for the distortion of the bonding angle of fluorenyl ring II with zinc. The shortest intramolecular interligand C–C separations are 4.064 (10) Å between C(3) and C(16) and 4.116 (10) Å between C(3) and C(17). The shortest intermolecular C–C distances of perpendicular rings are 3.589 (9) Å between C(6) and C(19) and 3.685 (9) Å between C(6) and C(18). These values are in good agreement with those found in solid benzene, i.e. a center-center separation of 5.1 Å.[26]

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Registry No. $Zn(C_5H_5)_2$, 11077-31-9; $Zn(C_9H_7)_2$, 117958-66-4; $(C_9H_7)K$, 12128-56-2; $Zn(C_{13}H_9)_2$, 117958-67-5; $(C_{13}H_9)Na$, 3531-83-7; C_9H_8, 95-13-6; $C_{13}H_{10}$, 86-73-7; $ZnCl_2$, 7646-85-7; $Zn(C_{13}H_9)_2(THF)_2$, 117958-68-6.

Supplementary Material Available: Tables of anisotropic thermal parameters, all H-atom parameters, bond lengths, and bond angles (6 pages); a listing of observed and calculated structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

EPR Studies of the Paramagnetic Complexes Produced in the Photochemical Reactions of Hexacarbonylbis(η^5-2,4-cyclopentadien-1-yl)dimolybdenum, $[CpMo(CO)_3]_2$, with *p*-Benzoquinones

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The photochemical reactions of hexacarbonylbis(η^5-2,4-cyclopentadien-1-yl)dimolybdenum, $[CpMo(CO)_3]_2$, with a series of *p*-benzoquinones and the structure of the paramagnetic reaction products have been investigated by the EPR spectroscopy. The paramagnetic products can be assigned to complexes of the form of $CpMo(CO)_3$(*p*-benzoquinone), where $CpMo(CO)_3$ produced by photocleavage of the Mo–Mo bond in $[CpMo(CO)_3]_2$ is coordinated by the carbonyl oxygen in the *p*-benzoquinones; the *p*-benzoquinones trap $CpMo(CO)_3$ as monodentate ligands, yielding the paramagnetic complexes. From the *g* and hyperfine (hf) coupling values of the complexes, the unpaired electron is considered to be mostly on the benzoquinone ligand. At temperatures around −40 °C, the *p*-benzoquinone ligands show hf couplings symmetrical about the axis connecting their two C–O bonds, but at lower temperatures near −90 °C, the line-width alternation effect is observed in the hf lines due to the protons at the positions meta to the coordinating carbonyl oxygen; the paramagnetic complex has a C_s symmetry as a "*time average*", and the *p*-benzoquinone ligands are rapidly rotating about the C–O(–Mo) bond at most of the temperatures studied.

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.[2-5] In the previous paper we have shown that the photochemical reactions of hexacarbonylbis(η^5-2,4-cyclopentadien-1-yl)dimolybdenum, $[CpMo(CO)_3]_2$, with a series of *o*-quinones and 1,2-diketones give the paramagnetic chelate complexes of *o*-quinones (or 1,2-diketones) and $CpMo(CO)_2$.[6] The chelate complexes were thought to be formed by coordination of the *o*-quinones or 1,2-diketones to $CpMo(CO)_3$, which was produced by photocleavage of the Mo–Mo bond of $[CpMo(CO)_3]_2$ followed by elimination of one of the CO groups and then the formation of the chelate structure.

On the other hand, it has been shown that *p*-benzoquinones coordinate to the metal by one of their carbonyl oxygens in the complexes of group IVB organometallics[7,8] and some transition metals.[9-12] However, in studies of the photochemical reaction of $Mn_2(CO)_{10}$ with *p*-benzoquinones,[13,14] Foster et al. have postulated the formation of the paramagnetic complexes in which *p*-benzoquinones bind to $Mn(CO)_5$ by their quinoid π systems, forming a carbon–manganese bond.[13] In connection with these metal complexes of *p*-benzoquinones and the photochemical reactions of $[CpMo(CO)_3]_2$ with

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(1) Chemical Research Institute of Non-Aqueous Solutions, Tohoku University.

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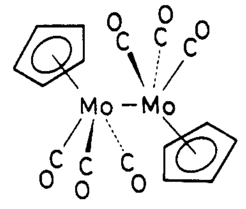
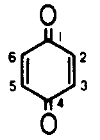


o-quinones or 1,2-diketones, it seemed of interest to investigate the photochemical reaction of $[CpMo(CO)_3]_2$ with *p*-benzoquinones and to elucidate the structural details of the products. We therefore attempted to examine them by EPR spectroscopy.

Experimental Section

$[CpMo(CO)_3]_2$ was commercially obtained from Strem Chemicals and used as received. 1,4-Benzoquinone (BQ), 2-methyl-1,4-benzoquinone (2-MBQ), 2,5-di-*tert*-butyl-1,4-benzoquinone (2,5-DBBQ), and 2-phenyl-1,4-benzoquinone (2-PBQ) were sublimed. 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), 2,5-diphenyl-1,4-benzoquinone (2,5-DPBQ), 2,3,5,6-tetramethyl-1,4-benzoquinone (TMBQ), 2,3,5,6-tetrafluoro-1,4-benzoquinone (TFBQ), and 2,3,5,6-tetrachloro-1,4-benzoquinone (TCBQ) of the commercially available best grade were used without further purification. Toluene used as a solvent was purified and dried by distillation over molecular sieves in vacuo. Tetrahydrofuran (THF) was purified by distillation from $LiAlH_4$ and stored with the sodium perylene anion in vacuo. Acetonitrile was purified by distillation from P_2O_5 and stored with molecular sieves in vacuo. For EPR studies, these solvents were distilled through a vacuum line to a vessel containing the reagents.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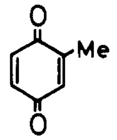
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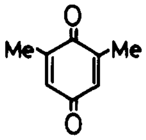
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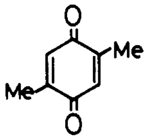
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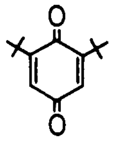
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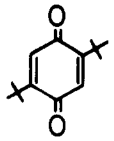
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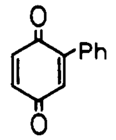
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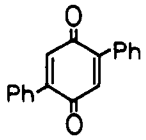
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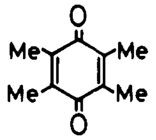
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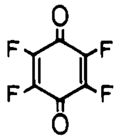
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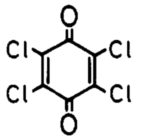
TCBQ

$[CpMo(^{13}CO)_3]_2$ was synthesized from $[CpMo(CO)_3]_2$ by the photosubstitution of CO with ^{13}CO under ^{13}CO atmosphere[15-17] in toluene. Almost complete substitution by ^{13}CO's was confirmed by the mass spectra.

Typical sample solutions containing $[CpMo(CO)_3]_2$ (1 mg) and the benzoquinone (1 mg) in 1 cm^3 of toluene were prepared in a vessel connected to a 5-mm o.d. quartz tube. The solutions were degassed on the vacuum line and kept at liquid-nitrogen temperature until just before photolysis. The solution in the quartz tube was cooled to −40 °C and irradiated in situ in an EPR cavity with a 100-W high-pressure mercury lamp equipped with a UV-cut filter (<310 nm) and a remote-controlled shutter.

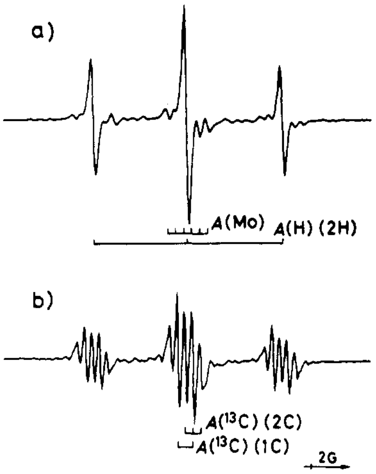

Figure 1. First-derivative X-band EPR spectra observed during photoirradiation of toluene solutions containing BQ and $[CpMo(CO)_3]_2$ (a) and $[CpMo(^{13}CO)_3]_2$ (b) at −40 °C.

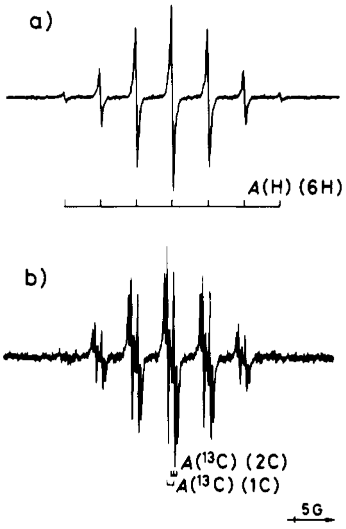

Figure 2. First-derivative X-band EPR spectra observed during photoirradiation of toluene solutions containing 2,6-DMBQ and $[CpMo(CO)_3]_2$ (a) and $[CpMo(^{13}CO)_3]_2$ (b) at −40 °C.

For BQ, acetonitrile was also used as a solvent, and for measurements at lower temperatures, THF was used instead of toluene since THF solutions gave better resolution of EPR spectra at low temperatures. For these solvents, 3-mm o.d. quartz tubes were used as EPR tubes.

EPR spectra were recorded on the JEOL JES-FE2XG X-band spectrometer using 100-kHz field modulation. The temperature was controlled by standard accessories. The microwave frequency was monitored with a Takedariken TR-5501 frequency counter equipped with a TR-5023 frequency converter. The magnetic field was measured with an Echo electronics EFM-2000 NMR oscillator, and the magnetic field difference between the NMR probe and the sample tube positions was caribrated by DPPH.

Results and Discussion

The degassed toluene solution containing $[CpMo(CO)_3]_2$ and BQ exhibited an EPR spectrum during photoirradiation (Figure 1a). This spectrum consists of a well-resolved triplet accompanied with six weak satelites, which are apparently due to the hyperfine (hf) interactions with two equivalent protons and the magnetic isotopes ^{95}Mo (15.8%, $I = {}^5/_2$, $\mu = -0.9099\ \mu_N$) and ^{97}Mo (9.6%, $I = {}^5/_2$,

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$\mu = -0.9290\ \mu_N$). When 2,6-DMBQ was used instead of BQ, the photoirradiation gave an EPR spectrum having a hf structure due to the interaction with six equivalent protons (Figure 2a).

The proton hf interactions observed above are obviously explained as arising from the interactions with the benzoquinone protons—the interaction with two ring protons in the former and that with the two equivalent methyl protons in the latter. These results show that the proton hf interactions are symmetrical about the axis connecting the two benzoquinone carbonyl groups. Such symmetrical proton hf interactions have also been reported for the paramagnetic complexes in which the *p*-benzoquinones coordinate to metals by one of their carbonyl oxygens.[7-10,12,14] If these complexes had a C–Mo bond as in the complexes formed from $Mn(CO)_5$ and *p*-benzoquinones,[13] such symmetrical proton hf interactions would not be observed. It is considered, therefore, that the *p*-benzoquinones coordinate to Mo by one of their two carbonyl oxygens in the above complexes.

On the other hand, when TMBQ was used, there was no indication of the formation of a paramagnetic complex under photoirradiation. This is because of the steric hinderance of the methyl groups impeding the coordination of the carbonyl oxygen to Mo. 2,6-DMBQ has two nonequivalent carbonyl oxygens, and the above result indicates that the coordination of 2,6-DMBQ occurs by the C_4 oxygen.

In order to obtain more information on these paramagnetic complexes, we attempted to observe EPR spectra of the complexes derived from $[CpMo(^{13}CO)_3]_2$. The paramagnetic complexes produced by the photochemical reaction with BQ exhibited an EPR spectrum having an additional doublet of triplets hf structure besides the splittings due to the interactions with Mo and the protons, and this doublet of triplets hf coupling can be assigned to interactions with ^{13}C nuclei in the complex (Figure 1b). This clearly indicates that the complex has two sets of CO's; two equivalent CO's and another CO. The EPR spectrum obtained by the photochemical reaction of $[CpMo(^{13}CO)_3]_2$ with 2,6-DMBQ also shows the doublet of triplet hf structure due to the interactions with three CO's as in the case of BQ (Figure 2b). From the number of the CO's in the paramagnetic complexes, *p*-benzoquinone is considered to coordinate to Mo of $CpMo(CO)_3$ as a monodentate ligand. Consequently, the paramagnetic complexes formed from $CpMo(CO)_3$ and *p*-benzoquinones have a structure in which Mo is coordinated by the carbonyl oxygen, and if *p*-benzoquinone has substituents, the sterically less hindered carbonyl oxygen is coordinated to Mo.

It is known that $[CpMo(CO)_3]_2$ primarily undergoes photocleavege of the Mo–Mo bond or loss of CO, forming the monomeric intermediate $CpMo(CO)_3$ in the former and the dimeric one $Cp_2Mo_2(CO)_5$ in the latter.[2,4,16-18] However, visible flash photolysis in THF yields the monomeric intermediates more than the dimeric ones, in a relative ratio of ~4/1.[4,19] On the other hand, the photoproduced $CpMo(CO)_3$ is trapped by a spin trap reagent, 2,3,5,6-tetramethyl-1-nitrosobenzene,[20] and reacts with carbon tetrachloride yielding $CpMo(CO)_3Cl$.[21] It is also known that $CpMo(CO)_3$ interacts with ligands or coordinating solvents to initiate the disproportionation reaction.[4,5,22-26] Our previous investigation exhibited that $CpMo(CO)_3$ is trapped by *o*-quinones and 1,2-diketones.[6] In view of these facts, the reaction of $[CpMo(CO)_3]_2$ with *p*-benzoquinones may be written as in Scheme I.

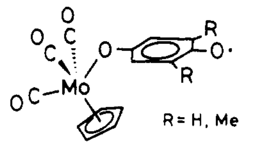
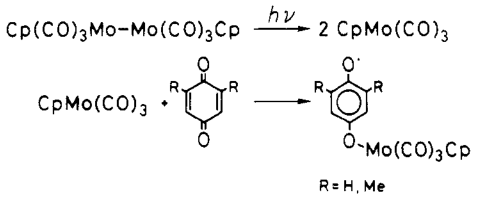


Figure 3. The postulated structure of the paramagnetic complexes.

Scheme I



According to the hf couplings of the complexes, these complexes are considered to have C_s symmetry as a "*time average*"; two of the three CO's and *p*-benzoquinone are symmetrically oriented to the symmetry plane as in Figure 3. However, when the temperature is lowered to −90 °C, the line-width alternation effect was observed in the proton hf splittings of the spectrum for the BQ complex;[27] the central line in the triplet splittings broadens and diminishes in amplitude due to incomplete averaging of the hf couplings of two different protons. This line-width alternation indicates that the most stable conformation of the complex is not the conformation having the *p*-benzoquinone symmetrically oriented to the symmetry plane.

As an origin of the line-width alternation effect, two types of molecular motions are considered: one is the rotation of the *p*-benzoquinone group about the C–O(–Mo) bond and the other is that of $CpMo(CO)_3$ group about the Mo–O bond. It is known that the stable structure of the monoprotonated *p*-benzosemiquinone is the one where the OH proton is in the aromatic plane; the EPR spectrum shows the symmetrical hf interactions about the axis connecting the two C–O bonds at room temperature by rapid rotation of the OH group, but as the temperature is lowered to −70 °C, the hf couplings of the C_2 and C_6 protons[28] become different from each other by the restricted OH group rotation between the most stable conformations (Table I).[29] In view of these facts, the line-width alternation observed for the present system seems more likely to attribute to the restricted rotation of the *p*-benzoquinone group about the C–O(–Mo) bond by as-

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[27] We used THF as a solvent because of its low viscosity at low temperatures. THF was effective to observe a well-resolved hf pattern at low temperatures.

[28] The numbering of the carbons of the monoprotonated *p*-benzosemiquinone is according to the assumption that the C_4 oxygen is protonated.

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Table I. EPR Parameters for the Paramagnetic Complexes and Related Compounds

substrate	solvent	temp, °C	g value	a_{Mo}/G	$a_{\mathrm{H}}2$/G	$a_{\mathrm{H}}3$/G	$a_{\mathrm{H}}5$/G	$a_{\mathrm{H}}6$/G	$a_{^{13}\mathrm{C(CO)}}$/G[a]
BQ[b]	toluene	-40	2.0047	0.4	4.69			4.69	0.73 (1 C), 0.38 (2 C)
	MeCN	-30	2.0046	0.5	4.22	0.50	0.50	4.22	
	THF	-40	2.0047	0.4	4.56	0.20	0.20	4.56	
BQ[c]	THF	-70		1.90[d]	5.69	0.57	0.57	5.34	
		RT[g]		1.54[d]	5.56	0.70	0.70	5.56	
BQ[e]	MeCN	RT[g]			2.42	2.42	2.42	2.42	
2-MBQ[b]	toluene	-40	2.0045	0.3	4.2 (Me)	0.3	0.3	4.8	0.7 (1 C), 0.3 (2 C)
2,6-DMBQ[b]	toluene	-40	2.0044		4.20 (Me)			4.20 (Me)	0.77 (1 C), 0.29 (2 C)
2,5-DMBQ[b]	toluene	-40	2.0045		5.2 (Me)	0.4		3.7	unresolved
2,6-DTBQ[b]	toluene	-40	2.0044	0.4					1.0 (1 C)
2,5-DTBQ[b]	toluene	-40	2.0045	0.7				4.07	1.10 (1 C)
2-PBQ[f]	toluene	-40	2.0047			4.12	5.12		1.1 (1 C), 0.6 (2 C)
2-PBQ[b]	toluene	-40	2.0046		0.6 (para) 0.6 (ortho) 0.3 (meta)			4.45	unresolved
2,5-DPBQ[b]	toluene	-40	2.0047		0.7 (para) 0.7 (ortho) 0.3 (meta)			3.90	
TFBQ[b]	toluene	-40	2.0052		10.0 (F)	1.7 (F)	1.7 (F)	10.0 (F)	
TCBQ[b]	toluene	-40	2.0063	3.2					

[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] The EPR parameters for monoprotonated *p*-benzosemiquinone in which the proton is bound to the C_4 oxygen.[29,30] [d] The hf coupling constant of the proton in the OH group. [e] The EPR parameters for *p*-benzosemiquinone.[31] [f] The EPR parameters for the complex in which the C_1 oxygen coordinates to Mo. [g] RT = room temperature.

suming that the most stable conformation of the complex is the following: the Mo–O bond is in the benzoquinone plane as in the case of the monoprotonated *p*-benzosemiquinone in which the π electrons of BQ can be more delocalized.[32]

In the photochemical reaction of [CpMo(CO)$_3$]$_2$ with other *p*-benzoquinones, the EPR spectra due to paramagnetic complexes could also be observed. The derived EPR parameters of the complexes are listed in Table I. The EPR spectra of these complexes exhibited hf splittings due to the quinone protons, ^{95,97}Mo, and ^{13}C's of ^{13}CO's as in the BQ and 2,6-DMBQ complexes. From the facts that the hf coupling constants of the quinone protons at the meta positions are larger than those at the positions ortho to the metalated oxygen and that the hf coupling constant of one nonequivalent ^{13}CO is larger than that of two equivalent ^{13}CO's, these paramagnetic complexes are also thought to have the same structures as shown in Figure 3. It should be noted that TFBQ and TCBQ in which all the hydrogens are substituted by halogen atoms also produce the paramagnetic complexes by photochemical reaction.

The EPR spectrum observed for the photochemical reaction with 2-PBQ shows the formation of two kinds of paramagnetic complexes (Figure 4; Table I). One of the complexes reveals the hf structure of a doublet of doublets, and it can be assigned to the complex in which the C_1 oxygen is coordinating to Mo. The other complex exhibits a doublet of multiplets, and it is assigned to the complex in which the C_4 oxygen is coordinating to Mo. The relative ratio of the integrated intensities of the EPR spectra of the two species is about 1/3, reflecting that the coordination by the C_1 oxygen is less preferential by the steric reason. In the reaction of 2-MBQ, the same trend was observed by EPR but reliable EPR parameters for the complex in which 2-MBQ is coordinated by the C_1 oxygen and the relative ratio of the two species could not be obtained because of the poor separation of the signals of the two species. However, it is evident from the spectrum that the complex in which the C_4 oxygen is coordinated to Mo is predominantly formed in the photochemical reaction.

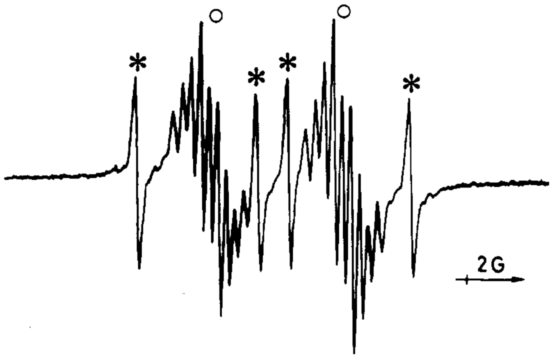

Figure 4. First-derivative X-band EPR spectrum observed during photoirradiation of a toluene solution containing 2-PBQ and [CpMo(CO)$_3$]$_2$ at -40 °C. The signal having a doublet of doublets hyperfine (hf) structure (*) was assigned to the complex in which the C_1 oxygen is coordinating to Mo, and the signal having a doublet of multiplets hf structure (O) was assigned to the C_4 oxygen coordinating complex.

As shown above, the formation of these complexes largely depends on the substituents of the *p*-benzoquinones; in particular, the steric factors around the carbonyl oxygen strongly affects the complex formation. Thus, 2,6-substituted *p*-benzoquinones give only one complex in which the C_4 oxygen coordinates to Mo, and no complex formation was observed for TMBQ (vide supra).

Giannotti et al. previously reported on the electron-transfer reaction between [CpMo(CO)$_3$]$_2$ and BQ in acetonitrile induced by photoirradiation.[33] They proposed, based on the observation of CH_2CN radicals trapped by spin trap reagents, that the free semiquinone anion radical is formed by the electron transfer from CpMo(CO)$_3$ to BQ, and the resulting anion radical abstracts hydrogen atoms from solvent molecules. Further, it has been also suggested that CpMo(CO)$_3$ is coordinated by a solvent molecule in potentially coordinating solvents such as acetonitrile, and the solvent-bound complex CpMo(CO)$_3$S (S = solvent molecule) will act as a reductant in outer-sphere elec-

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(32) The line-width alternation effects are being studied in detail for other quinone complexes too, and the results will be published elsewhere.

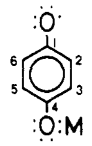
(33) Giannotti, C.; Mousset, G. *Tetrahedron Lett.* **1980**, *21*, 2155.

tron-transfer reactions to form $CpMo(CO)_3S^+$.[4] In the present work, we observed the formation of the paramagnetic complex for the same solvent system as Giannotti et al., but no evidence for the existence of the semiquinone anion radical was obtained. This result shows that the paramagnetic complex formation, not the electron-transfer reaction, occurs even in the coordinating solvent acetonitrile, and this suggests that there must be another reaction path for the formation of the CH_2CN radical than that proposed by Giannotti et al.

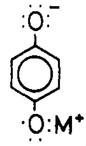
In the previous work, we observed that the photochemical reactions of $[CpMo(CO)_3]_2$ with *o*-quinones and 1,2-diketones in toluene yield paramagnetic complexes in which $CpMo(CO)_2$ is chelated by two carbonyl oxygens of *o*-quinones or 1,2-diketones. The chelate complexes were thought to be formed by coordination of the *o*-quinones or 1,2-diketones to the photoproduced $CpMo(CO)_3$ by one of their two carbonyl oxygens, followed by elimination of a CO group and then the formation of the chelate structure.[6] The present results indicate that *p*-benzoquinones coordinate to Mo as monodentate ligands as in the first step of the photochemical reactions with *o*-quinones and 1,2-diketones, and this supports the proposed scheme for the formation of the chelate complexes.

It has been shown that the paramagnetic chelate complexes show considerable variations in *g* values and the Mo hf coupling constants with *o*-quinone or 1,2-diketone ligands.[6] These variations were attributed to the marked variations of spin distribution between the metal moiety, $CpMo(CO)_2^+$, and the *o*-quinone or 1,2-diketone ligands. In the present complexes, no remarkable variations of *g* values were observed with *p*-benzoquinones, and the *g* values were almost identical with those of the corresponding free *p*-benzosemiquinone anion radicals. Further, in the BQ complex, the mean value of the proton hf coupling constants of the benzoquinone ligand is nearly equal to that of the free *p*-benzosemiquinone anion radical. These facts indicate that the unpaired electron is mostly transferred from $CpMo(CO)_3$ to *p*-benzoquinones, forming complexes of $CpMo(CO)_3^+$ ligated by *p*-benzosemiquinone anion radicals; i.e., most of the unpaired electron resides on the π^*-orbital of *p*-benzoquinones and Mo forms an 18-electron center.

We made EPR measurements for the BQ complex in three different solvents—toluene, THF, and acetonitrile—and observed that the proton hf coupling constants change with the polarity of solvents; the hf coupling constants of C_2 and C_6 protons decrease in the order toluene, THF, and acetonitrile solution while those of C_3 and C_5 protons increase (Table I). If the complex has an electronic configuration like I, the C_2 and C_6 protons will have larger hf coupling constants than the C_3 and C_5 protons, while in the complex having an electronic configuration like II, the ordering of proton hf coupling constants will be vice versa. The observed solvent effect indicates that the increase of the solvent polarity increases the contribution of configuration II.[34]



I



II

(M=CpMo(CO)3)

The complexation via the quinoid π-electron systems has been reported for the reactions of $Mn(CO)_5$, photochemically generated from $Mn_2(CO)_{10}$, with *p*-benzoquinones to form C-Mn bonds in benzene solutions.[13] However, no observation of the formation of such a complex has been reported for the reaction of $Mn_2(CO)_{10}$ with 2,6-DBBQ in toluene.[14] It has been also shown in the latter work that the formation of the ion pair $[Mn^I(CO)_{6-n}(S)_n{}^+]\cdot[p\text{-DBSQ}^-]$ ($n = 1$–3; S = solvent molecule; *p*-DBSQ = 2,6-di-*tert*-butyl-1,4-benzosemiquinone) occurs in coordinating solvents, followed by the photochemical formation of the paramagnetic complex $[Mn^I(CO)_{5-m}(S)_m(p\text{-DBSQ})]$ ($m = 0$–2), in which *p*-DBSQ coordinates to Mn by its C_4 oxygen. It seems interesting that $CpMo(CO)_3$ forms only the oxygen coordinating complexes and does not form the paramagnetic complexes having the C–Mo bond or ion pairs of the type mentioned above even in THF or acetonitrile, though it is a 17-electron species as $Mn(CO)_5$.

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[34] The same trend has been observed for monoprotonated *p*-benzosemiquinone.[30]