Journal of Organometallic Chemistry, 172 (1979) 309—315
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PHOTOLYSIS OF η-CYCLOPENTADIENYLMETHYLTRICARBONYL DERIVATIVES OF CHROMIUM, MOLYBDENUM AND TUNGSTEN: FORMATION OF PARAMAGNETIC ALKYL—METAL SPECIES BY PHOTOCHEMICALLY-INDUCED ELECTRON AND METHYL TRANSFER

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(Received January 16th, 1979)

Summary

Photo-induced methyl—metal bond cleavage in $CpM(CO)_3CH_3$ compounds (M = Cr, Mo, W) has been studied by ESR techniques. The Cr and Mo compounds exhibit signals due to paramagnetic species in which the methyl—metal bond is preserved; no such signals were observed for the W analog. Photolyses of these compounds in the presence of spin trapping reagents have led to the formation of methyl spin adducts which were unambiguously identified in the case of the Mo analog. The formation of these paramagnetic species is believed to proceed by both electron and methyl transfer. A mechanism is proposed for these processes.

Introduction

Photolysis of various organometallic compounds of the type $RMn(CO)_5$ (R = CH_3, $CH_2C_6H_5$) has recently been shown to proceed by homolytic cleavage of the metal—carbon σ-bond and concomitant formation of alkyl and metal-centered radicals, both of which could be spin-trapped in solution [1]. We now present evidence from ESR studies on compounds of the type $CpM(CO)_3CH_3$ (M = Cr or Mo) which indicate that, while M—CH_3 cleavage is most likely a predominant mechanism, electron and methyl transfer reactions occur during the photo-degradation process. These reactions are responsible for the formation of photo-generated, metal-centered radical species in which the metal—alkyl bond is retained.

Results

Recent studies on the photolysis of $CpM(CO)_3CH_3$ compounds (I, M = Cr; II, M = Mo; III, M = W) in hydrocarbon solvents have been carried out, and it was shown that the corresponding methyl-free dimers $[CpM(CO)_3]_2$ were the major isolable organometallic species to be formed after prolonged periods of photolysis [2,3]. Interestingly, methane was the major gaseous product to be detected, together with small amounts of carbon monoxide. In an effort to investigate the mechanistic pathways by which these photochemical processes occur, we have undertaken a study of the photolysis of compounds I, II and III in an ESR cavity in toluene solution. Reported here are the results of our investigation.

Photolysis of I. Irradiation in the ESR cavity of a 10^{-4} *M* solution of I in toluene gives rise after a short exposure time (ca. 2 min) to a signal which is best resolved at —30°C (Fig. 1). This signal is attributed to the formation of a metal-centered paramagnetic species. It is composed of an intense central line at $g = 2.011$ flanked by satellite lines due to ^{53}Cr isotopes ($I = 3/2$, natural abundance 9.5%). Furthermore, the central line is split into a quartet, obviously due to interaction of the unpaired electron with protons of the methyl

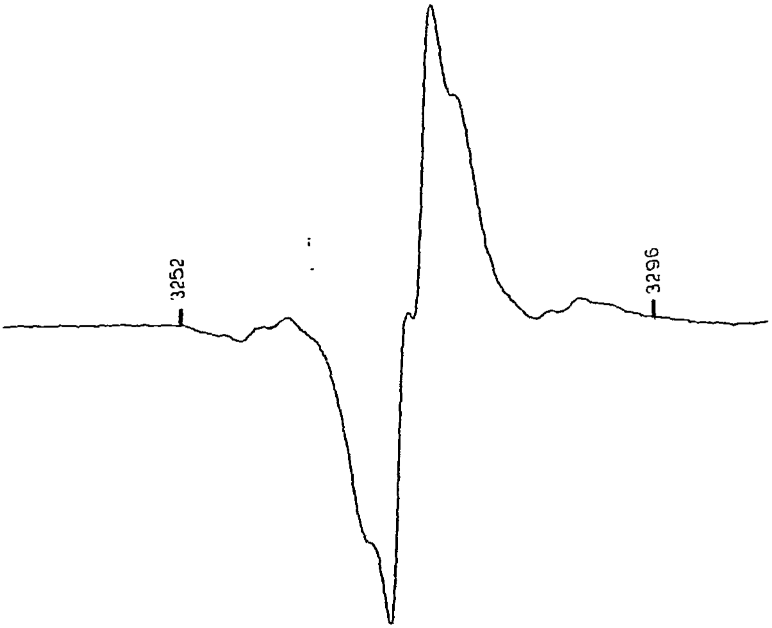

Fig. 1. ESR spectrum of the photolysis product of $CpCr(CO)_3CH_3$ in toluene at —30°C. Field in gauss. Gain 2 × 10^5. Frequency modulation intensity 1 G.

group which is σ-bonded to the metal. Superhyperfine interaction is also observed on each of the outer satellite lines.

Photolysis of II. In an analogous manner, irradiation of II as above generates a signal clearly resolved at room temperature, the pattern of which is also attributable to a paramagnetic metal-centered radical in which the methyl group is still σ-bonded to the metal (Fig. 2). The central line is likewise clearly resolved into a quartet superhyperfine splitting, due to interaction of the unpaired electron with the protons of the methyl group. Moreover, the presence of six satellite lines can be clearly detected, two lines on each side of the central line, and two lines overlapping with it. These lines are assignable to hyperfine interaction of the unpaired electron with ^{95}Mo and ^{97}Mo isotopes (^{95}Mo, $I = 5/2$; ^{97}Mo, $I = 5/2$) present in 15.78 and 9.60% natural abundance, respectively. The hyperfine lines for the two isotopes are superimposed due to the near equivalence of the respective μ_N/I values ($\mu_N = -0.9099$ and -0.9290 nuclear magnetons for ^{95}Mo and ^{97}Mo, respectively).

In order to insure that the superhyperfine splitting in the photolysis products derived from I and II was due to interaction of the unpaired electron with protons of the methyl group on the metal, and not due to other organic radicals which might be generated in the medium, photolysis was performed on the

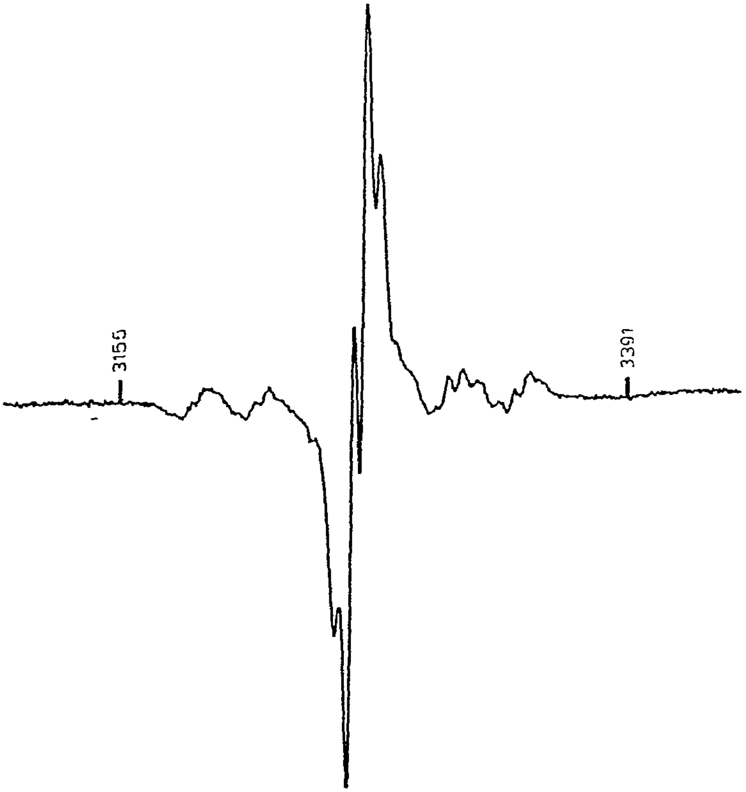

Fig. 2. ESR spectrum of the photolysis product of CpMo(CO)$_3$CH$_3$ intoluene at 20°C. Field in gauss. Gain 5 X 10^5. Frequency modulation intensity 0.5 G.

TABLE 1

ESR PARAMETERS OF THE SPECTRA OBTAINED BY PHOTOLYSIS OF $CpM(CO)_3CH_3$ (M = Cr, Mo) IN TOLUENE. ^aH IS RELATED TO THE METHYL PROTONS

Compound	g	A_M	a_H
$CpCr(CO)_3CH_3$	2.011	9.04	2.7
$CpMo(CO)_3CH_3$	2.016	29.4	6.4

deuterated compound $CpMo(CO)_3CD_3$. The ESR spectrum was very similar to that obtained for the protonated analog II, but with unresolved superhyperfine splitting due to the expected reduction of the superhyperfine interaction $a_H/a_D = 6$. The ESR parameters relative to these experiments are summarised in Table 1. It is noteworthy that the paramagnetic species described above have a relatively long lifetime (ca 1 h), and can also be detected by photolysis outside the ESR cavity.

Photolysis of other η^5-cyclopentadienylmethylmetal carbonyls. Under the same experimental conditions as described above for I and II, irradiation of toluene solutions of either III or $CpFe(CO)_2CH_3$ (IV) did not give any detectable signal even after prolonged photolysis.

Discussion

Earlier studies have been concerned with the relative stabilities of M—CH_3 versus M—CO bonds in this class of compounds under photolytic conditions [3,4]. Our observations of paramagnetic organometallic species which contain intact metal—alkyl bonds upon the photolysis of I and II is a novel and somewhat unexpected result.

In order to gain further insight into the mechanism of these processes, experiments have been carried out to spin-trap the photochemically generated methyl radicals which are expected to be formed if cleavage of the M—CH_3 bond is homolytic. Conclusive results have been obtained in the case of the photolysis of II, where methyl radical could be spin-trapped with PBN * and identified from the ESR spectrum of the spin adduct (a_N 15.1 G; a_H 3.56 G). The signal of the spin adduct appeared immediately upon irradiation and disappeared after termination of the photolysis.

For the chromium analog (I), attempts to spin-trap methyl radicals using PBN or other spin-trap reagents such as DMPO or nitrosodurene gave complex signals which could not be assigned to any identifiable spin adduct species. These results may be attributed to secondary reactions of the spin-trap reagent with the substrate.

In the case of the tungsten analog (III), only very weak signals due to the PBN-methyl adduct could be observed within a few minutes of photolysis. As for the iron compound (IV), no ESR signals could be detected upon photolysis either in the presence or absence of spin-trap reagents. It should be mentioned, however, that spin adducts attributed to the $CpFe(CO)_2$ radical formed upon

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* PBN = phenyl-N-t-butylnitrone.

photolysis of the iron carbonyl dimer $[CpFe(CO)_2]_2$ with UV light in the presence of spin traps have been reported [5].

Photolysis of either I or II in the presence of excess triphenylphosphine did not produce any detectable ESR signal, and gas evolution was clearly visible in the ESR tube. It is known that under these conditions, substitution of CO by phosphine ligands occurs to give primarily complexes of the type $CpM(CO)_2(PR_3)CH_3$ and not the respective dimers [2,6,7].

From the experimental observations, it can be assumed that the species responsible for the ESR signal ((C) in eq. 5 below) is produced by reaction pathways involving photo-induced formation of a metal carbonyl radical (A), followed by electron transfer from this radical to the alkylmetal carbonyl intermediate (B). We postulate the following series of reactions to account for the observed results (M = Cr or Mo):

$$CpM(CO)_3CH_3 \rightleftharpoons CpM(CO)_2CH_3 + CO \qquad (1)$$

$$CpM(CO)_2CH_3 \rightleftharpoons CpM(CO)_2^{\cdot} + CH_3^{\cdot} \qquad (2)$$

$$CpM(CO)_2^{\cdot} \underset{-CO}{\overset{CO}{\rightleftharpoons}} CpM(CO)_3^{\cdot} \rightleftharpoons [CpM(CO)_3]_2 \qquad (3)$$

$$CpM(CO)_3^{\cdot} + CH_3^{\cdot} \rightarrow CpM(CO)_3CH_3 \qquad (4)$$

$$\underset{(A)}{CpM(CO)_3^{\cdot}} + \underset{(B)}{CpM(CO)_2CH_3} \rightleftharpoons \underset{(C)}{CpM(CO)_2CH_3^{-\cdot}} + CpM(CO)_3^{+} \qquad (5)$$

Equations 1 and 2 have previously been proposed [4] to account for the photochemical cleavage of M—CH_3 in the tungsten compound (III). The metal carbonyl radical (A) can exist in photo-equilibrium with the dimer [8,9] (eq. 3) or else undergo electron transfer to the coordinatively unsaturated species (B) which acts as an electrophile (eq. 5). Such a process would generate the 17-electron species (C) which we believe is responsible for the observed ESR signals.

The reaction depicted in eq. 4 is of particular importance, as it implies that I or II can be formed in situ from recombination of the methyl and metal-based radicals. Equation 4 would also suggest that a methyl group could be transferred from one metal to another by a photo-induced radical process. The overall reaction mechanism may be viewed as involving both electron and methyl radical transfer.

In order to provide evidence for the concomitant occurrence of these two processes, we sought to demonstrate that (C) can be generated by a radical recombination reaction involving starting materials other than I or II. For this purpose, we photolyzed IV in the presence of the molybdenum dimer $[CpMo(CO)_3]_2$ (equimolar proportions in toluene) under the same photolysis conditions as above. After several minutes of irradiation, an ESR signal identical with the one shown in Fig. 2 developed. The iron compound IV was chosen for this experiment since, when photolyzed by itself, it does not give rise to any paramagnetic species which might interfere with the detection of the paramagnetic molybdenum complex (C) (vide supra). We believe that this experiment not only provides confirmation for the mechanism postulated above, but also reveals a new reaction by which methyl transfer from one transition metal to another can take place photochemically. Thermal reactions leading to such methyl transfer have already been described in the literature [10—12], although they remain rather scarce.

Attempts to induce electron transfer by chemical means have thus far been unsuccessful. For example, attempted reactions of I or II with either sodium amalgam or potassium metal in toluene or THF failed to give any detectable ESR signal. It should be noted, however, that ESR signals ($g = 2.0043$) attributed to $[Fe_3(CO)_{12}]^{-\bullet}$ were observed upon electrochemical reduction of $Fe_3(CO)_{12}$ [13], so the latter type of reduction of I or II to form paramagnetic species such as (C) remains a possibility.

The g value for both paramagnetic species derived from the photolysis of I and II are close to the free electron values (see Table 1), indicating predominant spin delocalization on the methyl group. This is further confirmed by the low isotropic interaction constants A_{iso} for I and II compared to the theoretically expected and observed values close to 20 G and 50 to 70 G, respectively [14—16]. It is interesting to note that a much lower A_{iso} (4 G) was reported for molybdenum in the $CpMo(CO)_3$ spin adduct with nitrosodurene [1]. The a_H values are of the same order as those known for paramagnetic alkyl-transition metal compounds (a_H 4.74 G in $Cp_2V(CH_3)_2$ [17] and 6.3 G in $Cp_2Nb(CH_3)_2$ [18]), and show the same increase in magnitude when proceeding from the first to the second row of the periodic table. To our knowledge, these are the first reported examples of paramagnetic mixed alkyl-carbonyl derivatives of the transition metals showing superhyperfine interaction with the σ-bonded substituent [19].

Finally, it is difficult at this stage of our investigations to speculate whether or not the formation of paramagnetic species such as (C) constitutes a major pathway in the photochemically induced cleavage of methyl—metal bonds. A rough measurement of spin concentration on II at the steady state under photolytic conditions gave a value of 10^{-3} *M*. Nevertheless, the role of intermediate organometallic radicals in electrophilic cleavage reactions and in electron transfer is now well-established [20].

Experimental

The $CpM(CO)_3CH_3$ compounds were prepared by literature methods [2,21]. Solutions of these compounds (2.3×10^{-2} *M*) in dry toluene were added under argon to a 4 mm cylindrical quartz ESR tube in the dark, and then flushed for 20 min with a slow stream of argon. The tubes were introduced into an ER 400 X-RL cavity of a Bruker ER-420 spectrometer equipped with B-ST 100/700, B-MN-12 and B-A6 accessories of the same origin for variable temperature, magnetic field calibration and frequency measurements, respectively. Irradiation was conducted with a Hanovia 977-B-0090, 1000 W Hg-Xe arc lamp in a Model LH 15-1H Schoeffel lamp housing. The light was focused by means of quartz lenses and filtered through a 15 cm flowing water filter and a Corning 3-73 or Pyrex filter. Spin concentration was determined by measuring the integrated signal area relative to known concentrations of α,α'-diphenyl-β-picrylhydrazyl (DPPH). The spin traps used, phenyl-*N*-t-butylnitrone (PBN), 5,5,-dimethyl-1-pyrroline-1-oxide (DMPO) and nitrosodurene, were synthesized by

TABLE 2

UV-VISIBLE ABSORPTION BANDS OF $CpM(CO)_3CH_3$ COMPOUNDS (M = Cr, Mo, W) IN TOLUENE

Compound	λ (nm)	ε
$CpCr(CO)_3CH_3$	238	600
	356	90
	395	br, sh
$CpMo(CO)_3CH_3$	242	20,000
	320	200
	370	75
$CpW(CO)_3CH_3$	210	5.6×10^3
	260	2.4×10^3
	315	4.3×10^2
	360	sh

literature methods and were introduced in 5×10^{-2} *M* concentrations. The UV-visible absorption data for the comppunds studied are summarized in Table 2.

Acknowledgements

E.S. and M.D.R. are grateful for partial support of this research program by a NATO research grant; E.S. and C.G. are also grateful to the Délégation Générale pour la Recherche Scientifique et Technique and M.D.R. to the National Research Foundation for partial support. The authors also wish to express their appreciation to Dr. H.G. Alt for assistance, to Mr. P. Maillard for supply of spin traps and to Prof. A. Wojcicki for making available results of his studies prior to their publication.

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