# Kinetics and Mechanism of Ring Closure for a Series of Photoproduced $[M(CO)_5L]$ Intermediates (M = Cr, Mo, or W; L = Pyridine 2-Carbaldehyde Imine Ligand)

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Light irradiation of a solution of $[M(CO)_6]$ (M = Cr, Mo, or W) in the presence of a pyridine 2-carbaldehyde imine ligand $2\text{-}C_5H_4NCHNR$ (L; R = Ph, Bu$^t$, Bu$^n$, or Pr$^i$) produced a transient complex $[M(CO)_5L]$, in which the normally bidentate ligand is co-ordinated in a monodentate fashion. The photoproduced complex $[M(CO)_5L]$ complex subsequently extrudes CO thermally to form a bidentate product $[M(CO)_4L]$; this process is relatively slow and its time-dependent behaviour has been monitored with a diode-array u.v.–visible spectrophotometer for each of the ligands L. Kinetic data obtained for these chelation reactions indicate that the pyridine nitrogen atom in L preferentially scavenges the photoproduced $[M(CO)_5]$ intermediate. Rate and activation energy parameters closely relate to the nature of the ligand L and imply varying degrees of associative character in the ring-closure transition state.

Despite extensive studies of the ligand photosubstitution processes of metal carbonyl complexes, relatively little is known about the nature of their intermediates in solution.[1] Spectral characterization of these intermediates and quantitative measurements of their reactivity are usually unavailable. Most investigations have been concerned with light irradiation of the $[M(CO)_6]$ (M = Cr, Mo, or W) system and have illustrated that the $[M(CO)_5]$ primary photoproduct is extremely reactive in solution, co-ordinating with even poor ligands at diffusion-controlled rates.[2] However, further information about ligand substitution processes of metal carbonyl intermediates is important to a continuing development of mechanistic organometallic chemistry and the use of metal carbonyls in homogeneous catalytic processes.[3]

In recent articles we have reported electronic absorption spectra recorded immediately following the photolysis of $[M(CO)_6]$ (M = Cr, Mo, or W) solutions containing the bidentate ligands RNCHCHNR (R = Bu$^t$, Pr$^i$, or $C_6H_{11}$), 2,2′-bipyridine, and 1,10-phenanthroline with the use of a rapid-scanning, diode-array u.v.–visible spectrophotometer.[4–6] These studies have provided spectral evidence for transient $[M(CO)_5L]$ complexes in which the normally bidentate ligand L is co-ordinated in a monodentate fashion. Subsequent kinetic results have shown that these photochemically generated $[M(CO)_5L]$ species undergo ring closure *via* a thermal process, equations (1) and (2).

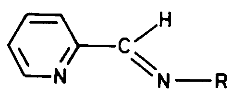
$$[M(CO)_6] \xrightarrow[L]{h\nu} [M(CO)_5L] + CO \qquad (1)$$

$$[M(CO)_5L] \xrightarrow{\text{Heat}} [M(CO)_4L] + CO \qquad (2)$$

Here we report further kinetic studies of the reaction of photoproduced $[M(CO)_5L]$ complexes, where L is a series of pyridine 2-carbaldehyde imine ligands, $2\text{-}C_5H_4NCHNR$ (L; R = Pr$^i$, pycipi; Bu$^n$, pycnbi; Bu$^t$, pyctbi; Ph, pycpi). In particular this investigation is concerned with the detailed nature of the $[M(CO)_5L]$ ring-closure mechanism.

## Results

A typical spectral sequence, recorded following 5-s u.v. irradiation of a benzene solution containing $5 \times 10^{-4}$ mol dm$^{-3}$ $[W(CO)_6]$ and $1 \times 10^{-2}$ mol dm$^{-3}$ pycpi ligand, is shown in Figure 1. In this experiment the initial spectrum was obtained approximately 2 s after excitation and spectra were recorded thereafter at 1-min time intervals. These spectra indicate an immediate absorbance increase at *ca.* 400 nm and then relatively slow growth of an intense feature centred at 574 nm which is characteristic of the metal-to-ligand charge-transfer (m.l.c.t.) transition of the product $[W(CO)_4(pycpi)]$. This light-initiated thermal process appears to proceed uncomplicated by subsequent or side reactions, maintaining a sharp isosbestic point at 482 nm.



L

| R | |
|---|---|
| Pr$^i$ | pycipi |
| Bu$^n$ | pycnbi |
| Bu$^t$ | pyctbi |
| Ph | pycpi |

Similar spectral results were observed from the other ligands studied. U.v.–visible spectra have been obtained from isolated $[M(CO)_4L]$ (M = Cr, Mo, or W) complexes and are listed in Table 1; these spectra were determined to be coincident with those observed at the end of the kinetic experiment.

Difference u.v.–visible spectra were obtained with the use of the data storage and software facilities of the microprocessor-controlled spectrophotometer. The difference u.v.–visible absorption spectrum obtained by subtracting the spectral data of the unphotolyzed solution containing $[W(CO)_6]$ and pycpi from those recorded immediately after photolysis is shown in Figure 2.

Reaction rates have been determined by monitoring the growth of the long-wavelength m.l.c.t. features of the $[M(CO)_4L]$ products. For each run, the growth from $A_0$ to $A_\infty$ was exponential; that is, plots of $\ln[(A_\infty - A_0)/(A_\infty - A_t)]$ *versus* time were linear, with gradient $k_{obs.}$. Here $A_0$ is defined as the initial absorbance recorded following excitation, $A_t$ is the absorbance at time $t$, and $A_\infty$ is the final absorbance reached; all absorbance values being recorded at fixed wavelength in the m.l.c.t. region. A typical plot representing the time dependence

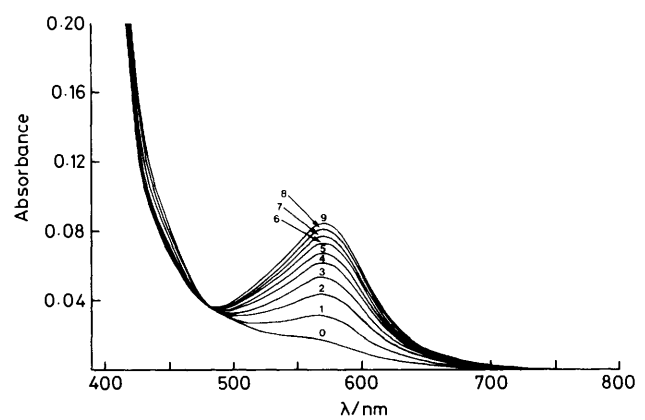


**Figure 1.** Electronic absorption spectral sequence following 5-s u.v. photolysis of 5 × $10^{-4}$ mol dm$^{-3}$ [W(CO)$_6$] and $10^{-2}$ mol dm$^{-3}$ pycpi in benzene at 298 K. Curve 0: initial spectrum recorded 2 s after photolysis. Curves 1—9: subsequent spectra at time intervals of 1 min

**Table 1.** Electronic absorption spectra and assignments for [M(CO)$_5$L][a] and [M(CO)$_4$L][b] in benzene at 293 K

| Complex | Band maxima (nm) |
|---|---|
| [Cr(CO)$_5$(pyctbi)] | 406 (*d–d*) |
| [Cr(CO)$_5$(pycpi)] | 408 (*d–d*) |
| [Cr(CO)$_5$(pycipi)] | 406 (*d–d*) |
| [Cr(CO)$_5$(pycnbi)] | 402 (*d–d*) |
| [Mo(CO)$_5$(pyctbi)] | 385 (*d–d*) |
| [W(CO)$_5$(pyctbi)] | 390 (*d–d*), 438 (*d–d*)[c] |
| [W(CO)$_5$(pycpi)] | 404 (*d–d*), 450 (*d–d*)[c] |
| [W(CO)$_5$(pycipi)] | 390 (*d–d*), 440 (*d–d*)[c] |
| [W(CO)$_5$(pycnbi)] | 402 (*d–d*), 452 (*d–d*)[c] |
| | |
| [Cr(CO)$_4$(pyctbi)] | 391 (*d–d*), 552 (m.l.c.t.) |
| [Mo(CO)$_4$(pyctbi)] | 369 (*d–d*), 518 (m.l.c.t.) |
| [Mo(CO)$_4$(pycpi)] | 375 (*d–d*), 564 (m.l.c.t.) |
| [Mo(CO)$_4$(pycipi)] | 368 (*d–d*), 524 (m.l.c.t.) |
| [Mo(CO)$_4$(pycnbi)] | 366 (*d–d*), 528 (m.l.c.t.) |
| [W(CO)$_4$(pyctbi)] | 375 (*d–d*), 534 (m.l.c.t.) |
| [W(CO)$_4$(pycpi)] | 378 (*d–d*), 574 (m.l.c.t.) |
| [W(CO)$_4$(pycipi)] | 376 (*d–d*), 538 (m.l.c.t.) |
| [W(CO)$_4$(pycnbi)] | 374 (*d–d*), 542 (m.l.c.t.) |

[a] Difference spectra obtained immediately following photolysis of [M(CO)$_6$] solutions containing excess ligand. Monodentate intermediates were not observed for the complexes [Mo(CO)$_5$L] (L = pycpi, pycipi, or pycnbi). [b] Spectra obtained from solutions of the isolated compounds. The complexes [Cr(CO)$_4$L] (L = pycpi, pycipi, or pycnbi) exhibit thermal decomposition in solution at room temperature and absorption data were not recorded. [c] Spin-forbidden transition observed as a shoulder.

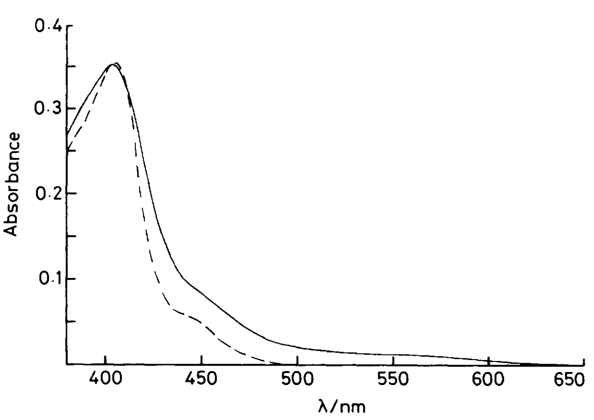


**Figure 2.** Difference absorption spectrum (———) representing the transient [W(CO)$_5$(pycpi)] obtained by subtracting the spectrum of the unphotolysed solution from that immediately after photolysis (curve 1 of Figure 1). The spectral features (– – – –) of [W(CO)$_5$(pip)] are included for comparison and its spectrum is scaled arbitrarily

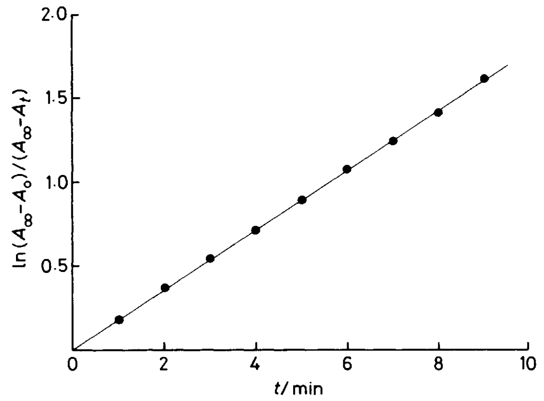


**Figure 3.** Time-dependent behaviour of the absorption data recorded at 574 nm corresponding to the formation of [W(CO)$_4$(pycpi)] (data taken from the experiment shown in Figure 1)

of the formation of [W(CO)$_4$(pycpi)], as monitored by its m.l.c.t. maximum at 574 nm (these absorption values were recorded from the experiment depicted in Figure 1), is shown in Figure 3. A single first-order rate constant ($k_{obs.}$) was recorded from each kinetic experiment; the values obtained for all the ligands in this study at several temperatures are given in Table 2. Each measurement is a mean value of at least three kinetic runs. Activation energy parameters have been obtained from Arrhenius plots of the rate data and are included in Table 2. Reaction rates were found to be independent of ligand concentration over the range 1 × $10^{-3}$ to 2 × $10^{-2}$ mol dm$^{-3}$, consistent with a first-order process in which the rate depends only on the metal complex concentration. Also, rate data were observed to be unaffected by variations in the spectrophotometer acquisition time; therefore, source light from this instrument was concluded to have no measurable effect on the reaction kinetics.

Similar photolysis experiments were also carried out on benzene solutions that contained 5 × $10^{-4}$ mol dm$^{-3}$ [W(CO)$_6$] and $10^{-3}$ mol dm$^{-3}$ primary amine (L′). Here the primary amines have the same functional groups (R) as the series of ligands L. For L′ = NH$_2$Pr$^i$, NH$_2$Bu$^n$, or aniline, the corresponding complexes [W(CO)$_5$L′] were observed to be completely formed immediately after photolysis, as noted by their u.v.–visible maxima in the 400—410 nm region. In contrast, when L′ = NH$_2$Bu$^t$ absorption features recorded immediately after photolysis at $\lambda_{max.}$ = 422 nm correspond to species [W(CO)$_5$-(solvent impurity)][5] and this complex was observed to form [W(CO)$_5$(NH$_2$Bu$^t$)] with a rate constant of 3.63 × $10^{-2}$ s$^{-1}$ at 20 °C.

## Discussion

The spectral data illustrated in Figure 1 are consistent with rapid scavenging of the photoproduced [M(CO)$_5$] intermediate by the ligand L and subsequent thermal ring closure to form the product [M(CO)$_4$L]. Previously it has been shown that the primary photoproduct of [M(CO)$_6$] (M = Cr, Mo, or W) is

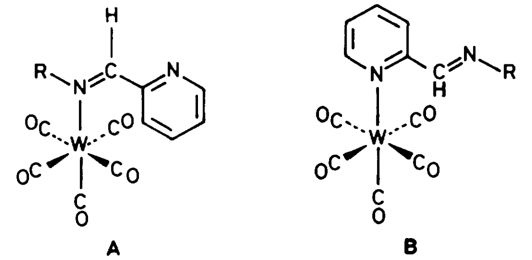


**Figure 4.** Stereochemistry of the linkage isomers of [W(CO)$_5$L]

[M(CO)$_5$] which is rapidly scavenged by even poor ligand donors such as cyclohexane or dinitrogen at rates approaching the diffusion-controlled limit.[2] Therefore, it is assumed that [M(CO)$_5$] will be scavenged rapidly in the presence of an approximately 100-fold excess of L to form [M(CO)$_5$L]. A high ligand concentration also precludes the scavenging of [M(CO)$_5$] intermediates by solvent impurities and the spectral results obtained show no indication of this.[5] Thus, the initial species observed immediately following photolysis is attributed to [M(CO)$_5$L], where the normally bidentate ligand is co-ordinated in a monodentate manner.

Each of the reaction products [M(CO)$_4$L] was isolated as a solid complex and yielded absorption spectra identical to the final spectra recorded in the kinetic experiment. Consistent with earlier studies of these compounds, the intense low-energy features are attributed to m.l.c.t. transitions, whereas the higher-energy absorptions are assigned to *d–d* bands.[7]

Further evidence for the monodentate nature of the reaction intermediate is obtained from the difference electronic absorption spectra (see Table 1), as these features are characteristic of [W(CO)$_5$L] type complexes.[8] For example, Figure 2 illustrates the close comparison that exists between [W(CO)$_5$(pycpi)] and [W(CO)$_5$(pip)] (pip = piperidine). Hence, the absorption features of the complexes [W(CO)$_5$L] are assigned to ${}^1A(e^4b_2{}^2) \longrightarrow {}^1E(e^3b_2{}^1a_1{}^1)$ and ${}^1A(e^4b_2{}^2) \longrightarrow {}^3E(e^3b_2{}^2a_1{}^1)$ ligand-field transitions.[8] The corresponding ${}^1A \longrightarrow {}^3E$ ligand-field absorptions were not observed in the spectra of chromium and molybdenum complexes in accordance with the spin-forbidden assignment. The remaining weak absorption centred at 574 nm (see Figure 2) is attributed to a small amount of product [W(CO)$_4$(pycpi)] formed during irradiation and before the initial reading.

For each of the ligands L the determination of a single rate constant illustrates that only one process is involved in the chelation mechanism. That is, only *one* product results from the reaction of photoproduced [W(CO)$_5$] and L. Importantly, our kinetic data indicate that the rate of ring closure depends significantly on the ligand substituent group, following the order R = Bu$^n$ > Pr$^i$ ~ Ph > Bu$^t$ (see Table 2). This order relates closely to the extent of steric hindrance about the aliphatic nitrogen atom of the ligand; for instance, the bulky ligand pyctbi exhibits the slowest chelation process. It should also be noted that ligand basicity does not appear to be a factor in influencing the rate of chelation; for example, the reaction rates of the ligands where R = Bu$^n$ and Bu$^t$ differ by approximately three orders of magnitude, yet their parent amines have almost the same p$K_a$ values.[9] Therefore, the experimental data lead us to suggest that it is the pyridine nitrogen atom which preferentially scavenges the photoproduct [W(CO)$_5$] and that subsequent ring closure involves co-ordination by the free aliphatic nitrogen atom. The other possible mechanism is that the aliphatic nitrogen atom scavenges the [W(CO)$_5$] photoproduct and that chelation results from the co-ordination of the pyridine nitrogen atom. Chelation in this manner would, however, not be expected to give rise to such great variations in reaction rates.

**Table 2.** First-order rate constants and derived activation energy parameters for the reaction of [M(CO)$_5$L] to form [M(CO)$_4$L] and CO[a]

| M | R | $T$/K | $k_{\mathrm{obs.}}$/s$^{-1}$ | $\Delta H^{\ddagger}$/ kJ mol$^{-1}$ | $\Delta S^{\ddagger}$/ J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|---|
| Cr | Bu$^t$ | 293 | $4.17 \times 10^{-5}$ | 86.5(±5.0) | —31.7(±8.0) |
| | | 303 | $1.98 \times 10^{-4}$ | | |
| | | 313 | $5.73 \times 10^{-4}$ | | |
| | | 323 | $1.25 \times 10^{-3}$ | | |
| Mo | Bu$^t$ | 293 | $2.86 \times 10^{-3}$ | 44.8(±8.0) | −140.6(±16.0) |
| | | 298 | $3.82 \times 10^{-3}$ | | |
| | | 303 | $5.11 \times 10^{-3}$ | | |
| | | 308 | $7.71 \times 10^{-3}$ | | |
| | | 313 | $9.25 \times 10^{-3}$ | | |
| Mo | Ph | 293 | >0.40[b] | | |
| Mo | Pr$^i$ | 293 | >0.40[b] | | |
| Mo | Bu$^n$ | 293 | >0.40[b] | | |
| W | Bu$^t$ | 293 | $1.50 \times 10^{-5}$ | 82.0(±6.0) | −56.9(±12.0) |
| | | 303 | $5.30 \times 10^{-5}$ | | |
| | | 313 | $1.28 \times 10^{-4}$ | | |
| | | 323 | $4.04 \times 10^{-4}$ | | |
| W | Ph | 283 | $1.08 \times 10^{-3}$ | 45.6(±8.0) | −140.2(±16.0) |
| | | 288 | $1.67 \times 10^{-3}$ | | |
| | | 293 | $1.97 \times 10^{-3}$ | | |
| | | 298 | $2.97 \times 10^{-3}$ | | |
| | | 303 | $4.37 \times 10^{-3}$ | | |
| W | Pr$^i$ | 283 | $9.76 \times 10^{-4}$ | 57.5(±7.0) | −98.2(±14.0) |
| | | 288 | $1.77 \times 10^{-3}$ | | |
| | | 293 | $2.79 \times 10^{-3}$ | | |
| | | 298 | $3.75 \times 10^{-3}$ | | |
| | | 303 | $5.47 \times 10^{-3}$ | | |
| W | Bu$^n$ | 283 | $1.07 \times 10^{-2}$ | 26.8(±8.0) | −179.0(±18.0) |
| | | 288 | $1.32 \times 10^{-2}$ | | |
| | | 293 | $1.67 \times 10^{-2}$ | | |
| | | 298 | $1.95 \times 10^{-2}$ | | |
| | | 303 | $2.44 \times 10^{-2}$ | | |

[a] Data were not obtained for the formation of [Cr(CO)$_4$L] (L = pycpi, pycipi, or pycnbi) because these complexes undergo thermal decomposition in benzene. [b] This value represents a lower limit as [Mo(CO)$_4$L] is formed immediately following photolysis on the experimental time-scale.

Experimental and theoretical studies on various di-imine ligands have illustrated that they normally exist in an approximately *s-trans* conformation in both solid and solution phases.[10,11] Ring closure involves rotation about the ligand C$^2$–CHNR bond to produce the necessary *cis* arrangement, and previously it has been estimated that an energy barrier of 20—28 kJ mol$^{-1}$ must be overcome to achieve this di-imine conformation.[11,12] However, as these rotational energy barriers are fairly small and not expected to be greatly dependent on the nature of the di-imine substituent,[12] they would not appear to bring about such significant variations in chelation rates. In the light of both interpretations we prefer the former reasoning that the marked rate differences are caused by steric differences in the ligand substituent groups. Specifically, for L = pyctbi, it appears that the bulky Bu$^t$ group hinders the co-ordination of the free aliphatic nitrogen atom and prevents rapid chelation. In contrast, pycnbi has the least steric hindrance about the aliphatic nitrogen atom and the corresponding [M(CO)$_5$L] complex undergoes much more rapid ring closure. These results clearly demonstrate the importance of the associative nature of the unco-ordinated nitrogen atom in determining the rate of the chelation mechanism.

A possible explanation of the preferential scavenging of the [W(CO)$_5$] photoproduct by the pyridine nitrogen atom is now discussed. A comparison of the stereochemistries of the two possible monodentate co-ordination forms of [W(CO)$_5$L] is depicted in Figure 4. It can be seen that during the scavenging of [W(CO)$_5$] to form structure **A**, the incoming aliphatic nitrogen atom will be hindered substantially by the interaction of the adjacent pyridine ring with the CO groups. This interaction will result in significant steric crowding and electronic repulsion. On the other hand, scavenging of [W(CO)$_5$] leading to structure **B**, where the monodentate complex is co-ordinated through the pyridine nitrogen atom, involves considerably less steric hindrance. Kinetic data obtained following photolysis of [W(CO)$_6$] with NH$_2$Bu$^t$ have provided a further illustration of slow ligand scavenging because of a bulky substituent group.

The ring-closure rates follow the order Mo > Cr > W as previously recorded for [M(CO)$_4$L] complexes, where L = RNCHCHNR ligand.[5] This order parallels the reactivity of the parent hexacarbonyls[13] and the calculated M–C force constants of [M(CO)$_6$] in solution.[14] These comparisons indicate that the relative ease of CO extrusion from [M(CO)$_5$L] is an important factor in controlling the rate of ring closure.

Previously a number of complexes [M(CO)$_5$L], where L = bidentate phosphorus or arsenic ligand, have been observed to undergo a slow chelation reaction.[15] For example, [W(CO)$_5$(PPh$_2$CH$_2$CH$_2$PPh$_2$)] undergoes ring closure with $k_{\text{obs.}} = 4.47 \times 10^{-6}$ s$^{-1}$ at 123 °C, and activation energy parameters have been reported as $\Delta H^‡ = 155$ kJ mol$^{-1}$ and $\Delta S^‡ = 40$ J K$^{-1}$ mol$^{-1}$. Furthermore, the chelation of these complexes has been concluded to proceed *via* a largely dissociative mechanism.[15] In contrast, the rapid rates recorded here for the complexes [M(CO)$_5$L] illustrate a more substantial contribution to the CO extrusion process by the associating ligand. Moreover, the negative entropy values obtained in this work tend to suggest an associative component in the reaction transition state. Accompanying this increase in the associative character is a reduction in the activation barrier to ring closure as reflected by the lower enthalpy values.

## Experimental

*Materials.*—The metal hexacarbonyls were purchased from Strem Chemical Co. and used without further purification. Materials used in the preparation of the ligands were obtained from Aldrich Chemical Co. or Fisher Scientific Co. as reagent grade quality. Benzene used in the kinetic experiments was obtained from J. T. Baker Chemical Co. as spectroscopic grade and further purified by absorptive filtration through Woelm basic alumina of activity grade 1 (ICN Pharmaceuticals Co.). Solvents used in the preparation of metal complexes were reagent grade. Nitrogen used for sample purging was obtained from Union Carbide at high purity and was dried and deoxygenated using a procedure described previously.[5]

*Synthesis of Ligands.*—The pyridine 2-carbaldehyde imine ligands L were prepared by the 1:1 condensation of pyridine-2-carbaldehyde and primary amine.[16] Primary amine (0.03 mol) was added dropwise to a diethyl ether solution (50 cm$^3$) of pyridine-2-carbaldehyde (0.03 mol) and stirred for 3 h at room temperature. The solution was dried by addition of CaSO$_4$, filtered, and then evaporated to an oil. Distillation at 140 °C under low pressure yielded the pure ligands as oily yellow liquids (yields 35—40%).

*Synthesis of Complexes* [M(CO)$_4$L].—The complexes [M(CO)$_4$L] (M = Cr, Mo, or W) were prepared following approximately 30-min u.v. irradiation of hexane solutions containing [M(CO)$_6$] (0.02 mmol) and excess ligand (0.3 mmol) with a 200-W Hg lamp.[17] The solution was purged with nitrogen for 15 min prior to photolysis and throughout photolysis to avoid oxidation of the metal complex. The tetracarbonyl products were obtained by filtration and purified by repeated washings with hexane to remove unreacted starting materials. Infrared and u.v.–visible spectra of the products [M(CO)$_4$L] are in agreement with those previously obtained.[17]

*Kinetic Measurements.*—Samples containing $5 \times 10^{-4}$ mol dm$^{-3}$ [M(CO)$_6$] and $1 \times 10^{-2}$ mol dm$^{-3}$ L in rigorously purified benzene (3 cm$^3$) were deoxygenated by purging with nitrogen for 15 min prior to light excitation. Typically, the samples were irradiated for 5 s with the 313 nm line of a 200-W medium-pressure Hg lamp (Ealing Corporation). The samples were stirred during photolysis and before each absorbance reading to ensure uniform concentration of photoproduct throughout the cell. Approximately $2 \times 10^{-4}$ mol dm$^{-3}$ [M(CO)$_6$] is photodissociated during this light irradiation; this value has been estimated by determining the incident light intensity using ferrioxalate actinometry[18] and the known quantum efficiency ($\varphi = 0.67$—$0.70$) of [M(CO)$_6$].[19] This value was accurately determined from the amount of complex [M(CO)$_4$L] produced at the end of the kinetic experiment. Varying amounts of [M(CO)$_6$] photodissociation ($1 \times 10^{-4}$ to $4 \times 10^{-4}$ mol dm$^{-3}$) did, however, have no effect on the obtained rate constant data. Electronic absorption data were obtained on a spectrophotometer which incorporates a microprocessor-controlled diode-array detector; this enabled full-range spectra to be recorded every 1 s. The initial spectrum was recorded within 2 s after light irradiation and subsequent spectra were recorded at suitable time intervals thereafter.

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