Photochemistry of Phosphorus(III) Complexes of Bromocarbonyl(π-cyclopentadienyl)iron(II) and Dicarbonylchloro(π-cyclopentadienyl)-molybdenum(II) and -tungsten(II)

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Photolysis with visible light in pyridine or dimethyl sulphoxide solutions of the complex [(cp)Fe(CO)LBr] yields $[(cp)Fe(CO)_2]_2$ when L = $P(OPh)_3$ but $[(cp)Fe(CO)_2(PPh_3)]^+Br^-$ when L = PPh_3 (cp = π-cyclopentadienyl). Solutions of the complexes $[(cp)M(CO)_2LCl]$[M = Mo or W; L = $P(OPh)_3$, PPh_3, or $P(C_6H_{11})_3$] yield $[(cp)M(CO)_2Cl]_2$ on irradiation under similar conditions. Possible mechanisms for these photoreactions are discussed.

WE recently reported[1] that the complexes $[(cp)M(CO)_3Cl]$ (M = Mo or W; cp = π-cyclopentadienyl) undergo photolysis ($\lambda > 400$ nm) in pyridine and dimethyl sulphoxide (DMSO) to yield $[(cp)M(CO)_2Cl]_2$ in contradistinction to the Fe analogues, $[(cp)Fe(CO)_2X]$ (X = Cl or Br) which give $[(cp)Fe(CO)_2]_2$, implying loss of halide rather than CO. Mawby and his co-workers also found the complex $[(cp)Mo(CO)_3I]$ gave $[(cp)Mo(CO)_2I]_n$ on photoirradiation in hexane.[2] In the same paper they reported on thermal substitution of CO by phosphorus(III) ligands (L) in the complexes $[(\pi\text{-}C_9H_7)Mo(CO)_3X]$, $[(\pi\text{-}C_9H_7)Mo(CO)_2X]_2$, and $[(cp)Mo(CO)_2I]_2$ (X = halide, C_9H_7 = indenyl) to give $[(\pi\text{-}arene)Mo(CO)_2XL]$ with X and L probably in a *cis*-configuration. Here we report the effects of substitution of one CO molecule in these complexes by a phosphorus(III) ligand. Replacement of CO in the complex $[(cp)Fe(CO)_2Br]$ by $P(OPh)_3$ has little effect on the photodimerisation and $[(cp)Fe(CO)_2]_2$ is formed *via* loss of Br and $P(OPh)_3$, but the major product of photolysis of $[(cp)Fe(CO)(PPh_3)Br]$ is $[(cp)Fe(CO)_2(PPh_3)]^+Br^-$, *i.e.* the phosphine ligand is retained. The Mo and W analogues, $[(cp)M(CO)_2LCl]$ [L = $P(OPh)_3$, PPh_3, or $P(C_6H_{11})_3$], all yield $[(cp)M(CO)_2Cl]_2$.

EXPERIMENTAL

The following complexes were prepared by established procedures: $[(cp)Fe(CO)\{P(OPh)_3\}]Br$, (I);[3] $[(cp)Fe(CO)(PPh_3)Br]$, (II);[4] $[(cp)Fe(CO)_2(PPh_3)]^+Br^-$, (III);[4] and $[(cp)_2Fe_2(CO)_3\{P(OPh)_3\}]$, (IV) (cp = π-cyclopentadienyl).[5] M.p.s and spectral data agreed well with those given in the literature. The complexes $[(cp)Mo(CO)_2LCl]$[L = $P(OPh)_3$ (V), PPh_3 (VI), or $P(C_6H_{11})_3$ (VII)] and $[(cp)W(CO)_2(PPh_3)Cl]$, (VIII), were prepared by the standard method of heating $[(cp)M(CO)_3Cl]$ (M = Mo or W) under reflux, in benzene under an atmosphere of nitrogen, with a 1·25—

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[4] P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, 1966, **5**, 1177.

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1·5 fold molar excess of P^{III} ligand. All m.p.s and spectral data accorded with literature figures. Solvents were of AnalaR grade throughout except that DMSO was distilled from reagent grade DMSO, over CaH_2 under reduced pressure, and stored over a molecular sieve. Spectra were recorded using Perkin-Elmer 621 i.r., Perkin-Elmer R12 n.m.r., and Unicam SP 800 u.v.-visible spectrophotometers.

Irradiation Technique.—The source was a high-pressure mercury arc (Wotan HBO 200 W), equipped with a constant-current power supply stabilised to 0·1%, and parts of the visible spectrum were isolated by means of Balzer metal interference filters, *e.g.* blue (435 ± 20 nm) or green light (542 ± 20 nm). Reactions were monitored by both i.r. and u.v. spectroscopy, normally by *in situ* irradiation of samples (1 cm depth in quartz cells for u.v. investigation, 0·1 mm depth in NaCl solution cells). Yields were estimated *in situ* by determination of the i.r. absorbances of reactant and product, absorption coefficient data for these being obtained by measurements on unreacted starting material and synthesised product respectively. For example, in the case of conversion of $[(cp)Fe(CO)(PPh_3)Br]$, (II), to $[(cp)Fe(CO)_2(PPh_3)]^+Br^-$, (III), $\varepsilon(II) = 1·36 \times 10^3$ at 1 947 cm^{-1} and ε (III) $= 1·91 \times 10^3$ l mol^{-1} cm^{-1} at 2 048 cm^{-1} in pyridine solution.

RESULTS

Iron Complexes.—$[(cp)Fe(CO)\{P(OPh)_3\}Br]$, (I). Irradiation with blue or green light of complex (I) (5×10^{-4}M, pyridine solution; $\lambda_{max.}$ 350, 415, and *ca.* 570 nm) produced an isosbestic point at 421 nm and product absorptions in the u.v. region. Monitoring the reaction in the i.r. region [$1·1 \times 10^{-1}$M; $\bar{\nu}$(CO) 1 978 cm^{-1}] showed $\bar{\nu}$(CO) (products) at 2 042vw, 2 010w, 1 990s, 1 933s, 1 773m, 1 743w, and 1 720m cm^{-1}, and an isosbestic point at 1 955 cm^{-1}.

A solution of complex (I) (6×10^{-2}M) in pyridine was photolysed in a Pyrex vessel (2 h, $\lambda_{irr} > 400$ nm), the solvent removed under high vacuum at room temperature, and the residue chromatographed on silica gel using benzene as eluent. A red compound (R_f 0·78) was separated having m.p. 189 °C, strong $\bar{\nu}$(CO) at 1 985, 1 945, and 1 773 cm^{-1} (pyridine), and showing n.m.r. absorption at τ 5·05 in $[^2H_6]$DMSO. The data match those of authentic $[(cp)Fe(CO)_2]_2$, (IX). Traces of another red component (R_f 0·35) had $\bar{\nu}$(CO) at 2 042 and 1 992 cm^{-1} (pyridine), matching the spectrum of the complex $[(cp)Fe(CO)_2Br]$. Free triphenyl phosphite was also separated by chromatography and identified by i.r. ($\bar{\nu}$ 1 485, 1 193, 1 162, and 860 cm^{-1} in pyridine) and n.m.r. spectroscopy (multiplet τ 2·75 in $CDCl_3$). No other products were isolated. The molar percentage yield of complex (IX), based on i.r. measurements during reaction, was 10·8%. Irradiation of (I) in DMSO led to similar changes: i.r. monitoring of the reaction showed $\bar{\nu}$(CO) (I) 1972 cm^{-1}, converting to $\bar{\nu}$(CO) (products) 2 035w, 2 004s, 1 983s, 1 940s, 1 767m, 1 740m, and 1 735m cm^{-1}.

$[(cp)Fe(CO)(PPh_3)Br]$, (II). Irradiation with blue or green light of complex (II) ($\lambda_{max.}$ 444 and 620 nm in pyridine) produced an isosbestic point at 423 nm and general product absorption below 400 nm. Monitoring the reaction in the i.r. region in pyridine [9×10^{-2}M, $\bar{\nu}$(CO) 1948 cm^{-1}] showed $\bar{\nu}$(CO)(products) at 2 052s, 2 005s, *ca.* 1 915s, 1 773vw, and 1 720vw cm^{-1}. A similar reaction was observed in DMSO, $\bar{\nu}$(CO)(II) at 1 945 cm^{-1} being replaced by $\bar{\nu}$(CO)(products) at 2 048s, 2 000s, and 1 767vw cm^{-1} only.

Complex (II) (0·1 g) was dissolved in DMSO (10 cm^3) and on irradiation with visible light the green solution became brown. Products were isolated by extracting the DMSO into diethyl ether in which the product was insoluble. The dried, brown residue was found to be insoluble in most organic solvents and therefore extraction and chromatography on silica gel were carried out in acetone. This unfortunately resulted in decomposition of much of the product. However the presence of a yellow compound possessing a pair of CO stretching frequencies (2 046 and 2 004 cm^{-1} in Nujol, 2 048 and 2 000 cm^{-1} in DMSO, and 2 050 and 2 004 cm^{-1} in pyridine) was indicated. These data match those for the complex $[(cp)Fe(CO)_2(PPh_3)]^+Br^-$, (III), prepared by the method of Treichel *et al.*[4] The molar percentage yield of (III) [per mol of (II)], based on i.r. measurements at the end of reaction, was 21%.

Molybdenum and Tungsten Complexes.—The Table describes the changes in the carbonyl stretching frequencies of the solutes on photoirradiation with light of wavelength $\lambda = 435 \pm 20$ nm, *i.e.* corresponding to absorption in the visible bands of the complexes [$\lambda_{max.}$ 466 (V), 476 (VI), 500 (VII), and 465 nm (VIII), all measured in pyridine]. All the above reactions appear to be remarkably ' clean ' and are characterised by isosbestic points in the i.r. region using pyridine or DMSO as solvent. The secondary reaction of the complexes $[(cp)M(CO)_2Cl]_2$ in pyridine solution, which is accelerated if light of shorter wavelength ($\lambda > 280$ nm) is used, has been discussed elsewhere.[1] Visible bands prominent in complexes (V)—(VIII) were gradually destroyed on irradiation, giving way to unstructured absorptions in the u.v. region.

Changes in i.r. wavenumbers/cm^{-1} on irradiating (λ 435 ± 20 nm) solutions in pyridine and dimethyl sulphoxide of P^{III} complexes of dicarbonylchloro(π-cyclopentadienyl)-molybdenum(II) and -tungsten(II)

Solvent	L	$\bar{\nu}$(CO) (initial)	$\bar{\nu}$(CO) (product)	$\bar{\nu}$(CO) (secondary product)
$[(cp)Mo(CO)_2LCl]$				
py	CO	2 047, 1 960	1 955, 1 858	1 892, 1 778
	$P(OPh)_3$	1 982, 1 904	1 956, 1 857	1 893, 1 773
	PPh_3	1 959, 1 870	1 955, 1 857	1 892, 1 772
	$P(C_6H_{11})_3$	1 950, 1 863	1 955, 1 858	1 893, 1 772
DMSO	CO	2 042, 1 955	1 935, 1 825	
	$P(OPh)_3$	1 980, 1 901	1 936, 1 825	
	PPh_3	1 955, 1 865	1 935, 1 823	
$[(cp)W(CO)_2LCl]$				
py	CO	2 042, 1 950	1 940, 1 839	1 887, 1 764
	PPh_3	1 948, 1 856	1 939, 1 839	1 886, 1 766
DMSO	CO	2 036, 1 930	*ca.* 1 920,* 1 800	
	PPh_3	1 943, 1 851	1 917, 1 800	

* Overlapped by broad absorption of starting material.

The complex $[(cp)W(CO)_3Cl]$ (0·1 g) was dissolved in pyridine (10 cm^3) and irradiated in a Pyrex vessel under N_2. The reaction was monitored by i.r. spectroscopy and was stopped when all the starting material had reacted. The solvent was removed under high vacuum at room temperature to leave a red-brown residue. The latter was dissolved in sodium-dried benzene and its i.r. spectrum [$\bar{\nu}$(CO) 1 950s, 1 921m, 1 842m, and 1 808s] slowly transformed to that of the complex $[(cp)W(CO)_3Cl]$ [$\bar{\nu}$(CO) 2 042 and 1 960 cm^{-1}], in a manner analogous to that we have found for $[(cp)Mo(CO)_2Cl]_2$ in benzene and which has been reported for $[(cp)Mo(CO)_2I]_2$ in hexane.[2] The residue has been formulated as $[(cp)W(CO)_2Cl]_2$. It shows $\bar{\nu}$(CO) at 1 916 and 1 799 cm^{-1} in DMSO, but its mass spectrum could not be obtained because of decomposition during the determination.

DISCUSSION

Photolysis of complex (I) gives $[(cp)Fe(CO)_2]_2$, (IX), as the major product, in 10·8% molar percentage yield [based on 1 mol of (I)], and $[(cp)Fe(CO)_2Br]$, (X), as a minor one. Under the experimental conditions the latter will photoreact to give the former.[1] The secondary product with $\bar{\nu}$(CO) 1 720 (pyridine) and 1 736 cm^{-1} (DMSO) has been formulated[1] as $[(cp)_2Fe_2(CO)_3$ (solvent)], *i.e.* it is considered to arise by replacement of one CO molecule in complex (IX) by a molecule of pyridine or DMSO. Its i.r. spectra display the following bands which are of approximately equal intensity: $[(cp)_2Fe_2(CO)_3(py)]$ (py = pyridine), 1 934 and 1 720 cm^{-1}; $[(cp)_2Fe_2(CO)_3(dmso)]$, 1955 and 1736 cm^{-1}. In conformity with this assignment, the i.r. spectrum of authentic $[(cp)_2Fe_2(CO)_3\{P(OPh)_3\}]$ in pyridine shows $\bar{\nu}$(CO) at 1 952 and 1 744 cm^{-1}. This complex was not isolated from the photochemical reaction but may be formed in very small proportions, as a weak absorption at 1 743 cm^{-1} was present in the i.r. spectrum of the products. [It is also photolabile, the major product being complex (IX).] Photolysis of complex (I) in benzene or diethyl ether yields (X) as the major product (30%) but no (IX) was isolated.

The overall reaction scheme appears to be as in equations (1) and (2). There appears to be a solvent selectivity associated with the above photochemical reactions, photolysis of complex (I) in benzene, diethyl ether, acetonitrile or dimethylformamide leading to products other than those formed in pyridine or DMSO.

$$\underset{\text{(I)}}{[(cp)Fe(CO)\{P(OPh)_3\}Br]} \xrightarrow{h\nu} \underset{\text{(X)}}{[(cp)Fe(CO)_2Br]} \quad (1)$$

$$\underset{\text{(X)}}{[(cp)Fe(CO)_2Br]} \xrightarrow[\text{DMSO or py}]{h\nu}$$

$$\underset{\text{(IX)}}{[(cp)Fe(CO)_2]_2} \xrightarrow[\text{DMSO or py}]{h\nu} [(cp)_2Fe_2(CO)_3\,(\text{solvent})] \quad (2)$$

It is clear from the spectroscopic evidence that the product on photolysis of the complexes $[(cp)M(CO)_2LCl]$ [M = Mo or W; L = $P(OPh)_3$, PPh_3, or $P(C_6H_{11})_3$] in pyridine or DMSO is the dimer $[(cp)M(CO)_2Cl]_2$. The mechanism is postulated to be as in equation (3) and (4). The postulated primary photochemical process is unusual in that CO is normally eliminated from organometallic carbonyl complexes.[6] It appears that, as with the complexes $[(cp)Fe(CO)_2X]$ (X = Cl, Br) and $[(cp)Mo(CO)_3Cl]$, the reactions show a strong solvent selectivity. The strongly co-ordinating solvents prevent the dimer from decomposing (*cf.* benzene) and may also stabilise the $[(cp)M(CO)_2Cl]$ species or even form loose (but short-lived) $[(cp)M(CO)_2$ (solvent) Cl] complexes.

$$[(cp)M(CO)_2LCl] \xrightarrow[\text{py or DMSO}]{h\nu} [(cp)M(CO)_2Cl] + L \quad (3)$$

$$2[(cp)M(CO)_2Cl] \longrightarrow [(cp)M(CO)_2Cl]_2$$

$$\text{or } [(cp)M(CO)_2Cl] + [(cp)M(CO)_2LCl] \longrightarrow [(cp)M(CO)_2Cl]_2 + L \quad (4)$$

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