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Dynamic Structure of Paramagnetic Complexes, $MeCpMo(CO)_3$(p-benzoquinone) (MeCp = η^5-$CH_3C_5H_4$), Formed by Photochemical Reaction of $[MeCpMo(CO)_3]_2$ with p-Benzoquinones as Studied by EPR Spectroscopy

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The existence of the intramolecular motion and the most stable structure of the paramagnetic complexes, $MeCpMo(CO)_3$(p-benzoquinone), formed by photochemical reaction of $[MeCpMo(CO)_3]_2$ with p-benzoquinones were revealed by the EPR spectroscopic study.

There have been extensive studies on the photochemical reactions of metal carbonyl complexes containing a metal-metal bond, because the molecules display fascinating and diverse photochemical properties.1,2) In the previous paper, we reported the photochemical reaction of $[CpMo(CO)_3]_2$ (Cp = η^5-C_5H_5) with p-benzoquinones and showed the formation of complexes, $CpMo(CO)_3$(p-benzoquinone), in which p-benzoquinones coordinate monodentately by one of their two carbonyl oxygens to $CpMo(CO)_3$ produced by photocleavage of the Mo-Mo bond.3) Recently we observed that the methyl substituted compound, $[MeCpMo(CO)_3]_2$ (MeCp = η^5-$CH_3C_5H_4$), also undertakes the similar photochemical reaction with p-benzoquinones and forms paramagnetic complexes of the type of $MeCpMo(CO)_3$(p-benzoquinone). In this system, however, we observed EPR spectra showing temperature dependence over a wide temperature range. The present communication reports that the observed temperature dependence of the spectra can be explained by the restricted intramolecular motion of the complexes, and shows the dynamic structure and the most stable coordination structure of the complexes.

The degassed toluene solution (1 cm^3) of $[MeCpMo(CO)_3]_2$ (1 mg) and 1,4-benzoquinone (BQ) (1 mg) exhibited an EPR spectrum during photo-irradiation4) at -40 °C (Fig. 1,a). The spectrum consists of a well resolved triplet accompanied with six weak satellites, which are apparently attributable to the hyperfine (hf) interactions with two equivalent BQ protons and the magnetic isotopes, ^{95,97}Mo. $[MeCpMo(^{13}CO)_3]_2$ being used, the EPR spectrum exhibited an additional triplet of doublets hf structure which can be assigned to the hf couplings with two equivalent ^{13}C's and a different single ^{13}C (Fig. 1,b), indicating the presence of three CO's in the paramagnetic product. These facts clearly indicate that the photochemically produced $MeCpMo(CO)_3$ was trapped by BQ, yielding a paramagnetic complex, $MeCpMo(CO)_3$(BQ). The EPR features of the complex well resemble, in most part, to those of the complex derived from $[CpMo(CO)_3]_2$ reported in the previous paper[3] (Table 1). It is considered, therefore, that the complexes in the both systems have common structure in which Mo is coordinated by BQ with one of its two carbonyl oxygens.

Interesting features were observed in the EPR spectra of the complex by changing temperatures. As was mentioned above, at -40 °C the complex shows proton hf couplings symmetrical about the axis connecting the two carbonyl groups of BQ ligand, but at the lower temperatures[5] the line-width alternation effect clearly appears in the proton hf splittings, and as the temperature is lowered further the triplet splitting by the couplings with the C_2 and C_6 protons becomes the pattern due to the couplings with the non-equivalent two protons, i.e., it becomes a doublet of doublets pattern as is shown in Fig. 2.

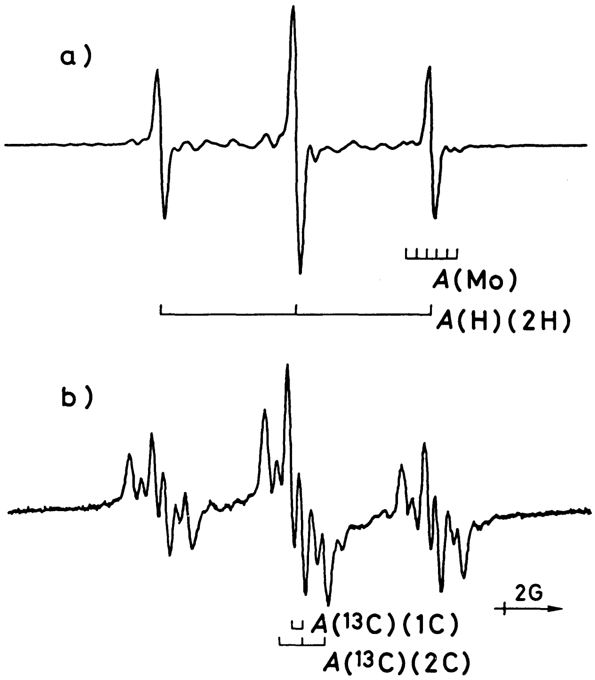

Fig. 1. First-derivative X-band EPR spectra observed during photoirradiation of toluene solutions at -40 °C ; a) $[MeCpMo(CO)_3]_2$ and BQ, b) $[MeCpMo(^{13}CO)_3]_2$ and BQ.

Table 1. EPR Parameters for the Paramagnetic Complexes

p-Benzo-quinone	Metal	Solvent	t/°C	g value	a_{Mo}/G	a_H2/G	a_H3/G	a_H5/G	a_H6/G	$a_{13C(CO)}$/G[a]
BQ[b]	$CpMo(CO)_3$[c]	toluene	-40	2.0047	0.4	4.69	--	--	4.69	0.73(1C), 0.38(2C)
	$MeCpMo(CO)_3$	toluene	-40	2.0048	0.3	4.65	--	--	4.65	0.78(2C), 0.35(1C)
		2-Me-THF	-40	2.0048	0.4	4.57	0.19	0.19	4.57	
			-105	2.0048	--	3.85	--	--	5.00	
2,6-DMBQ[b]	$CpMo(CO)_3$[c]	toluene	-40	2.0044	--	4.20(Me)	--	--	4.20(Me)	0.77(1C), 0.29(2C)
	$MeCpMo(CO)_3$	toluene	-40	2.0045	0.1	4.20(Me)	--	--	4.20(Me)	0.65(2C), 0.41(1C)
		2-Me-THF	-40	2.0045	0.2	4.05(Me)	--	--	4.05(Me)	
			-102	2.0045	--	3.5(Me)	--	--	4.4(Me)	

a) The hyperfine (hf) coupling constants of ^{13}C's in carbon monoxides. The number of equivalent carbons is indicated in parentheses. b) The EPR parameters for the complex in which the C_4-oxygen coordinates to Mo. c) Ref. 3.

It has been reported that a mono-protonated p-benzosemiquinone shows the line-width alternation effect due to the restricted rotation of the OH group.[6] It seems most likely to attribute the observed line-width alternation effect to the restricted rotation of the BQ ligand around the C-O(-Mo) bond as in the case of the mono-protonated p-benzosemiquinone. The most stable conformation is not, therefore, that the metal moiety, $MeCpMo(CO)_3$, situates symmetrically to the BQ so as the Mo-O bond is in the plane perpendicular to the BQ, but that the Mo-O bond is in the BQ plane in which the π electrons of BQ can be more delocalized. In order to estimate the thermodynamic parameters for the restricted rotation, the temperature dependence of the spectra was analyzed by using the modified Bloch equations assuming the two-jump model as a function of the correlation time τ for the restricted rotation of BQ. The examples of the observed and simulated spectra are shown in Fig. 2. From the plot of $\log_{10}(1/\tau)$ against inverse of the absolute temperature, the activation energy for the rotation was determined to be 25±2 kJ/mol.

When 2,6-dimethyl-1,4-benzoquinone (2,6-DMBQ) was used instead of BQ, EPR spectra evidenced the formation of the paramagnetic complex in which 2,6-DMBQ coordinates to the Mo of $MeCpMo(CO)_3$ by its C_4-oxygen (Table 1). This complex also showed the line-width alternation effect by the restricted rotation of 2,6-DMBQ ligand in the EPR spectra, and the activation energy for the rotation was estimated to be 29±2 kJ/mol by the computer simulation of the spectra.

In the system of $[CpMo(CO)_3]_2$, such a line-width alternation effect was slightly observed only at the temperatures near the freezing point of the solvent, and the information of details of the intramolecular motion could not be obtained. However, the use of the methyl substituted compound clarified the presence of the dynamical motion in the

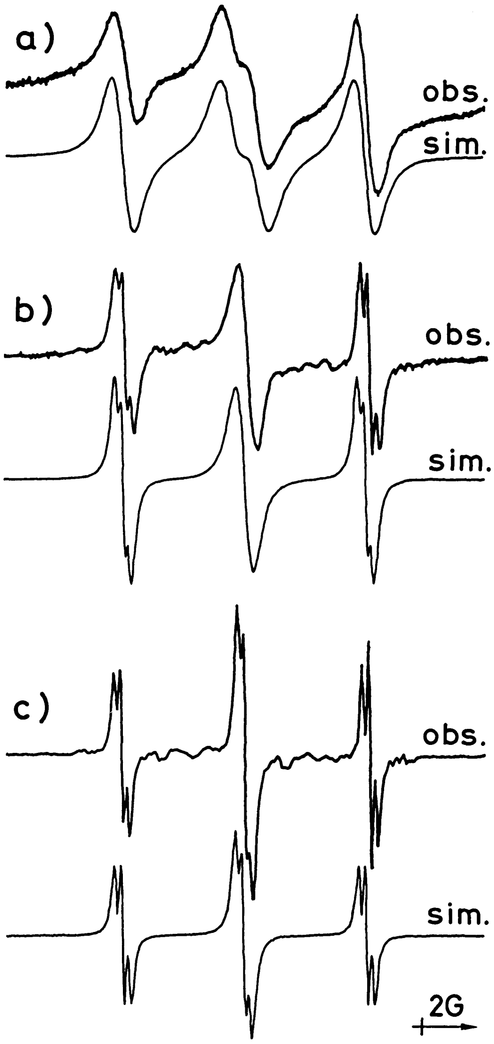

Fig. 2. First-derivative X-band EPR spectra of the paramagnetic complex, $MeCpMo(CO)_3(BQ)$, in 2-Me-THF at different temperatures, and their simulated spectra obtained by use of the modified Bloch equations assuming the two-jump model ; a) spectra observed at -105 °C and simulated with $\tau = 0.23\times10^{-5}$s, b) spectra observed at -80 °C and simulated with $\tau = 0.40\times10^{-6}$s, and c) spectra observed at -60 °C and simulated with $\tau = 0.80\times10^{-7}$s.

complex molecules and its details. The fact that the complexes derived from $[MeCpMo(CO)_3]_2$ show the line-width alternation effect at higher temperatures than in the case of $[CpMo(CO)_3]_2$ suggests that they have higher activation energies for the rotation and that the methyl group makes an appreciable effect on the intramolecular motion of the complex; the methyl group makes the transition states in the intramolecular motion of the complexes unstable by the steric interaction with the other ligands.

It is known that p-benzoquinones coordinate to group 4B organometallics and also to some transition metals by one of the carbonyl oxygens forming paramagnetic complexes.[7-12] However, neither details of the coordination structures nor dynamic motions of the complexes have been known. The present paper is the first case showing clearly the most stable conformation of the p-benzoquinone ligands and their restricted rotation in such a type of complexes. It must be notable that the structures obtained from the information of EPR spectra at high temperatures are not necessarily for the most stable conformation.

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4) The photo-irradiation was accomplished in situ in an EPR cavity with a 100-W high-pressure mercury lamp equipped with a UV-cut filter (< 310 nm).
5) 2-Me-THF was used as a solvent because of its low viscosity at low temperatures. In toluene, the observed proton hf structure is the triplet splitting due to the interactions with the C_2 and C_6 protons (Fig. 1,a), but in 2-Me-THF additional splittings which can be assigned to the couplings with the C_3 and C_5 protons were observed (Fig. 2,b and c), though they were not resolved at the low temperatures by the line-width broadening (Fig. 2,a).
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