

and Cp*₂Ce(amido) complexes (11, 12), respectively. Reaction of 8 with LiCl in the presence of basic ligands; e.g., TMEDA gives Cp*₂CeCl₂Li(TMEDA)₂ (3) and LiCH(SiMe₃)₂, indicating that alkylation of Ce-Cl bonds by metathetical reactions with a main-group hydrocarbyl is thermodynamically very critical. Despite the paramagnetic character of these bis(pentamethylcyclopentadienyl)cerium complexes, ¹³C NMR spectra are readily interpreted and provide valuable information.

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Note Added in Proof. After submission of this paper Evans et al. reported the synthesis of 4 and 5.⁴⁶

Registry No. 1, 106043-06-5; 2, 116635-57-5; 3, 116635-58-6; 4, 98789-69-6; 5, 111559-69-4; 6, 116635-59-7; 7, 113132-51-7; 8, 106333-13-5; 9, 116635-60-0; 10, 106433-89-0; 11, 116635-61-1; 12, 116635-62-2; CeCl₃, 7790-86-5; CeO₂, 1306-38-3; Cp*Li, 51905-34-1; LiCH(SiMe₃)₂, 41823-71-6; *t*-BuCN, 630-18-2; (Cp*₂CeD)₂, 116635-63-3; HN(SiMe₃)₂, 999-97-3; NaN(SiMe₃)₂, 1070-89-9; *t*-BuNH₂, 75-64-9.

Supplementary Material Available: An ORTEP drawing and tables of atom coordinates, thermal parameters, bond distances and angles, and hydrogen coordinates for 8 (23 pages); a listing of structure factors for 8 (21 pages). Ordering information is given on any current masthead page.

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Photoexcitation of Tungsten Hexacarbonyl in Solutions Containing Pyridine-2-carbaldehyde Imine Ligands. Spectral Characterization and Reaction Kinetics of the Photoproduced Monodentate W(CO)₅L Intermediate

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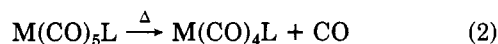
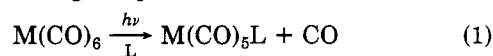
UV photolyses of W(CO)₆ in solutions containing pyridine-2-carbaldehyde N-substituted imine (R-pyca) or 6-methyl-pyridine-2-carbaldehyde N-substituted imine (R-pyca') ligands produce transient species that are attributed to W(CO)₅L complexes, where the normally chelating ligands are coordinated in a monodentate configuration. Electronic absorption and Fourier transform infrared spectra recorded immediately following light excitation using rapid scanning techniques have enabled characterization of this monodentate W(CO)₅L species. Kinetic data have been obtained for the chelation reactions of W(CO)₅L to form W(CO)₄L and CO; in each case the ring closure reaction proceeds via a first-order mechanism. From the ligand dependence of the kinetic data it is inferred that R-pyca scavenges the primary photoproduct exclusively at the pyridine nitrogen atom whereas R-pyca' initially coordinates at the aliphatic nitrogen atom. These kinetic results are discussed in terms of steric hindrance during the ligand scavenging process.

Introduction

Photochemical studies of metal carbonyl complexes have been greatly stimulated by the importance of these molecules as models in mechanistic organometallic chemistry and in the design of homogeneous catalytic processes.¹ Although unsaturated species are believed to be involved in a number of these processes, direct spectral observation and quantitative measurements of their reactivity have rarely been reported. In fact, our current knowledge of the identity and reactivity of intermediates involved in ligand substitution events at low-valent transition-metal centers remains fairly limited.

Recently, several reports have appeared concerned with the nature of reaction intermediates that are produced during the photochemical formation of chelated M(CO)₄L

complexes from M(CO)₆ (M = Cr, Mo, W) solutions containing bidentate ligands (L).²⁻⁴ Spectral data obtained using rapid-scanning Fourier transform infrared spectroscopy³ and diode-array UV-visible spectroscopy⁴ have provided a direct characterization of the monodentate M(CO)₅L intermediate, where L is a series of substituted 2,2'-bipyridine, 1,4-diazabutadiene, or pyridine-2-carbaldehyde imine ligands. Consequently, the photochemical formation of the chelated M(CO)₄L complex is believed to proceed according to eq 1 and 2. In a further extension



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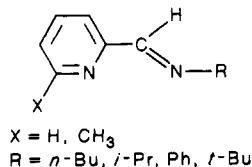
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of this work a number of stable monodentate, $M(\text{CO})_5\text{L}$ ($M = \text{Cr}, \text{Mo}, \text{or W}$ and $\text{L} = \text{di-2-pyridylmethane}, 1,2\text{-di-2-pyridylethane}, 1,8\text{-diazabiphenylene}, \text{or ethylenediamine}$) complexes have now been isolated and $M(\text{CO})_5\text{-}(\text{phen})$ transients have been identified following pulsed laser flash photolysis.⁵

This paper deals with spectral characterization, and the reaction kinetics of monodentate $\text{W}(\text{CO})_5\text{L}$ intermediates produced on photoexcitation of $\text{W}(\text{CO})_6$ solutions containing the ligands pyridine-2-carbaldehyde *N*-substituted imine (*R*-pyca) and 6-methylpyridine-2-carbaldehyde *N*-substituted imine (*R*-pyca').



The goals of this research have been to determine the ligand coordination site with the photoproduct $\text{W}(\text{CO})_5$ species and to assess the influence of hindering substituent groups *X* and *R* on this reaction and on the subsequent chelation step. Comparing the kinetic data obtained not only reveals mechanistic details on the nature of the ring closure process for the $\text{W}(\text{CO})_5\text{L}$ intermediates but also provides an insight into how the highly reactive $\text{W}(\text{CO})_5$ photoproduct is scavenged in these ligand solutions.

Experimental Section

Materials. Tungsten hexacarbonyl was obtained from Strem Chemical Co. and used without further purification. Reagents used in the ligand synthesis were obtained from Aldrich Chemical Co. or Fisher Scientific Co. at 99% purity and used without further purification. Alumina (80–200 mesh, activity grade 1) used in the chromatographic purification of the $\text{W}(\text{CO})_5\text{L}$ complexes was purchased from Fisher Chemical Co. Spectroscopic grade benzene (Photrex, Baker Chemical Co.) was further purified before use by absorptive filtration through Woelm basic alumina of activity grade 1 (ICN Pharmaceuticals Co.). All other solvents used were reagent grade. The impurities in benzene were monitored by gas chromatography on a Carle Instruments Model 6500 gas chromatograph equipped with a polar column and by infrared spectroscopy on a Perkin-Elmer 283B spectrometer. Nitrogen used in the purging experiments was rigorously purified to remove H_2O and O_2 by passage through two 1-m by 2-cm tubes, the first containing dry CaSO_4 and P_2O_5 in alternating 20 cm lengths and the second containing a Cu catalyst (BASF R3-11, Chemical Dynamics Corp.). The catalyst is activated by heating to 120 °C while flushing with hydrogen prior to use. In the activated form the catalyst effectively removes O_2 from gases. *Caution:* the activated catalyst is pyrophoric.

Synthesis of *R*-pyca and *R*-pyca' Ligands. The pyridine-2-carbaldehyde *N*-substituted imine ligands were prepared by the condensation reaction of 2-pyridinecarboxaldehyde (or 6-methyl-2-pyridinecarboxaldehyde) and the appropriate primary amine.⁶ The amine (30 mmol) was added dropwise to a solution of 2-pyridinecarboxaldehyde (30 mmol) in diethyl ether (50 mL) and stirred for 3 h at 25 °C. The solution was dried overnight on addition of CaSO_4 (5 g) and then filtered and evaporated to a pale yellow oil (6–10 mL). Kugelrohr distillation (twice) under reduced pressure at 120–140 °C gave pure *R*-pyca and *R*-pyca' ligands as oily yellow liquids in 35–40% yields.

Synthesis of $\text{W}(\text{CO})_5\text{L}$ ($\text{L} = \text{R-pyca}$ or $\text{R-pyca}'$) Complexes. The $\text{W}(\text{CO})_5\text{L}$ complexes were prepared by UV irradiation with a 200-W Hg lamp of solutions of $\text{W}(\text{CO})_6$ (20 mmol) and excess

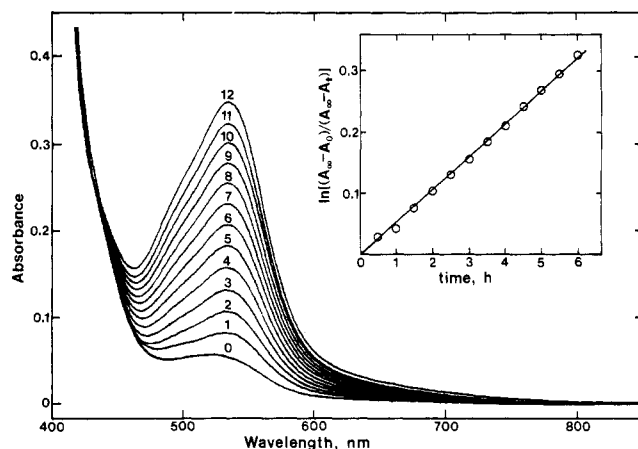


Figure 1. Electronic absorption spectra recorded following 10-s UV irradiation of a deoxygenated benzene solution containing $5 \times 10^{-4} \text{ M W}(\text{CO})_6$ and $1 \times 10^{-2} \text{ M } t\text{-Bu-pyca}$ at 20 °C. Initial spectrum observed $\sim 5 \text{ s}$ after excitation is shown by curve 0. Subsequent spectra at 30 min intervals are shown by curves 1–12. The spectra depict the formation of $\text{W}(\text{CO})_4(t\text{-Bu-pyca})$ with its characteristic MLCT absorption maximum at 534 nm. The inset illustrates the time-dependent behavior of absorption readings taken at 534 nm.

ligand (30 mmol) in hexane (200 mL), according to published procedures.⁷ The solution was deoxygenated to prevent oxidation of the metal complex during photolysis. The $\text{W}(\text{CO})_5\text{L}$ complexes are sparingly soluble in hexane and precipitated during light excitation. These were then purified by repeated hexane washings to remove unreacted starting materials, followed by column chromatography on alumina, if necessary. Typical yields were 60–80%. Representative samples gave satisfactory chemical (C, H, N) analyses, and their infrared and UV–visible spectra were in good agreement with those previously reported.^{7a}

Photolysis and Kinetic Studies. Samples (3 mL) of $5 \times 10^{-4} \text{ M W}(\text{CO})_6$ and $1 \times 10^{-2} \text{ M}$ ligand in deoxygenated benzene at 20 °C were typically irradiated for 5–10 s with the 313-nm line of a 200-W medium-pressure Hg lamp (Ealing Corp.). Approximately $1 \times 10^{-4} \text{ M W}(\text{CO})_6$ undergoes photodissociation during this excitation; this amount was determined from the absorbance of the $\text{W}(\text{CO})_5\text{L}$ complex formed at the end of the kinetic experiment. The extent of $\text{W}(\text{CO})_6$ photodissociation was also confirmed by a ferrioxalate determination⁸ of incident light intensity and the reported quantum yield value of 0.72 (± 0.04) for $\text{W}(\text{CO})_6$.⁹ Variations in the degree of $\text{W}(\text{CO})_6$ photodissociation over the 8×10^{-5} to $4 \times 10^{-4} \text{ M}$ concentration range had no effect on the observed rate data. In the kinetic experiment the concentrations of $\text{W}(\text{CO})_5\text{L}$ intermediates and $\text{W}(\text{CO})_4\text{L}$ products were monitored by UV–visible absorption spectroscopy on a Hewlett-Packard 8450A microprocessor-controlled diode-array spectrometer and by Fourier transform infrared (FT-IR) spectroscopy on a Nicolet 20SXC spectrometer. Samples were stirred during light excitation and before each spectral reading to ensure uniform concentration of photoproduct throughout the cell. Reported rate constants are the mean of at least three kinetic measurements.

Results and Discussion

A typical kinetic experiment consisted of 5–10-s UV irradiation of a deoxygenated benzene solution containing $5 \times 10^{-4} \text{ M W}(\text{CO})_6$ and $1 \times 10^{-2} \text{ M}$ entering ligand. Electronic absorption data were subsequently acquired at time intervals varying between 5 s and 30 min utilizing the rapid-scanning facilities of the diode-array spectrometer. Figure 1 illustrates the spectral sequence obtained from

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Table I. Electronic Absorption Spectral Data (nm) and Assignments for Photoproduced Transient $W(CO)_5L$ Complexes^a and Product $W(CO)_4L$ Complexes^b in Benzene at 20 °C

complex	band maxima, nm
$W(CO)_5(n\text{-Bu-pyca})$	402 (d → d), 452 (d → d) ^c
$W(CO)_5(i\text{-Pr-pyca})$	390 (d → d), 440 (d → d) ^c
$W(CO)_5(\text{Ph-pyca})$	404 (d → d), 450 (d → d) ^c
$W(CO)_5(t\text{-Bu-pyca})$	390 (d → d), 438 (d → d) ^c
$W(CO)_5(n\text{-Bu-pyca}')$	389 (d → d), 468 (d → d) ^c
$W(CO)_5(i\text{-Pr-pyca}')$	396 (d → d), 463 (d → d) ^c
$W(CO)_5(\text{Ph-pyca}')$	404 (d → d), 478 (d → d) ^c
$W(CO)_5(t\text{-Bu-pyca}')$	400 (d → d), 466 (d → d) ^c
$W(CO)_4(n\text{-Bu-pyca})$	374 (d → d), 542 (MLCT)
$W(CO)_4(i\text{-Pr-pyca})$	376 (d → d), 538 (MLCT)
$W(CO)_4(\text{Ph-pyca})$	333 (d → d), ^d 378 (d → d), ^d 574 (MLCT)
$W(CO)_4(t\text{-Bu-pyca})$	321 (d → d), ^d 375 (d → d), 534 (MLCT)
$W(CO)_4(n\text{-Bu-pyca}')$	348 (d → d), 391 (d → d), ^d 534 (MLCT)
$W(CO)_4(i\text{-Pr-pyca}')$	346 (d → d), 385 (d → d), ^d 532 (MLCT)
$W(CO)_4(t\text{-Bu-pyca}')$	350 (d → d), 384 (d → d), ^d 524 (MLCT)
$W(CO)_4(\text{Ph-pyca}')$	324 (d → d), 380 (d → d), ^d 566 (MLCT)

^a Difference spectra recorded following UV photolysis of 5×10^{-4} M $W(CO)_6$ in deoxygenated benzene containing 1×10^{-2} M ligand.

^b Spectra recorded from solutions of the isolated complexes.

^c Spin-forbidden transition observed as a weak shoulder.

^d Observed as a shoulder.

$L = t\text{-Bu-pyca}$ at 20 °C, which is representative of those observed from the R-pyca ligand series. Here the initial spectrum was recorded approximately 5 s after irradiation, and subsequent spectra were recorded at 30-min intervals in the dark. Approximately 1×10^{-4} M $W(CO)_6$ has been determined to undergo photodissociation (see Experimental Section). These absorption spectra depict an absorbance increase at ~400 nm immediately following photolysis and then a relatively slow growth centered at 534 nm that is characteristic of the metal to ligand charge-transfer (MLCT) transition of the chelated $W(CO)_4(t\text{-Bu-pyca})$ product. A sharp isosbestic point observed at 430 nm indicates that this reaction is uncomplicated by side or subsequent thermal processes. Similar spectral sequences were observed for each of the other R-pyca ligands studied, although the spectral changes took place much more rapidly in these molecules.

In the case of the R-pyca' ligands the spectral sequence during the first minute of reaction is complicated by competitive scavenging of solvent impurities; the spectral sequence is analogous to that observed from the closely related 1,4-di-*tert*-butyl-1,4-diazabutadiene ligand, previously studied in much detail.^{4b} Absorption spectra recorded immediately following photolysis exhibit maxima in the 400–420 nm region, with considerable variation noted between individual experiments and different methods of solvent purification. This type of behavior indicates that the R-pyca' ligands are relatively poor scavengers of the primary photoproduct and that solvent impurities are involved in the complex coordination. After the initial 1-min scavenging period the reaction proceeds in a manner identical with that of the above R-pyca system.

Reaction products are $W(CO)_4L$ complexes in each case, and these have been independently isolated and characterized. Electronic absorption data and assignments for these compounds are summarized in Table I; each complex exhibits a low-lying MLCT transition and ligand field (LF) transitions are observed at higher energy.^{7,10} Importantly, the final absorption spectra (A_∞) in the kinetic experiments

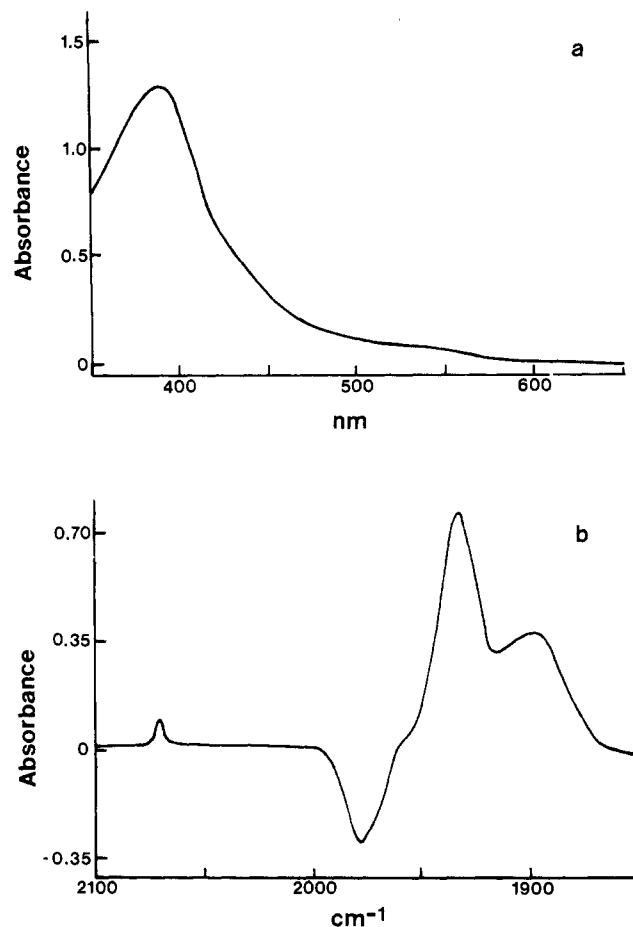


Figure 2. Difference (a) electronic absorption and (b) FT-IR spectra obtained by subtracting spectral data of unphotolyzed solution from that recorded immediately after photolysis at 20 °C. Visible and FT-IR data were recorded from deoxygenated benzene and methylene chloride solutions, respectively. Spectra represent the monodentate $W(CO)_5(t\text{-Bu-pyca})$ transient species.

are identical with the isolated $W(CO)_4L$ complexes, confirming the reaction products.

Figure 2a depicts the difference electronic absorption spectrum obtained in the above experiment. Here the spectral data of the unphotolyzed solution (5×10^{-4} M $W(CO)_6$ and 1×10^{-2} M $t\text{-Bu-pyca}$) have been subtracted from the data recorded immediately after photoexcitation. The difference spectrum is consistent with a monodentate $W(CO)_5(t\text{-Bu-pyca})$ reaction intermediate, as it exhibits characteristic LF absorptions at 404 and 478 (sh) nm corresponding to the $^1A(e^4b_2^2) \rightarrow ^1E(e^3b_2^2a_1^1)$ and $^1A(e^4b_2^2) \rightarrow ^3E(e^3b_2^2a_1^1)$ transitions, respectively.¹¹ As noted previously, it is not uncommon to observe the spin-forbidden $^1A \rightarrow ^3E$ LF band in the absorption spectra of $W(CO)_5L$ type complexes.¹² The weak absorption noted at 534 nm (see Figure 2a) is associated with a small amount of $W(CO)_4(t\text{-Bu-pyca})$ that is photochemically formed in the experiment. The difference spectra obtained for all the ligands studied exhibit similar features, and these are summarized in Table I. At this time we have been unable to isolate any of the $W(CO)_5L$ intermediates, although a number of other stable monodentate species (where $L =$ a normally chelating ligand) have recently been reported.⁵

FT-IR spectra have been recorded throughout the kinetic experiment, and the difference spectrum obtained

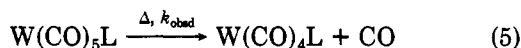
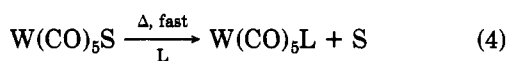
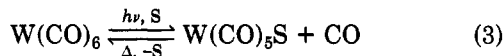
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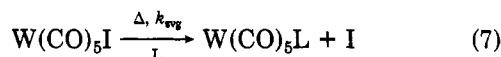
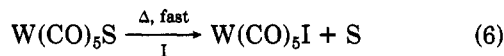
(12) Lees, A. *J. Chem. Rev.* 1987, 87, 711 and references therein.

immediately after irradiation when L = *t*-Bu-pyca is shown in Figure 2b. This result strongly supports the existence of the monodentate W(CO)₅L species as the reaction intermediate because the bands at 2072, 1929, and 1898 cm⁻¹ are consistent with the C_{4v} arrangement of the carbonyl ligands in this complex; these features correspond to the A₁¹, E, and A₁² modes, respectively.¹³ The intense negative absorption band centered at 1974 cm⁻¹ represents W(CO)₆ that is consumed during the photolysis. At the end of the kinetic experiment the infrared features of W(CO)₄(*t*-Bu-pyca) at 2008, 1895, 1878, and 1827 cm⁻¹ were recorded; these bands are the A₁^{1a}, B₁, A₁^{1b}, and B₂ modes, respectively, for this C_{2v} symmetry species.

The following sequence (eq 3-5) is consistent with these spectral observations.



The initial photoproduct of W(CO)₆ has been established to be the unsaturated species W(CO)₅, which is known to react rapidly to form the weakly bound solvent complex W(CO)₅S (eq 3).¹⁴ In the case of L = R-pyca the experimental data indicates that the solvent complex is efficiently scavenged by the approximately 100-fold concentration excess of L to form the W(CO)₅(R-pyca) intermediate, where the normally bidentate ligand is coordinated in a monodentate fashion. In contrast, when L = R-pyca' the initial coordination is relatively slow and involves competitive scavenging by solvent impurities (I), as noted above.^{4b} However, the subsequent conversion to W(CO)₅(R-pyca') is complete within 1 minute of reaction, that is, $k_{\text{avg}} > 3.5 \times 10^{-2} \text{ s}^{-1}$ at 10⁻² M [L]. Therefore, for L = R-pyca', eq 4 is replaced by eq 6 and 7. In all these



reactions no IR or UV-visible spectral evidence was obtained indicating the formation of ligand-bridged (OC)₅W-L-W(CO)₅ species,¹⁵ although it is not anticipated that these molecules would be produced with such an excess concentration of scavenging ligand available. Furthermore, the scavenging rates were determined to be independent of primary photoproduct concentration (this was varied by changing the photolysis time), and this observation is not supportive of binuclear complexation.

Kinetic data have been obtained for each of the reactions where monodentate W(CO)₅L extrudes CO and forms the chelated W(CO)₄L complex (eq 5). In each reaction the growth of absorbance representing W(CO)₄L product was observed to be exponential, that is, plots of ln [(A_∞ - A_t)/(A_∞ - A_i)] vs time are linear, with slope = k_{obsd}. Here A₀ is defined as the initial absorbance, A_t is the absorbance at time *t*, and A_∞ is the final absorbance reached. All

Table II. First-Order Rate Constants for the Reaction of Photoproduct W(CO)₅L To Form W(CO)₄L and CO in Deoxygenated Benzene at 20 °C^a

ligand (L)	k _{obsd} , s ⁻¹
<i>n</i> -Bu-pyca	1.7 (± 0.1) × 10 ⁻²
<i>i</i> -Pr-pyca	2.8 (± 0.2) × 10 ⁻³
Ph-pyca	2.0 (± 0.2) × 10 ⁻³
<i>t</i> -Bu-pyca	1.5 (± 0.1) × 10 ⁻⁵
<i>n</i> -Bu-pyca'	8.2 (± 0.8) × 10 ⁻³
<i>i</i> -Pr-pyca'	8.6 (± 0.9) × 10 ⁻³
Ph-pyca'	3.2 (± 0.3) × 10 ⁻³
<i>t</i> -Bu-pyca'	2.6 (± 0.3) × 10 ⁻³

^a W(CO)₅L complex is generated in ~1 × 10⁻⁴ M concentration following UV photolysis of 5 × 10⁻⁴ M W(CO)₆ solutions containing 1 × 10⁻² M entering ligand.

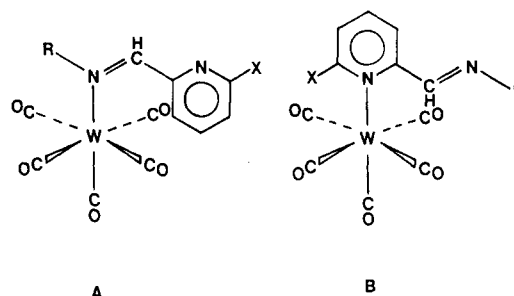


Figure 3. Stereochemistry of the linkage isomers of the monodentate W(CO)₅L intermediate.

absorbance values were recorded at a fixed wavelength in the MLCT region. A typical kinetic plot is shown in Figure 1. Each of the reactions yielded a single first-order rate constant (k_{obsd}) and these values are listed in Table II. In accordance with a first-order kinetic process for W(CO)₅L the rates were observed to be independent of ligand concentration over the 1 × 10⁻³–5 × 10⁻² M range. In addition, source light from the spectrometer was determined to have no measurable effect on the reaction kinetics as the rate data were not changed on varying the spectrometer acquisition time.

It is noticeable that the observed chelation rate data for these photoproduct W(CO)₅L intermediates are considerably increased over the rates known for the ligand substitution of CO¹⁶ or L¹⁷ from M(CO)₅L type complexes and of CO loss from M(CO)₆ (M = Cr, Mo, W) in solution.¹⁸ Clearly when the ligand is already attached in a monodentate configuration, the associating nucleophile contributes substantially to the CO extrusion process.

Significantly, a single reaction rate constant was determined for each of the ligands studied; thus only one process occurs in the ring closure mechanism. Although these diimine ligands have two possible sites for coordination to the metal center, the results suggest that a single W(CO)₅L species is obtained in each photoreaction. When L = R-pyca, the kinetic data illustrate that the rate of chelation depends substantially on the nature of the ligand substituent group R, following the order R = *n*-Bu > *i*-Pr ~ Ph > *t*-Bu (see Table II). We note that this order is closely related to the amount of steric hindrance about the aliphatic nitrogen atom of the R-pyca ligand. The ligand basicity does not appear to account for these rate differ-

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ences because the reactions for $R = t\text{-Bu}$ and $n\text{-Bu}$ differ by approximately 3 orders of magnitude in k_{obsd} , yet the pK_a values for their corresponding parent amines are almost equivalent.¹⁹ Therefore, it is concluded that for $L = R\text{-pyca}$ the pyridine nitrogen atom initially scavenges the $W(\text{CO})_5\text{S}$ photoproduct and that the slow chelation reaction occurs via the coordination of the aliphatic nitrogen atom. Contrastingly, when $L = R\text{-pyca}'$, the kinetic data illustrate little dependence on the ligand substituent group R (see Table II). Thus, it is concluded that for $L = R\text{-pyca}'$ the aliphatic nitrogen atom initially scavenges the $W(\text{CO})_5\text{S}$ photoproduct and the ring closure process involves coordination by the pyridine nitrogen atom.

Figure 3 depicts the stereochemistries of two possible monodentate $W(\text{CO})_5\text{L}$ intermediates. The diimine ligands are shown in a trans configuration as both theoretical and experimental studies on related systems have concluded that the free ligands exist in this conformation as solids and in solution.²⁰ Rotation about the $\text{C}_2\text{-C}_2'$ bond is needed to produce the cis chelation arrangement, although this energy barrier may be rather small as it has been calculated to be between 20 and 28 kJ mol^{-1} for other diimines.^{20g} Structure A illustrates the monodentate $W(\text{CO})_5\text{L}$ intermediate that results when the aliphatic nitrogen atom of the ligand has scavenged the $W(\text{CO})_5\text{S}$ photoproduct. It is noted that this arrangement involves substantial steric hindrance and electronic repulsion by the interaction of the pyridine ring with the carbonyl ligands. Structure B depicts the monodentate $W(\text{CO})_5\text{L}$ intermediate that is formed when the initial scavenging takes place at the pyridine nitrogen atom, and it can be

seen that this conformation involves much less steric hindrance. Hence, the observed kinetic data suggesting exclusive formation of structure B for the $W(\text{CO})_5(R\text{-pyca})$ intermediates may be rationalized on the basis of steric constraint. On the other hand, for $L = R\text{-pyca}'$ the kinetic results imply that structure A is predominantly formed, presumably because the methyl group precludes initial coordination at the pyridine nitrogen atom.

The ligand scavenging observations are also in accordance with this reasoning. This is because when $L = R\text{-pyca}$, the initial scavenging of $W(\text{CO})_5\text{S}$ by L was seen to be efficient and take place rapidly, and when $L = R\text{-pyca}'$, the scavenging was relatively slow and it suffered competition from solvent impurities. It is striking that the increased steric hindrance about the pyridine nitrogen atom in $R\text{-pyca}'$ has such a significant effect on the ability of this ligand (even at 10^{-2} M) to scavenge $\sim 10^{-4}$ M of the $W(\text{CO})_5\text{S}$ photoproduct, whereas extremely poor donor ligands such as N_2 or Ar can scavenge the unsaturated $W(\text{CO})_5$ species at near diffusion-controlled rates.^{14c,d} The results presented here clearly demonstrate that the steric properties of the entering ligand is a major factor in determining the scavenging mechanism of the $W(\text{CO})_5$ primary photoproduct.

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Registry No. $n\text{-Bu-pyca}$, 7032-24-8; $i\text{-Pr-pyca}$, 7032-23-7; Ph-pyca , 7032-25-9; $t\text{-Bu-pyca}$, 21478-42-2; $n\text{-Bu-pyca}'$, 71769-88-5; $i\text{-Pr-pyca}'$, 78004-29-2; $\text{Ph-pyca}'$, 27768-36-1; $t\text{-Bu-pyca}'$, 106155-16-2; $W(\text{CO})_6$, 14040-11-0; $W(\text{CO})_5(n\text{-Bu-pyca})$, 107339-94-6; $W(\text{CO})_5(i\text{-Pr-pyca})$, 107339-93-5; $W(\text{CO})_5(\text{Ph-pyca})$, 102190-24-9; $W(\text{Co})_5(t\text{-Bu-pyca})$, 102190-23-8; $W(\text{CO})_5(n\text{-Bu-pyca}')$, 117203-02-8; $W(\text{CO})_5(i\text{-Pr-pyca}')$, 117203-03-9; $W(\text{CO})_5(\text{Ph-pyca}')$, 117203-04-0; $W(\text{CO})_5(t\text{-Bu-pyca}')$, 117203-05-1; $W(\text{CO})_4(n\text{-Bu-pyca})$, 107339-96-8; $W(\text{CO})_4(i\text{-Pr-pyca})$, 36107-20-7; $W(\text{CO})_4(\text{Ph-pyca})$, 36107-21-8; $W(\text{CO})_4(t\text{-Bu-pyca})$, 107339-95-7; $W(\text{CO})_4(n\text{-Bu-pyca}')$, 117203-06-2; $W(\text{CO})_4(i\text{-Pr-pyca}')$, 117203-07-3; $W(\text{CO})_4(t\text{-Bu-pyca}')$, 117203-08-4; $W(\text{CO})_4(\text{Ph-pyca}')$, 117203-09-5.

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Laser-Ion Beam Photodissociation Studies of Ionic Cluster Fragments of Iron Carbonyls: $\text{Fe}_x(\text{CO})_y^+$ ($x = 1-3$; $y = 0-6$)

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Ionic cluster fragments of the type $\text{Fe}_x(\text{CO})_y^+$ ($x = 1-3$; $y = 0-6$) are mass resolved by high-resolution mass spectrometry ($R = 7500$) and then photodissociated. The photofragment ions are mass analyzed by an electrostatic analyzer. The ions studied include $\text{Fe}(\text{CO})_y^+$ ($y = 1-5$), $\text{Fe}_2(\text{CO})_y^+$ ($y = 0-6$), and $\text{Fe}_3(\text{CO})_y^+$ ($y = 0-4$) derived from $\text{Fe}_3(\text{CO})_{12}$ neutral. Relative photofragment ion yields for each photodissociating ion and upper and lower limits to the average bond dissociation energies for both $\text{Fe}^+\text{-CO}$ and $\text{Fe}^+\text{-Fe}$ bonds are reported. Average metal-ligand binding energies in the range 19.5-58.6 kcal/mol are measured for iron-carbonyl bonds. The photodissociation threshold for $\text{Fe}_3^+ \rightarrow \text{Fe}_2^+ + \text{Fe}$ is found to be <27.8 kcal/mol. The Fe_2^+ ion does not photodissociate over the wavelength range (458-514.5 nm), placing the lower limit for the bond dissociation energy at <62.4 kcal/mol.

Introduction

The chemical and physical properties of ionic transition-metal species, e.g., monatomic bare and ligated metals, as well as dimer, trimer, and small metal clusters, have been the subject of intense research over the past decade.¹⁻⁶

There have been numerous recent studies that demonstrate the change in chemical reactivities as a function of

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