Photolysis of Tungsten Hexacarbonyl with Bidentate Ligands. Characterization and Reaction Kinetics of a $W(CO)_5L$ Intermediate by Diode-array Electronic Absorption Spectroscopy

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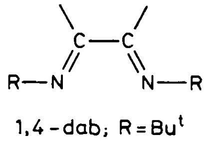
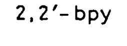
Electronic absorption spectra of a monodentate $W(CO)_5L$ intermediate have been recorded during the photoinitiated reaction of $W(CO)_5L$ with L = 1,4-di-t-butyl-1,4-diazabutadiene and 2,2′-bipyridine; the $W(CO)_5L$ species subsequently extrudes CO in a first order kinetic process to form $W(CO)_4L$.

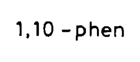
A knowledge of the identity, structure, and reaction kinetics of photochemically generated intermediates is important to a further understanding of organometallic photochemistry. There have been extensive spectroscopic studies of $M(CO)_5$ intermediates produced in the photolysis of Group 6 hexacarbonyls, either in a rigid environment as glasses[1] and matrices[2] or in room temperature solution by conventional flash photolysis techniques.[3] In this paper, we report u.v.–visible spectra recorded during the photoinitiated reaction of $W(CO)_6$ with three different types of di-imine ligands: 1,4-di-t-butyl-1,4-diazabutadiene[4] (1,4-dab; R = Bu^t), 2,2′-bipyridine (2,2′-bpy), and 1,10-phenanthroline (1,10-phen).



1,4-dab; R = Bu^t



2,2′-bpy



1,10-phen

This reaction has been monitored by recording electronic absorption data every 1.5 s with a microprocessor-controlled diode-array detector. The u.v.–visible spectra provide direct evidence for the formation of monodentate $W(CO)_5$(di-imine) following photolysis, and subsequent thermal displacement of CO to form bidentate $W(CO)_4$(di-imine).[5] The sequence of reactions (1)—(4) is presented to account for the observation of $W(CO)_5L$ (L = di-imine, S = solvent: benzene in this work).

$$W(CO)_6 \overset{h\nu,\ S}{\rightleftharpoons} W(CO)_5S + CO \tag{1}$$

$$W(CO)_5S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} W(CO)_5 + S \tag{2}$$

$$W(CO)_5 + L \xrightarrow{k_2} W(CO)_5L \tag{3}$$

$$W(CO)_5L \xrightarrow{k_3} W(CO)_4L + CO \tag{4}$$

Previously it has been determined that the initial photoproduct of $W(CO)_6$ is unsaturated $W(CO)_5$ which rapidly forms a weakly co-ordinated solvent complex $W(CO)_5S$, reaction (1).[3] It has also been shown that this solvent complex reacts rapidly in the presence of scavenging ligand to form $W(CO)_5L$, reactions (2) and (3).[3,6] The relatively slow subsequent reaction (4) is studied here. Figure 1 illustrates the spectral sequence observed following *ca.* 2 s irradiation with a

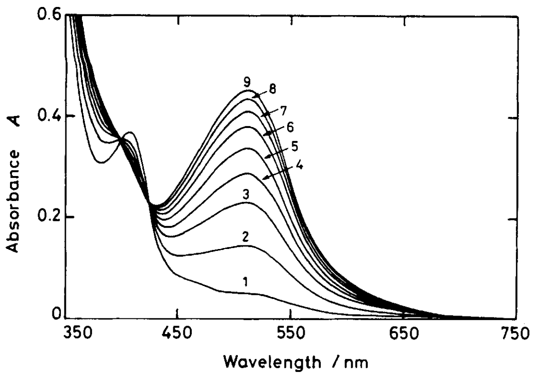


Figure 1. Spectral sequence recorded following *ca.* 2 s irradiation with a 200 W Hg lamp of a solution of 5×10^{-4} M $W(CO)_6$ in benzene at 20 °C containing 10^{-2} M 2,2′-bipyridine. Curve 1, initial spectrum recorded within 4 s after photolysis. Curves 2—9, spectra at 15 s time intervals. The absorption at 514 nm is characteristic of $W(CO)_4$(2,2′-bpy).

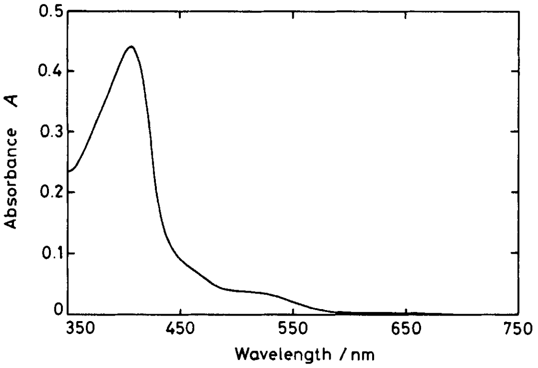


Figure 2. Difference absorption spectrum obtained by subtracting spectral data of unphotolysed solution from curve 1 of Figure 1.

200 W Hg lamp of 5×10^{-4} M $W(CO)_6$ in benzene containing 10^{-2} M 2,2′-bpy. The formation of the $W(CO)_4$(2,2′-bpy) product is monitored by the growth of its characteristic metal to ligand charge-transfer (MLCT) absorption at 514 nm.[7] The presence of sharp isosbestic points at 397 and 424 nm indicates that this reaction appears to be uncomplicated by side or subsequent reactions. Figure 2 illustrates the difference u.v.–visible spectrum obtained by subtracting the spectral data before photolysis from that immediately after. The close similarity of this spectrum to the absorption spectra of $W(CO)_5$(pyridine) and $W(CO)_5$(piperidine) is strong evidence for the monodentate character of the intermediate species. The absorptions of $W(CO)_5$(2,2′-bpy) in benzene at 406 and 460 nm (Figure 2) are consequently assigned to be ${}^1A(e^4b_2^2) \rightarrow {}^1A(e^3b_2^2a_1^1)$ and ${}^1A(e^4b_2^2) \rightarrow {}^3E(e^3b_2^2a_1^1)$ transitions respectively.[8] The weak absorption at 514 nm is due to a small amount of $W(CO)_4$(2,2′-bpy) formed in the 4 s taken to record the data after photolysis. Electronic absorption data recorded for all the $W(CO)_5L$ and $W(CO)_4L$ complexes studied are listed in Table 1.

The rate of reaction (4) was determined by following the growth of the MLCT absorption of $W(CO)_4L$. Reaction rates were found to be independent of ligand concentration over the 1×10^{-3}—1×10^{-2} M range. The growth of A_0 to A_∞ is exponential, and plots of $\ln(A_\infty - A_0/A_\infty - A)$ *vs.* time are linear, yielding slope k_3. The first order rate constant, k_3, is observed to depend greatly on the nature of the di-imine. For L = 1,10-phen no discernible $W(CO)_5$(1,10-phen) intermediate was observed within 4 s after photolysis, thus $k_3 > 0.2\ s^{-1}$. For L = 2,2′-bpy, $k_3 = 1.5 \times 10^{-2}\ s^{-1}$ at 20 °C, corresponding to a half-life of *ca.* 50 s. For L = 1,4-dab; R = Bu^t, $k_3 = 1.1 \times 10^{-4}\ s^{-1}$ at 20 °C, corresponding to a half-life of *ca.* 6300 s. The large differences in k_3 are presumably associated with steric constraints for the bidentate co-ordination of L; for 1,10-phen the nitrogen atoms are held coplanar in contrast to the approximately s-*trans* conformation of 2,2′-bpy in solution,[9] whereas in the 1,4-dab ligand it appears that the bulky Bu^t groups hinder rapid chelation. The relative rates of chelation are in good agreement with those recently obtained with the use of rapid-scan Fourier transform (FT) i.r. spectroscopy for the reaction of $M(CO)_5L$ to $M(CO)_4L$, where M = Cr, Mo, or W, and L = 4,4′-dialkyl-2,2′-bpy or 4,7-diphenyl-1,10-phen.[5] However, this FT i.r. study was limited to the substituted di-imines because of solubility restrictions.

Table 1. Electronic absorption spectra and assignments for $W(CO)_5L^a$ and $W(CO)_4L^b$ (L = di-imine) complexes in benzene at 20 °C.

Complex	Band maxima, nm
$W(CO)_5$(1,4-dab; R = Bu^t)	385(d → d), 425(d → d)^c
$W(CO)_5$(2,2′-bpy)	406(d → d), 460(d → d)^c
$W(CO)_5$(1,10-phen)	^{d}
$W(CO)_4$(1,4-dab; R = Bu^t)	375(d → d), 540(MLCT)
$W(CO)_4$(2,2′-bpy)	364(d → d), 387(d → d),^{c} 514(MLCT)
$W(CO)_4$(1,10-phen)	340(d → d), 396(d → d),^{c} 510(MLCT)

^{a} Difference spectra obtained from photolyses of 5×10^{-4} M $W(CO)_6$ in benzene containing 10^{-2} M L. ^{b} Spectra recorded from solutions of the solid complexes. ^{c} Observed as a shoulder. ^{d} Not observed.

A further intermediate (λ_{max} = 416 nm) is observed immediately following the irradiation of 5×10^{-4} M $W(CO)_6$ in benzene containing 10^{-2} M 1,4-dab; R = Bu^t. This species decays with a *pseudo* first order rate constant $k_{app.} = 1.8 \times 10^{-2}\ s^{-1}$ at 20 °C. The spectral features of this intermediate are also observed following photolysis of $W(CO)_6$ solutions that exclude scavenging ligand; it is therefore assigned to be a solvent impurity species $W(CO)_5$-(impurity). Hence for L = 1,4-dab; R = Bu^t reaction (3) is replaced by the sequence (5)—(6).

$$W(CO)_5 + \text{impurity} \xrightarrow{\text{fast}} W(CO)_5(\text{impurity}) \qquad (5)$$

$$W(CO)_5(\text{impurity}) + L \xrightarrow{k_{app.}} W(CO)_5L + \text{impurity} \qquad (6)$$

The appearance of $W(CO)_5$(impurity) illustrates that 1,4-dab (where R = Bu^t) is a relatively poor scavenging di-imine, due to steric hindrance around the co-ordinating atom.

This paper demonstrates the potential of diode-array electronic absorption spectroscopy as a technique to monitor relatively slow reactions. A prerequisite for its employment is that reactant or product exhibit an identifiable absorption that can be monitored (in our case the low-energy MLCT feature). A considerable advantage of this technique over FT i.r. spectroscopy is that if the identifiable transition is in the visible or near u.v. spectral region, one's choice of solvent is virtually unlimited.

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