Photochemical Metathesis of a Tungsten–Carbene Complex

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Abstract: Photolysis of $[W(CO)_5CPh_2]$ (**1**) in the presence of $CH_2{=}CPh(C_6H_4\text{-}p\text{-}OCH_3)$ results in metathetical exchange of the alkylidene ligand with the aromatic alkylidene moiety of the alkene to form the new carbene complex $[W(CO)_5CPh(C_6H_4\text{-}p\text{-}OCH_3)]$ (**2**), which has also been prepared by alkylation of $[W(CO)_5C(OMe)Ph]$. The quantum yield for the photochemical metathesis is lower at 12–14 °C than at 27–29 °C. Experiments with filters have shown that the reaction is wavelength dependent and follows irradiation into an absorption of **1** at 375 nm which is assigned to a ligand field excitation in which the $d_{x^2-y^2}$ orbital is occupied. The photochemical methathesis is suppressed by an atmosphere of CO, and it is suggested that occupation of the $d_{x^2-y^2}$ orbital, which is σ^* with respect to the cis carbonyl ligands of **1**, results in dissociation of a cis carbonyl ligand to form a $[W(CO)_4CPh_2]$ fragment. Coordination of the alkene to this unsaturated fragment results in metallacyclobutane formation and subsequent metathetical exchange.

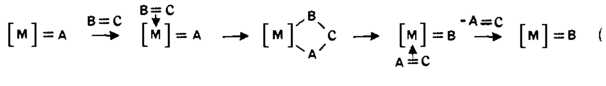
There have been few studies to date of the photochemistry of transition-metal carbene complexes, despite the recent general interest in the chemistry of such complexes.[1] This is particularly surprising in the case of the pentacarbonyl/carbene complexes of the group 6A metals ($[M(CO)_5L]$, M = Cr, Mo, W) since other aspects of the chemistry of these systems have been extensively studied,[1] the complexes are readily available, and the complexes contain two potentially photoactive ligands in their coordination spheres.

Photolysis of carbonyl/carbene complexes could, in principle,[2] lead to photochemistry based on primary dissociation of a carbonyl ligand or of the carbene ligand or involving direct reaction of a suitable substrate with an excited state of the complex. In practice, carbonyl loss is the only well-documented reaction pathway for such systems: although several of the previous photochemical studies of carbonyl/carbene complexes have reported overall loss or transfer of the carbene ligand,[3-5] there is little mechanistic data supporting primary loss of the carbene in these reactions. The existence of photochemical reaction pathways involving CO loss is, however, indicated by a report from Fischer's laboratories describing the stereospecific (at low temperatures) synthesis of tetracarbonyl/phosphine/carbene complexes of Cr and W by photolysis of $[M(CO)_5C(OR)R']$ complexes in the presence of phosphines (eq 1).[6] More recently, Casey has used photochemical

$$[M(CO)_5C(OR)R'] + PPh_3 \xrightarrow{h\nu} cis\text{-}[M(CO)_4(PPh_3)C(OR)R'] + CO \quad (1)$$

dissociation of CO to prepare cis carbene/alkene complexes of W.[7] The most convincing evidence for the importance of primary CO loss in these systems, however, comes from the elegant study by Geoffroy and co-workers,[8] published after the experiments described below were completed, in which they demonstrated that loss of a cis CO ligand is the only detectable photoreaction of $[W(CO)_5C(OMe)Ph]$ in the presence of a variety of trapping agents.

Photochemical loss of a carbonyl ligand from an $[M(CO)_5]$ carbene complex would form a coordinatively unsaturated species which could undergo subsequent thermal reaction sequences. In the presence of an alkene, for example, formation of a cis alkene/carbene complex could lead to facile exchange of the carbene ligand with one of the alkylidene moieties of the alkene by the well-known metallacyclobutane mechanism for alkene metathesis (eq 2).[9]



(2)

Fischer-type carbene complexes, containing α-heteroatomic substituents,[1a-c] are unlikely to be good substrates for such metathetical reaction sequences, since the known thermal reactions of those complexes with alkenes result in cyclopropanation rather than metathesis.[10,1f] A much more promising substrate is the closely related complex $[W(CO)_5CPh_2]$ (**1**) first reported by Casey[11] and prepared independently by Fischer.[12] Studies of the thermal reactions of alkenes with $[W(CO)_5CPh_2]$ have shown, for example, that reaction of **1** with vinyl ethers results in metathetical transalkylidenation to give isolable alkoxy-stabilized carbene complexes[13,14] (e.g., eq 3), and even in the case of alkenes

$$[W(CO)_5CPh_2] \xrightarrow{CH_2{=}C(OCH_3)Ph} [W(CO)_5C(OCH_3)Ph] + CH_2{=}CPh_2 \quad (3)$$

which could not give rise to stabilized carbene complexes, analysis of the organic products indicated that **1** had reacted metathetically with the alkenes;[13] unstable carbene complexes were presumably formed and then decomposed to the observed $[W(CO)_6]$.

In view of these results it seemed possible that photolysis of **1** in the presence of suitable alkenes could lead to formation of carbene complexes lacking stabilizing heteroatomic substituents (typically unstable under the conditions necessary for thermal metathesis of **1**) if photolysis of **1** resulted in loss of a carbonyl ligand. We now wish to report that **1** does undergo a photochemically promoted metathesis reaction and that mechanistic studies have shown that the reaction occurs via initial carbonyl dissociation from **1**. Evidence has been obtained that this dissociation is highly wavelength dependent, and examination of the electronic spectra of **1** and its metathesized product have led to an interpretation of this dependence in terms of carbonyl dissociation from a ligand field excited state.

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Experimental Section

General. All manipulations were carried out under dry nitrogen by using standard Schlenk tube techniques. Spectral grade cyclohexane was used as received. AR grade CCl_4 was used as received.

The literature methods were used to prepare $[W(CO)_5CPh_2]$[15] and $[W(CO)_5COMePh]$.[16] The method reported for the preparation of $CH_2{=}CPh_2$[17] was used to convert $CH_3CO(C_6H_4\text{-}p\text{-}OCH_3)$ on a 30-g scale (50% yield after distillation and recrystallization from pentane) into $CH_2CPh(C_6H_4\text{-}p\text{-}OCH_3)$: bp 140–142 °C (16 mm); ^1H NMR (80 MHz, $CDCl_3$) δ 7.41 (s, 5, C_6H_5), 7.38 (d, 2, J = 8.8 Hz, $C_6H_2^AH_2^B$), 6.95 (d, 2, J = 8.8 Hz, $C_6H_2^AH_2^B$), 5.50 (d, 1, J = 1.3 Hz, $=CH^AH^B$), 5.45 (d, 1, J = 1.3 Hz, $=CH^AH^B$), 3.80 (s, 3, OCH_3).

All photolyses used a Hanovia 450-W medium-pressure Hg arc lamp in a water-cooled jacket. Photolyses were carried out in 30-mm quartz or Pyrex Schlenk tubes placed at 23 cm from the lamp.

Photochemical Preparation of $[W(CO)_5C(C_6H_5)(C_6H_4\text{-}p\text{-}OCH_3)]$. A solution of $[W(CO)_5C(C_6H_5)_2]$ (0.038 g, 0.078 mmol) in cyclohexane (5 mL) was added to a solution of $CH_2{=}C(C_6H_5)(C_6H_4\text{-}p\text{-}OCH_3)$ (1.64 g, 7.8 mmol) in cyclohexane (35 mL) and the mixture was placed in a Schlenk tube 23 cm from the lamp. The solution was irradiated through a Pyrex filter using a thermocouple in the solution to monitor the reaction temperatures, which stayed at 25 ± 1 °C throughout. After 4 h absorption spectra showed that λ_{max} of the solution (in the visible) had changed from 485 to 509 nm.

When irradiation was completed the solution was concentrated to dryness under reduced pressure. Extraction with cold pentane (−10 °C) was continued until the solid was colorless. The pentane extracts were concentrated to dryness and redissolved in 5 mL of CCl_4 before being placed on top of a silica gel chromatography column (150 g) packed under pentane and flushed with degassed CCl_4. The silica gel (100–200 mesh) had been deactivated by addition of water until the R_f for $PhN{=}N(C_6H_4\text{-}p\text{-}NH_2)$ was 0.50 in a dry packed capillary using 1:1 benzene–pentane as eluant. The jacketed column was cooled to −15 °C with chilled 2-propanol and the products were eluted with CCl_4. The two colored bands were collected in Schlenk tubes cooled to 0 °C and the solvent was removed under reduced pressure. Occluded CCl_4 was removed by dissolving the samples in pentane and removing the pentane under vacuum to give pure (^1H NMR, solution IR in pentane) samples of $[W(CO)_5CPh_2]$ (first band, 7.4 mg, 0.015 mmol) and $[W(CO)_5CPh(C_6H_4\text{-}p\text{-}OCH_3)]$ (15.1 mg, 0.029 mmol ≡ 37% yield); IR (cyclohexane, ν C≡O) cm^{-1} 2063 m (equatorial A_1), 1956 s (E; the axial A_1 is presumably coincident); ^1H NMR (80 MHz, C_6D_6) δ 7.17 (m, 9, C_6H_5 and C_6H_4), 3.22 (s, 3, OCH_3); ^{13}C NMR (75.45 MHz, THF, 240 K; ppm) 346.3 (W═C), 211.7 (satellites, J_{W-C} = 126 Hz, trans CO), 197.2 (satellites, J_{W-C} = 126 Hz, cis CO), 165.8 (t, ^3J = 7 Hz, ipso C of $PhOCH_3$), 165.7 (s, *p*-C of $PhOCH_3$), 155.0 (t, ^3J = 7 Hz, ipso C of Ph), 134.5 (dd, ^1J = 160 Hz, ^3J = 8 Hz, *m*-C of $PhOCH_3$), 127.3 (dt, ^1J = 161 Hz, ^3J = 7 Hz, *p*-C of Ph), 126.3 (dd, ^1J = 162 Hz, ^3J = 7 Hz, *o*-C of $PhOCH_3$), 121.2 (dt, ^1J = 159 Hz, ^3J = 6 Hz, *o*-C of Ph), 113.3 (dd, ^1J = 163 Hz, ^3J = 4 Hz, *m*- C of Ph), 54.8 (q, J = 146 Hz, OCH_3); mass spectrum (parent ion, ^{184}W), *m/e* 522. Anal. Calcd for $C_{19}H_{12}O_6W$: C, 43.87; H, 2.33. Found (Galbraith Laboratories, Knoxville, TN): C, 44.07; H, 2.38.

$[W(CO)_5C(C_6H_5)(C_6H_4\text{-}p\text{-}OCH_3)]$ from $[W(CO)_5C(OCH_3)(C_6H_5)]$. This reaction was based on the literature preparation of $[W(CO)_5CPh_2]$.[15] A solution of $[W(CO)_5C(OCH_3)(C_6H_5)]$ (0.514 g, 1.16 mmol) in diethyl ether (30 mL) was cooled to −78 °C, and 5.35 mL of a 0.32 M solution of $LiC_6H_4\text{-}p\text{-}OMe$ (prepared by treatment of $BrC_6H_4\text{-}p\text{-}OCH_3$ with 3 equiv of Li dispersion in diethyl ether) was added dropwise to the solution. The resulting red-brown solution was stirred at −78 °C for 1 h before addition of 5.2 mL of 0.43 M HCl in diethyl ether at −78 °C. After 45 min the intensely colored purple solution was warmed slowly to 0 °C and 5 g of SiO_2 added. The solvent was removed under vacuum and the solids were transferred to the top of a jacketed chromatography column containing 250 g of SiO_2 packed in pentane. The column was eluted with pentane at −15 °C to remove excess $[W(CO)_5C(OCH_3)(C_6H_5)]$ as a red band, and $[W(CO)_5C(C_6H_5)(C_6H_4\text{-}p\text{-}OCH_3)]$ was then eluted as a purple band by gradually adding diethyl ether to the eluant. The product was collected at 0 °C and the solvent removed under vacuum until the solution was saturated. Cooling to −78 °C gave 0.323 g (0.62 mmol ≡ 53%) of $[W(CO)_5C(C_6H_5)(C_6H_4\text{-}p\text{-}OCH_3)]$ as a purple crystalline solid.

Thermal Reaction of $[W(CO)_5C(C_6H_5)_2]$ with $CH_2{=}C(C_6H_5)(C_6H_4\text{-}p\text{-}OCH_3)$. A solution of $[W(CO)_5C(C_6H_5)_2]$ (0.246 g, 0.50 mmol) in cyclohexane (≈50 mL) was added to a solution of $CH_2{=}C(C_6H_5)(C_6H_4\text{-}p\text{-}OCH_3)$ (1.051 g, 5.00 mmol) in cyclohexane (≈150 mL). The mixture was wrapped with Al foil and placed in a 30 °C water bath. Aliquots of 0.25 mL were removed at intervals and their absorbance spectra recorded after dilution to 10 mL. After 2 weeks the solvent was removed under vacuum and the mixture chromatographed on a silica gel column to give $[W(CO)_6]$ (0.054 g, 30%), $CH_2{=}C(C_6H_5)_2$ (0.020 g, 22%), and a complex mixture of other organic products.

Photochemical Reaction of $[W(CO)_5CPh_2]$ with $CH_2{=}C(C_6H_5)(C_6H_4\text{-}p\text{-}OCH_3)$: Spectroscopic Studies Using Electronic Absorption. These experiments were carried out with use of an ≈2 × 10^{-3} M solution of $[W(CO)_5CPh_2]$ in cyclohexane which was ≈200 × 10^{-3} M in $CH_2{=}C(C_6H_5)(C_6H_4\text{-}p\text{-}OCH_3)$.

(1) CO Inhibition. For the CO inhibition experiment 10 mL of this solution was put under an atmosphere of CO in a Pyrex Schlenk tube and the sample irradiated for 3 h. Absorption spectra of a 1.0-mL aliquot diluted to 10 mL showed that λ_{max} of the solution had not changed from 485 nm while the absorbance had decreased from 0.980 to 0.793.

(2) Wavelength Dependence. For the wavelength dependence studies, similar samples under an atmosphere of N_2 were irradiated through a variety of filter combinations and absorption spectra of 0.25-mL aliquots diluted to 10 mL recorded at intervals. Two experiments were carried out:

(a) A sample with initial λ_{max} 485 nm, A = 0.48, was irradiated through a Hoya L-42 filter (transmittance <10% below 420 nm) for 2 h to give a solution with λ_{max} 485 nm, A = 0.35. The filter was removed and irradiation continued for a further 2 h to give a solution with λ_{max} 502 nm, A = 0.26.

(b) A sample with initial λ_{max} 485 nm, A = 0.53, was irradiated through a combination of a Hoya U-330 and Hoya JD-48 filters (maximum transmittance 45% at 380 nm, <5% transmittance above 410 nm and below 360 nm) to give after 2.5 h a solution with λ_{max} 490 nm, A = 0.38. After 4.5 h the solution had λ_{max} 495 nm, A = 0.295.

(3) Temperature Dependence. The temperature-dependent studies were carried out by dividing a sample between two Schlenk tubes maintained in identical well-stirred Pyrex water baths, one of which was at ambient temperature while the other was maintained approximately 15 °C below ambient by means of an ice-filled cooling finger. The temperatures of the two solutions were monitored intermittently by means of a thermocouple inserted through a serum cap into the solutions and remained within the ranges 27–29 and 12–14 °C, respectively. The solutions were placed 23 cm from the lamp and irradiated simultaneously. Irradiation was stopped at 30-min intervals and the absorption spectrum of 0.25-mL aliquots diluted to 10 mL recorded. The solutions were maintained at 27–29 and 12–14 °C, respectively, for the time (20 min) between irradiation periods. The results of these experiments are recorded in the supplementary table and in Figure 1.

Results

Photolysis of $[W(CO)_5CPh_2]$ (**1**) in the presence of 10 equiv of $CH_2{=}CPh(C_6H_4\text{-}p\text{-}OCH_3)$ in cyclohexane resulted in a gradual change in the color of the solution from red to red/purple as the alkene reacted with the alkylidene complex to give a new alkylidene complex $[W(CO)_5CPh(C_6H_4\text{-}p\text{-}OCH_3)]$ (**2**) and the metathesized alkene (TLC) (eq 4).

$$\underset{\mathbf{1}}{[W(CO)_5CPh_2]} + CH_2{=}CPh(C_6H_4\text{-}p\text{-}OCH_3) \xrightarrow{h\nu} \underset{\mathbf{2}}{[W(CO)_5CPh(C_6H_4\text{-}p\text{-}OCH_3)]} + CH_2{=}CPh_2 \quad (4)$$

Absorption spectroscopy was used to monitor the course of the reaction at ambient temperatures, and it was observed that λ_{max} of the principal visible absorption of the solution changed from 485 to 511 nm over a period of ca. 6 h. The ratio of **1**:**2** at various intermediate times was determined from the corresponding λ_{max} by examination of a plot of λ_{max} vs. composition (calculated from the absorption spectra of pure **1** and **2** in the presence of 100 equiv of the alkene) on the assumption that **1** and **2** are the only materials present with absorptions in the visible (solution IR showed that **1**, **2**, and $[W(CO)_6]$ were the only metal carbonyls present). The concentrations of **1** and **2** present were then calculated from their ratios and the corresponding absorbance. Data from a typical experiment are recorded in Table SIa of the supplementary material and the calculated concentrations of **1** and **2** are plotted against irradiation time in Figure 1a.

The increase in concentration of **2** slows markedly during the photolysis (and eventually becomes negative), and maximum yields

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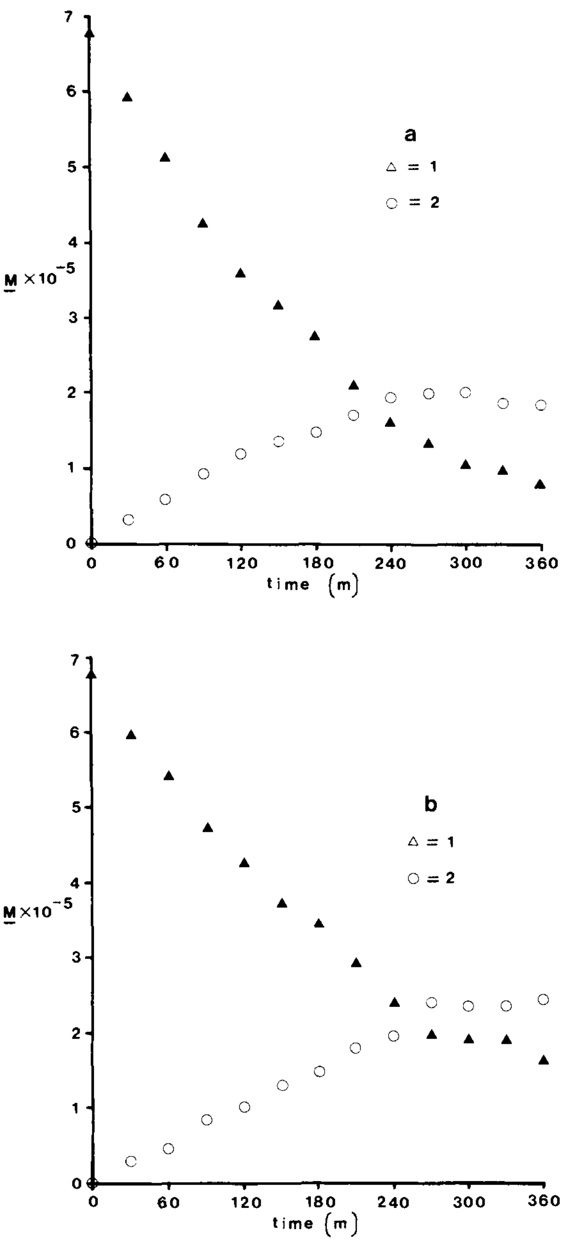

Figure 1. Composition of the reaction mixture during photolysis as determined by absorption spectroscopy: (a) at 27–29 °C; (b) at 12–14 °C.

are obtained if the reaction is stopped at concentrations corresponding to λ_{max} ~508 nm. This limitation on the optimum extent of reaction reflects a number of factors, including the ability of the **2** being formed to act as an internal filter and the increasing rate of loss of **2** by thermal decomposition and photochemical degradation as the concentration of **2** increases.

The course of the photochemical reaction is sensitive to the temperature of the solution: attempts to carry out the photolysis in a commercial immersion photoreactor resulted in extensive decomposition, probably as a consequence of thermal hot spots on the internal surface of the reactor, and the reaction proceeded more slowly below ambient temperatures. This phenomenon was observed in several experiments carried out at ca. −20 °C and has been examined quantitatively by using absorption spectroscopy to monitor the course of photolysis of a solution of **1** and $CH_2{=}CPh(C_6H_4\text{-}p\text{-}OCH_3)$ maintained at 12–14 °C under conditions otherwise identical with those used for the photolysis at ambient temperatures. (This experiment was run in parallel with the experiment for which ambient data are reported in Figure 1a; see Experimental Section). The changing values of λ_{max} and *A* for the solution are recorded in Table SIb in the supplementary material, together with the changing composition of the solution as calculated from these data. The composition of the solution is plotted against elapsed irradiation time in Figure 1b. It was not possible to examine the reaction quantitatively at temperatures much below 12 °C, since (i) the alkene has limited solubility in cold hydrocarbons and begins to precipitate at temperatures below 10 °C and (ii) the reaction does not proceed cleanly in more polar solvents. In diethyl ether at ~10 °C, for example, the formation of $[W(CO)_5C(C_6H_5)(C_6H_4\text{-}p\text{-}OCH_3)]$ was accompanied by extensive decomposition, as indicated by the decrease in absorbance of the peak in the visible and the appearance of a new peak at 413 nm.

Pure **2** was isolated from the photolysis of **1** in the presence of the alkene at ambient temperatures in 37% yield as described in the Experimental Section. The ratio of alkene:**1** used is not critical; values of 10:1 and 100:1 resulted in similar reactions; the experiment described used a ratio of 100:1. The low solubility of the alkene in hydrocarbon solvents at −10 °C permitted preliminary separation of the organometallics from the bulk of the excess alkene, and the product was then purified by chromatography on deactivated silica gel at −15 °C. Successful separation depended critically on the activity of the chromatographic medium (Experimental Section), since **2** decomposed rapidly on both Fluorosil and active silica gel.

The new alkylidene complex was also prepared from $[W(CO)_5C(OCH_3)Ph]$ and $LiC_6H_4\text{-}p\text{-}OCH_3$ by using the method reported by Casey for the preparation of **1**.[15] Characterization was based on analysis and on spectroscopic data (^{1}H NMR, ^{13}C NMR, IR, and mass spectrum) reported in the Experimental Section.

The photochemical nature of the transalkylidenation was confirmed by a control experiment in which a mixture of **1** and 10 equiv of $CH_2{=}CPh(C_6H_4\text{-}p\text{-}OCH_3)$ in cyclohexane was allowed to stand in the dark at 30 °C and subsequent reaction monitored by absorption spectroscopy. After 17.5 h λ_{max} of the solution had shifted from the initial value of 485 (A = 0.920) to 491 nm (A = 0.342), and after 48 h to 495 nm (A = 0.065). The slow shift to the red indicates that there is some thermal transalkylidenation, but the reaction is much slower than the photochemical reaction and thermal decomposition is competitive, as indicated by the marked decrease in the absorbance of the solution. The only organometallic product isolated from the reaction was $[W(CO)_6]$, which could have been formed by decomposition of either **1** or **2**, but the isolation of a 22% yield of $CH_2{=}CPh_2$ did indicate that some metathesis had occurred.

It is clear from several considerations that photolysis must be effected by absorptions of **1** in the visible region. (i) The reaction proceeds just as well in Pyrex Schlenk tubes (cut-off at 320 nm) as it does in quartz Schlenk tubes. (ii) The alkene, with λ_{max} at 204 (ϵ 34 500), 237 (20 200) and 260 nm (12 700), is present in large excess and would in any case act as an internal filter. Surprisingly, however, experiments with filters established that the principal visible absorption at 485 nm is photochemically inactive: absorption spectroscopy showed that no metathesis occurred when a 1:100 mixture of **1** and $CH_2{=}CPh(C_6H_4\text{-}p\text{-}OCH_3)$ in cyclohexane was irradiated through a filter that cut off radiation with a wavelength <420 nm and that metathesis began at a normal pace when the filter was removed. This shows that the 485-nm band is photochemically inactive and suggests that the remaining visible feature at 375 nm must be the photoactive absorption. This was confirmed by using absorption spectroscopy to monitor a similar sample which was irradiated with a narrow band of light centered at 380 nm. Metathesis proceeded normally under these conditions; the shift in λ_{max} indicated that the reaction occurred at less than half the speed observed with unfiltered light, but this can be attributed to the low transmittance of the filter combination used (45% maximum at 380 nm, 43% at 375 nm). In view of the thermal instability of both **1** and **2** no attempt was made to determine the quantum yield for the photochemical metathesis.

The alkylidene complex **2**, like **1**,[11a] is thermally unstable in solution. The stability depends to some extent on the nature of the solvent, and we have monitored the thermal decomposition

Table I. Solvent Dependence of Extinction Coefficients of 1 and 2 (Principal Absorption Only)

complex	solvent	λ_{max}, nm	ϵ
1	pentane	485	15 000
1	cyclohexane	485	14 200
1	Et_2O	485	12 000
2	pentane	513	20 300
2	cyclohexane	513	23 100
2	Et_2O	513	23 200

of the alkylidene complexes in both pentane and diethyl ether at 30 °C using absorption spectroscopy. Both compounds undergo decomposition reactions which initially appear to be first order in the tungsten complex, but which accelerate markedly after approximately 25% of the complex has decomposed. This differs from the bimolecular decomposition observed previously for a related carbene complex,[18] but may be consistent with the occurrence of an autocatalytic pathway analogous to that observed by Casey during the decomposition of $[W(CO)_5C(C_6H_4\text{-}p\text{-}CH_3)O(CH_2)_2CH{=}CH_2]$.[19] The overall observed half-lives for **1** are 11.1 h in pentane and 5.5 h in diethyl ether, and the observed half-lives for **2** are 15.0 and 8.0 h, respectively, in the same solvents. The increased stability of **2** relative to **1** is presumably a consequence of the electron-donating abilities of the *p*-methoxy substituent. In the course of these experiments we also observed that the extinction coefficients for the principal absorptions of the complexes in the visible region are dependent on the solvent medium (see Table I).

Discussion

The most probable mechanism for the photochemical metathesis reaction is that shown in eq 2, in which [M]=A is an unsaturated $[W(CO)_4CPh_2]$ fragment formed by photolytic loss of a carbonyl ligand from **1**. Coordination of the alkene to this fragment would then give an alkylidene/alkene complex, which could form the metathesized alkylidene/alkene complex via a six-coordinate tetracarbonylmetallocyclobutane. Replacement of the alkene by CO (present in solution from the photolysis) would generate the observed products.

Direct support for a reaction mechanism involving CO dissociation is provided by our observation that photolysis of **1** in the presence of $CH_2{=}CPh(C_6H_4\text{-}p\text{-}OCH_3)$ under an atmosphere of CO does not result in any metathesis. This experiment argues strongly against alternative mechanisms which have not been observed in thermal metatheses but which might become operative under photolytic conditions, such as direct $\pi + \pi$ addition of the C=C bond to the W=C bond to form a seven-coordinate metallacyclobutane. The proposed mechanism is also consistent with recent results from Casey's laboratories on a closely related system,[7] in which photolysis of $[W(CO)_5C(NHCH_2CH{=}CH_2)(C_6H_4\text{-}p\text{-}CH_3)]$, containing an alkene functionality attached to the carbenoid center through a side chain, leads to slow CO loss and formation of a remarkably stable cyclic tungsten–carbene–alkene complex. Formation of this molecule provides support both for the feasibility of photodissociation of a carbonyl ligand from a $[W(CO)_5L]$ complex and for the possible intermediacy of an alkene/carbene complex in the metathesis of **1**.

An important implication of CO inhibition of the metathesis reaction is that CO loss is probably a primary photoreaction of **1**. Geoffroy's work[8] has resolved conflicts between earlier reports on the photochemistry of [W(CO)$_5$C(OMe)Ph] and established that CO loss is the only detectable photoreaction of this typical heteroatom-substituted carbene complex, but the photochemistry of **1**, an archetypal carbonyl/carbene complex lacking a heteroatomic substituent, has remained confused. It has been reported[3] that photodecomposition of **1** in hexane was not inhibited by an atmosphere of CO, but Casey has also indicated that exchange of ^{13}CO for CO in **1** can be photochemically promoted.[20] Our results suggest that CO loss is a primary photoreaction, and the observation of a moderate yield of **2** despite the losses due to thermal decomposition and photodecomposition suggests that this may be the dominant photoreaction of **1** at 25 °C. These results are clearly consistent with Casey's data.

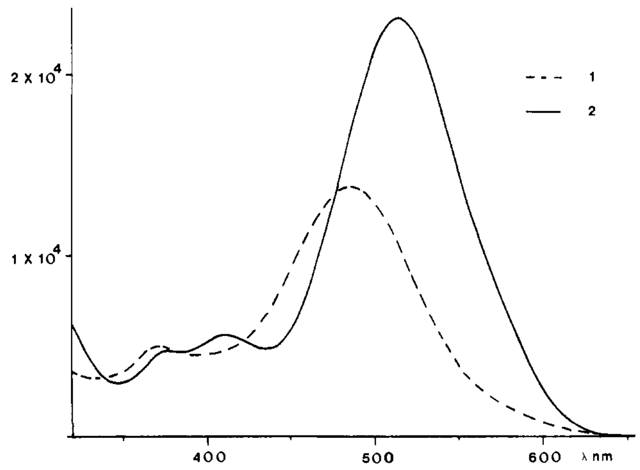

Figure 2. Absorption spectra of **1** and **2**.

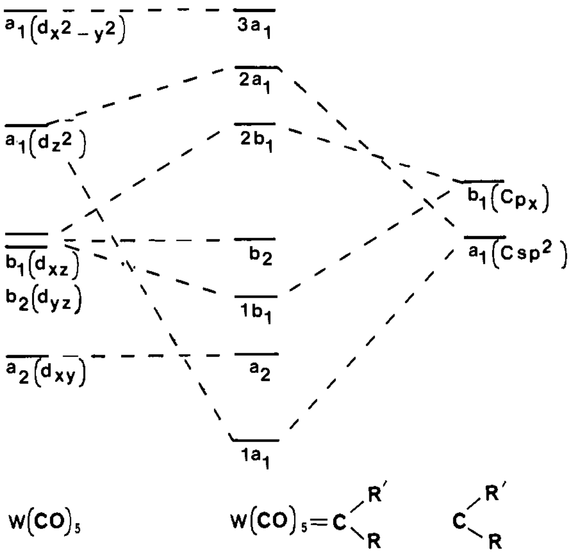

Figure 3. One-electron energy level diagram for $[W(CO)_5(\text{carbene})]$ complexes (C_{2v} symmetry).

The small but synthetically important temperature dependence observed for the photochemical metathesis of **1** is unlikely to reflect thermal effects on the primary photochemical process, since changes in product quantum yields for photochemical reactions more typically reflect differing temperature dependencies for competing secondary reactions[23] (although the photophysics of some d^6 carbonyl complexes is temperature dependent in the range 10–100 K[21,22]). One possible interpretation is that one of the thermal steps following CO loss (such as metallacyclobutane formation) proceeds at a rate which does not compete effectively with decomposition reactions below ambient temperatures. It is also possible that the efficiency of recombination of CO with the unsaturated $[W(CO)_4CPh_2]$ fragment decreases markedly around room temperature, possibly because more of the dissociated CO molecules leave the solvent cage.

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Table II. Absorption Spectra of $[W(CO)_5L]$ Carbene and Alkylidene Complexes

L	LF $^1A_1(b_2^2) \rightarrow {}^1B_2(b_2^1 3a_1^1)$ λ_{max} $(\epsilon)^c$	LF $^1A_1(b_2^2) \rightarrow {}^1B_2(b_2^1 2a_1^1)$ λ_{max} $(\epsilon)^c$	MLCT $^1A_1(b_2^2) \rightarrow {}^1A_2(b_2^1 2b_1^1)$ λ_{max} $(\epsilon)^c$	MLCT $^1A_1(b_2^2) \rightarrow {}^3A_2(b_2^2 2b_1^1)$ λ_{max} $(\epsilon)^c$
C(OMe)Ph^a (data from ref 8)	352 (6080)	n.o.^{d}	402 (10 500)	521 (576)
CPh_2^{b}	375 (5250)	n.o.^{d}	485 (14 200)	n.o.^{d}
$CPh(C_6H_4$-*p*-$OCH_3)$^{b}	376 (5500)	413 (6350)	513 (23 100)	n.o.^{d}

^{a} Hexane solution. ^{b} Cyclohexane solution. ^{c} λ_{max} in nm; ϵ in L mol^{-1} cm^{-1}. ^{d} Not observed.

Interpretation of the wavelength dependence observed for the metathesis of **1** depends on the assignment of the electronic spectrum of **1**. The spectra of **1** are **2** are shown in Figure 2 and tabulated in Table II together with our assignments. These are based on previous literature assignments[8] for the spectra of **1** and $[W(CO)_5C(OMe)Ph]$, with modifications necessitated by the observation that the spectrum of **2** contains three low-energy absorptions.

The assignments refer to the schematic one-electron energy level diagram for $[W(CO)_5(\text{carbene})]$ complexes shown in Figure 3.[8] This assumes C_{2v} local symmetry and that the carbene ligand acts as a σ-donor through a filled C_{sp^2} orbital directed along the *z* axis and as a π-acceptor through the empty C_{p_x} orbital. The important feature of the ordering of the occupied levels is that the b_2 (d_{yz}) level is expected to be the HOMO: the $1b_1$ (d_{xz}) and b_2 (d_{yz}) orbitals will be less stabilized by π-acceptor interactions with CO than the a_2 (d_{xz}) orbital, and the $1b_1$ orbital will have a stabilizing π-interaction with the C_{p_x} orbital on the carbene which will bring it below the b_2 orbital. The LUMO must be the $2b_1$ (π^*), primarily ligand C_{p_x} in character, since the lowest allowed absorption in **1**, **2**, and $[W(CO)_5C(OMe)Ph]$ is almost certainly metal to ligand charge transfer (MLCT) on several grounds: (a) the band is intense in all cases; (b) the intensity of the band is solvent dependent in both **1** and **2**; and (c) the position of the band is very sensitive to changes in the ligand. Thus the band shifts from 402 nm in $[W(CO)_5C(OMe)Ph]$ to 485 nm in **1** and to 513 nm in **2**. The shift from **1** to **2**, which differ only by a *p*-methoxy substituent in one of the phenyl rings, provides a particularly strong argument against a ligand field (LF) origin for this absorption.

Interpretation of the absorption spectrum of **2** is straightforward. The 513-nm band is the MLCT transition $^1A_1(b_2^2) \rightarrow A_2(b_2^1 2b_1^1)$ discussed above, and the 413- and 376-nm bands are the LF transitions $^1A_1(b_2^2) \rightarrow {}^1B_2(b_2^1 2a_1^1)$ and $^1A_1(b_2^2) \rightarrow {}^1B_2(b_2^1 3a_1^1)$, respectively. There is no obvious alternative assignment for these transitions: they are too low in energy to be ligand based or to be MLCT excitation to the carbonyl ligands (cf. 289 nm for the lowest energy MLCT in $[W(CO)_6]$[26]), and they are an order of magnitude more intense than the spin-forbidden (singlet → triplet) absorptions seen for some other $d^6[M(CO)_5L]$ complexes of third-row metals.[8,22,24] Both transitions are orbitally allowed under C_{2v}, consistent with their similar intensities.

Assigning the lowest energy LF absorption to excitation into the d_{z^2} orbital rather than the $d_{x^2-y^2}$ is entirely consistent with previous assignments for $[W(CO)_5L]$ and $[Re(CO)_5X]$ complexes,[22,24,25] supported by MCD and emission studies, and comparison with these assignments suggests that the carbene ligand is comparable to a halide as a σ donor (cf. 414 nm for the $^1A_1(e^4b_2^2) \rightarrow {}^1E(e^3b_2^2a_1^1)$ transition in $[W(CO)_5Br]^-$[22]). (The strong field character of the carbene presumably arises largely because of its π-acceptor capabilities.)

The proposed assignments for **2** suggest that the 375-nm absorption of **1** and 352-nm absorption of $[W(CO)_5(OMe)Ph]$[8] are not in fact the lowest energy LF transitions for these systems, but are instead the $^1A_1(b_2^2) \rightarrow {}^1B_2(b_2^1 3a_1^1)$ transitions, occurring at positions very close to those at which they are observed in **2**. LF transitions should be relatively insensitive to changes in the carbene ligands, and it is difficult to imagine, for example, that the 375-nm band of **1** corresponds to the 413-nm band of **2**. These assignments imply that the $^1A_1(b_2^2) \rightarrow {}^1B_2(b_2^1 2a_1^1)$ LF transitions of both **1** and $[W(CO)_5C(OMe)Ph]$ are masked by their respective MLCT transitions at 485 and 402 nm, and examination of the spectra shows that this is indeed possible.

These assignments lead to a straightforward interpretation of the photochemistry of **1**. Irradiation of the 485-nm absorption should lead to MLCT excitation, and since it is well established that carbonyl dissociation is a function of LF excitation,[22,24] the failure to observe metathesis at this wavelength is consistent with the suggestion that the primary photochemical process in the metathesis sequence is CO dissociation. Initial CO loss following irradiation at 375 nm, on the other hand, would be consistent with excitation into the $d_{x^2-y^2}$ orbital.

Since the $d_{x^2-y^2}$ orbital is antibonding with respect to the cis carbonyls, 375-nm excitation could also lead to specific loss of a cis carbonyl, as has been observed in wavelength dependent photolysis of other d^6 ($[Re(CO)_5X]$[22] and $[W(CO)_5L]$[27]) complexes. Specific cis carbonyl loss would allow direct access to the cis alkene/alkylidene complex required for metallacyclobutane formation without rearrangement of an intermediate $[W(CO)_4L]$ complex, and it is interesting to note that the reassignment suggested for the spectrum of $[W(CO)_5C(OMe)Ph]$ could account similarly for the wavelength-dependent formation of *cis*-$[W(CO)_4(L)\{C(OMe)Ph\}]$ complexes without requiring the assumption that initial loss of a trans CO is followed by rapid rearrangement of a coordinatively unsaturated intermediate.[8,28]

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Registry No. 1, 50276-12-5; **2**, 76096-47-4; $[W(CO)_5C(OCH_3)Ph]$, 37823-96-4; $[W(CO)_6]$, 14040-11-0; $CH_2CPh(C_6H_4$-*p*-$OCH_3)$, 1142-15-0; LiC_6H_4-*p*-OMe, 14774-77-7; $CH_2{=}C(C_6H_5)_2$, 530-48-3.

Supplementary Material Available: Table of λ_{max} and *A* during photolyses of solutions of $[W(CO)_5CPh_2]$ with $CH_2{=}CPh(C_6H_4$-*p*-$OCH_3)$ in cyclohexane at 27–29 and 12–14 °C (1 page). Ordering information is given on any current masthead page.

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(28) A referee has pointed out that this interpretation requires that internal conversion of the $^1B_2(b_2^1 3a_1^1)$ and $^1B_2(b_2^1 2a_1^1)$ LF states is sufficiently slow to allow CO loss from the higher energy LF state. Although this spin-allowed conversion would be expected to be quite fast, the previous observation of higher quantum yields for CO dissociation in some d^6 carbonyl complexes following population of a higher energy $d_{x^2-y^2}$ orbital[22] does suggest that this is feasible.