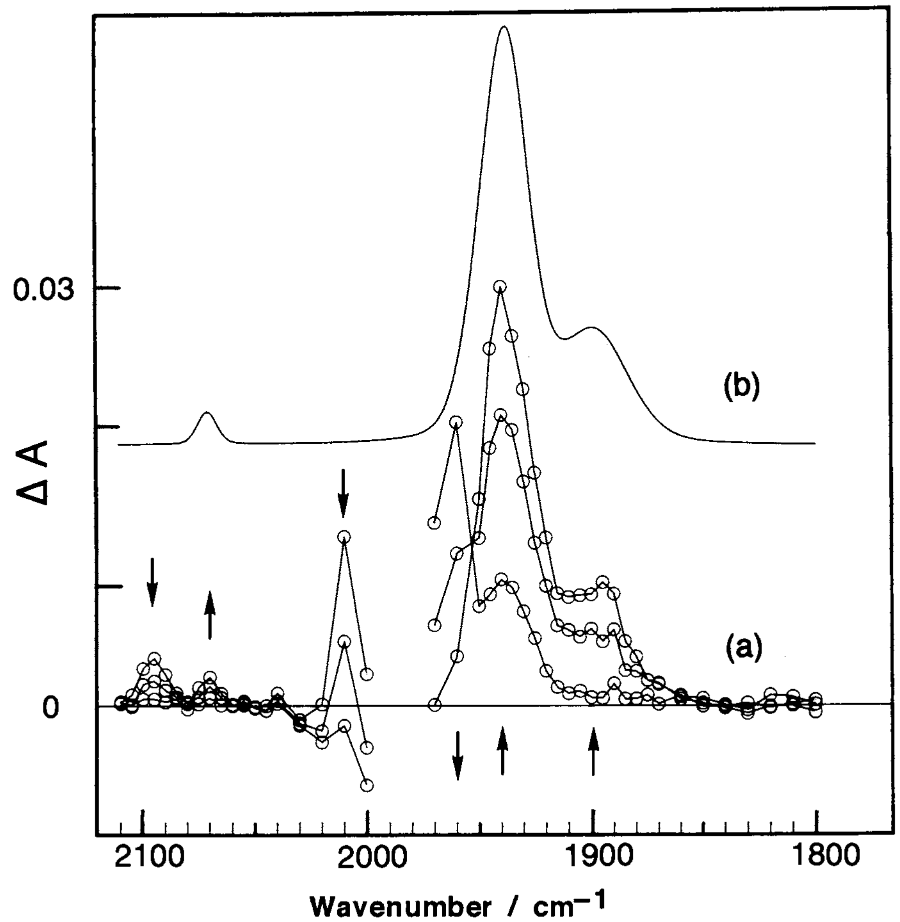


Fig. 2. (a) Time-resolved infrared spectra just after the laser pulse, at 130 μs, and at 370 μs. Spectral changes with time are indicated by arrows. Bleaching at around 1980 cm^{-1} due to the photolysis of $Cr(CO)_6$ is not shown. (b) Simulation spectrum for $Cr(CO)_5$(phen) assuming a capped octahedral geometry. Force constants and a dipole moment derivative ratio used in the calculation can be seen in the text.

The force constants obtained above were similar to those calculated for $Cr(CO)_5$(pyridine) where the plane of pyridine staggers the Cr–CO(eq) bonds,[16] being consistent with a capped-octahedral geometry of $Cr(CO)_5$(phen). An octahedral-wedge type structure is energetically unfavorable because of the loss of effective overlap between a lone pair orbital of nitrogen and d orbital of Cr, particularly, the back lobe of σ bond to an axial carbonyl.[17] Moreover, if we assume this, the $A_1^{(2)}$ mode which mainly reflects the vibration of an axial carbonyl is expected to exhibit a band at a higher frequency because the back-donation assisted by a trans ligand decreases. An octahedral wedge geometry, therefore, is eliminated.

In conclusion, $Cr(CO)_5$(phen) has a capped-octahedron type structure, which should be considered to obey the18-electron rule though the "non-coordinating" nitrogen is interacting to such an extent that the shift of d-d absorption takes place.[3] The interaction will be more significant with increasing size of central metal, as revealed in the order of the rate for the carbonyl extrusion.[3] The geometrical reorganization to approach the transition state of the carbonyl extrusion will be more important in Cr than in Mo and W. This is consistent with the results by Zhang et al. that the entropy of activation for Cr is more negative than those for Mo and W.[5]

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