

## PHOTOSUBSTITUTION REACTIONS ON DI- $\eta^5$ -CYCLOPENTADIENYL-MOLYBDENUM AND -TUNGSTEN COMPLEXES \*

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(Received December 1st, 1978; in revised form March 13th, 1979).

### Summary

Irradiation of di- $\eta^5$ -cyclopentadienyl-molybdenum and -tungsten complexes (in pyridine, acetonitrile, or dimethylphenylphosphine) leads to photoinduced substitution. The product formed depends on the radiation wavelength; thus at 390–450 nm (*d-d* transition) monosubstitution results, whereas irradiation at  $390 > \lambda > 220$  nm (charge transfer transition) gives disubstitution.

The non-dependence of the quantum yield upon the ligand concentration is accounted for in terms of a dissociative mechanism for the monosubstitution.

### Introduction

There is an increasing interest in the photochemistry of organometallic compounds [1]. Photosubstitution reactions of coordination compounds remain the most studied, and extensive investigations have dealt with metal carbonyl complexes in which carbon monoxide photoinduced substitution by various ligands is observed [2]. Studies of the photochemistry of complexes  $[M(\eta^5-C_5H_5)_2H_2]$  ( $M = Mo, W$ ) by Green [3,4] and Geoffrey [5], of  $[W(\eta^5-C_5H_5)_2CO]$  by Thomas [6], and of  $[Ti(\eta^5-C_5H_5)_2X_2]$  ( $X = Cl, Br, Me$ ) by Gray [7] and Rausch [8], demonstrate the photolability of those organometallic compounds.

In order to gain insight into the photoreactions of the di- $\eta^5$ -cyclopentadienyl-molybdenum (and -tungsten) system and to devise new convenient synthetic routes we have begun a study of the photosubstitution reactions of some  $M(\eta^5-C_5H_5)_2$  derivatives, namely the compounds  $\{[M(\eta^5-C_5H_5)_2(L)Br]PF_6\}$  (I) ( $L = py, Ph_3P, MeCN, CO$ ),  $[M(\eta^5-C_5H_5)_2Br_2]$  (II) and  $[M(\eta^5-C_5H_5)_2(Me)_2]$  (III)

\* Presented in part at the 3rd Microsymposium of Photochemistry and Photophysics of Coordination Compounds, Köln, 1978.

(M = Mo, W), and a comparison with the related thermal reactions. We now describe results on the irradiation of complexes (I) and (II) which leads to photoinduced substitution, in which the products depend on the irradiation wavelength used. Complex III is not photoreactive, but if the oxidized compound  $\{[\text{Mo}^{\text{V}}(\eta^5\text{-C}_5\text{H}_5)_2(\text{Me})_2]\text{PF}_6\}$  is irradiated it behaves like I and II.

## Experimental

All the preparations and subsequent manipulations were carried out under nitrogen. All solvents were dried and distilled.  $^1\text{H}$  NMR spectra were determined using a JEOL JNM 100 PF instrument. The EPR spectrum was determined using a Bruker ER 200 tt instrument. Infrared spectra were recorded as mulls on a Perkin-Elmer 457 instrument and were calibrated with polystyrene film. Microanalyses were by H. Malissa and G. Reuter or by the microanalytical department of this laboratory.  $[\text{M}(\eta^5\text{-C}_5\text{H}_5)_2\text{Br}_2]$  (M = Mo, W) were prepared by the reported method [9]; compounds  $[\text{M}(\eta^5\text{-C}_5\text{H}_5)_2(\text{L})\text{Br}]\text{PF}_6$  (L = py, MeCN, PPh<sub>3</sub>, CO) were prepared by reaction of  $[\text{M}(\eta^5\text{-C}_5\text{H}_5)_2\text{Br}_2]$  and the ligand L in the presence of TlPF<sub>6</sub> according to the general method described in ref. 10. The compounds were purified by column chromatography (except when L = MeCN) followed by recrystallization) and were identified by comparison of their IR and NMR spectra with those of authentic samples.

$[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{Me}_2]$  was prepared according to the published method [11];  $[\text{M}(\eta^5\text{-C}_5\text{H}_5)_2(\text{Me})_2]\text{PF}_6$  was prepared as described below.

The complete characterization of the new complexes mentioned in this article is given in Table 1.

### (1) Synthesis of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{Me})_2]\text{PF}_6 \cdot \frac{1}{2} \text{H}_2\text{O}$

A solution ( $5 \times 10^{-2} \text{ M}$ ) of iodine in diethyl ether was added to a stirred solution of  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{Me}_2]$  (0.3 g) in the same solvent ( $50 \text{ cm}^3$ ) until no further precipitation occurred; after filtration the precipitate was extracted into acetone/water (1/1);  $\text{NH}_4\text{PF}_6$  was added to the solution, and on reduction of the volume under vacuum, a red solid appeared. This was recrystallized from acetone/ethanol. Yield ca. 70%. The compound analysed correctly for  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{Me})_2]\text{PF}_6 \cdot \frac{1}{2} \text{H}_2\text{O}$ , the presence of water being visible in the IR spectrum even after prolonged drying of the sample under vacuum at  $80^\circ \text{C}$ .

### (2) Photolysis of $[\text{M}(\eta^5\text{-C}_5\text{H}_5)_2(\text{L})\text{Br}]\text{PF}_6$

A typical experiment is described: a solution ( $10^{-2} \text{ M}$ ) of  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{PPh}_3)\text{Br}]\text{PF}_6$  in acetonitrile was irradiated for one hour in a  $100 \text{ cm}^3$  reactor with a Pyrex jacket containing a sodium nitrite filter (aqueous solution,  $75 \text{ g dm}^{-3}$ ) and fitted with a medium pressure 90 W mercury lamp. The mixture was taken to dryness under vacuum. The residue was extracted with acetone and recrystallized from acetone/ethanol to give a bluish green crystalline solid, which was identified as  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{NCMe})\text{Br}]\text{PF}_6$  by comparison of its IR and NMR spectra with those of an authentic sample.

### (3) Photolysis of $[\text{M}(\eta^5\text{-C}_5\text{H}_5)_2\text{Br}_2]$

A typical experiment is described: a suspension of  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{Br}_2]$

(500 mg) in acetonitrile was irradiated for three hours in a 100 cm<sup>3</sup> reactor with a quartz jacket. The solvent was removed under vacuum, the residue was extracted with water and upon addition of excess NH<sub>4</sub>PF<sub>6</sub> to the aqueous solution, a red solid precipitated. The crude product was washed with water and recrystallized from acetone/ethanol, to give red crystals which were identified as  $\{[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{MeCN})_2](\text{PF}_6)_2\}$  by comparison of the IR and NMR spectra with those of an authentic sample prepared by a different thermal route [12]. The analogous tungsten compound is characterized in Table 1.

*(4) Photolysis of  $\{[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{MeCN})\text{Br}]\text{PF}_6\}$*

A typical run is described: in conditions identical to those described in (1) but using a methanol filter gave  $\{[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{MeCN})_2](\text{PF}_6)\text{Br}\}$ . Treatment of this compound with an excess of TlPF<sub>6</sub> gave a precipitate of TlBr and  $\{[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{MeCN})_2](\text{PF}_6)_2\}$ , which was identified as in (2).

*(5) Photolysis of  $\{[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{Me})_2]\text{PF}_6\}$*

A solution (10<sup>-2</sup> M) of  $\{[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{Me})_2]\text{PF}_6\}$  in acetonitrile was irradiated for one hour in a 100 cm<sup>3</sup> reactor with a pyrex jacket. The solvent was removed under vacuum, the residue was extracted with acetone and an aqueous solution of NH<sub>4</sub>PF<sub>6</sub> was added yielding a brown precipitate. This was washed with water, dried in vacuum and dissolved in acetone; ethanol was added to the solution and careful removal of acetone under vacuum gave first a precipitate identified as  $\{[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{MeCN})_2](\text{PF}_6)_2\}$  as described [3], and upon further removal of the solvent a mixture of  $\{[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{MeCN})_2](\text{PF}_6)_2\}$  and  $\{[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{MeCN})(\text{Me})]\text{PF}_6\}$ . These were separated by repeated recrystallization and identified on the basis of their analyses and their IR and NMR spectra.

*(6) Quantum yield determinations*

The quantum yield measurements were carried out using a 1 cm quartz cell with a degassing bulb attached. The samples were degassed using three cycles (freeze-pump-thaw) up to 10<sup>-4</sup> Torr. The cell was then brought to atmospheric pressure by filling the cell with nitrogen. The sample was irradiated with a 250 W mercury discharge lamp mounted in an optical bench with a lens and a three compartment filter with a chemical filter (NaNO<sub>2</sub>, 75 g dm<sup>-3</sup> and CuSO<sub>4</sub> 5 H<sub>2</sub>O, 0.44 g/100 cm<sup>3</sup> and 2.7 M NH<sub>4</sub>OH) with a pathlength of 10 cm to isolate the 435.8 nm line of the mercury lamp.

The absorption spectra were taken at regular intervals and the quantum yields were determined using the ferrioxalate actinometer [13].

## Results

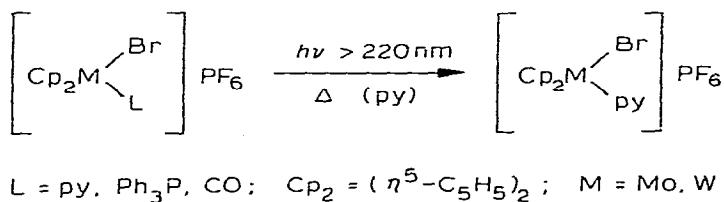
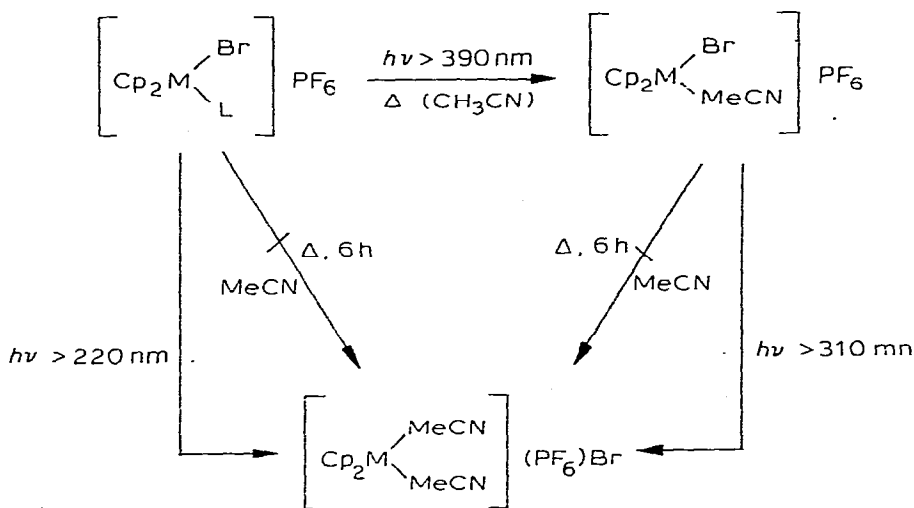
The thermal and photochemical reactions of complexes I are presented in Scheme 1. The monosubstituted product can be obtained either photochemically using wavelengths longer than 390 nm or thermally in refluxing acetonitrile after six hours. However, irradiation at shorter wavelengths ( $\lambda > 220$  nm) yields the disubstituted compound which could not be obtained directly via a thermal reaction in the absence of TlPF<sub>6</sub>. The disubstituted compound is also

TABLE I  
ANALYTICAL AND SPECTROSCOPIC DATA

Compound	Colour	Analysis (calcd. (%))			IR NMR data <sup>a</sup>	Selected IR data (cm <sup>-1</sup> ) <sup>f</sup>
		C	H	N		
{[W(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> (NCCH <sub>3</sub> ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub> }	dark yellow	24.6(24.5)	2.2(2.3)	4.1(4.1)	3.9, 10, <u>2</u> , <u>7</u> , <u>2</u> , <u>6</u> , <u>c</u> , <u>2</u>	3140m <i>h</i> , 2942 w <i>h</i> , 2322 w <i>i</i> , 2298 <i>j</i> , w 840s <i>h</i> , 560s <sup>h</sup>
{[Mo(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> (CH <sub>3</sub> )(NCCH <sub>3</sub> )]PF <sub>6</sub> }	red-brown	36.3(36.55)	3.6(3.8)	3.3(3.3)	4.6, 10, <u>2</u> , <u>7</u> , <u>4</u> , <u>3</u> , <u>c</u> , <u>2</u> , <u>9</u> , <u>9</u> , <u>3</u> , <u>2</u> , <u>d</u>	3140m <i>h</i> , 2980m <i>h</i> , 2808m <i>h</i> , 2820 <i>h</i> , 2320 <i>i</i> , w 2290 <i>i</i> , w 840s <i>h</i> , 560s <i>k</i>
{[Mo(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> (CH <sub>3</sub> )(C <sub>5</sub> H <sub>5</sub> N)]PF <sub>6</sub> }	red	41.4(41.3)	4.0(3.9)	2.8(3.0)	1.26, <u>2</u> , <u>1</u> , <u>e</u> , <u>1.92</u> , <u>1</u> , <u>e</u> , <u>e</u> , <u>2.6</u> , <u>2</u> , <u>e</u> , <u>1</u> , 4.6, 10, <u>2</u> , <u>7</u> , <u>9</u> , <u>8</u> , <u>3</u> , <u>2</u> , <u>d</u>	3138m <i>h</i> , 2960 <i>h</i> , 2910m <i>h</i> , 2842 <i>h</i> , m 1610 <i>j</i> , m 1492 <i>j</i> , m 1455 <i>j</i> , s 1230 <i>j</i> , m 840 <i>s</i> , <i>k</i> , 560 <i>s</i> , <i>k</i>
{[Mo(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub> · ½ H <sub>2</sub> O}	red	35.1(35.15)	4.1(4.1)	—	—	3440br <i>m</i> , 3120m <i>h</i> , 2950m <i>h</i> , 2880m <i>h</i> , 840s <i>h</i> , 560s <i>h</i>

<sup>a</sup> Given as: Chemical shift (τ), relative intensity, multiplicity; in (CD<sub>3</sub>)<sub>2</sub>CO, *b* η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>, *c* NCH<sub>3</sub>, *d* M-CH<sub>3</sub>, *e* C<sub>5</sub>H<sub>5</sub>N, *f* Nujol mulls, *h* ν(C-H) of η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>, *j* ν(C-H) of CH<sub>3</sub>, *i* ν(N≡C), *k* typical frequencies of N-coordinated pyridine, *l* PF<sub>6</sub><sup>-</sup>, *m* Paramagnetic μ = 2.003, *n* ν(O-H).

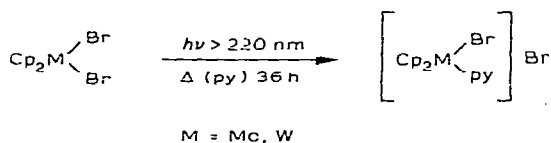
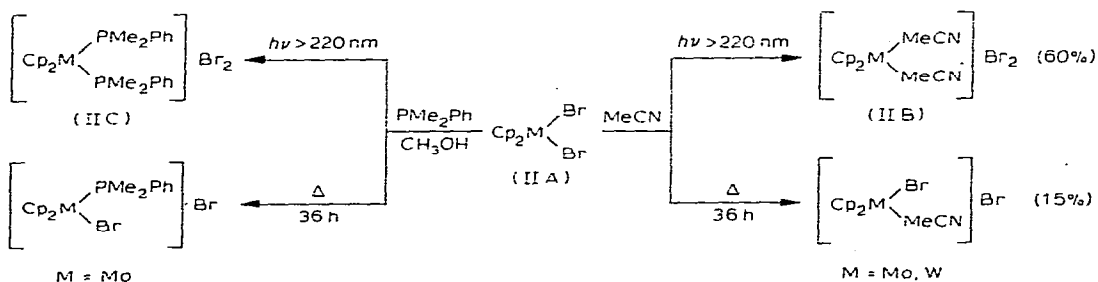
SCHEME 1



formed when the monosubstituted product is irradiated with  $\lambda > 310$  nm. Using pyridine as a solvent we were unable to obtain the disubstituted derivatives. At wavelengths longer than 530 nm only the tungsten derivatives are photosubstituted, the molybdenum complexes remaining unchanged.

Compounds II in acetonitrile or in the presence of dimethylphenylphosphine

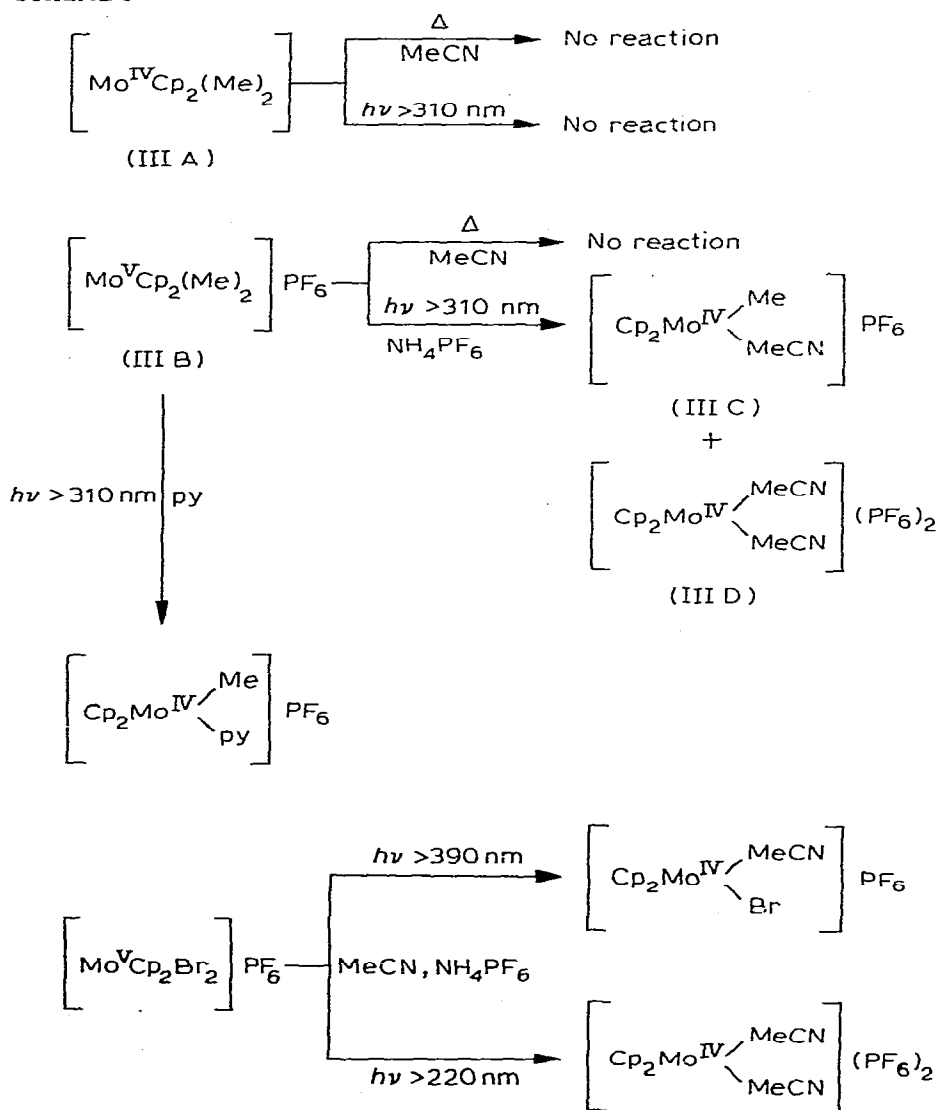
SCHEME 2



in methanol yield disubstitution compounds at short wavelengths ( $\lambda > 220$  nm), but it is impossible in this case to isolate the monosubstituted compound since the starting material is not photolabile at lower energies. However, as in the case of complexes I, photolysis in pyridine yields only the monosubstituted derivative, which was also the only product of the corresponding thermal reaction in the presence of TlPF<sub>6</sub> [10] (Scheme 2).

The complexes III are not reactive towards substitution photochemically or thermally. However the oxidized compound  $\{[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{Me})_2]\text{PF}_6\}$  in acetonitrile yields a mixture of the monosubstituted III C and disubstituted III D compounds when irradiated in a Pyrex reactor; in pyridine only the monosubstituted derivative is formed. The dibromide analogue undergoes a similar photoreaction (Scheme 3).

SCHEME 3



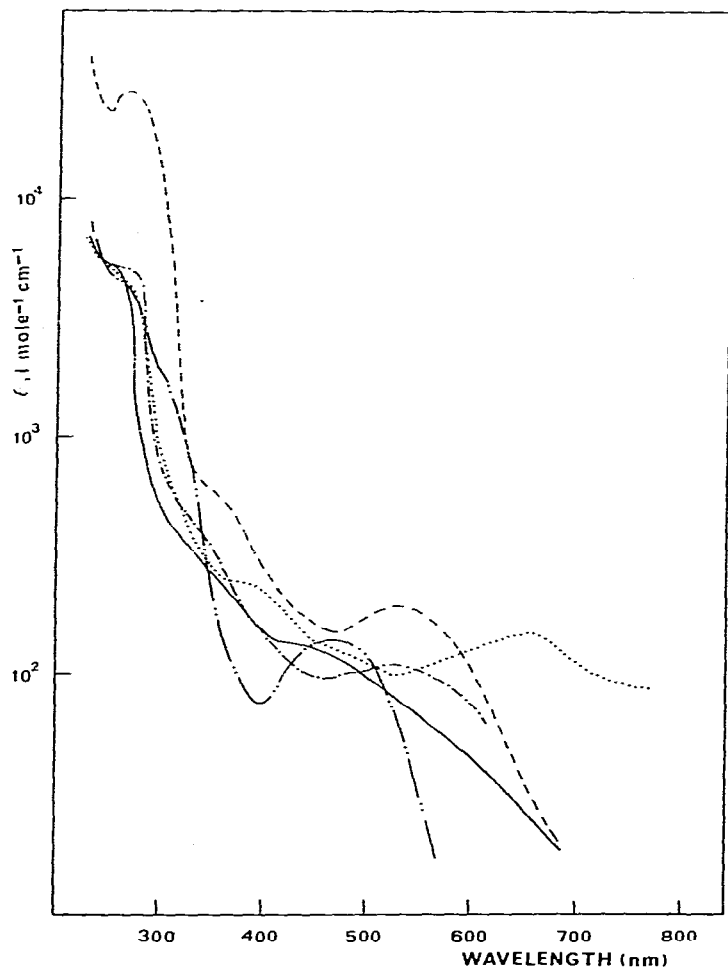


Fig. 1. Absorption spectra of di- $\eta^5$ -cyclopentadienyltungsten complexes:  $\{[W(\eta^5-C_5H_5)_2(PPh_3)Br]PF_6\}$  (-----);  $\{[W(\eta^5-C_5H_5)_2(MeCN)Br]PF_6\}$  (- · - · - ·);  $[W(\eta^5-C_5H_5)_2Br_2]$  (· · · · ·);  $\{[W(\eta^5-C_5H_5)_2(MeCN)_2](PF_6)_2\}$  (————);  $\{[W(\eta^5-C_5H_5)_2(CO)Br]PF_6\}$  (- · - · - ·).

## Discussion

The electronic spectra of the tungsten derivatives are shown in Fig. 1 and those of the molybdenum species in Fig. 2. The electronic spectra of compounds IIIA and IIIB are shown in Fig. 3. It is possible to distinguish essentially three bands, the natures of which have been previously discussed [14]. The long wavelength band  $\lambda_A$  centered around 550–600 nm is attributed to a  $d-d$  transition, since it has a very low extinction coefficient and follows the spectrochemical series for ligand substitution. The second band  $\lambda_B$ , which in most compounds is centered around 350–400 nm, must, again in the light of low extinction coefficient, be essentially  $d-d$  in character even for iodine complexes, for which a second  $d-d$  bond has been recently identified [15]. These two bands overlap to a certain extent in the tungsten complexes, whereas in

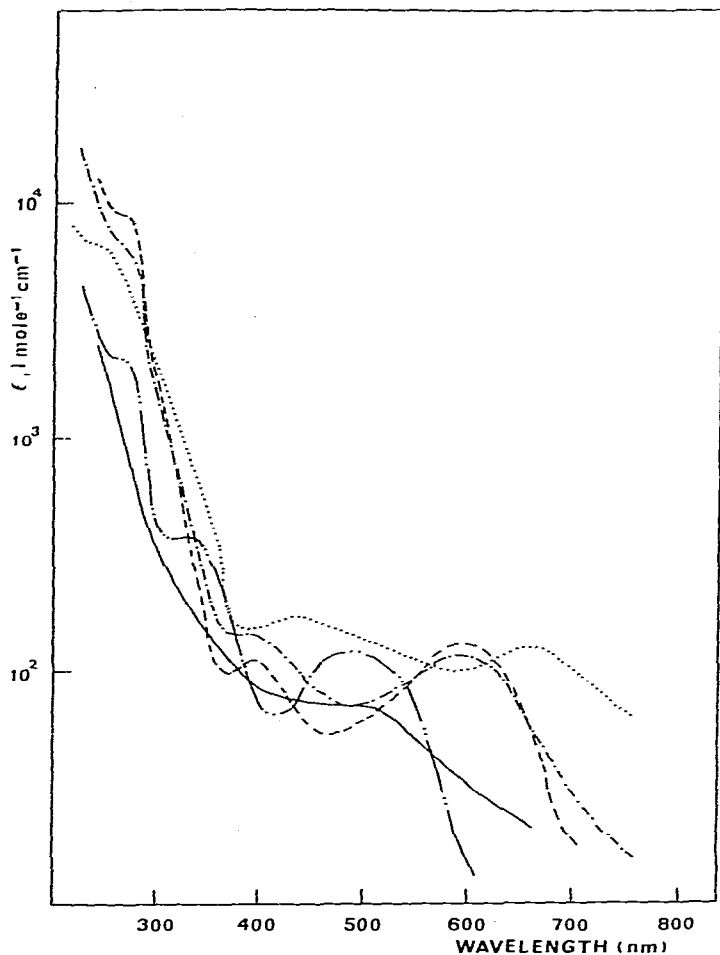


Fig. 2. Absorption spectra of di- $\eta^5$ -cyclopentadienylmolybdenum complexes:  $\{[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{PPh}_3)\text{Br}]\text{-PF}_6\}$  (-----);  $\{[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{MeCN})\text{Br}]\text{PF}_6\}$  (- - - - -);  $\{[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{Br}_2]\}$  (· · · · ·);  $\{[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{MeCN})_2](\text{PF}_6)_2\}$  (—————);  $\{[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})\text{Br}]\text{PF}_6\}$  (- · - · - · - ·).

molybdenum complexes they are distinct. Finally the third band  $\lambda_C$  has marked charge transfer character [14] and probably has contributions from a cyclopentadienyl-metal transition and also a ligand-metal transition.

According to the molecular orbital model of  $\text{Cp}_2\text{MLL}'$  proposed by Hoffman [16] and in agreement with photoelectron studies by Green [17], the remaining orbitals of the bent  $\text{Cp}_2\text{M}$  fragment lie in the plane of the ligands,  $\text{L}, \text{L}'$ . The two  $d-d$  transitions are expected to be from the nonbonding  $1a_1$  orbital to orbitals  $b_2$  and  $2a_1$  [16] which have antibonding character in relation to  $\text{M-L}, \text{L}'$  bonding. Hence, the transitions associated with excitation  $\lambda_B$  must weaken the metal-ligand bond, and the replacement of the neutral ligand by the solvent would be favoured, since it is less strongly bound to the metal than the other halogen ligand.

If the ligand is a  $\pi$ -acceptor, as in the case of CO, we expect a bonding char-



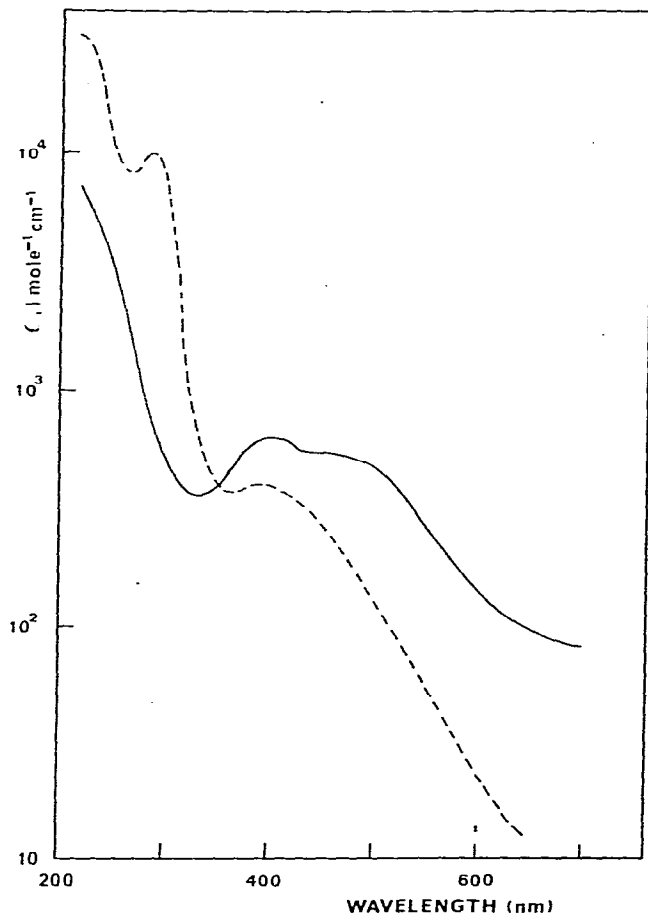


Fig. 3. Absorption spectra of di- $\eta^5$ -cyclopentadienyldimethylmolybdenum complexes:  $[\text{Mo}^{\text{IV}}(\eta^5\text{-C}_5\text{H}_5)_2(\text{Me})_2]$  (-----);  $[\text{Mo}^{\text{V}}(\eta^5\text{-C}_5\text{H}_5)_2(\text{Me})_2]\text{PF}_6$  (—).

acter for the orbital  $2a_1$  [16]. In this case the population of the antibonding orbital will tend to labilize both ligands, but the depopulation of the level  $2a_1$  will reduce the  $\pi$ -bonding character, and therefore cleavage of the metal-carbonyl bond would be feasible [18]. The photolabilization of the metal-halogen bond is explicable if the excitation is associated with the metal-ligand charge transfer transition.

Another possible mechanism may involve a direct excitation of the charge transfer cyclopentadienyl-metal band, which could promote delocalization from the ring to the metal. An increase of the electronic density on the metal favoured by solvation in acetonitrile would enhance an heterocyclic cleavage, the leaving bromide ion remaining as a counterion. The excitation of that band may alternatively induce an  $\eta^5$ - $\eta^3$  ring shift, and an associative mechanism would then follow [19].

Interestingly, complex III is not photoreactive under the experimental conditions used. The photocleavage assisted by the ring would not be expected in complex III since in this compound the sigma bonds would be relatively stable,

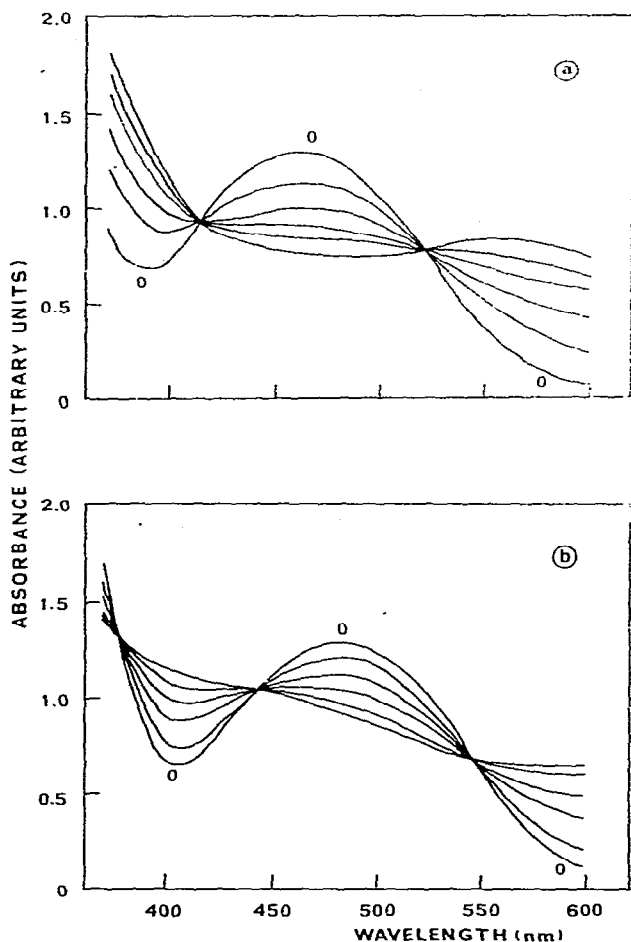
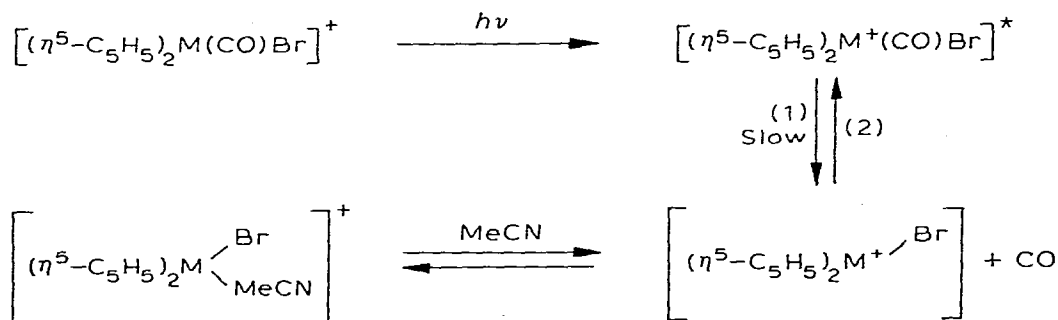


Fig. 4. Absorption changes ( $\lambda_{\text{exc}}$  435 nm) of (a)  $\{[W(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})\text{Br}]\text{PF}_6\}$  ( $4 \times 10^{-3}$  M)/acetonitrile (2 M) in acetone; (b)  $\{[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})\text{Br}]\text{PF}_6\}$  ( $4 \times 10^{-3}$  M)/acetonitrile (2 M) in acetone. 0: Absorption before irradiation.

and the electron donating ability of the methyl groups has already increased the electron density on the central metal atom.

The titanium analogue complexes are known to break the metal–methyl bond homolytically on excitation [20], and given the bond enthalpy contributions for Ti–CH<sub>3</sub> [21] and Mo–CH<sub>3</sub> [22] this apparent lack of photoreactivity towards homolytic cleavage in complex III seems to be due to kinetic rather than thermodynamic factors.

The quantum yield of the monosubstitution was determined for the compounds which seemed most appropriate in terms of the difference between the absorption spectrum of the starting material and that of the photoproduct. The changes in the absorption spectra with excitation at 435 nm ( $\lambda_{\text{B}}$ ) are shown for both molybdenum and tungsten derivatives in Fig. 4. The irradiated samples were always compared with non-irradiated ones to ensure that no thermal reaction was taking place. At several concentrations of acetonitrile the quantum yields obtained were found to be independent of the ligand concentration. It is



thus possible to explain the monosubstitution in terms of a dissociation mechanism followed by a nucleophilic attack by acetonitrile (Scheme 4). The proposed mechanism is consistent with the fact that irradiation of complexes I in presence of excess NaBr leads to complexes II  $\text{M}(\eta^5\text{-C}_5\text{H}_5)_2\text{Br}_2$ .

The quantum yields determined for type I complexes ( $\text{L} = \text{CO}$ ) were  $\phi$   $0.95 \pm 0.05$  and  $\phi$   $0.97 \pm 0.05$  for molybdenum and tungsten complexes, respectively. These values of near unity are in good agreement with the quantum yields reported for  $\text{S}_\text{N}^1$  type photosubstitution reactions in metal carbonyls [23], implying that step (1) in Scheme 4 is the rate controlling process and that the pathways leading to recombination, which have been observed in monosubstituted carbonyls [24], are not important in these systems.

The quantum yield ( $\lambda$  366 nm) for halogen substitution in compound I ( $\text{M} = \text{Mo}$ ,  $\text{L} = \text{MeCN}$ ) dropped to  $0.1 \pm 0.05$ , indicating that a less efficient nucleophilic attack still takes place even when a charge transfer excitation is involved.

The mechanism for the photoreactions shown in Scheme 3, when the metal is in the oxidation state (+5), is likely to be of radical nature. The cleavage leading to methyl (or bromine) radical would lead to reduction of  $\text{Mo}^{\text{V}} \rightarrow \text{Mo}^{\text{IV}}$ . However, the simultaneous formation of disubstituted components is rather intriguing and we are now investigating this reaction further.

A more detailed interpretation of the photochemical reactions of this class of compounds requires further experimental data and more complete MO diagrams for these compounds.

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