

PHOTOCHEMISTRY OF METHYL- AND η^1 -BENZYL- η^5 -CYCLOPENTADIENYLTRICARBONYLTUNGSTEN(II) *

ROLAND G. SEVERSON and ANDREW WOJCICKI *

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210 (U.S.A.)

(Received February 21st, 1978)

Summary

Irradiation of solutions of η^5 -C₅H₅W(CO)₃R (R = CH₃, η^1 -CH₂C₆H₅) in cyclohexane at ca. 310–490 nm leads to the formation of [η^5 -C₅H₅W(CO)₃]₂ and methane and of η^5 -C₅H₅W(CO)₂(η^3 -CH₂C₆H₅) and some [η^5 -C₅H₅W(CO)₃]₂, respectively. When the irradiation is carried out in the presence of excess P(C₆H₅)₃, the photoproducts are η^5 -C₅H₅W(CO)₂[P(C₆H₅)₃]CH₃ (R = CH₃) and η^5 -C₅H₅W(CO)₂(η^3 -CH₂C₆H₅) and trace [η^5 -C₅H₅W(CO)₃]₂ (R = η^1 -CH₂C₆H₅). Photolysis of the η^5 -C₅H₅W(CO)₃R in the presence of benzyl chloride affords η^5 -C₅H₅W(CO)₃Cl (R = CH₃) and both η^5 -C₅H₅W(CO)₂(η^3 -CH₂C₆H₅) and η^5 -C₅H₅W(CO)₃Cl (R = η^1 -CH₂C₆H₅), the relative amounts of the latter products depending on the quantity of added C₆H₅CH₂Cl. Irradiation of η^5 -C₅H₅W(CO)₃-CH₃ in the presence of both P(C₆H₅)₃ and C₆H₅CH₂Cl affords η^5 -C₅H₅W(CO)₂-[P(C₆H₅)₃]CH₃, but no η^5 -C₅H₅W(CO)₃Cl. It is proposed that the primary photo-reaction in these transformations is dissociation of a CO group from η^5 -C₅H₅W(CO)₃R to generate η^5 -C₅H₅W(CO)₂R, which can either combine with L to form a stable 18-electron complex, η^5 -C₅H₅W(CO)₂(L)R (L = CO, P(C₅H₅)₃; LR = η^3 -CH₂C₆H₅), or lose the group R in a competing, apparently slower step. This proposal receives support from the observation that, light intensities being equal, η^5 -C₅H₅W(CO)₃CH₃ undergoes a considerably faster photoconversion to [η^5 -C₅H₅W(CO)₃]₂ under argon than under carbon monoxide.

Introduction

The behavior of transition metal–carbon σ bonds in the alkyl, aryl, and related complexes has not been systematically examined under photolytic conditions. Scattered literature data appear to indicate that for the complexes containing carbonyl ligands the observed reactions are initiated either by disso-

* Experimental work performed during the tenure of A.W. and R.G.S. at the Institut für Strahlenchemie im Max-Planck-Institut für Kohlenforschung, Mülheim a.d. Ruhr, W. Germany.

ciation of carbon monoxide or by cleavage of the metal—carbon σ bond.

The first type of behavior is illustrated by the formation of substituted $\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_{x-1}(\text{L})\text{R}$ upon irradiation of $\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_x\text{R}$ ($\text{M} = \text{Fe}$, $x = 2$ or $\text{M} = \text{Mo}$, W , $x = 3$; $\text{R} = \text{alkyl}$ or aryl) in the presence of L ($\text{L} = \text{tertiary phosphine}$ or phosphite) [1–4]. When the ligand R is a potential three-electron donor, photolysis of $\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_x\text{R}$ affords $\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_{x-1}(\eta^3\text{-R})$. Examples include conversion of $\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_x(\eta^1\text{-CH}_2\text{CH}=\text{CH}_2)$ ($\text{M} = \text{Fe}$, $x = 2$ or $\text{M} = \text{Mo}$, W , $x = 3$) and $\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_3(\eta^1\text{-CH}_2\text{C}_6\text{H}_5\text{-R}_x)$ ($\text{M} = \text{Mo}$, W ; $\text{R} = \text{alkyl}$) to $\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_{x-1}(\eta^3\text{-CH}_2\text{:CH:CH}_2)$ [5–7] and $\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}_6\text{H}_5\text{-R}_x)$ [8,9], respectively.

The second type of photochemical behavior is indicated by the formation of $[\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_x]_2$ from $\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_x(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ ($\text{M} = \text{Fe}$, $x = 2$ or $\text{M} = \text{Mo}$, $x = 3$) ($\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_{x-1}(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)$ is also formed when $\text{M} = \text{Mo}$, *vide supra*) [8,10] and of $[\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_3]_2$ ($\text{M} = \text{Cr}$, Mo , W) and $[\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_2]_2$ ($\text{M} = \text{Cr}$, Mo) from $\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{CH}_3$ [11,12]. Moreover, irradiation of $\text{Mn}(\text{CO})_5\text{R}$ ($\text{R} = \text{CH}_3$, $\eta^1\text{-CH}_2\text{C}_6\text{H}_5$) has afforded the radical fragments R^\cdot and $\text{Mn}(\text{CO})_5^\cdot$, both of which were spin-trapped with nitrosodurene [13]. Photoassisted insertion of tetrafluoroethylene into the $\text{Mn}\text{—C}_6\text{H}_5$ bond of $\text{Mn}(\text{CO})_5\text{C}_6\text{H}_5$ [14] may also proceed by such metal—carbon bond homolysis. Elimination of the group R occurs upon irradiation of a number of transition metal-alkyl non-carbonyl complexes, including $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}(\text{CH}_3)_2$ ($\text{M} = \text{Ti}$, Zr , Hf) [15,16], $(\text{C}_{13}\text{H}_9)_2\text{Zr}(\text{CH}_3)_2$ [17], $\text{Co}(\text{CN})_5\text{CH}_2\text{C}_6\text{H}_5^{3-}$ [18], alkylcobaloximes [19], and related alkylcobalt compounds [20].

In an attempt to learn more about these two apparent types of primary photoprocess of transition metal-alkyl carbonyl complexes, we have examined the photochemistry of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{R}$ ($\text{R} = \text{CH}_3$, $\eta^1\text{-CH}_2\text{C}_6\text{H}_5$). Both of these compounds exhibit a high degree of stability at ambient temperatures in the absence of light, a property which we thought would render them well suited for the proposed study.

Reported here are the results of our investigation.

Results

Spectra of complexes

The UV-visible absorption spectra of the tungsten carbonyl starting materials and products are presented in Table 1. Good agreement exists between these data and those available in the literature for $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ [21] and $[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$ [22,23]. The spectra of the two reactant complexes $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ and $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ exhibit well-defined maxima at 312 (ϵ 2430 l mol⁻¹ cm⁻¹) and 303 nm (ϵ 10 800 l mol⁻¹ cm⁻¹), respectively, on the absorption curves that rise with decreasing wavelength below ca. 280 nm.

The IR $\nu(\text{CO})$ absorptions of the tungsten complexes are also listed in Table 1. The reported values agree well with those given in the literature [2,21,22,24]. These spectra were used for the analysis of the photoreactions of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ and $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$.

Photochemistry of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$

Solutions of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ (6×10^{-3} M) in cyclohexane under argon

TABLE 1

UV-VISIBLE AND IR $\nu(\text{CO})$ ABSORPTION DATA FOR TUNGSTEN CARBONYL COMPLEXES IN CYCLOHEXANE AT ROOM TEMPERATURE

Complex	UV-visible band maxima ^a (nm(ϵ) ^b)	IR $\nu(\text{CO})$ bands ^a (cm ⁻¹ (ϵ) ^b)
$\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$	350(sh), 312(2430), 256(sh)	2023(4300), 2012w, 1933(12 000), 1900w
$\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$	385(sh), 303(10 800), 268(sh)	2019s, 2008w, 1935s, 1927s, 1900w, 1893w
$[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$	490(2450), 361(20 160), 275(sh)	1963vs, 1914s, 1905w
$\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\text{CH}_3$	382(1600), 319(4400), 270(sh ^c)	1944s, 1866s
$\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)$	444(573), 358(3840), 280(12 300)	1954s, 1932w, 1881s, 1870w
$\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{Cl}$	460(510), 315(2200) [22] ^d	2053s, 1972s, 1953s

^a Abbreviations: vs, very strong; s, strong; w, weak; (sh), shoulder. ^b l mol⁻¹ cm⁻¹. ^c With sharp features.^d In CCl₄.

undergo no detectable chemical change in the dark for at least 30 h. By contrast, photolysis of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ (3×10^{-4} to 4×10^{-3} M) in cyclohexane under argon proceeds cleanly with the formation of $[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$. This photo-reaction slows down considerably as the concentration of the tungsten dimer builds up with time and conversions of only up to ca. 50% have been realized. The organometallic product was identified by its IR $\nu(\text{CO})$ absorptions and was subsequently isolated and compared with an authentic sample of the tungsten dimer. No other tungsten carbonyl species were detected by IR spectroscopy in short reaction times; prolonged irradiation (generally ≥ 2 h) leads to the appearance of other, weak IR $\nu(\text{CO})$ bands (2029, 1939, 1869 cm⁻¹) and to the formation of insoluble non-carbonyl decomposition products. Gas-liquid chromatography in conjunction with mass spectrometry showed that the only organic product present in the gases above the irradiated solution is methane. These results are in good agreement with those reported very recently [12] for photolysis of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ in several organic solvents.

The nature of the organometallic photoproduct appears to be independent of the wavelength of incident light when $\lambda \gtrsim 310$ nm. Thus $[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$ is the only observed tungsten carbonyl complex when $\lambda \sim 310$ (Osram HBO 200W lamp) and ≥ 330 , 417, and 490 nm (Osram XBO 1600W lamp). However, the formation of $[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$ slows down with increasing wavelength, becoming virtually arrested at $\lambda \geq 490$ nm.

The irradiation of cyclohexane solutions of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ (1.9×10^{-3} M) was also performed simultaneously under an atmosphere of each of argon and carbon monoxide. These experiments were conducted in pyrex tubes (8 total 4 under Ar and 4 under CO) using a merry-go-round Rayonet Model RPR-100 photochemical reactor equipped with eleven 300 nm lamps. The reactions were followed by measuring the absorbance of the 2023 cm⁻¹ band of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ and of the 1963 cm⁻¹ band of $[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$ as a function of time. The results are presented in Table 2. It is readily seen that the disappearance of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ and the appearance of $[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$ occur more rapidly under argon than under carbon monoxide.

Quantum yield measurements were carried out for the photoreaction of

TABLE 2
PHOTOREACTION AT ca. 300 nm OF $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3\text{CH}_3$ IN CYCLOHEXANE

Time (min)	Absorbance of			
	$\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3\text{CH}_3$ at 2023 cm^{-1}		$[\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3]_2$ at 1963 cm^{-1}	
	Under Ar	Under CO	Under Ar	Under CO
0	0.121	0.121	0	0
10	0.097	0.113	0.015	0.007
21	0.065	0.100	0.047	0.021
39	0.015	0.080	0.081	0.049
55	0.010	0.081	0.090	0.052

$\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3\text{CH}_3$ in cyclohexane under argon at ca. 310 nm. As shown in Fig. 1, the methyl complex exhibits an absorption band maximum at 312 nm whereas the photoproduct $[\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3]_2$ shows a minimum at approximately the same wavelength. However, at 312 nm the value of ϵ for $[\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3]_2$ is more than twice that for $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3\text{CH}_3$ (vide infra). For that reason the photoconversion was kept lower than 10% and a correction was applied for the absorption of light by $[\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3]_2$. The amounts of $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3\text{CH}_3$ consumed and $[\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3]_2$ produced were determined by UV-visible spectroscopy at 312 (ϵ 2.43×10^3 and $5.61 \times 10^3\text{ l mol}^{-1}\text{ cm}^{-1}$, respectively) and 490 nm (ϵ 0 and $2.45 \times 10^3\text{ l mol}^{-1}\text{ cm}^{-1}$, respectively). An average quantum yield, Φ , of 0.067 ± 0.001 was obtained for the appearance of $[\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3]_2$.

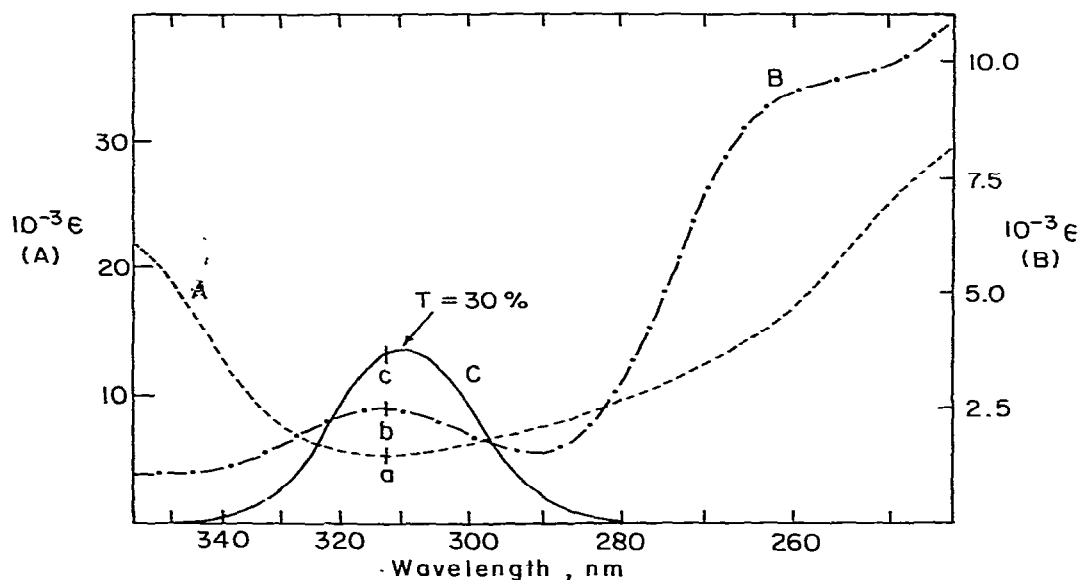


Fig. 1. Electronic absorption spectra of $[\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3]_2$ (A) and $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3\text{CH}_3$ (B) in cyclohexane and the percent transmittance curve of the 310 nm bandpass filter (C). Note the different ϵ scales for the spectra A and B. The points a, b, and c correspond to the respective ϵ or % T values of A, B, and C at 312 nm.

Photolysis of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ in CCl_4 under argon at $\lambda \geq 330$ and 417 nm rapidly leads to the formation of a brown/blue non-carbonyl precipitate as the solution changes color from yellow to deep blue. Weak IR $\nu(\text{CO})$ bands at 2053, 1972, and 1953 cm^{-1} indicate that small amounts of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{Cl}$ are also produced. A similar, but very slow, reaction appears to occur at $\lambda \geq 490$ nm. No attempt was made fully to characterize the insoluble photoproducts. These results may be contrasted with the reported [12] formation of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{Cl}$ in high yield upon photolysis of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ in CHCl_3 .

Solutions of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ in CCl_4 under argon remain unchanged for at least 40 h in the absence of light.

Photochemistry of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ in the presence of $\text{P}(\text{C}_6\text{H}_5)_3$

As a cyclohexane solution of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ ($6.6 \times 10^{-3} M$) and $\text{P}(\text{C}_6\text{H}_5)_3$ ($3.6 \times 10^{-2} M$) is photolyzed at ca. 310 nm, new IR $\nu(\text{CO})$ bands grow in at 1944 and 1866 cm^{-1} . These absorptions are assigned to $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\text{CH}_3$ by comparison of the isolated product with an authentic sample of the dicarbonyl. At longer reaction times, a non-carbonyl material separates from the solution and a new $\nu(\text{CO})$ band appears at 1782 cm^{-1} . The observed peak may be due to $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{CH}_3$, as the related $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})[\text{P}(\text{OCH}_3)_3]_2\text{CH}_3$ is reported [11] to absorb at 1833 cm^{-1} . These species were not characterized further.

Similar results were obtained when the irradiation was carried out at $\lambda \geq 417$ nm, except that $[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$ is also produced in a detectable concentration. Thus the photolysis of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ ($4.6 \times 10^{-3} M$) and $\text{P}(\text{C}_6\text{H}_5)_3$ ($5.7 \times 10^{-3} M$) in cyclohexane yields primarily $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\text{CH}_3$ ($\geq 90\%$) and some $[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$ ($\leq 10\%$). The conversion is virtually complete in less than 1 h.

Photochemistry of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ in the presence of $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$

Photolysis at $\lambda \sim 310$ or ≥ 417 nm of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ (6×10^{-3} to $2 \times 10^{-2} M$) and excess $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ (5×10^{-2} to $0.6 M$) in cyclohexane leads to the appearance of new IR $\nu(\text{CO})$ bands at 2053, 1972, and 1953 cm^{-1} . These absorptions correspond to those of an authentic sample of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{Cl}$. There is also formation of some insoluble non-carbonyl decomposition material. Toluene, but not ethylbenzene, was detected upon chromatography of the reaction mixture.

Under the conditions of same light intensity, the photoconversion of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ to $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{Cl}$ proceeds considerably slower than the photo-substitution to yield $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\text{CH}_3$. When $[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3]$ $2 \times 10^{-2} M$ and $[\text{C}_6\text{H}_5\text{CH}_2\text{Cl}]$ $0.28 M$, only about 10% of the methyltungsten complex is consumed in 1 h at ca. 310 nm.

Photochemistry of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ in the presence of both $\text{P}(\text{C}_6\text{H}_5)_3$ and $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$

A cyclohexane solution of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ ($6.6 \times 10^{-3} M$), $\text{P}(\text{C}_6\text{H}_5)_3$ ($3.6 \times 10^{-2} M$), and $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ ($0.56 M$) was irradiated at ca. 310 nm. The only product detected by IR spectroscopy was $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\text{CH}_3$; no $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{Cl}$ was observed. Prolonged irradiation leads to the appearance

of an IR band at 1795 cm^{-1} , which may possibly be due to $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{-}[\text{P}(\text{C}_6\text{H}_5)_3]\text{Cl}$, reported [25] to show the $\nu_{\text{as}}(\text{CO})$ absorption at 1780 cm^{-1} .

Photochemistry of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$

The electronic spectra of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ and the photoproducts $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)$ and $[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$ in cyclohexane in the 350–250 nm region are shown in Fig. 2. At 310 nm, the respective values of ϵ are 1.05×10^4 , 4×10^3 , and $5.61 \times 10^3\text{ l mol}^{-1}\text{ cm}^{-1}$.

Irradiation of a cyclohexane solution of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ ($4 \times 10^{-3}\text{ M}$) using the 310 nm bandpass filter (Fig. 2) results in the formation of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)$ as the major photoproduct and of $[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$ as the minor one. After ca. 1 h the starting complex is almost completely consumed and the ratio $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)/[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$ is approximately 4/1. Continued photolysis leads to the appearance of an insoluble decomposition material and the formation of a carbonyl species showing weak IR $\nu(\text{CO})$ bands at 2029 and 1939 cm^{-1} . This complex may possibly be $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{H}$, as the observed absorptions match those of an authentic sample of the hydride.

When $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ in cyclohexane is irradiated at $\lambda \geq 417$ nm, the product ratio $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)/[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$ becomes greater than 10/1. The photolysis at $\lambda \geq 490$ nm leads to a very slow disappearance of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$.

Solutions of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ in CCl_4 also were photolyzed at $\lambda \geq 417$ and 490 nm. At $\lambda \geq 417$ nm, there occurs a rapid change of color from yellow to blue/green which is accompanied by gas evolution. The IR $\nu(\text{CO})$ bands of the η^1 -benzyltungsten complex decrease in intensity and weak absorp-

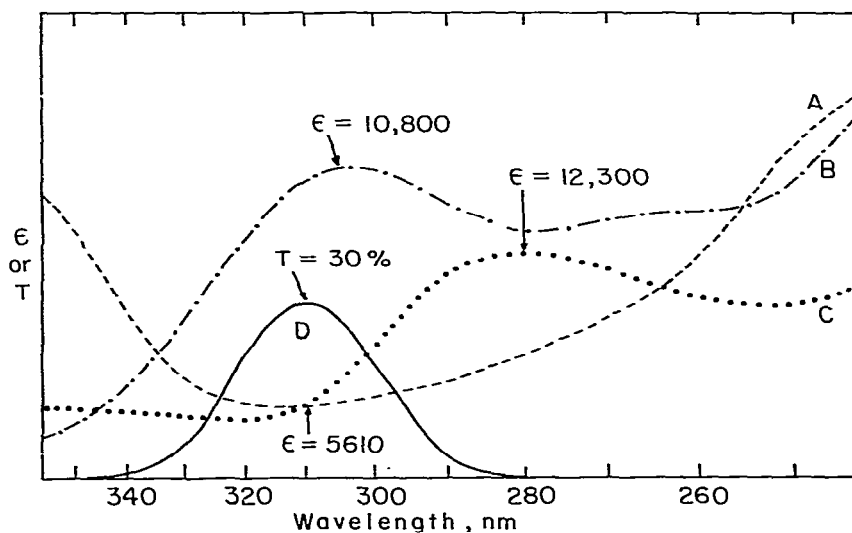


Fig. 2. Electronic absorption spectra of $[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$ (A), $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ (B), and $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)$ (C) in cyclohexane and the percent transmittance curve of the 310 nm bandpass filter (D). Note that the ϵ scales for the spectra A, B, and C are all different.

tions appear at 2053, 1972, and 1953 cm^{-1} . The three latter peaks are almost certainly due to $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{Cl}$ (cf. Table 1). After ca. 3 min only very weak absorptions of the η^1 -benzyl and the chloro complex are seen in the IR $\nu(\text{CO})$ region of the irradiated solution.

A similar, but considerably slower, photoreaction occurs at $\lambda \geq 490$ nm. After 20 min the IR $\nu(\text{CO})$ absorptions of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ have lost relatively little intensity. Weak $\nu(\text{CO})$ bands of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{Cl}$ are discernible.

Photochemistry of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ in the presence of $\text{P}(\text{C}_6\text{H}_5)_3$

Photolysis at ca. 310 nm of a cyclohexane solution of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ (4×10^{-3} M) and $\text{P}(\text{C}_6\text{H}_5)_3$ (6.3×10^{-2} M) for 1 h results approximately in a 50% conversion of the η^1 -benzyl complex to $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)$. Trace $[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$, but no other tungsten carbonyl species, was detected by IR spectroscopy. Under the conditions of same light intensity, this photoreaction proceeds more slowly than that of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3(\eta^1\text{-CH}_2\text{-C}_6\text{H}_5)$ without added $\text{P}(\text{C}_6\text{H}_5)_3$.

Photochemistry of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ in the presence of $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$

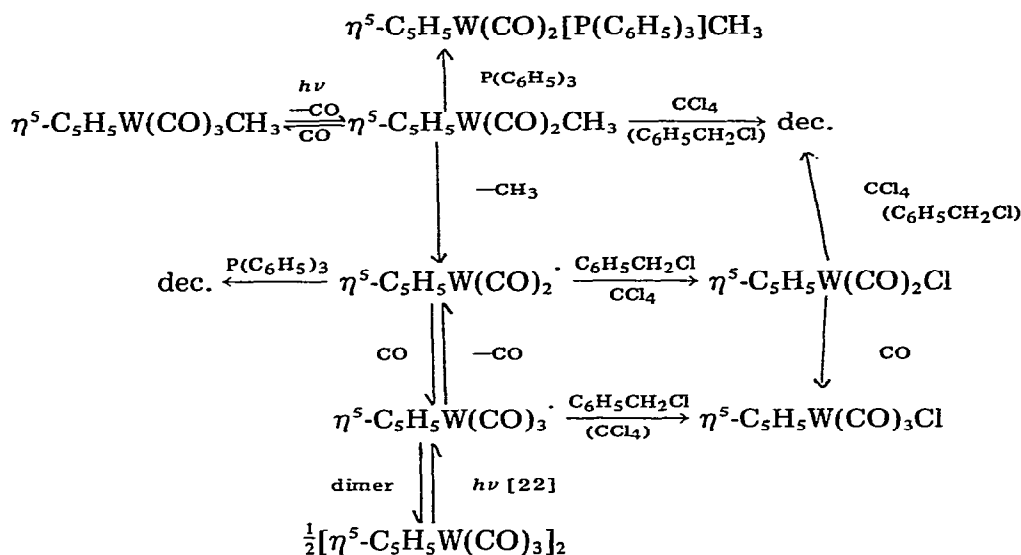
Solutions containing $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ (3.2×10^{-3} M) and $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ (0.11 to 3.07 M) in cyclohexane were irradiated at $\lambda \geq 417$ nm for ca. 10 min. The formation of both $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)$ and $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{Cl}$ was observed by IR spectroscopy, the ratio of the chloro to the η^3 -benzyl complex varying from less than 1/30 when $[\text{C}_6\text{H}_5\text{CH}_2\text{Cl}]$ 0.11 M to approximately 1/2 when $[\text{C}_6\text{H}_5\text{CH}_2\text{Cl}]$ 3.07 M. The η^3 -benzyl complex is stable to irradiation under these conditions in the presence or absence of $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$, whereas $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{Cl}$ shows signs of decomposition over longer periods of photolysis in cyclohexane solution containing $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$.

Discussion

The results on the photolysis of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ may be rationalized in terms of the reactions presented in Scheme 1.

The primary photoreaction of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ in cyclohexane leading to the formation of $[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$ and methane appears to be loss of carbon monoxide to afford a coordinatively unsaturated species, $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{CH}_3$. This proposal receives support from the faster disappearance of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{-CH}_3$ (and of the appearance of $[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$) when the photolysis is conducted under argon than when it is carried out under carbon monoxide using same light intensity. Little difference would be expected in the photoconversion under the two conditions if the initial reaction were homolysis of the W—CH₃ bond. Cleavage of the tungsten—carbon σ bond occurs after loss of a CO group; however, we cannot tell whether this process is initiated photochemically or thermally and by what mechanism it proceeds. Although the formation of methane as the only detectable organic product can be readily explained by homolytic scission of the W—CH₃ bond, mechanisms involving hydrogen abstraction by $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{CH}_3$ from C_5H_5 or the solvent and reductive elimination of CH_4 cannot be dismissed. Rausch and co-workers [12] have recently demon-

SCHEME 1



stated that the methane produced in photolysis of $\eta^5\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{CH}_3$ derives from C_5H_5 . A quantum yield of 0.067 for the photogeneration of $[\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3]_2$ under argon at ca. 310 nm appears consistent with the proposed reaction scheme. The low efficiency of this process may be ascribed to removal of the $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_2\text{CH}_3$ through back reaction with CO which occurs in competition with loss of the CH_3 group.

The nature of the organometallic photoproduct of $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3\text{CH}_3$ in cyclohexane (i.e., the tungsten dimer) is not affected by the wavelength of light in the range 310–490 nm. However, the conversion becomes slower as the wavelength increases, owing to a decreasing absorption of the methyltungsten complex and, possibly, to a difference in the intensity of light at various wavelengths. At $\lambda \geq 490$ nm, where the extinction coefficient of $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3\text{CH}_3$ is essentially zero, the formation of $[\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3]_2$ is immeasurably slow. At all wavelengths 310–490 nm, the photoreaction slows down with time, since the concentration of the strongly absorbing product $[\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3]_2$ increases.

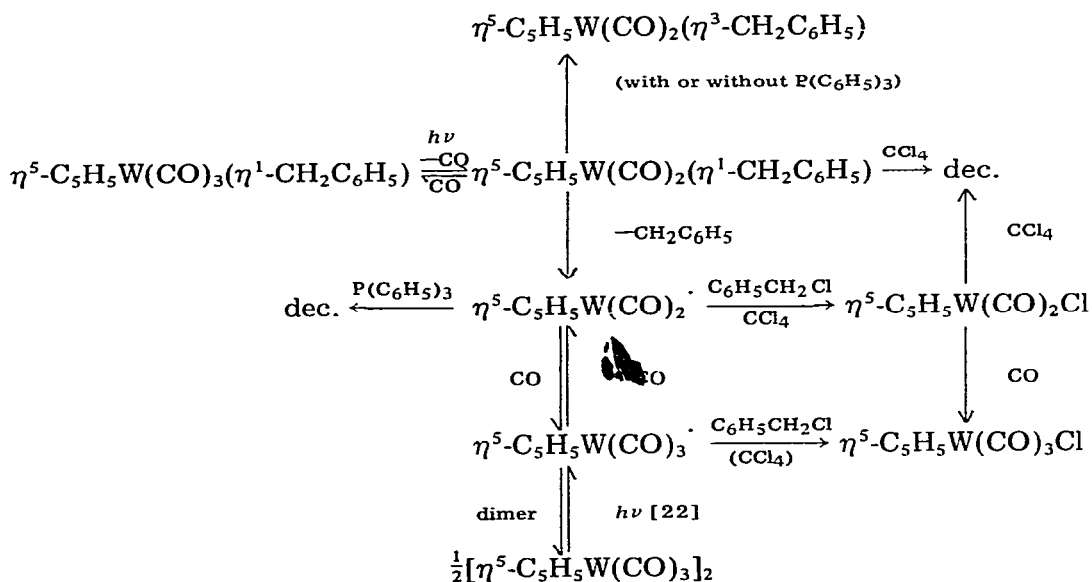
As shown in Scheme 1, the coordinatively unsaturated $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_2\text{CH}_3$ can be intercepted by carrying out photolysis of $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3\text{CH}_3$ in cyclohexane in the presence of $\text{P(C}_6\text{H}_5)_3$. The trapping is essentially complete, allowing at most only small amounts of $[\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3]_2$ to be formed along with some decomposition material. Since the substituted product $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_2[\text{P(C}_6\text{H}_5)_3]\text{CH}_3$ appears stable to the photolytic conditions employed, the observed partial decomposition may result from reaction of $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_x$ ($x = 2$ and/or 3) with $\text{P(C}_6\text{H}_5)_3$. It has been reported [2] that $[\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3]_2$ is unstable to photolysis in the presence of $\text{P(C}_6\text{H}_5)_3$.

Photolysis of $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3\text{CH}_3$ in CCl_4 results in rapid decomposition to non-carbonyl substances, possibly via the coordinatively unsaturated $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_2\text{CH}_3$ and/or $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_2$. Only a small amount of $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3\text{Cl}$

is produced. Wrighton has shown [22] that $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3$, photogenerated from $[\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3]_2$, reacts with CCl_4 to afford $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3\text{Cl}$, which is stable to irradiation. Accordingly, it appears unlikely that either $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3$ or $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3\text{Cl}$ arises along the path to decomposition in this work. By contrast however, photolysis of $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3\text{CH}_3$ in the presence of $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ does yield $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3\text{Cl}$ together with some non-carbonyl decomposition material, perhaps by the reactions shown in Scheme 1. The formation of $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3\text{Cl}$ by reaction of $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ with $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3$, generated photochemically from $[\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3]_2$, was demonstrated earlier [22]. It is of interest that irradiation of $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3\text{CH}_3$ in cyclohexane in the presence of both $\text{P(C}_6\text{H}_5)_3$ and $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ affords $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_2[\text{P(C}_6\text{H}_5)_3]\text{CH}_3$, and no $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3\text{Cl}$. This indicates that the coordinatively unsaturated $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_2\text{CH}_3$ adds $\text{P(C}_6\text{H}_5)_3$ very rapidly compared to elimination of the CH_3 group. Consistently, the relative velocities of these two processes also lead to a virtually complete photoconversion of $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3\text{CH}_3$ to $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_2[\text{P(C}_6\text{H}_5)_3]\text{CH}_3$ in the presence of $\text{P(C}_6\text{H}_5)_3$ rather than formation of $[\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3]_2$.

The reactions thought to be involved in the observed photochemistry of $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ comprise Scheme 2.

SCHEME 2



Although $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ was not investigated in as much detail as the methyl analogue, its photochemistry appears to exhibit gross features that are very similar to those of $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_3\text{CH}_3$. Thus loss of CO is again proposed to generate a coordinatively unsaturated species, $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_2(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ in this case. However, unlike the analogous methyltungsten dicarbonyl, this intermediate readily undergoes an intramolecular rearrangement, yielding the 18-electron $\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_2(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)$ [9], which is stable to the photochemical conditions employed in the present work. The facile and rapid η^1 -benzyl-to- η^3 -benzyl conversion accounts for a number of experimental results.

First, photolysis of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ affords mainly $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)$, and less $[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$. Second, irradiation in the presence of $\text{P}(\text{C}_6\text{H}_5)_3$ gives no $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3](\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$, only $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)$. Under the conditions of same light intensity, this photo-reaction proceeds more slowly than that without $\text{P}(\text{C}_6\text{H}_5)_3$, most likely because of the absorption of some light by the phosphine [26]. Third, photolysis with added $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ requires large amounts of the benzyl chloride for the formation of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{Cl}$ to compete reasonably effectively with the production of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)$.

Finally, we wish to address the question which is central to the goal of this investigation, namely why the primary photochemical process of the $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{R}$ complexes is dissociation of carbon monoxide rather than cleavage of the W-R bond. A reasonable answer to this question may lie in the recently reported [27] qualitative molecular orbital scheme based on the photoelectron spectrum of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$. The two highest energy occupied levels (HOMO), at IP 7.60 and 7.77 eV, have been assigned as metal-based MO's, whereas the next lower level, at IP 9.26 eV, has been assigned as the W-R σ -bonding MO. Thus it may be that the electronic transitions giving rise to the observed photochemistry of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{R}$ are of the metal-to-ligand charge transfer type, with the transitions from the W-R σ -bonding orbital occurring at higher energies. This would result in dissociation of a W-CO bond rather than the W-R bond, as we indeed observed. However, for this proposal to gain sound theoretical basis some information is required about the energies of the corresponding antibonding MO's, and such information is unfortunately lacking at present.

A further unresolved problem in the general context of this investigation is the relative lability of the W-R bond in the coordinatively unsaturated $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{R}$ vis-à-vis the starting $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{R}$. Is this a thermodynamic bond weakening or a kinetic phenomenon, attributable to a vacant coordination site on tungsten? Clearly, additional studies are needed to resolve these points; such studies are either contemplated or currently under way.

Experimental

UV-visible spectra were obtained using a SEM Brückl HRS 4001 C spectrophotometer. IR measurements were made on Perkin-Elmer 257 and 621 spectrophotometers. Proton NMR spectra were recorded on a Varian Associates A-60A spectrometer. Mass spectra were obtained on a Varian MAT CH-5 spectrometer. Melting points were taken on a hot stage apparatus and are uncorrected.

Except as noted, all reactions were carried out under an atmosphere of argon. Analytical grade cyclohexane (99.952%) from Merck was used at all times. Benzyl chloride (Merck) was distilled under reduced pressure and passed through a column of neutral alumina (grade III) and, immediately before use, through activated basic alumina. Triphenylphosphine was recrystallized from pentane and dried (3 h) under high vacuum. Other common chemicals and solvents were reagent grade or equivalent quality and were used without further purification. All solvents were degassed in three freeze-pump-thaw cycles before introduction of argon, or were treated by bubbling argon thereinto for 2-4 h prior to use.

Preparation of complexes

The tungsten dimer $[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$ was prepared by the method of King and Stone [28]. The methyl complex $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ was obtained in 80–90% yield by the general procedure of Piper and Wilkinson [21]. It was freed from the $\text{W}(\text{CO})_6$ contaminant by dissolution in minimum CHCl_3 and passage through a column packed with grade III neutral alumina in pentane, using pentane for washing and elution. Continuous washing of the column led to complete removal of $\text{W}(\text{CO})_6$ before the collection of the effluent containing $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$, as ascertained by IR spectroscopy in the $\nu(\text{CO})$ region. The $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ -containing effluent was evaporated to dryness and the complex was sublimed at 30°C (ca. 0.1 Torr).

The benzyl complex $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ was synthesized as reported in the literature [24]; vacuum sublimation at 40°C of the crude product removed most of the $\text{W}(\text{CO})_6$, and then final purification was effected on alumina as for the methyl analogue.

The known $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\text{CH}_3$ was synthesized according to a modified literature procedure [2] by irradiating (Pyrex, immersion lamp apparatus. Phillips HPK 125W lamp, GWV filter with 60% transmission at 400 nm and 1% at 366 nm) a mixture of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ (0.01 M) and $\text{P}(\text{C}_6\text{H}_5)_3$ (0.02 M) in cyclohexane. The product was isolated in 50% yield after chromatography of the reaction mixture on a column of grade III neutral alumina. Elution with pentane removed the starting materials, and then elution with benzene afforded $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\text{CH}_3$. $^1\text{H NMR}$ (CDCl_3) τ 9.46 d (J 2.8 Hz), 5.18 d (J 1.8 Hz), 2.58 m ppm.

The complex $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)$ was prepared by irradiating (vide supra for conditions) for 1 h a 0.03 M solution of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ in cyclohexane. Solvent was then removed, the residue was dissolved in CH_2Cl_2 , and the byproduct $[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$ (10% yield) was precipitated by the addition of pentane. The filtrate was evaporated to dryness, dissolved in minimum CH_2Cl_2 , and chromatographed on a 2×30 cm column of grade III neutral alumina in cyclohexane. Addition of cyclohexane first eluted unreacted $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ (26% recovery) and then $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)$ (40% yield). The solid product was purified by dissolution in 10/1 cyclohexane/ CH_2Cl_2 , filtration through activated neutral alumina, and concentration of the filtrate under reduced pressure to precipitate orange-brown crystals, m.p. $103\text{--}105^\circ\text{C}$, which were collected under argon. The compound was characterized by its IR $\nu(\text{CO})$ absorptions (Table 1), which closely match those of the similar derivative $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}_6\text{H}_4\text{CH}_3\text{-}p)$ [9].

Photolysis procedures

Solutions to be irradiated were prepared using degassed solvents and were hermetically sealed under argon (or carbon monoxide, when so stated). All photoreactions were conducted at room temperature. Analysis of photolyzed solutions were performed by IR spectroscopy (except those for quantum yield measurements, cf. Results section).

Several experiments were carried out with an Osram XBO 1600W xenon high-pressure arc lamp. For these irradiations, both the reaction vessel (12.5 or 25 ml volume, equipped with a stirrer) and the filter (when used) were immersed

in a water bath. Little light (<1%) with $\lambda \leq 330$ nm was transmitted to the sample under these conditions.

Most photolyses were performed using an Osram HBO 200W mercury vapor lamp in conjunction with an optical train. Quartz sample cells (1–5 cm path length, 3–18 ml volume) equipped with a stirrer were used.

A bandpass filter (combination of WG 305 and SFK-18, Jenaer Glaswerk Schott and Gen.) was employed to isolate (>1% transmittance) light with $285 \text{ nm} \leq \lambda \leq 339 \text{ nm}$ (maximum transmittance 30% at 310 nm) in photolysis experiments using the HBO 200W lamp. Glass filters were used in conjunction with the XBO 1600W lamp to cut off (<1% transmittance) light with $\lambda \leq 490$ and 417 nm (GG 435, Jenaer Glaswerk Schott and Gen.).

Lamp intensities for quantum yield measurements were determined using ferrioxalate actinometry [29]. They were of the order 1×10^{-6} einstein/min at ca. 310 nm. The reported quantum yield is based on two determinations.

Acknowledgements

A.W. thanks the Alexander von Humboldt-Stiftung for a Senior U.S. Scientist Award, whereas R.G.S. acknowledges a fellowship from the Max-Planck-Gesellschaft. The U.S. National Science Foundation is thanked for partial support of this work through a research associateship to R.G.S. and for continued support of research on metal-carbon bonds at The Ohio State University through a grant to A.W. (CHE76-02413 A02). We are indebted to W. Riemer for UV-visible spectroscopic measurements, to Dr. F.-W. Grevels for his help and hospitality, and, above all, to the late Professor E. Koerner von Gustorf for arranging various aspects of a collaborative study before his untimely death.

References

- 1 P.M. Treichel, R.L. Shubkin, K.W. Barnett, and D. Reichard, *Inorg. Chem.*, **5** (1966) 1177.
- 2 K.W. Barnett and P.M. Treichel, *Inorg. Chem.*, **6** (1967) 294.
- 3 A.N. Nesmeyanov, Yu.A. Chapovsky, I.V. Polovnyanyuk, and L.G. Makarova, *J. Organometal. Chem.*, **7** (1967) 329.
- 4 A.N. Nesmeyanov, L.G. Makarova, and I.V. Polovnyanyuk, *J. Organometal. Chem.*, **22** (1970) 707.
- 5 M. Cousins and M.L.H. Green, *J. Chem. Soc.*, (1963) 889.
- 6 M.L.H. Green and P.L.I. Nagy, *J. Chem. Soc.*, (1963) 189.
- 7 M.L.H. Green and A.N. Stear, *J. Organometal. Chem.*, **1** (1964) 230.
- 8 R.B. King and A. Fronzaglia, *J. Amer. Chem. Soc.*, **88** (1966) 709.
- 9 F.A. Cotton and T.J. Marks, *J. Amer. Chem. Soc.*, **91** (1969) 1339.
- 10 A.N. Nesmeyanov, T.B. Chenskaya, G.M. Babakhina, and I.I. Kritskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1970) 1187.
- 11 H.G. Alt, *J. Organometal. Chem.*, **124** (1977) 167.
- 12 M.D. Rausch, T.E. Gismondi, H.G. Alt, and J.A. Schwärzle, *Z. Naturforsch. B*, **32** (1977) 998.
- 13 A. Hudson, M.F. Lappert, P.W. Lednor, and E.K. Nicholson, *J. Chem. Soc., Chem. Commun.*, (1974) 966.
- 14 J.B. Wilford, P.M. Treichel, and F.G.A. Stone, *J. Organometal. Chem.*, **2** (1964) 119.
- 15 M.D. Rausch, T.E. Gismondi, H.G. Alt, and J.A. Schwärzle, *J. Amer. Chem. Soc.*, **96** (1974) 5936.
- 16 H.G. Alt and M.D. Rausch, *Z. Naturforsch. B*, **30** (1975) 813.
- 17 E. Samuel, H.G. Alt, D.C. Hrcir, and M.D. Rausch, *J. Organometal. Chem.*, **113** (1976) 331.
- 18 A. Vogler and R. Hirschmann, *Z. Naturforsch. B*, **31** (1976) 1082.
- 19 C. Giannotti and J.R. Bolton, *J. Organometal. Chem.*, **80** (1974) 379.
- 20 C.Y. Mok and J.F. Endicott, *J. Amer. Chem. Soc.*, **99** (1977) 1276.
- 21 T.S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3** (1956) 104.
- 22 M.S. Wrighton and D.S. Ginley, *J. Amer. Chem. Soc.*, **97** (1975) 4246.

- 23 J.L. Hughey, IV, Ph.D. Thesis, The University of North Carolina at Chapel Hill, 1975.
- 24 J.O. Kroll, M.S. Thesis, The Ohio State University, 1971; M. Graziani, J.P. Bibler, R.M. Montesano, and A. Wojcicki, *J. Organometal. Chem.*, **16** (1969) 507.
- 25 M. Cousins and M.L.H. Green, *J. Chem. Soc.*, (1964) 1567.
- 26 H.H. Jaffé and L.D. Freedman, *J. Amer. Chem. Soc.*, **74** (1952) 1069.
- 27 J.C. Green and S.E. Jackson, *J. Chem. Soc., Dalton Trans.*, (1976) 1698.
- 28 R.B. King and F.G.A. Stone, *Inorg. Synth.*, **7** (1963) 107.
- 29 P. Kirsch (private communication), adapted from C.G. Hatchard and C.A. Parker, *Proc. R. Soc. London, Ser. A.*, **235** (1956) 518.