GROUP VIA METAL PENTACARBONYL COMPLEXES OF 2- AND 4-VINYLPYRIDINE AND THEIR COPOLYMERS. PREPARATION, SPECTROSCOPIC CHARACTERISATION AND PHOTOCHEMICAL PROPERTIES

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Summary

$M(CO)_5(4\text{-VP})$ (M = Cr, Mo, or W) and $M(CO)_5$ (2-VP) (M = Cr, W), prepared from the reaction of $M(CO)_5(EtOH)$ and 2-vinylpyridine (2-VP) or 4-vinylpyridine (4-VP), have been characterised by IR, ^1H NMR, and UV/visible absorption spectroscopy. Copolymers of $M(CO)_5(VP)$ with vinylpyridine, styrene, or methyl methacrylate have been synthesised and spectroscopically characterised. Preliminary data on the photosubstitution reactions of $W(CO)_5$-(4-VP) and of its copolymers are presented, and the dependence of the spectroscopic and photochemical properties on the composition of the polymer backbone is reported.

Introduction

The potential use of synthetic polymers containing bound coordination compounds covers areas as diverse as those which utilise the improved mechanical properties of some types to those where bio-mimetic activity is exploited [1—6]. In the case of organometallic compounds, the catalytic properties of polymer-bound analogues of known homogeneous catalysts have been studied [3—6]. It has been found in many cases that the reactivity of the metal complex, in particular its specificity and selectivity, is retained on polymer-binding and, indeed, enhanced activity is sometimes observed. As the physical properties of the materials are determined principally by the polymer backbone, changes in solubility etc. can readily be effected, and this should prove useful in practical applications, e.g. in the separation of the catalyst from the products.

The use of polymer-bound metal complexes as photocatalysts can also be envisaged. Typical applications might be in the photodissociation of water [7,8], solar energy storage via strained ring compounds [9], and photoassisted

reactions of olefins [10,11]. It has been known for some time that the efficiency of homogeneous organometallic catalysts can be greatly enhanced by UV irradiation and that the possibility exists for both generation and regeneration of the catalyst by this means [12,13]. In most cases the effect of photo-exitation is to expel a ligand such as CO or PPh₃, forming a coordinatively unsaturated complex, a highly reactive species which acts as the active molecule in the process to be catalysed. Photodissociation reactions of metal carbonyls have been carefully studied [14,15], and the structure and reactivity of coordinatively unsaturated species such as $M(CO)_5$, $M(CO)_4py$, and $Cr(CO)_4PCl_3$ have been the subject of matrix isolation [16—18] and flash photolysis studies [19]. A particularly well-characterised photochemical system is that of $W(CO)_5(Xpy)$, where Xpy represents a substituted pyridine [20]. It seemed therefore that a study of $M(CO)_5$ complexes of polyvinylpyridine might prove useful in determining how the photoprocesses of a substituted metal carbonyl are affected by binding to a polymer and in seeing whether the photochemical properties of the complex can be "tuned" by systematic variation in the polymer backbone.

Two general routes may be considered for the synthesis of $M(CO)_5$ complexes of polyvinylpyridines or their copolymers. The first, and perhaps the most commonly employed, is to prepare well-characterised homopolyvinyl-pyridine or a vinylpyridine copolymer and allow it to react with $M(CO)_5$, generated in situ either photochemically or from some labile complex such as $M(CO)_5(EtOH)$. (We have used $M(CO)_5(EtOH)$ instead of the more commonly employed $M(CO)_5(THF)$ [21], because of the insolubility of poly-4-vinyl-pyridine in THF.) The other route, and the one used here principally, is to prepare and purify the $M(CO)_5(VP)$ complex and then cause it to copolymerise with other vinyl monomers.

The majority of vinylpyridine complexes which have been characterised, contain Co^{II}, Ni^{II}, Zn^{II} and Cu^{II} [22,23], and a number of these have been structurally characterised by X-ray crystallography [24]. A particular interest here is the possibility of inducing polymerisation of the vinylpyridine in the solid state [25]. In all previously reported complexes the vinylpyridine is bound to the metal via the nitrogen atom. However with metal carbonyl complexes the possibility of coordination to the vinyl group should be considered, and this type of bonding has been observed recently in $(\eta^5\text{-}C_5H_5)Mn(CO)_2$-(4-VP) and $(\eta^5\text{-}C_5H_5)Mn(CO)_2(\mu\text{-}4\text{-}VP)Mn(CO)_2(\eta^5\text{-}C_5H_5)$ [26,27].

In this paper we present details of the synthesis, spectroscopic, chemical and photochemical properties of $M(CO)_5$ (M = Cr, Mo or W) complexes of 2- and 4-vinylpyridine and their copolymers with vinylpyridines, styrene and methyl methacrylate. In a forthcoming paper results of an X-ray diffraction study of $M(CO)_5(4\text{-}VP)$ (M = Cr, W) and $Cr(CO)_5(2\text{-}VP)$ will be reported [28].

Results and discussion

All the monomer complexes described here were prepared by the same route involving the reaction of $M(CO)_5(EtOH)$ (M = Cr, Mo, or W) with a two-molar excess of either 2-vinylpyridine or 4-vinylpyridine in ethanol solution. $M(CO)_5(EtOH)$ is generated as a clear yellow solution by photolysis of a suspension of $M(CO)_6$ in ethanol, and any unreacted $M(CO)_6$ is removed by filtra-

tion before addition to the vinylpyridine solution. The compounds were all obtained as crystalline solids. W(CO)$_5$(4-VP) (I) and Cr(CO)$_5$(4-VP) (II) were purified by sublimation, the other complexes by recrystallisation from oxygen-free methanol or ethanol. No evidence was found for other complexes such as olefin-bound (η^2-VP)M(CO)$_5$, M(CO)$_5$(μ-VP)M(CO)$_5$, or M(CO)$_4$(VP)$_2$, indicating that these must be at very best minor products.

$$M(CO)_6 \xrightarrow[\text{EtOH}]{h\nu} M(CO)_5(\text{EtOH}) \xrightarrow[\text{VP}]{} M(CO)_5(VP) \qquad (1)$$
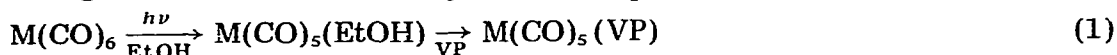
Although all complexes were handled as air-sensitive, I and II do show considerable stability even in aerated solution. The molybdenum complexes however are less stable, and Mo(CO)$_5$(4-VP) decomposed partially upon attempted sublimation. W(CO)$_5$(2-VP) (IV) and Cr(CO)$_5$(2-VP) (V) crystals deteriorate if left in air and V rapidly decomposes in ethanol solution even when degassed. Mo(CO)$_5$(2-VP) could not be isolated from reaction 1, presumably because of its propensity to dissociate. In general the stability of the complexes is in the order W > Cr ≫ Mo and 4-VP > 2-VP. The decreased stability of the 2-vinyl-pyridine complexes may be attributed to steric interaction of the M(CO)$_5$ group and the vinyl group, and this explanation is substantiated by the observation of a longer Cr—N bond in Cr(CO)$_5$(2-VP) (2.23(2) Å) than in Cr(CO)$_5$-(4-VP) (2.18(2) Å) [28].

Spectroscopic properties of complexes I—V

The infrared absorption spectra of the complexes show bands due to the C—O stretch of the carbonyl group (1900—2050 cm^{-1}), to the M—C stretch and M—C—O bend vibrations (300—700 cm^{-1}) (Table 1) and to coordinated vinyl-pyridine (700—1650 cm^{-1}) [27]. The pattern and position of the ν(CO) vibrations are those expected for a M(CO)$_5$ fragment bound to the nitrogen atom of a substituted pyridine [20] and the positions of the bands are quite different from those expected for a M(CO)$_5$ group bound to the vinyl group [20]. Coordination by M(CO)$_5$ causes substantial changes in the IR bands of the vinyl-pyridine. The intensity of some bands change markedly (e.g. the skeletal vibration of the pyridine ring for 4-VP at 1549 cm^{-1} is essentially absent in I—III), while others shift significantly (e.g. the skeletal pyridine ring vibration of 4-VP at 1599 cm^{-1} shifts to 1612—1618 cm^{-1} in I—III; the vinyl band vibration of 4-VP at 925 cm^{-1} is at 937—939 cm^{-1} in I—III, and the pyridine ring C—H
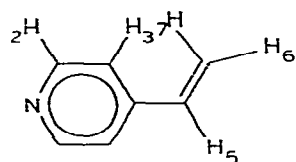
TABLE 1

FREQUENCY OF C=O STRETCH, M—C=O BEND AND M—C STRETCH VIBRATIONS FOR M(CO)$_5$(VP) COMPLEXES

Compound	ν(CO) (cm^{-1}) (in n-hexane)			ν(M—C) (cm^{-1}) (in KBr)	β(M—C—O) (cm^{-1}) (in KBr)
W(CO)$_5$(4-VP)	2072w	1931s	1919m	365	598, 578
Cr(CO)$_5$(4-VP)	2067w	1938s	1919m	440, 410 [a]	665, 650
Mo(CO)$_5$(4-VP)	2076w	1941s	1921m	365	615, 600
W(CO)$_5$(2-VP)	2075w	1934s	1918m	360	600, 580
Cr(CO)$_5$(2-VP)	2071w	1939s	1918m	440, 410 [a]	665, 651

[a] It is possible that one of these bands corresponds to a vinylpyridine-associated vibration.

TABLE 2

^{1}H NMR CHEMICAL SHIFTS (δ in ppm) AND COUPLING CONSTANTS (J in Hz) IN C_6D_6 FOR $M(CO)_5$ (4-VP)

Compound	H(2)	H(3)	H(5)	H(6)	H(7)
4-VP	8.51	6.77	6.28	5.06	5.53
	(4.4,1.4)	(4.4,1.4)	(17.6,10.7)	(10.7,1.0)	(17.6,1.0)
W(CO)$_5$ (4-VP)	8.06	6.06	5.94	5.02	5.32
	(6.0,1.4)	(6.0,1.4)	(18.0,10.2)	(10.2,0.8)	(18.0,0.8)
Cr(CO)$_5$ (4-VP)	7.81	6.03	5.90	4.99	5.30
	(5.1,1.4)	(5.1,1.4)	(17.2,10.3)	(10.3,1.0)	(17.2,1.0)
Mo(CO)$_5$ (4-VP)	7.89	6.13	5.94	5.04	5.35
	(4.9,1.6)	(4.9,1.6)	(17.4,10.2)	(10.2,1.4)	(17.4,1.4)

deformation vibration of 4-VP at 830 cm^{-1} is found at 839—848 cm^{-1} in I—III). In general, then, the major consequence to the vinylpyridine absorptions, which remain after complexation, is a shift towards higher energy. Similar blue shifts recorded for other vinylpyridine complexes, particularly for the pyridine ring C—H deformation, were explained by postulating a reduction in the π-electron density of the pyridine ring on complexation [23], and it is probable that the same effect is operative here.

The pattern of the resonances in the ^{1}H NMR spectra of I—V are, as expected, similar to those of the free ligand, although the signals of all protons are shifted to higher field, the effect being particularly marked for the protons of the pyridine ring. A possible explanation for this shift is a reduction in the deshielding effect of the ring current due to a decrease of the π-electron density in the pyridine ring upon complexation. Data for the 4-VP complexes are tabulated in Table 2.

TABLE 3

UV/VISIBLE ABSORPTION DATA ($\lambda > 300$ nm) FOR M(CO)$_5$(VP)

Compound	λ_{max} (nm)	ϵ (dm^3 mol^{-1} cm^{-1})	Solvent
W(CO)$_5$ (4-VP)	386	5.5×10^3	EtOH
	404	7.3×10^3	cyclohexane
Cr(CO)$_5$ (4-VP)	394	7.7×10^3	EtOH
	414	8.7×10^3	cyclohexane
Mo(CO)$_5$ (4-VP)	386	4.4×10^3	EtOH
	396	7.7×10^3	cyclohexane
W(CO)$_5$ (2-VP)	335,386	3.08×10^3, 3.28×10^3	EtOH
	392	4.1×10^3	cyclohexane
Cr(CO)$_5$ (2-VP) [a]	380		cyclohexane

[a] Unstable in solution.

The most significant feature of the UV/VIS absorption spectra is the band centred at ca. 400 nm. The position of this band depends somewhat on the constituent metal and markedly on the solvent (Table 3). A similar band is found in other $M(CO)_5(Xpy)$ complexes and has been shown to contain MLCT and $d-d$ (LF) components. For $W(CO)_5(Xpy)$ it was found that the λ_{max} of the MLCT band varies with both the pyridine ring substituent X and with the solvent (in isopentane λ_{max} is 351 nm for $W(CO)_5(4\text{-Mepy})$ and 470 nm for $W(CO)_5(4\text{-pyCHO})$), whereas that of the $d-d$ band is solvent and substituent independent [20]. For $W(CO)_5(4\text{-VP})$ in cyclohexane solution the MLCT and $d-d$ bands are not resolved implying that the λ_{max} for the MLCT band in alkane solvents is at about 400 ± 30 nm and that the electron-withdrawing of the vinyl group in the 4-position is similar to that reported for the 3-bromo or 3-acetyl substituents [20].

Copolymers of complexes I—V with vinyl monomers

Vinylpyridine copolymers of complexes I—V were formed by heating vinyl-pyridine solutions of I—V (5 mole %) with free-radical initiator azobisisobu-tyronitrile (AIBN) at 80°C, and also by reaction of $M(CO)_5(EtOH)$ and homo-polymer P(2-VP) or P(4-VP) in ethanol solution at room temperature. In each case the polymers were purified by repeated precipitation from dichloromethane solution by hexane, which is a solvent for I—V but not for the polymers. The incorporation of the metal carbonyl fragment into the polymers is confirmed by the infrared spectra, which show the expected carbonyl stretch absorption in the 1900—2100 cm^{-1} area and by the UV/VIS spectra (Table 4).

Copolymers of $W(CO)_5(4\text{-VP})$ with styrene or methyl methacrylate and terpolymers of $W(CO)_5(4\text{-VP})$ with styrene and 4-vinylpyridine were also prepared by AIBN-initiated polymerisation. Again incorporation of the complex into the polymer is confirmed by IR and UV/VIS spectra. Figure 1 compares the absorption spectra of benzene solutions of $W(CO)_5(4\text{-VP})$ and the copolymer $W(CO)_5(4\text{-VP})$/styrene (1/20 mole ratio). It will be noted that the absorption at about 330 nm in the copolymer is a striking difference. This band coincides in position with the MLCT band for $W(CO)_5(4\text{-Mepy})$ (λ_{max} in benzene 333 nm). As noted above, the wavelength of the λ_{max} for the MLCT

TABLE 4

CARBONYL STRETCH VIBRATIONS (in (a) chloroform and (b) KBr) AND UV/VIS ABSORPTION ($\lambda > 300$ nm) (in ethanol) OF COPOLYMERS $M(CO)_5(VP)$ AND VINYLPYRIDINE

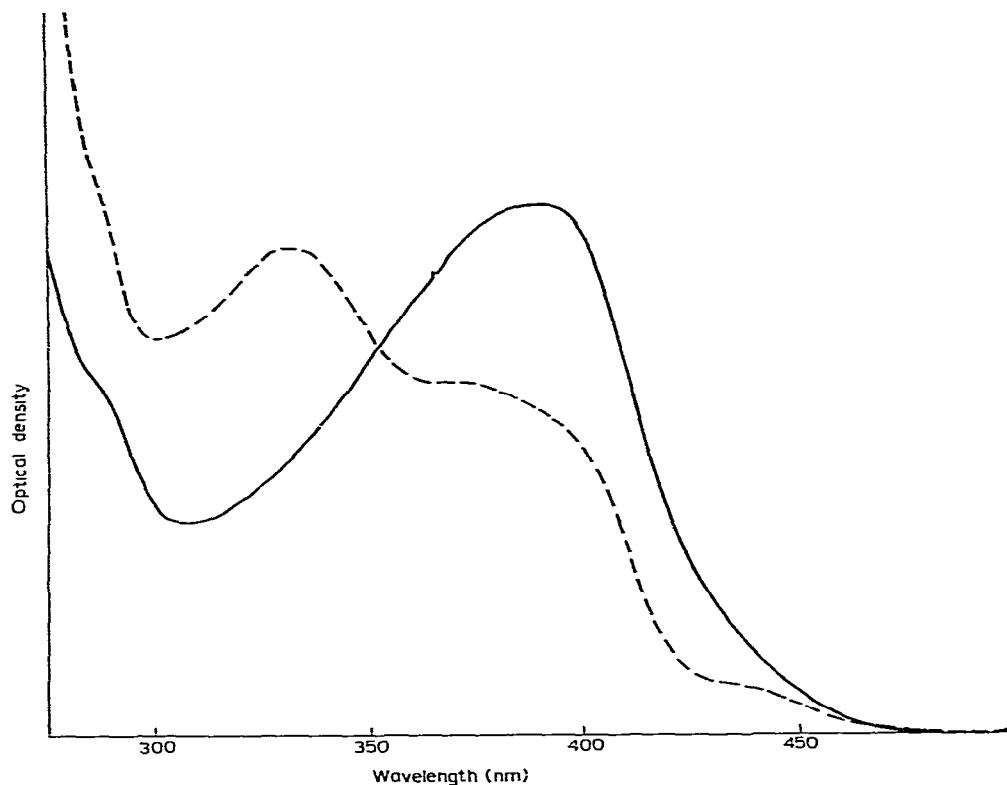| Polymer	ν(CO) (cm^{-1})		λ_{max} (nm)
$Cr(CO)_5$ (P(4-VP))	(a) 2071w	1933s broad	362, 402
	(b) 2071w	1933s 1886m	
$Cr(CO)_5$ (P(2-VP))	(a) 2072w	1938s 1905m	385
	(b) 2072w	1939s broad	
$Mo(CO)_5$ (P(4-VP))	(b) 2079w	1937s 1887m	330sh, 393
$W(CO)_5$ (P(4-VP))	(a) 2076w	1931s broad	337, 382sh
	(b) 2079w	1925s broad	
$W(CO)_5$ (P(2-VP))	(a) 2073w	1934s broad	375
	(b) 2073w	1930s broad	

Fig. 1. A comparison of the UV/VIS spectra of benzene solutions of (i) ——— W(CO)$_5$(4-VP) with (ii) ------ W(CO)$_5$(4-VP)-styrene copolymer (VI).

band of W(CO)$_5$(4-Mepy) was found to depend strongly on the polarity of the solvent [20], and we have also found a marked solvent dependence for the λ_{max} of the 330 nm-band for the polymer complexes. (Table 5 gives λ_{max} for the styrene/W(CO)$_5$(VP) (20/1) copolymer for a number of solvents). This band may therefore be assigned to the MLCT transition of the polymer bound W(CO)$_5$(py—CH—CH$_2$) group.

The position of this MLCT band in the copolymers of I is also sensitive to the composition of the polymer back-bone. (Table 6 gives some data for copolymers in chloroform solution). It will be noted that for the styrene-4-

TABLE 5

λ_{max} FOR MLCT OF W(CO)$_4$ (4-VP)-STYRENE COPOLYMER IN VARIOUS SOLVENTS

| Solvent	λ_{max} (nm)
C$_6$H$_6$	334
C$_6$H$_6$/Et$_2$O (50/50 v/v)	331
C$_6$H$_6$/Et$_2$O (25/75 v/v)	329
THF	325

TABLE 6

VARIATION WITH POLYMER BACKBONE COMPOSITION OF THE λ_{max} FOR THE MLCT BAND
OF $W(CO)_5$ (4-VP) COPOLYMERS IN CHLOROFORM SOLUTION

Polymer No.	4-VP	Mole% Styrene	$W(CO)_5$ (4-VP)	λ_{max} (nm)
VI	—	99.7	0.3	333
XIII	2.1	95.4	2.6	334
XII	5.1	92.3	2.5	335
XI	9.7	88.0	2.4	336
X	17.6	80.1	2.2	337
XIV	29.6	68.5	1.9	341
XV	89.4	8.3	2.3	350sh
MMA				
XVI	—	95.5	4.5	345

vinylpyridine-$W(CO)_5$(VP) terpolymers the position of the band shifts to longer wavelength as the proportion of vinylpyridine in the copolymer is increased. Surprisingly this shift is in the direction expected for an increasingly less-polar environment of the bound $W(CO)_5(pyCH—CH_2)$. Presumably the environment of the complex is determined both by the solvent and by the presence of the other polymer side chains, the extent of each being controlled by the tightness of the polymer coil in the solvent. Further experiments to investigate the nature of the factors controlling this wavelength shift are being carried out, and the matter will be the subject of a future publication.

Photochemical reactions of I and its copolymers

Upon irradiation (λ 436 nm) of degassed olefin-free isopentane solutions of $W(CO)_5$(4-VP) (1×10^{-3}—1×10^{-4} M), the complex decomposes giving $W(CO)_6$ as the only carbonyl product identifiable by IR. No evidence was found for the formation of π-bound $W(CO)_5$(VP), in contrast to the behaviour observed with $CpMn(CO)_2$(VP) [27]. If 1-pentene is present in the solution then the following reaction takes place (eq. 2), the reaction course being conveniently monitored by either IR or UV/VIS spectroscopic methods. The quantum yield for this photosubstitution reaction was determined as 0.66 ± 0.07. This behaviour is therefore very similar to that reported for $W(CO)_5$(Xpy) complexes having a $d—d$ (LF) state as the lowest excited state [20].

$$W(CO)_5\text{(4-VP)} + \text{1-pentene} \rightarrow W(CO)_5\text{(1-pentene)} + \text{4-VP} \qquad (2)$$
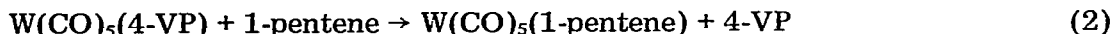
Photocleavage of the W—N bond is also found when $W(CO)_5$(VP)-copolymers are irradiated at λ 436 nm. Figure 2 shows the reaction course for a styrene-4-vinylpyridine-$W(CO)_5$ (VP) copolymer in 50% (v/v) benzene/1-pentene mixture monitored by UV/visible absorption spectroscopy. Preliminary data show that the relative quantum yield for photo-dissociation of the complex in styrene-4-vinylpyridine-$W(CO)_5$(4-VP) terpolymers is dependent on the nature of the polymer backbone and in particular on the proportion of uncoordinated vinyl-pyridine groups on the chain. (The relative quantum yield for a terpolymer containing 12% 4-vinylpyridine compared to that of a styrene copolymer is 0.3). This lower yield is most probably due to recombination of the initially
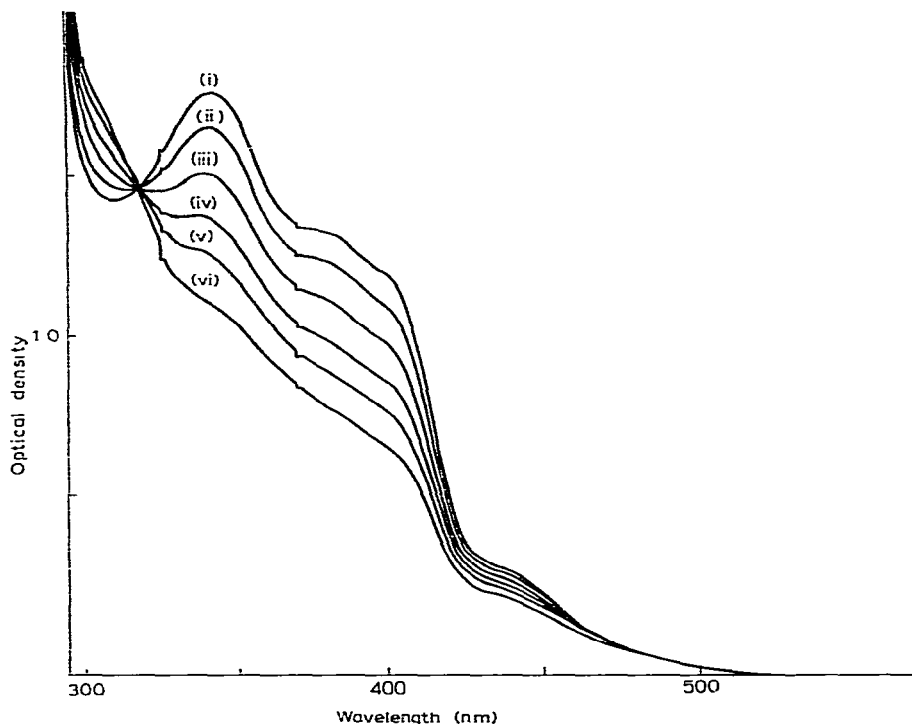
Fig. 2. UV/VIS spectra of W(CO)$_5$ (4-VP)-styrene copolymer (VI) in 50/50 v/v benzene/1-pentene: (i) before irradiation and (ii)—(vi) after irradiation with 436 nm light for successive periods of 1 min.

formed W(CO)$_5$ with other uncoordinated pyridine groups of the polymer, whose local concentration in the vicinity of the reaction centre may be high because of polymer coiling (eq. 3). Other possible explanations such as a lower

$$3$$
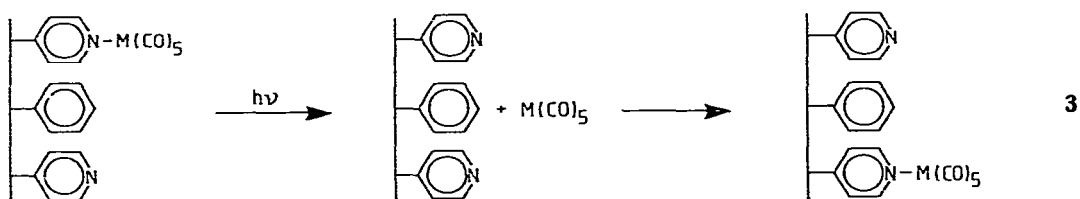
initial quantum yield for photodissociation or thermal back reaction (eq. 4)

$$4$$
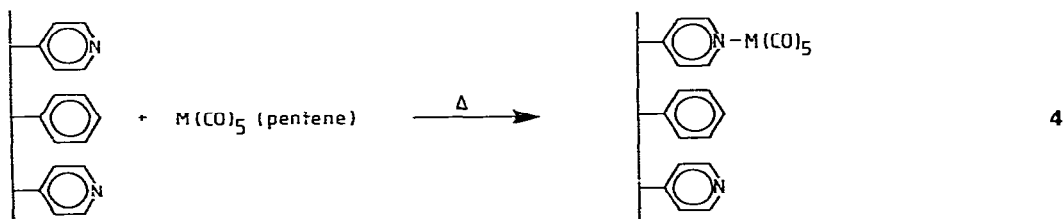
cannot be excluded at present, and this system will be the subject of further study with fully characterised copolymers.

Conclusion

The results reported here indicate that $M(CO)_5(4\text{-}VP)$ complexes have properties closely similar to those of other $M(CO)_5(4\text{-}Xpy)$ complexes and demonstrate the relative instability of the 2-vinylpyridine complexes. It has been found that $W(CO)_5(4\text{-}VP)$ readily copolymerises with other vinyl monomers and that by varying the composition of the monomer mixture it is possible to prepare a series of polymer-bound $W(CO)_5$ derivatives with chemically different polymer backbones. The distribution of monomer entities on the polymer chain, however, will depend on the relative reactivities of the monomers. It is known that the reactivity ratios of 4-vinylpyridine, styrene and methyl methacrylate are similar, and that therefore their copolymers possess a random distribution of functional groups. Although the relative reactivity of $W(CO)_5(4\text{-}VP)$ is not known, it would appear that the electron density in the vinyl group is not appreciably different from that in the uncomplexed monomer and steric hindrance should also be slight. We may presume therefore that the copolymers may be used to test the effect of the nature of the polymer backbone on the photochemical and photophysical properties of $W(CO)_5(\text{py-polymer})$ complexes. The preliminary results presented here appear to indicate that the energy of the MLCT state is sensitive to the nature of the polymer backbone, shifting to lower energy when vinylpyridine replaces styrene in the polymer chain. The finding that the quantum yield drops as the percentage of vinylpyridine in the backbone increases may be a result of intra-chain recombination, as has been previously observed with $[Ru(bpy)_2(PVP)X]^{n+}$ complexes [7], although further experiments will be required to clarify this matter. Both these observations confirm our view that it should be possible to "tune" the photochemical properties of organometallic compounds by binding them to polymers and hopefully it may be possible in this way to develop more effective photocatalysts.

Experimental

Infrared spectra were recorded on a Perkin—Elmer 599 grating spectrophotometer. Peak position are accurate to ± 4 cm^{-1} above 2000 cm^{-1} and ± 2 cm^{-1} below 2000 cm^{-1}. Ultraviolet spectra were recorded on a Pye Unicam SP8-200 single monochromator recording spectrophotometer. Peak positions are accurate to ± 1 nm. Extinction coefficients were measured on a Unicam SP500 or SP8-200 spectrophotometer and are accurate to 5%. ^{1}H NMR spectra were obtained either on a Bruker WP60 or WP80 Fourier transform spectrometer. Peak positions have an accuracy of 0.01 ppm and chemical shifts are measured relative to an internal TMS standard.

Materials. 2- and 4-vinylpyridine (Aldrich) and methyl methacrylate (Loctite) were distilled under reduced pressure and kept at -20°C until required. Styrene (Fluka) and $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ (BDH or Strem) were used as purchased. Spectroscopic grade cyclohexane (BDH) and ethanol (A.R. grade) (Burroughs) were used without purification. All other solvents were reagent grade and purified by fractional distillation before use. Perdeuteriobenzene (Merck or CEA Chemicals) was dried over calcium hydride before use.

TABLE 7

ELEMENTAL ANALYSIS FOR M(CO)₅ (VP) COMPLEXES

Compound	Found (calcd. (%))		
	C	H	N
W(CO)₅ (4-VP)	33.2	1.9	3.5
	(33.6)	(1.6)	(3.3)
Cr(CO)₅ (4-VP)	48.2	2.1	5.0
	(48.5)	(2.4)	(4.7)
Mo(CO)₅ (4-VP)	41.6	2.1	4.1
	(42.2)	(2.1)	(4.1)
W(CO)₅ (2-VP)	33.6	2.0	3.3
	(33.6)	(1.6)	(3.3)
Cr(CO)₅(2-VP)	47.7	2.7	4.6
	(48.5)	(2.4)	(4.7)

Preparation of pentacarbonyl-4-vinylpyridinetungsten(0) (I), pentacarbonyl-4-vinylpyridinechromium(0) (II), pentacarbonyl-4-vinylpyridinemolybdenum(0) (III), pentacarbonyl-2-vinylpyridinetungsten(0) (IV) and pentacarbonyl-2-vinyl-pyridinechromium(0) (V)

All complexes were prepared by the same route involving initial photolysis (8 h) of a suspension of the parent metal hexacarbonyl (1 g) in ethanol (150 cm³). The light source was a Phillips HPK 125W mercury lamp, and the light was filtered through pyrex glass. The photolysis solution was continually purged with a flow of N_2 gas to aid the removal of the carbon monoxide. Following the photolysis, the resulting clear solution was filtered and added to a two molar excess of the desired vinylpyridine, under a nitrogen atmosphere. The solution was stirred at room temperature for 15 min, prior to the removal of the solvent under reduced pressure at ambient temperature. The crude products were purified by either vacuum sublimation at pressures $<10^{-3}$ Torr and temperature $<100°C$ in the case of I and II, or by crystallisation from either degassed methanol or ethanol in the case of III, IV and V. Yields in all cases $>70\%$. Satisfactory elemental (C, H, N) analyses for complexes I—V were obtained (Microanalytical Labs, University College, Dublin) (Table 7). ¹H 60 MHz NMR spectrum of IV (in C_6D_6) 8.58—8.48 (2H,m), 7.33—6.63 (2H,m), 6.15—5.90 (1H,m) and 5.25—4.97 (2H,m) ppm. Other spectroscopic parameters of complexes (I—V) are collected in Tables 1, 2 and 3.

Preparation of polymer M(CO)₅ complexes

Poly-2-vinylpyridine ($|\eta|$(EtOH) = 0.291 dl g⁻¹; $\bar{M}_v$ = 37000) and poly-4-vinylpyridine ($|\eta|$[MeEtCO/Me₂CHOH (86/14 v/v)] = 0.129 dl g⁻¹; $\bar{M}_v$ = 27500) were prepared by AIBN-initiated radical polymerisation as already described [7]. M(CO)₅(PVP) (M/PVP = 1/20) * complexes were prepared either by mixing ethanol solutions of M(CO)₅(EtOH), prepared as above, and PVP in the

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* M/PVP refers to the molar ratio of metal complex centres to vinylpyridine moieties on the polymer chain.

TABLE 8

REACTION MIXTURES USED IN PREPARATION OF COPOLYMERS OF I WITH VINYLPYRIDINE, STYRENE AND METHYL METHACRYLATE

Polymer	Weight (g)			Mole%		
	4-VP	Styrene	W(CO)$_5$ (4-VP)	4-VP	Styrene	W(CO)$_5$ (4-VP)
VI	—	3.60	0.04	—	99.7	0.3
VII	0.50	3.60	0.04	12.1	87.7	0.3
VIII	0.20	3.60	0.04	5.2	94.6	0.3
IX	0.10	3.60	0.04	2.7	97.2	0.3
X	1.00	4.50	0.50	17.6	80.1	2.2
XI	0.50	4.50	0.50	9.7	88.0	2.4
XII	0.25	4.50	0.50	5.1	92.3	2.5
XIII	0.10	4.50	0.50	2.1	95.4	2.6
XIV	1.96	4.5	0.50	29.6	68.5	1.9
XV	4.90	0.45	0.50	89.4	8.3	2.3
		MMA			MMA	
XVI	—	5.0	1.0	—	95.5	4.5

required 1/20 molar ratio or by AIBN-initiated copolymerisation of a vinyl-pyridine solution of M(CO)$_5$(VP) at 80°C. Other copolymers were produced by AIBN-initiated copolymerisation at 80°C of the amounts shown in Table 8. The resulting polymers were purified by precipitation from CH$_2$Cl$_2$ solution by n-hexane.

Photochemical procedures. Irradiations were carried out using a Thorn MED 250 W medium pressure mercury lamp. Wavelengths (365 or 436 nm) were selected by an Applied Physics high radiance Monochromator (5 nm band pass). For quantum yield determinations samples, in standard 1 cm cuvettes, were irradiated in a merry-go-round apparatus and light intensities determined by ferrioxalate actinometry.

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