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## EPR studies of photochemical reactions of hexacarbonylbis( $\eta^5$ -2,4-cyclopentadien-1-yl)ditungsten, $[\text{CpW}(\text{CO})_3]_2$ , with quinones

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### Abstract

Photochemical reactions of hexacarbonylbis( $\eta^5$ -2,4-cyclopentadien-1-yl)ditungsten  $[\text{CpW}(\text{CO})_3]_2$  in the presence of *o*-quinones or *p*-benzoquinones were investigated by EPR. It was found that photoirradiation to the toluene solution of  $[\text{CpW}(\text{CO})_3]_2$  containing *o*-quinones produces successively two kinds of paramagnetic complexes,  $\text{CpW}(\text{CO})_3(\textit{o}\text{-quinone})$  and  $\text{CpW}(\text{CO})_2(\textit{o}\text{-quinone})$ . The former is observed during the photoirradiation and then it converts to the latter with the chelate type structure. Photoirradiation to the THF solution of  $[\text{CpW}(\text{CO})_3]_2$  containing *p*-benzoquinones produces the paramagnetic complexes in which *p*-benzoquinones are bound to W of  $\text{CpW}(\text{CO})_3$  by their carbonyl oxygen, but when toluene is used as a solvent another kind of complex, with a C–W bond, is formed in the reaction with 1,4-benzoquinone. The reaction schemes and the structural features of the paramagnetic products are discussed based on the EPR observations and compared with the system of molybdenum complexes.

### Introduction

The chemical reactivity of metal carbonyl complexes containing a metal–metal bond has been the subject of extensive study. It has been shown that photolytic cleavage of the metal–metal bonds commonly occurs and the resulting paramagnetic species undergo various reactions [1–4]. We have previously reported that photoirradiation of the toluene solutions of  $[\text{CpMo}(\text{CO})_3]_2$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) or  $[\text{MeCpMo}(\text{CO})_3]_2$  ( $\text{MeCp} = \eta^5\text{-CH}_3\text{C}_5\text{H}_4$ ) containing *o*-quinones, 1,2-diketones, or *p*-benzoquinones yields paramagnetic complexes having these quinones or ketones as a ligand. These complexes show interesting properties of spin distribution and intramolecular dynamic motions [5–9].

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Hexacarbonylbis( $\eta^5$ -2,4-cyclopentadien-1-yl)ditungsten,  $[\text{CpW}(\text{CO})_3]_2$ , which has a W–W bond [10], also gives the paramagnetic species  $\text{CpW}(\text{CO})_3$  by photolytic cleavage of the metal–metal bond as in  $[\text{CpMo}(\text{CO})_3]_2$  and  $[\text{MeCpMo}(\text{CO})_3]_2$  [1–3, 11–13]. It seems interesting to examine the photochemical reactions of the W complex in the presence of the quinones in comparison with those of the Mo complexes. In the present work, we extended our EPR study to the system of  $[\text{CpW}(\text{CO})_3]_2$  to obtain further information about the photochemistry of these kind of complexes and to elucidate structural features of the paramagnetic products generated in the photochemical reactions.

## Experimental section

$[\text{CpW}(\text{CO})_3]_2$  was commercially obtained from Aldrich and used as received. The  $^{13}\text{C}$  enriched sample,  $[\text{CpW}(^{13}\text{CO})_3]_2$ , was synthesized from  $[\text{CpW}(\text{CO})_3]_2$  by photosubstitution of CO with  $^{13}\text{CO}$  under  $^{13}\text{CO}$  atmosphere in toluene [14]. The concentration of  $^{13}\text{C}$  in the sample was estimated to be higher than 95% from the  $^{13}\text{C}$  content in the  $^{13}\text{CO}$  gas and the experimental procedure used [14]. The quinones used were 1,2-acenaphthenequinone (AQ), 9,10-phenanthrenequinone (PQ), 1,4-benzoquinone (*p*-BQ), 2-methyl-1,4-benzoquinone (2-MBQ), 2,5-di-*tert*-butyl-1,4-benzoquinone (2,5-DBBQ), 2-phenyl-1,4-benzoquinone (2-PBQ), 2,6-dimethyl-1,4-benzoquinone (2,6-DMBQ), 2,5-dimethyl-1,4-benzoquinone (2,5-DMBQ), 2,6-di-*tert*-butyl-1,4-benzoquinone (2,6-DBBQ), and 2,5-diphenyl-1,4-benzoquinone (2,5-DPBQ). The sources of the quinones and purification were as described previously [5,6,9].

Toluene used as a solvent was purified by distillation over molecular sieves. Tetrahydrofuran (THF) was purified by distillation from  $\text{LiAlH}_4$  under a nitrogen atmosphere and stored in an ampule with the sodium perylene anion on a vacuum line. Typical sample solutions, containing  $[\text{CpW}(\text{CO})_3]_2$  (1 mg) and the quinones (1 mg) in approx.  $1\text{ cm}^3$  of toluene, were prepared in a vessel connected to a quartz EPR tube by using a vacuum line. For the reactions with *p*-benzoquinones, THF was also used as a solvent. The solutions were degassed on the vacuum line and kept the temperature of liquid nitrogen until just before photolysis. The solution in the quartz EPR tube was irradiated *in situ* in an EPR cavity with a 100 W high pressure mercury lamp equipped with a UV-cut filter ( $< 310\text{ nm}$ ) at room temperature or lower.

EPR spectra were recorded on a Jeol JES-FE2XG X-band spectrometer. The temperature was controlled by standard accessories. The microwave frequency was monitored with a Takedariken TR5501 frequency counter equipped with a TR5023 frequency converter. The magnetic field strength was measured with an Echo electronics EFM2000 NMR oscillator, and the magnetic field difference between the NMR probe and the sample position was calibrated by DPPH.

## Results and discussion

### *Photochemical reactions of $[\text{CpW}(\text{CO})_3]_2$ with o-quinones*

The degassed toluene solution of  $[\text{CpW}(\text{CO})_3]_2$  and PQ exhibited two kinds of EPR spectra by photoirradiation (Figs. 1 and 2). During photoirradiation the solution showed an EPR spectrum with well resolved hyperfine (hf) structure

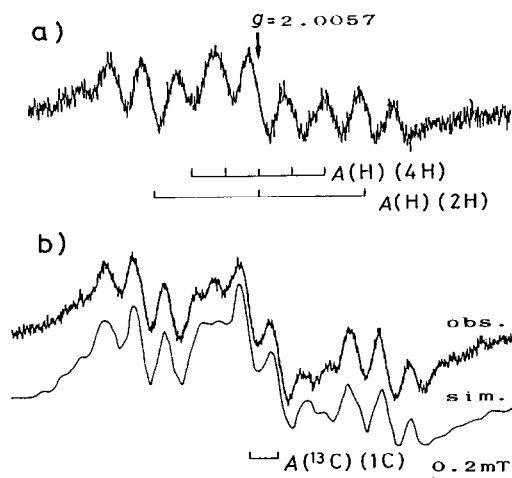


Fig. 1. First-derivative X-band EPR spectra observed during photoirradiation of the toluene solutions of: (a)  $[\text{CpW}(\text{CO})_3]_2$  and PQ; (b)  $[\text{CpW}^{13}\text{C}(\text{CO})_3]_2$  and PQ at  $-40^\circ\text{C}$ . The simulation spectrum obtained by adding the  $^{13}\text{C}$  hf splittings to the spectrum (a) is shown in (b) for comparison.

which can be explained as arising from the interaction with the PQ protons (Fig. 1(a)). When the  $^{13}\text{C}$  enriched sample  $[\text{CpW}^{13}\text{C}(\text{CO})_3]_2$  was used, additional hf splittings due to  $^{13}\text{C}$  were observed (Fig. 1(b)). These indicate formation of a paramagnetic W complex containing PQ and CO as ligands. It is known that photoirradiation to  $[\text{CpW}(\text{CO})_3]_2$  gives a paramagnetic species  $\text{CpW}(\text{CO})_3$  formed

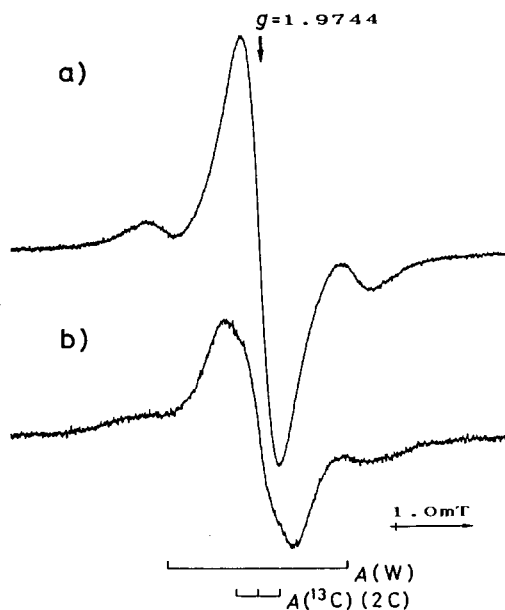
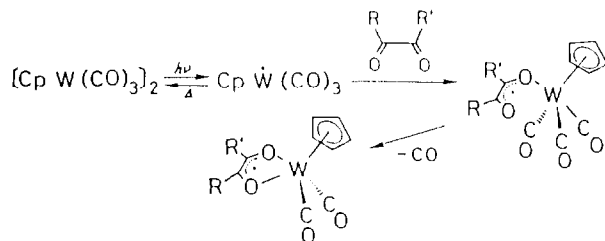


Fig. 2. First-derivative X-band EPR spectra observed after photoirradiation of the toluene solutions of: (a)  $[\text{CpW}(\text{CO})_3]_2$  and PQ; (b)  $[\text{CpW}^{13}\text{C}(\text{CO})_3]_2$  and PQ at  $-40^\circ\text{C}$ .



Scheme 1.

by photolytic cleavage of the W–W bond and CO loss species [1–3,11–13]. It is reasonable to consider that only the paramagnetic species  $\text{CpW}(\text{CO})_3$  is concerned with the formation of the paramagnetic product, as in the reaction between  $[\text{CpW}(\text{CO})_3]_2$  and halocarbons [3,12]. Since the observed EPR spectra resemble well those of the paramagnetic complexes in which PQ is bound to the Mo of  $\text{CpMo}(\text{CO})_3$  or  $\text{MeCpMo}(\text{CO})_3$  by one of its carbonyl oxygen [7,9], the paramagnetic complex product formed is assigned to the complex containing PQ as a ligand monodentately bound to the W of  $\text{CpW}(\text{CO})_3$  [15\*].

On the other hand, after ceasing photoirradiation the solution showed an EPR spectrum exhibiting weak satellites arising from the hf interaction with the isotope  $^{183}\text{W}$  (14.3%,  $I = 1/2$ ,  $\mu = 0.1172\mu_{\text{N}}$ ) and when the  $^{13}\text{C}$  enriched sample  $[\text{CpW}(^{13}\text{CO})_3]_2$  was used, the EPR spectrum exhibited additional hf splittings due to two equivalent  $^{13}\text{CO}$ s (Fig. 2). Although these EPR spectra exhibited no hf splittings due to the PQ protons, the spectral features correspond well to those of the spectra observed for the chelate type complexes formed in the photochemical reactions of  $[\text{CpMo}(\text{CO})_3]_2$  or  $[\text{MeCpMo}(\text{CO})_3]_2$  with PQ [5,9], and hence the complex observed after photoirradiation is assigned to the chelate type complex of the form  $\text{CpW}(\text{CO})_2(\text{PQ})$ , in which PQ is bound bidentately to the W of  $\text{CpW}(\text{CO})_2$  generated by elimination of one of the COs from  $\text{CpW}(\text{CO})_3$ , as in the reaction of  $[\text{CpMo}(\text{CO})_3]_2$  with PQ evidenced by EPR spectroscopy [7]. In the present case, the hf splittings due to the two equivalent  $^{13}\text{CO}$ s support the chelate structure [16\*].

Photoirradiation to  $[\text{CpW}(\text{CO})_3]_2$  under the presence of AQ also generated successively two types of paramagnetic complex; one is the complex where AQ is bound monodentately to  $\text{CpW}(\text{CO})_3$ , and the other is the complex where AQ is bound to  $\text{CpW}(\text{CO})_2$  in the chelate form. The reaction mechanism is shown in Scheme 1 and the EPR parameters of the complexes are listed in Table 1.

The  $g$  values of the chelate type complexes deviate from those of the free semiquinone radicals ( $g_{\text{O}^-} = 2.0048$ ), and the larger the W hf couplings, the larger the deviation of the  $g$  values (Fig. 3). This correlation between the W hf couplings and the  $g$  values indicates that the deviation of the  $g$  value from the free semiquinone value arises mainly from the spin-orbit coupling effect of the unpaired electron on W.

It is notable that the  $^{13}\text{C}$  hf coupling constants of the CO groups obtained for the chelate type complexes are larger than those of the corresponding Mo

\* Reference with asterisk indicates a note in the list of references.

Table 1

EPR parameters for the paramagnetic complexes formed in the photochemical reactions of  $[\text{CpW}(\text{CO})_3]_2$  with *o*-quinones in toluene

Quinone	Metal	<i>g</i> value	$a_{\text{W}}$ (mT)	$a_{\text{H}}$ (mT) <sup>a</sup>
PQ	$\text{CpW}(\text{CO})_3$ <sup>b</sup>	2.0057	–	$a_{\text{H}} 1,3 = 0.27$ (2H), $a_{\text{H}} 2,4,6,8 = 0.08$ (4H), $a_{13\text{C}} = 0.06$ (1C) <sup>c</sup>
	$\text{CpW}(\text{CO})_2$ <sup>d</sup>	1.9744	2.30	$a_{13\text{C}} = 0.28$ (2C) <sup>c</sup>
AQ	$\text{CpW}(\text{CO})_3$ <sup>e</sup>	2.0038	–	$a_{\text{H}} 3,5 = 0.27$ (2H), $a_{13\text{C}} = 0.07$ (2C) <sup>c</sup>
	$\text{CpW}(\text{CO})_2$ <sup>d</sup>	1.9899	1.02	$a_{13\text{C}} = 0.13$ (2C) <sup>c</sup>

<sup>a</sup> The number of equivalent protons is indicated in parentheses. <sup>b</sup> The complex with a quinone ligand monodentately coordinated to W by the C<sub>10</sub> oxygen. <sup>c</sup> The hyperfine (hf) coupling constants of <sup>13</sup>Cs observed for the <sup>13</sup>C enriched sample,  $[\text{CpW}(\text{C}^{13}\text{O})_3]_2$ . The number of equivalent <sup>13</sup>Cs is indicated in parentheses. <sup>d</sup> The complex with a chelate structure. <sup>e</sup> The complex with a quinone ligand monodentately coordinated to W by the C<sub>2</sub> oxygen.

complexes reported previously [5]. It may be also notable that the quinone proton hf couplings in the W complexes of the chelate type are considered to be smaller than those in the corresponding Mo complexes since they are not resolved in the EPR spectra of the W complexes, while they are clearly observed for the Mo complexes [5,9]. These facts imply that the unpaired electron distribution shifts partly from the quinone ligand to the metal moiety  $\text{CpM}(\text{CO})_2^+$  (M = Mo, W) by the change of the central metal from Mo to W.

According to the extended Hückel MO calculation, the unpaired electron orbital, SOMO, of the chelate type complexes is formed by the antibonding combination of the HOMO of the metal moiety  $\text{CpM}(\text{CO})_2^+$  and the lowest vacant  $\pi$  orbital of the *o*-quinone ligands [17\*]. In this MO model, contribution of the metal moiety HOMO to the SOMO of the product complexes is increased by

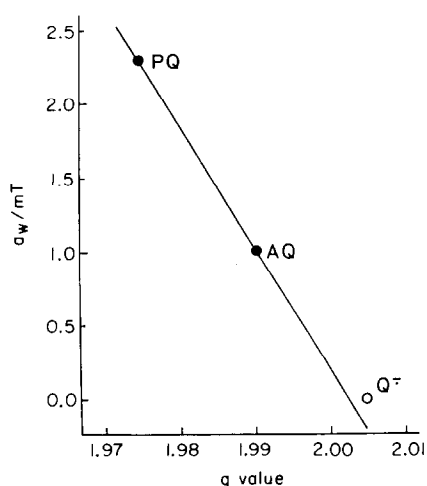


Fig. 3. Plots of  $a_{\text{W}}$  versus *g* values for the chelate paramagnetic complexes (●) and the *o*-semiquinone anion radical ( $\text{Q}^{\bullet-}$ , ○).

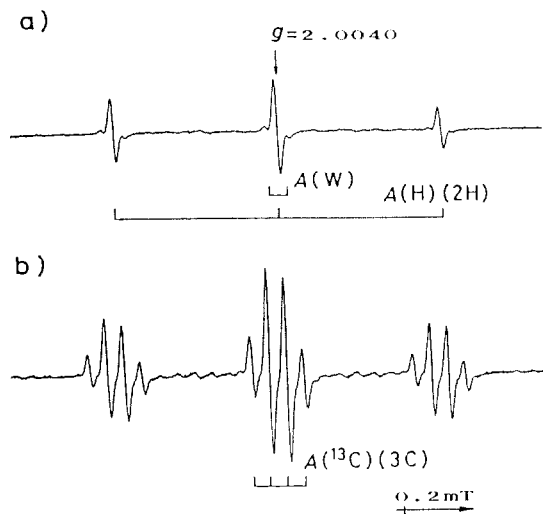


Fig. 4. First-derivative X-band EPR spectra observed during photoirradiation of the THF solutions of: (a)  $[\text{CpW}(\text{CO})_3]_2$  and *p*-BQ; (b)  $[\text{CpW}^{(13}\text{C})_3]_2$  and *p*-BQ at  $-40^\circ\text{C}$ .

elevation of the energy of the metal moiety HOMO. Since the metal moiety HOMO is considered to be elevated by change of the central metal from Mo to W, the unpaired electron density on the metal moiety is expected to become larger in the W complex than in the Mo complex. This is consistent with the experimental results, indicating the feasibility of the model for the SOMO.

#### *Photochemical reactions of $[\text{CpW}(\text{CO})_3]_2$ with *p*-benzoquinones*

Photoirradiation to the THF solution of  $[\text{CpW}(\text{CO})_3]_2$  in the presence of *p*-BQ gave an EPR spectrum exhibiting a triplet hf splitting due to two equivalent protons of *p*-BQ and satellites arising from hf interaction with the magnetic isotope  $^{183}\text{W}$ , and when the  $^{13}\text{C}$ -enriched sample  $[\text{CpW}^{(13}\text{C})_3]_2$  was used, additional hf splittings due to three  $^{13}\text{C}$  nuclei were observed in the spectrum (Fig. 4). These EPR spectra suggest formation of a paramagnetic complex of the type of  $\text{CpW}(\text{CO})_3(\textit{p}\text{-BQ})$  where *p*-BQ is monodentately bound to W of the  $\text{CpW}(\text{CO})_3$  produced by photocleavage of  $[\text{CpW}(\text{CO})_3]_2$ .

The formation of this type of complex was also observed when toluene was used as a solvent and in reactions with other *p*-benzoquinones. The complex formation is largely affected by steric factors around the quinone carbonyl oxygens; 2,6-substituted *p*-benzoquinones yield only the complexes in which the  $\text{C}_4$ -oxygen coordinates to W, and in the reactions with 2-MBQ or 2-PBQ, the  $\text{C}_4$ -oxygen coordinating complexes are formed in preference to the  $\text{C}_1$ -oxygen coordinating complexes. The EPR parameters of the complexes are listed in Table 2.

As Table 2 shows, the W hf coupling constants are so small that they are not observable in many cases and the *g* values are near to those of the *p*-benzosemiquinone radicals, indicating that the unpaired electron may be mostly populated on the *p*-benzoquinone ligands in these complexes. The deviation of the *g* values from those of the *p*-benzosemiquinone radicals is slight, but it is larger than that in

Table 2

EPR parameters for the paramagnetic complexes formed in the photochemical reactions of  $[\text{CpW}(\text{CO})_3]_2$  with *p*-benzoquinones in solutions at  $-40^\circ\text{C}$

Quinone	Solvent	<i>g</i> value	$a_{\text{W}}$ (mT)	$a_{\text{H}2}$ (mT)	$a_{\text{H}3}$ (mT)	$a_{\text{H}5}$ (mT)	$a_{\text{H}6}$ (mT)	$a_{^{13}\text{C}(\text{CO})}$ (mT) <sup>a</sup>
<i>p</i> -BQ <sup>b</sup>	Toluene	2.0040	–	0.485	–	–	0.485	0.06(1C), 0.04(2C)
	THF	2.0040	0.05	0.468	–	–	0.468	0.049(3C)
2-MBQ <sup>b</sup>	Toluene	2.0038	–	0.44(Me)	0.01	0.04	0.49	
2,6-DMBQ <sup>b</sup>	Toluene	2.0037	–	0.438(Me)	0.016	0.016	0.438(Me)	0.074(1C) 0.033(2C)
	THF	2.0037	–	0.418(Me)	–	–	0.418(Me)	
2,5-DMBQ <sup>b</sup>	Toluene	2.0037	–	0.54(Me)	–	–	0.39	
2,6-DBBQ <sup>b</sup>	Toluene	2.0036	–	–	–	–	–	
2,5-DBBQ <sup>b</sup>	Toluene	2.0037	–	–	–	–	0.42	
2-PBQ <sup>c</sup>	Toluene	2.0040	–	–	0.42	0.53	–	
2-PBQ <sup>b</sup>	Toluene	2.0038	–	0.06(para)	–	–	0.46	
				0.06(ortho)				
				0.03(meta)				
2,5-DPBQ <sup>b</sup>	Toluene	2.0039	–	–	–	–	0.40	

<sup>a</sup> The hyperfine (hf) coupling constants of  $^{13}\text{C}$ s observed for the  $^{13}\text{C}$  enriched sample,  $[\text{CpW}(^{13}\text{CO})_3]_2$ . The number of equivalent  $^{13}\text{C}$ s is indicated in parentheses. <sup>b</sup> The complex with a quinone ligand coordinated to W by the C<sub>4</sub> oxygen. <sup>c</sup> The complex with a quinone ligand coordinated to W by the C<sub>1</sub> oxygen.

the corresponding Mo complexes [6,8,9]; this may be due to the larger spin-orbit coupling effect of W than that of Mo.

In a previous paper, we showed that the most stable conformation of the coordinating *p*-benzoquinones in the Mo complexes is that the Mo–O bond is in the *p*-benzoquinone plane, and the quinones are rotating about the C–O (–Mo) axis [6]. It was also shown that the complexes derived from  $[\text{MeCpMo}(\text{CO})_3]_2$  exhibit the line width alternation effect in the EPR spectra, which is attributable to the restricted rotation of the quinone ligands [8,9]. In the present case, however, the line width broadening effect attributable to the restricted rotation of the quinone ligands was not observed; the quinone ligands are rotating freely in the EPR time scale. In the case of the complexes derived from  $[\text{CpMo}(\text{CO})_3]_2$  too, no line width broadening effect attributable to the restricted rotation was observed at the same temperature range. The presence of substituents on the cyclopentadienyl ring, such as a methyl group, seems to have an appreciable effect on the rotation of the *p*-benzoquinone ligands, and there seemed no appreciable difference between the Mo–O and the W–O bonds for the restricted rotation of the quinone ligands.

The formation of the paramagnetic complexes, in which *p*-benzoquinones are bound to W by their carbonyl oxygen, has been ascertained above. However, when toluene was used as a solvent, another type of complex was observed in the reaction with *p*-BQ; photoirradiation to the toluene solution of  $[\text{CpW}(\text{CO})_3]_2$  and *p*-BQ gave an EPR spectrum exhibiting a doublet of triplet hf splittings besides the triplet pattern signal due to the complex of the type mentioned above (Fig. 5(a)). When  $[\text{CpW}(^{13}\text{CO})_3]_2$  was used, the hf splittings attributable to the  $^{13}\text{C}$  hf couplings were also observed in the doublet of triplet hf pattern (Fig. 5(b)). It has been reported that a photochemical reaction of  $\text{Mn}_2(\text{CO})_{10}$  with *p*-benzoquinones

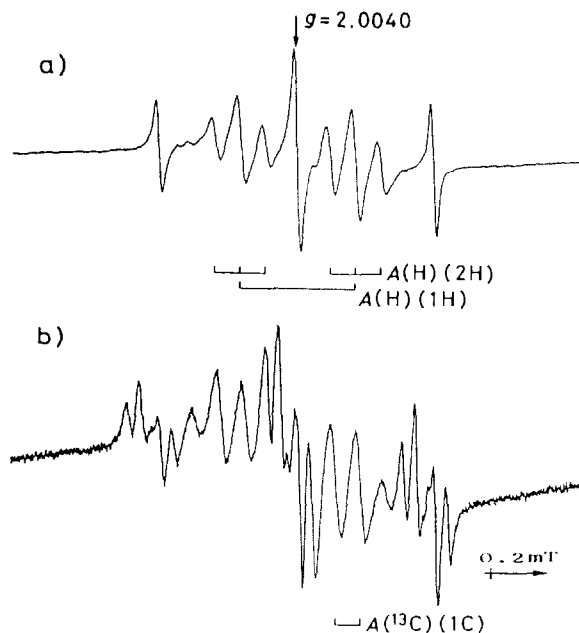


Fig. 5. First-derivative X-band EPR spectra observed during photoirradiation of the toluene solutions of: (a)  $[\text{CpW}(\text{CO})_3]_2$  and *p*-BQ at  $-39^\circ\text{C}$ ; (b)  $[\text{CpW}^{(13)\text{C}}_3]_2$  and *p*-BQ at  $-27^\circ\text{C}$ .

in benzene yields paramagnetic complexes with a C–Mn bond formed between  $\text{Mn}(\text{CO})_5$  and the  $\pi$  electron system of the *p*-benzoquinones [18]. Formation of the complexes with a C–Si or a C–P bond has been also reported in the reactions of organosilicon or organophosphorus compounds with *p*-benzoquinones [19,20]. The hf couplings of the *p*-BQ protons observed here indicate the formation of a complex with the C–W bond formed between  $\text{CpW}(\text{CO})_3$  and the  $\pi$  electron system of *p*-BQ; the estimated structure is shown in Fig. 6.

Such a complex with a C–W bond was not observed when THF was used as a solvent. The formation of C–Mo bonded complexes was not observed in the reactions of  $[\text{CpMo}(\text{CO})_3]_2$  and  $[\text{MeCpMo}(\text{CO})_3]_2$  with quinones. It seems interesting which type of complex, O–metal bonded or C–metal bonded, is formed under what kind of conditions. The above experimental results suggest that the softness/hardness of the metal moiety and the coordination sites of the ligand play

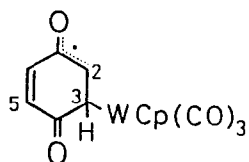


Fig. 6. The structure of the paramagnetic complex with a C–W bond formed in the toluene solution of  $[\text{CpW}(\text{CO})_3]_2$  and *p*-BQ. The EPR parameters of the complex are  $g = 2.0040$ ,  $a_{\text{H}2} = 0.405$  mT, and  $a_{\text{H}3.5} = 0.088$  mT.



an important role on the type of reactions, and the interaction is also influenced by the polarity of the solvents, *i.e.*,  $\text{CpW}(\text{CO})_3$ , which is softer than  $\text{CpMo}(\text{CO})_3$  or  $\text{MeCpMo}(\text{CO})_3$ , can produce the C–metal bonded complex by interaction with the softer part in the quinone, and non-polar solvents seem to make the soft interaction more preferable.

### Acknowledgment

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### References and notes

- 1 G.L. Geoffroy and M.S. Wrighton, *Organometallic Photochemistry*, Academic Press, New York, 1979.
- 2 G.L. Geoffroy, *J. Chem. Educ.*, 60 (1983) 861.
- 3 T.J. Meyer and J.V. Caspar, *Chem. Rev.*, 85 (1985) 187.
- 4 A.E. Stigman and D.R. Tyler, *Coord. Chem. Rev.*, 63 (1985) 217.
- 5 M. Hanaya, S. Tero-Kubota and M. Iwaizumi, *Organometallics*, 7 (1988) 1500.
- 6 M. Hanaya and M. Iwaizumi, *Organometallics*, 8 (1989) 672.
- 7 M. Hanaya and M. Iwaizumi, *Bull. Chem. Soc. Jpn.*, 63 (1990) 275.
- 8 M. Hanaya and M. Iwaizumi, *Chem. Lett.*, (1989) 1381.
- 9 M. Hanaya and M. Iwaizumi, *J. Organomet. Chem.*, 417 (1991) 407.
- 10 R.D. Adams, D.M. Collins and F.A. Cotton, *Inorg. Chem.*, 13 (1974) 1086.
- 11 M.S. Wrighton and D.S. Ginley, *J. Am. Chem. Soc.*, 97 (1975) 4246.
- 12 R.M. Laine and P.C. Ford, *Inorg. Chem.*, 16 (1977) 388.
- 13 A.F. Hepp and M.S. Wrighton, *J. Am. Chem. Soc.*, 103 (1981) 1258.
- 14 D.S. Ginley, C.R. Bock and M.S. Wrighton, *Inorg. Chim. Acta*, 23 (1977) 85.
- 15 In the spectrum of Fig. 1(b), the observed  $^{13}\text{C}$  hf splittings are attributed to the interaction with a single  $^{13}\text{CO}$  group. The hf couplings with the other two  $^{13}\text{CO}$  groups may be too small to be resolved, as in the case of  $\text{CpMo}(\text{CO})_3(\text{PQ})$  [7].
- 16 Unfortunately quantitative information about quantum yields for the conversion of  $\text{CpW}(\text{CO})_3(\text{PQ})$  to  $\text{CpW}(\text{CO})_2(\text{PQ})$  could not be obtained because of instability of the complexes observed here.
- 17 The MO calculation was made according to the same procedure as that in ref. 5, and the parameters for W were taken from: C.N. Wilker and R. Hoffmann, *J. Am. Chem. Soc.*, 105 (1983) 5285.
- 18 T. Foster, K.S. Chen and J.K.S. Wan, *J. Organomet. Chem.*, 184 (1980) 113.
- 19 M.T. Craw, A. Alberti, M.C. Depew and J.K.S. Wan, *Bull. Chem. Soc. Jpn.*, 58 (1985) 3675.
- 20 A. Alberti, A. Hudson, G.F. Pedulli, W.G. McGimpsey and J.K.S. Wan, *Can. J. Chem.*, 63 (1985) 917.