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Time-Resolved IR Characterization of *cis*- and *trans*-[$LW(CO)_4$(solvent)] [L = PPh_3, P(O-*i*-Pr)$_3$, and $P(OEt)_3$] in *n*-Heptane Solution: The Solvent as a Token Ligand in Short-Lived Reaction Intermediates

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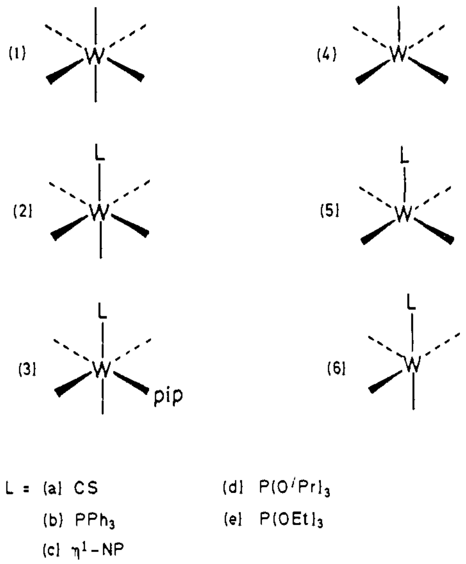
Abstract: Time-resolved IR spectroscopy is used to identify the cis (**6**) and trans (**5**) isomers of [$LW(CO)_4$(s)] (L = PPh_3, P(O-*i*-Pr)$_3$ and $P(OEt)_3$, (s) = solvent) as the major primary photoproducts of the photolysis of $LW(CO)_5$ (**2**) and *cis*-(pip)$LW(CO)_4$ (**3**) (pip = piperidine) in *n*-heptane solution at room temperature. Matrix isolation experiments in solid Ar at 20 K with (PPh_3)$W(CO)_5$ help with the interpretation of these time-resolved spectra. In *n*-heptane solution, for each L, the cis isomer (**6**) is shorter lived than the trans (**5**), and there is no evidence for thermal interconversion of the two isomers, which react with CO at different rates. Intermediates with bulky ligands react with CO faster than those with sterically less demanding ligands. For all L, both isomers react with CO faster than does [$W(CO)_5$(s)] (**4**), the intermediate generated by flash photolysis of $W(CO)_6$ under similar conditions. All of these formally unsaturated species appear to be solvated even in *n*-heptane solution, to give pseudooctahedral "quasicoordination compounds". The term "Token Ligand" is proposed to signify this specific interaction of a solvent molecule with an otherwise vacant coordination site in reaction intermediates.

Coordinatively unsaturated metal carbonyl compounds are of increasing interest because of their relevance to the mechanisms of substitution reactions and the reactivities of species important in homogeneous catalysis.[1] In particular, intermediates formed from substituted group 6 metal carbonyls have been studied in detail[2,3] via both continuous wave (cw) and flash photolysis under ambient conditions and via matrix isolation techniques.[4] The information gained through these investigations shows these intermediates to be attractive candidates for study via flash photolysis with infrared detection, so-called time-resolved IR (TRIR).[5]

Matrix isolation studies of $M(CO)_6$ (**1**: M = Cr, Mo, W) have demonstrated that the $M(CO)_5$ intermediates **4**, generated upon photolysis, retain geometries based upon the octahedron.[6] Matrix molecules such as CH_4 or even the inert gases, particularly Xe, occupy the coordination site vacated by the ejected CO group and interact sufficiently strongly with the metal center to produce substantial changes in the electronic spectrum of the $M(CO)_5$ fragment.[6]

For $Cr(CO)_6$, flash photolysis studies in solution indicate[7] that within 0.8 ps the photofragment [$Cr(CO)_5$] is deactivated and solvated to give [$Cr(CO)_5$(s)]. Other studies are also consistent with the very rapid formation of specifically solvated five-coordinate intermediates.[8] Since such solvated intermediates appear to be widespread, we propose the term "*Token Ligand*" to describe a weakly interacting solvent molecule, (s), occupying a specific coordination site.

For $M(CO)_5L$ compounds, several intermediates may be produced upon initial photolysis. Matrix isolation studies of $W(CO)_5CS$ (**2a**) showed that both the C_{4v} (**5a**) and C_s (**6a**) isomers of square-pyramidal [$W(CO)_4CS$] are generated.[9] Darensbourg and Murphy have shown in cw photolysis investigations on $Ph_3PW(CO)_5$ (**2b**) that either CO or PPh_3 can be lost and all three intermediates which can be formed through rupture of a single coordinate bond, [$W(CO)_5$] (**4**) (loss of PPh_3) and *cis*- and *trans*-[$Ph_3PW(CO)_4$] (**6b** and **5b**) (loss of CO), are in fact produced.[10] More recently, flash photolysis studies of (NP)$M(CO)_4$ complexes (M = Cr, Mo, W; NP = $R_2N(CH_2)_n(PPh_3)_2$) have demonstrated that the N–M bond is broken in preference to the M–P or M–CO bonds, affording *cis*-[(η^1-NP)$M(CO)_4$] (**6c**). This intermediate was identified on the basis of the *two-term* rate law for its decay in the presence of "trapping agents" L; the two terms correspond to the competing processes of unimolecular chelate ring reclosure and bimolecular reaction with L to give *cis*-(η^1-NP)$M(CO)_4L$.[11] For some of these (NP)$M(CO)_4$ compounds,



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a second intermediate with a slower decay was identified as ***trans***-$[(\eta^1\text{-NP})M(CO)_4]$ (**5c**) although the identification was not unequivocal.[11a,c] Parallel investigations with flash photolysis and conventional kinetics on the closely related *cis*-(pip)$(Ph_3P)W(CO)_4$ complex (**3b**: pip = piperidine) in chlorobenzene have also supported the formation of solvated *cis*-$[(Ph_3P)W(CO)_4]$ (**6b**).[12]

Flash photolysis investigations typically employ UV–visible detection. The identification of intermediates formed via photolysis of unsubstituted metal carbonyls poses little difficulty because the number of possible primary photoproducts is extremely limited. For substituted metal carbonyls, however, the problem is more complicated, as we have already indicated. Several possible photogenerated intermediates could arise from either M–CO or M–L bond breaking or from isomerization. Such intermediates are not readily identifiable from their relatively featureless and similar UV–visible spectra, which provide little information about structural and bonding properties. Infrared spectroscopy is a far more informative means of probing these intermediates.[5]

Paradoxically, however, the very richness of ν(C–O) IR spectra, which provides both conclusive identification of intermediates and information about their stereochemistry and bonding, can lead to complicated time-resolved IR because several five-coordinated species can be produced by photolysis of a single $M(CO)_{6-x}L_x$ precursor. Thus, the identification of particular intermediates is greatly simplified by studying the photolysis of a series of related precursor compounds, which all yield the same intermediates.

In this paper, we apply this approach to the photolysis of $LM(CO)_5$ compounds. We report time-resolved IR studies on a series of complexes, $W(CO)_6$, $LW(CO)_5$ (L = P(O-*i*-Pr)$_3$), and *cis*-(pip)$LW(CO)_4$ (L = P(OEt)$_3$, P(O-*i*-Pr)$_3$ and PPh$_3$), which are photochemical precursors for the solvated intermediates, $[W(CO)_5(s)]$, and both *cis*- and *trans*-$[LW(CO)_4(s)]$. These species are identified through ν(C–O) IR spectra, and their reactivities toward CO are probed in *n*-heptane solution. Most of the published time-resolved IR studies on organometallic compounds have used data from matrix isolation experiments to help in interpreting the spectra,[5] and since such data are unavailable for $W(CO)_5L$ compounds, we begin with a brief account of the photolysis of matrix-isolated $(PPh_3)W(CO)_5$, an experiment that underpins our time-resolved results in solution.

Experimental Section

Materials. $W(CO)_6$, purchased from Pressure Chemical Co., and carbon monoxide (BOC Research Grade) were used without further purification and *n*-heptane (Aldrich, HPLC grade) was distilled from CaH_2 before use. All syntheses were carried out at North Texas State University. (P(O-*i*-Pr)$_3$)$W(CO)_5$ was prepared by employing the method of Strohmeier and Müller[13] as discussed by Brown and Dobson.[14] It was identified through its characteristic carbonyl stretching spectrum.[14] The *cis*-(pip)$LW(CO)_4$ (L = PPh$_3$, P(OEt)$_3$, P(O-*i*-Pr)$_3$) complexes were prepared from *cis*-(pip)$_2W(CO)_4$ (pip = piperidine) through use of a modified method employed by Darensbourg and Kump[15] for the synthesis of the PPh$_3$ complex. This complex, originally identified through its carbonyl stretching spectrum[15,16] (Table 1), has also been synthesized photolytically.[16] The other complexes have not previously been reported.

***cis*-(pip)(P(OEt)$_3$)W(CO)$_4$ (3e).** *cis*-(pip)$_2W(CO)_4$ (3.0 g, 6.1 mmol) and P(OEt)$_3$ (1.2 g, 7.2 mmol) were warmed in 100 mL of 1,2-dichloroethane under nitrogen at 50 °C for 30 min, during which time the *cis*-(pip)$_2W(CO)_4$ dissolved. The reaction solution was filtered warm, and the volume of the solution was reduced to 20 mL. The product was precipitated by addition of methanol (1/1, v/v) and by cooling overnight in a freezer. The bright yellow product was obtained by suction filtration and was recrystallized from dichloromethane/methanol. Anal. (Midwest Microlab, Indianapolis, IN) Calcd for $C_{15}H_{26}NO_7PW$: C, 32.92; H, 4.79. Found: C, 32.72; H, 5.01. The other *cis*-(pip)$LW(CO)_4$ complexes were prepared analogously. For L = P(O-*i*-Pr)$_3$, calculated for $C_{18}H_{32}NO_7PW$: C, 36.69; H, 5.47. Found: C, 36.89; H, 5.58. For L = PPh$_3$, calculated for $C_{27}H_{26}NO_4PW$: C, 50.41; H, 4.07. Found: C, 50.63; H, 4.06. Carbonyl stretching IR data are presented in Table I.

Table I. Wavenumbers (cm^{-1}) of ν(C–O) IR Bands of Compounds Used in This Work, Measured in *n*-Heptane Solution

(a) $LW(CO)_5$ (**2**)		
L = PPh$_3$	**2b**	2075, 1942, 1915
L = P(O-*i*-Pr)$_3$	**2d**	2075, 1952, 1937
(b) *cis*-(pip)$LW(CO)_4$ (**3**)		
L = PPh$_3$	**3b**	2013, 1904, 1888, 1865
L = P(O-*i*-Pr)$_3$	**3d**	2018, 1913, 1889, 1867
L = P(OEt)$_3$	**3e**	2019, 1914, 1891, 1870

Matrix Isolation. The low-temperature apparatus and Nicolet MX-3600 FTIR interferometer (0.7-cm^{-1} resolution) have been described previously.[17] $(PPh_3)W(CO)_5$ was deposited into the Ar matrix by "slow-spray-on" techniques. The UV photolysis source was a Philips HPK 125W lamp with appropriate filters.[17]

Time-Resolved IR Studies. The time-resolved TRIR instrumentation employed a Lumonics Hyperex HE-440 excimer laser (10–15-ns FWHI, 200-mJ energy) operating on XeCl (308 nm) as the photolysis source. The IR signal was digitized by employing a Datalab DL912 digitizer (50 ns/point). An iris was employed to attenuate the output of the Edinburgh Instruments PL3 line-tunable cw CO laser. Otherwise, the equipment was as described elsewhere.[18] Solutions approximately 10^{-4} M in metal complex were employed and all solutions for photolysis were degassed under vacuum prior to use. A fresh sample was employed for each UV laser shot.

The CO laser is line-tunable, giving output at any one of a series of frequencies (2020 1700 cm^{-1}) separated by ~4 cm^{-1}. For each UV flash, therefore, a kinetic trace, such as is shown in Figure 5, is recorded at a single frequency. An IR spectrum, therefore, can be created from data for a series of lines over the wavelength range of interest. The spectra are actually "IR difference spectra" of (absorbance after flash) minus (absorbance before flash) in which products appear as positive peaks and reactants destroyed by the flash appear as negative peaks. The observed data points are interpolated with use of a "cubic spline" to create the spectra,[18] which are of surprisingly high quality. For example, Figure 4 compares the TRIR difference spectrum taken 1500 μs after the UV flash (long after the intermediates have completely decayed) with a routine FT–IR spectrum generated by computer subtraction of spectra due to the product and to the reactant.

Results and Discussion

Photolysis of Matrix-Isolated $(PPh_3)W(CO)_5$ (2b). Figure 1a shows part of the FT IR spectrum obtained after brief broad band UV photolysis of $(PPh_3)W(CO)_5$ (**2b**) isolated in an Ar matrix at 20 K. The six bands labeled **C** or **T** are due to photoproducts. The labeling is based on the results of narrow band photolyses (with 367 nm or visible light), which confirm that there are two photoproducts, photochemically interconvertible. The spectra in parts b and c of Figure 1 show that one product has *two* ν(C–O) bands labeled **T** while the other has *four* bands, marked **C**.

We assign these bands to the trans **5b** and cis **6b** isomers of $[(PPh_3)W(CO)_4]$, *very* weakly coordinated to Ar for the following reasons: (i) The *number* of IR bands is consistent with **5b** (a_1 + e) and **6b** (3a′ + a″). (ii) Formation of both photoproducts involves loss of CO from $(PPh_3)W(CO)_5$—a band due to free CO appears at 2138 cm^{-1}, not illustrated. (iii) Both photoproducts recombine photochemically with CO to regenerate $(PPh_3)W(CO)_5$. (iv) The two species appear to be isomeric since their interconversion does not involve the formation or loss of uncoordinated CO. (v) The pattern of IR bands, **C**, is similar in intensity to those of *cis*-(pip)$(PPh_3)W(CO)_4$ (**3b**) but shifted ~30 cm^{-1} to higher frequency (see Table II). A similar wavenumber shift has been observed both in a methane matrix and in cyclohexane solution

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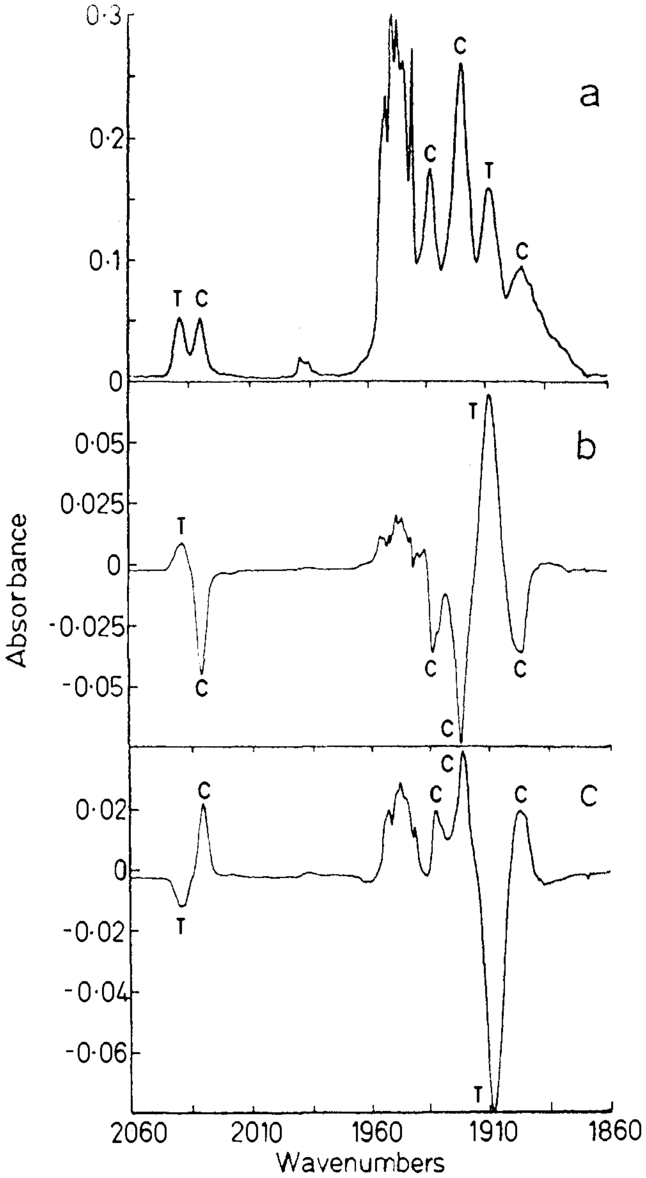

Figure 1. FTIR spectra showing the results of the photolysis of $(PPh_3)W(CO)_5$ (**2b**) in an Ar matrix at 20 K (approximate dilution 1:2000). (a) After 10 min of photolysis with an unfiltered Hg arc. Unlabeled bands are due to unphotolysed **2b**; bands labeled **C** are due to *cis*-$[(PPh_3)W(CO)_4]$ (**6b**) and **T** are due to the trans isomer (**5b**). (b) IR difference spectrum, i.e. (spectrum after photolysis) *minus* (spectrum before), showing the cis → trans isomerization (**6b** → **5b**) induced by 10 min of irradiation with filtered light, 367 nm. (c) IR difference spectrum showing trans → cis isomerization (**5b** → **6b**) induced by 2 min of irradiation with visible light.

Table II. Wavenumbers[a] (cm^{-1}) of IR Bands of $(PPh_3)W(CO)_5$ and Its Photoproducts Isolated in an Ar Matrix at 20 K (Cf. Figure 1)

$(PPh_3)W(CO)_5$	**2b**	2077, 1953, 1948,[b] 1945[b]
trans-$[(PPh_3)W(CO)_4]$	**5b**[c]	2038 (a_1), 1908 (e)
cis-$[(PPh_3)W(CO)_4]$	**6b**[d]	2030, 1933, 1919, 1895
cis-(pip)$(PPh_3)W(CO)_4$	**3b**[e]	2013, 1904, 1888, 1865

[a] Error ±0.5 cm^{-1}. [b] Matrix split bands. [c] Bands labeled T in Figure 1. [d] Bands labeled C in Figure 1. [e] Bands measured in *n*-heptane solution, 25 °C. The fragments **5b** and **6b** are *very* weakly coordinated to argon.

Table III. Wavenumbers (cm^{-1}) of ν(C–O) Bands of $W(CO)_5(s)$ Species

	S			
assignment	*n*-heptane[a,b]	cyclohexane[b,c]	CH_4[d]	pip[a]
a_1	*e*	2082	2092	2073
e	1959	1958	1957	1930
a_1	1929	1932	1926	1919

[a] This work, room temperature, *n*-heptane solution. [b] Time-resolved IR measurements, error ±2 cm^{-1}. [c] Room temperature, ref 22. [d] Solid CH_4 20K, ref 6. [e] Not observed, outside range of TRIR spectrometer, see ref 21.

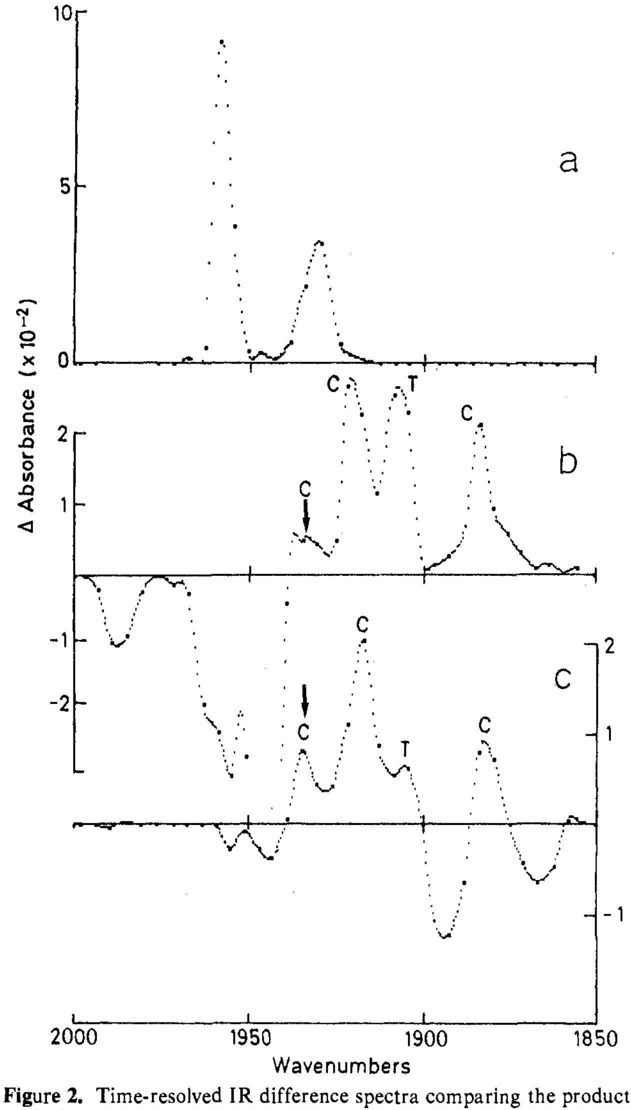

Figure 2. Time-resolved IR difference spectra comparing the products 1 μs after flash photolysis of (a) $W(CO)_6$ (**1**), (b) $(P(O\text{-}i\text{-}Pr)_3)W(CO)_5$ (**2d**), and (c) *cis*-(pip)$(P(O\text{-}i\text{-}Pr)_3)W(CO)_4$ (**3d**) in *n*-heptane solution at room temperature. Details of the spectra are as follows: (a) Unlabeled bands due to $[W(CO)_5(s)]$ (**4**) with a token *n*-heptane ligand (note that the negative peak due to $W(CO)_6$ is not shown). (b) Bands labeled **C** due to *cis*-$[(P(O\text{-}i\text{-}Pr)_3)W(CO)_4(s)]$ (**6d**) and T due to the trans isomer **5d**. Unlabeled negative peaks due to **2d**. (c) Bands labeled as in spectrum b; negative peaks due to **3d** and a trace of **2d**.

for $[W(CO)_5(hydrocarbon)]$ (**4**), where carbonyl stretching bands[6] are significantly higher in energy than those[14] of (pip)$W(CO)_5$ (see Table III). This shift is consistent with less donation of charge to the metal by the matrix than by amines. The greater shift to higher energy of the e mode than the a_1 (axial) mode in $[W(CO)_5(CH_4)]$, relative to (pip)$W(CO)_5$, is consistent with decreased Fenske–deKock "direct donation"[19] of electron density by the solvent to the equatorial carbonyls than by piperidine.

Our overall conclusions are similar to those of Black and Braterman, who reported carbonyl stretching bands for cis and trans species analogous to **6b** and **5b** produced by photolysis of $LMo(CO)_5$ (L = tri(cyclohexyl)phosphine) in a methylcyclohexane/isopentane glass at 77 K.[20]

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We now show how these matrix results can be combined with time-resolved IR experiments to provide conclusive identification of *cis-* and *trans-*[LW(CO)$_4$(s)] intermediates in *n*-heptane solution at room temperature.

Time-Resolved IR Experiments. Figure 2 illustrates carbonyl stretching spectra corresponding to a time 1 μs after the flash photolysis of (a) W(CO)$_6$ (**1**), (b) (P(O-*i*-Pr)$_3$)W(CO)$_5$ (**2d**), and (c) *cis*-(pip)(P(O-*i*-Pr)$_3$)W(CO)$_4$ (**3d**) in *n*-heptane. The spectra show that the major photolysis products of **2d** and **3d** are similar but different from the photolysis product of W(CO)$_6$. We shall therefore consider the photolysis of W(CO)$_6$ before identifying the other photoproducts.

For W(CO)$_6$ (Figure 2a) two new bands are evident. These bands both decay at the same rate under an atmosphere of CO, and this decay mirrors the growth in intensity of a band at 1985 cm^{-1} due to the t$_{1u}$ band of W(CO)$_6$.

Thus, the bands may be reasonably assigned to the reversible formation of W(CO)$_5$ (**4**) here solvated by *n*-heptane.

$$\mathrm{s} + \mathrm{W(CO)_6} \underset{k[\mathrm{CO}]}{\overset{h\nu}{\rightleftharpoons}} [\mathrm{W(CO)_5(s)}] \qquad (1)$$

(s = *n*-heptane)

The bands,[21] Table III, are close in frequency to those assigned as [W(CO)$_5$(cyclohexane)], observed by Skibbe[22] employing the TRIR equipment described by Schaffner, Grevels, and co-workers.[23] Also, similar bands have been observed for [W(CO)$_5$(CH$_4$)] in a CH$_4$ matrix at 20 K where it has been proposed that CH$_4$ is a Token Ligand occupying the vacant coordination site of the pentacarbonyl.[6] The bands in Table III have been assigned by analogy with assignments for matrix-isolated [W(CO)$_5$(CH$_4$)] and for various (amine)W(CO)$_5$ complexes.[14] Since both methane and *n*-heptane are probably bound weakly to the metal atom, intermediates generated through matrix-isolation photolysis might be expected to be similar to those generated in solution at ambient temperatures. The close agreement between the carbonyl stretching frequencies for [W(CO)$_5$(CH$_4$)] and for [W(CO)$_5$(C$_7$H$_{16}$)] provides support for this view.

Figure 2b shows the spectrum produced by flash photolysis of (P(O-*i*-Pr)$_3$)W(CO)$_5$ (**2d**) in *n*-heptane under Ar. Three intense carbonyl stretching bands appear in the region 1845–1945 cm^{-1}, none of which are those observed upon flash photolysis of W(CO)$_6$. Under an atmosphere of CO two of these bands, labeled "C", decay at the same rate while the third, labeled "T", decays at a significantly slower rate (Figure 3). The decays obey pseudo-first-order kinetics. Thus, it may be concluded that the "C" and "T" bands correspond to the formation of two major species, neither of which is [W(CO)$_5$(s)]. If any [W(CO)$_5$(s)] is formed, it is at best a minor photoproduct, as was noted by Darensbourg and Murphy in their cw photolysis studies of (PPh$_3$)W(CO)$_5$.[10]

The spectrum in Figure 2c shows that the same intermediates are generated by photolysis of *cis*-(pip)(P(O-*i*-Pr)$_3$)W(CO)$_4$ (**3d**) in *n*-heptane. The frequencies of the bands labeled "C" and "T" are clearly the same as those shown in Figure 2b, but their relative intensities are different. Although it is of course possible that the two reactants **2d** and **3d** afford differing relative amounts of the photoproducts, the observed intensity differences are at least partly the result of comparing IR difference spectra rather than conventional absorption spectra. Thus, the **T** band in Figure 2c is weaker than that in Figure 2b because it overlaps a band of the starting material, **3d**, destroyed by the flash. Similarly, the **C** band, arrowed in Figure 2c, appears weaker in Figure 2b because, there, it partially overlaps the strong negative absorption of the destroyed starting material. This arrowed band **C** is definitely due to the same intermediate as the other two **C** bands because all three bands are observed to decay at the same rate under both Ar[24] and CO.

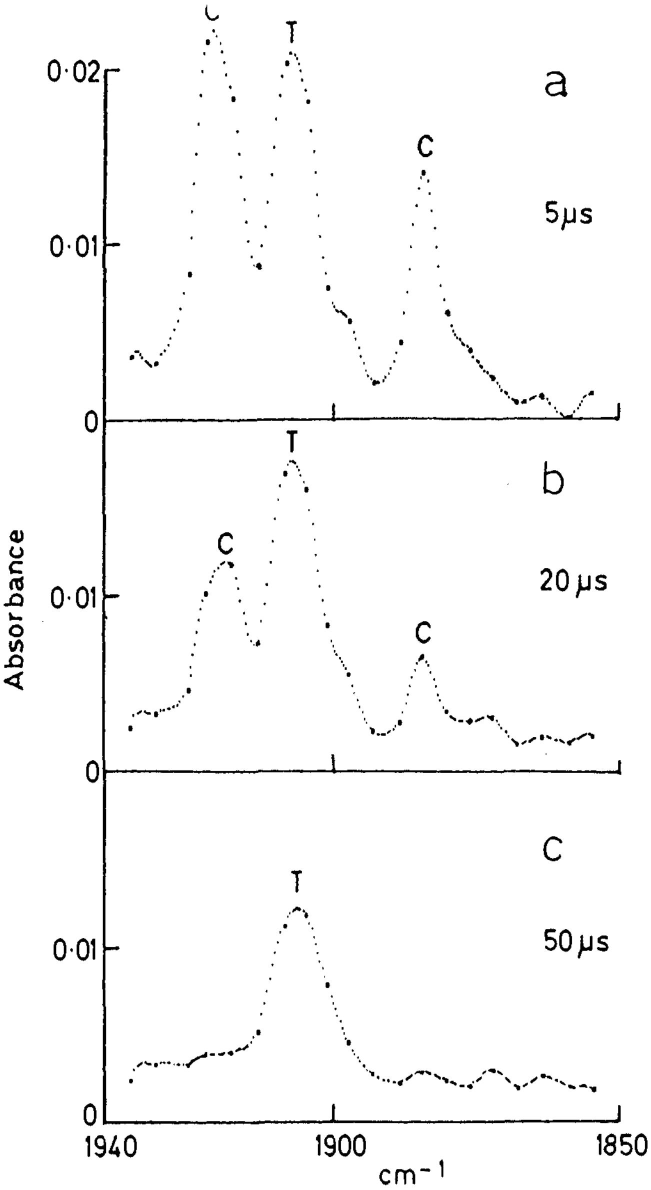

Figure 3. Time-resolved IR spectra corresponding to (a) 5 μs, (b) 20 μs, and (c) 50 μs after the flash photolysis of (P(O-*i*-Pr)$_3$)W(CO)$_5$ (**2d**) in *n*-heptane under 1 atm of CO. As in Figure 2, bands labeled **C** are due to **6d** and **T** are due to **5d**. Note that these spectra cover a more restricted wavenumber range than those in Figure 2.

In all of our experiments, the **C** and **T** bands, generated from (P(O-*i*-Pr)$_3$W(CO)$_5$ (**2d**), decayed at the same rate as the **C** and **T** bands, generated from *cis*-(pip)(P(O-*i*-Pr)$_3$)W(CO)$_4$ (**3d**), under similar conditions. The decay of the **C** bands was always faster than the decay of **T** and both **C** and **T** decayed faster under an atmosphere of CO than under Ar. For **2d**, photolysis under CO

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[24] In the absence of CO there is a slow decay of bands attributed to **C** and **T** with the concomitant growth of unassigned product bands at 1856, 1899, 1924, and 1946 cm^{-1}. Fortunately, the identification of **C** and **T** does not rely on the detailed characterization of this product. It is not formed by reaction with H$_2$O because the rates of formation and decay of these bands were similar in both cyclohexane and *n*-heptane purified by various different routes to remove traces of water. It appears to be formed by reaction of the intermediates **C** and **T** with the unphotolyzed parent *cis*-(pip)LW(CO)$_4$, since the rate of formation of this product was found to increase with increasing concentration of *cis*-(pip)LW(CO)$_4$. For further discussion of this phenomenon see ref 34. In the presence of CO, the formation of this product from **C** is competitive with the reaction with CO to give LW(CO)$_5$ and consequently, the rate of decay of bands due to **C** is faster than the rate of formation of LW(CO)$_5$ from C, Table V. However, the formation of this product from **T** is much slower than CO addition, and thus the rate of decay of bands due to **T** is equal to the rate of formation of LW(CO)$_5$ via the slower pathway.

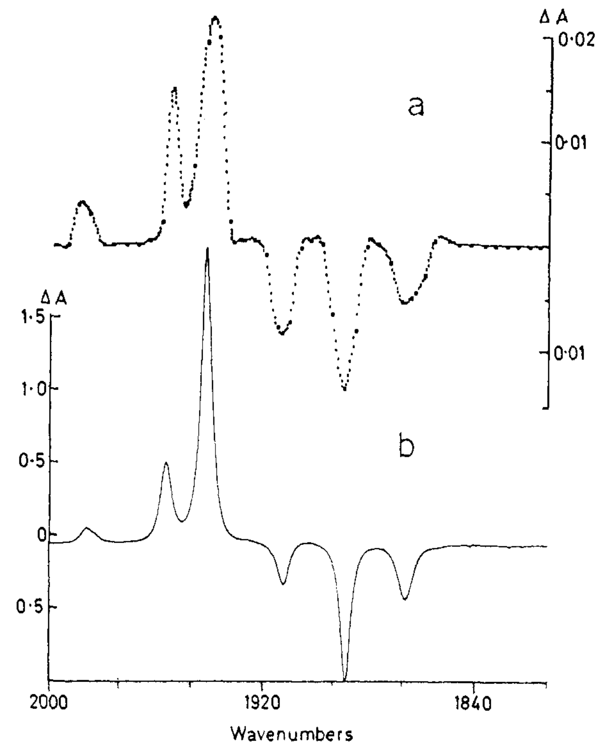


Figure 4. (a) Time-resolved IR difference spectrum corresponding to 1500 μs after the flash photolysis of *cis*-(pip)(P(O-*i*-Pr)$_3$)W(CO)$_4$ (**3d**) under 1 atm of CO. Positive peaks are due to the final product (P(O-*i*-Pr)$_3$)W(CO)$_5$ (**2d**) and negative peaks due to the reactant **3d**, destroyed by the flash. (b) An FTIR difference spectrum (0.7-cm^{-1} resolution) obtained by computer subtraction of spectra of authentic samples of **2d** and **3d**. Note the good overall agreement between the two spectra. Differences in the relative intensities of the peaks between the two spectra are an artefact of the "point-by-point" data collection of the time-resolved spectrum (see ref 18b). Note that this artefact has no effect on the kinetic measurements. As in Figures 2 and 3, points marked ■ are recorded data points while those marked · were obtained by computer interpolation.

Table IV. Wavenumbers[a] (cm^{-1}) of Time-Resolved IR Bands of *trans*- and *cis*-[LW(CO)$_4$(s)] Intermediates in *n*-heptane Solution

	trans-[LW(CO)$_4$(s)]	
L = PPh$_3$	**5b**	1904
L = P(O-*i*-Pr)$_3$	**5d**	1907
L = P(OEt)$_3$	**5e**	1907
	cis-[LW(CO)$_4$(s)]	
L = PPh$_3$	**6b**	1938, 1916, 1886
L = P(O-*i*-Pr)$_3$	**6d**	1937, 1916, 1882
L = P(OEt)$_3$	**6e**	1937, 1920, 1882

[a] Error ±2 cm^{-1}.

is reversible (eq 2) while for **3d** photolysis under CO results in the formation of **2d** (eq 3).

$$\mathbf{2d} \underset{CO}{\overset{h\nu}{\rightleftharpoons}} \mathrm{C} + \mathrm{T} \qquad (2)$$

$$\begin{tikzcd} & \mathrm{C} \arrow[dr, "CO"] & \\ \mathbf{3d} \arrow[ur, "h\nu"] \arrow[dr, "h\nu"'] & & \mathbf{2d} \\ & \mathrm{T} \arrow[ur, "CO"'] & \end{tikzcd} \qquad (3)$$

The overall stoichiometry of eq 3 is confirmed by the TRIR spectrum illustrated in Figure 4a. The kinetic traces in Figure 5 show that, under CO, the exponential decays of bands due to **C** and **T** are accompanied by the growth of an absorption due to **3d**. This band increases in intensity via two independent first-order processes which mirror the decays of **C** and **T**.

We identify **C** as the cis isomer of [(P(O-*i*-Pr)$_3$)W(CO)$_4$(s)] (**6d**) and **T** as the trans isomer (**5d**) for the following reasons.

(i) Since **C** and **T** can be generated from both **2d** and **3d**, they must have four CO groups and cannot contain piperidine.

(ii) Since **C** and **T** both react with CO to form **2d**, they must contain P(O-*i*-Pr)$_3$.

(iii) The frequencies of the IR bands, Table IV, are similar to those of the matrix-isolated cis and trans isomers **6b** and **5b** (see Table I and Figure 1).

(iv) The shift to higher wavenumber of the carbonyl stretching frequencies of **C** compared to those of the pip complex **3d** parallels that noted above between the solvated W(CO)$_5$ and (pip)W(CO)$_5$.[14] This wavenumber shift is also observed when the carbonyl stretching frequencies for *cis*-[LW(CO)$_4$(s)] (L = P(OEt)$_3$ (**6e**) or PPh$_3$ (**6b**)) are compared to those for the analogous *cis*-(pip)LW(CO)$_4$ complexes (Table IV).

Rate data for the reaction of each photogenerated intermediate with CO are presented in Table V. The overall photolysis reactions in *n*-heptane solution under an atmosphere of CO are summarized in Scheme I.

Table V. Pseudo-First-Order Rate Constants (s^{-1}) for the Reaction of *trans*- and *cis*-[LW(CO)$_4$(s)] (**5** and **6**) with CO in *n*-heptane Solution[a] at 25 °C and the Corresponding Rates of Formation of W(CO)$_5$L (**2**)

trans-[(LW(CO)$_4$(s)] (**5**)

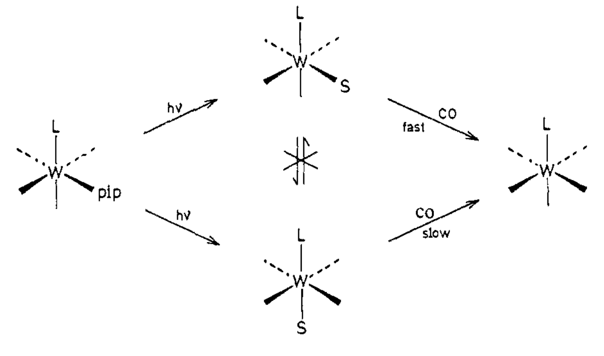
L	rate of decay of **5**	rate of formation of **2**
PPh$_3$	3.5 ± 1 × 10^4	3 ± 1 × 10^4
P(O-*i*-Pr)$_3$	2.0 × 10^4	1.7 × 10^4
P(OEt)$_3$	1.2 × 10^4	1.3 × 10^4
CO	1 × 10^4	1 × 10^4

cis-[(LW(CO)$_4$(s)] (**6**)

L	rate of decay of **6**[c]	rate of formation of **2**[c]
PPh$_3$[b]	14 × 10^4	9.5 × 10^4
P(O-*i*-Pr)$_3$	11.5 × 10^4	3.7 × 10^4
P(OEt)$_3$	8.63 × 10^4	4.6 × 10^4

[a] Pressure of CO 1 atm which will give a concentration of dissolved CO ~1.1 × 10^{-2} M (see, e.g., ref 22 and 23). [b] These values are only approximate, estimated from half-life values. Error probably ±30%. Other rates ±10%. [c] See ref 24 for explanation of why the rates of decay are faster than rates of growth.

Scheme I



(L = PPh$_3$, P(OEt)$_3$ or P(O^{i}Pr)$_3$; S = n-heptane; pip = piperidine)

Reactivities of the Intermediates: The Role of Solvent as a Token Ligand. Although our experiments do not provide direct spectroscopic evidence for coordination of a solvent molecule into the vacant coordination site of the [LW(CO)$_4$] intermediates, our kinetic measurements suggest that such solvation is occurring. Previous work on other d^6 metal centers indicates that the strength of interaction with solvents decreases in the order chloroalkane > chloroarene[5a] > arene[5a,25] > alkane[26] > perfluoroalkane,[8a] the order of decreasing solvent polarity. In agreement with this, our rate constants, measured in *n*-heptane, are substantially larger than the corresponding rate constants in chlorobenzene solution.[12,25]

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(26) Mansour, S. E.; Dobson, G. R., unpublished results.

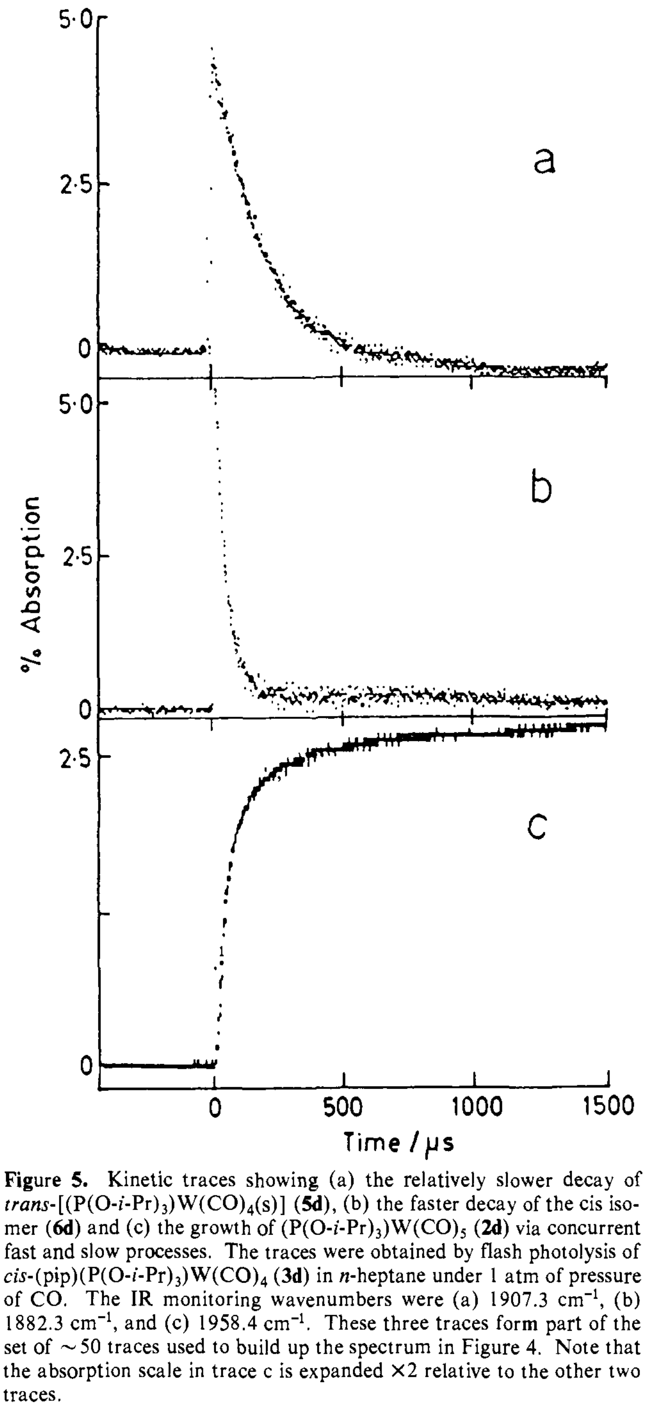

Figure 5. Kinetic traces showing (a) the relatively slower decay of $trans$-[(P(O-i-Pr)$_3$)W(CO)$_4$(s)] (**5d**), (b) the faster decay of the cis isomer (**6d**) and (c) the growth of (P(O-i-Pr)$_3$)W(CO)$_5$ (**2d**) via concurrent fast and slow processes. The traces were obtained by flash photolysis of cis-(pip)(P(O-i-Pr)$_3$)W(CO)$_4$ (**3d**) in n-heptane under 1 atm of pressure of CO. The IR monitoring wavenumbers were (a) 1907.3 cm^{-1}, (b) 1882.3 cm^{-1}, and (c) 1958.4 cm^{-1}. These three traces form part of the set of ~50 traces used to build up the spectrum in Figure 4. Note that the absorption scale in trace c is expanded ×2 relative to the other two traces.

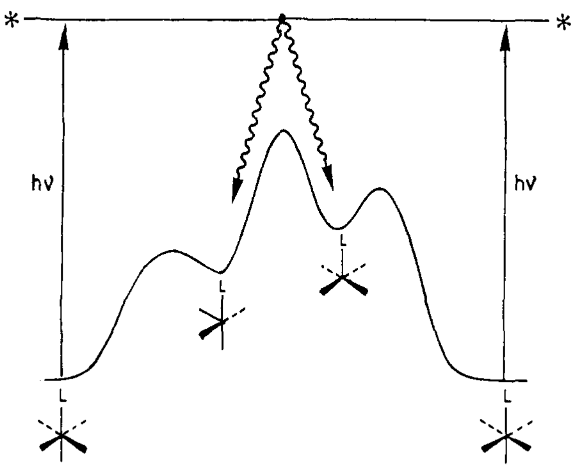

Figure 6. A qualitative plot showing the relative ground energies of LW(CO)$_5$ (**2**) and the two isomers of [LW(CO)$_4$] (**5** and **6**). The asterisk indicates the photoactive excited state. The diagram is based on a combination of our results and those of Brown[32] and Veillard.[33]

As noted earlier, the rate of reaction of CO with cis-[LW(CO)$_4$(s)] (**6**) is significantly faster than its rate with the trans isomer (**5**). Thus, for L = P(O-i-Pr)$_3$ the ratio $k_{\mathrm{cis}}/k_{\mathrm{trans}}$ is 5.75 and both k_{cis} and k_{trans} are *larger* than the rate constant for [W(CO)$_5$(s)]. This ratio of rate constants is exactly the opposite of what would be expected for a coordinatively unsaturated intermediate [LW(CO)$_4$] with a bulky phosphine impeding the approach of an incoming ligand. The behavior is, however, similar to that observed in systems where the bulky group facilitates the loss of a cis ligand, in the present case the cis ligand being the solvent (s). Thus Darensbourg and Graves[27] noticed a similar effect in the dissociation of PPh$_3$ from cis- and $trans$-(PPh$_3$)$_2$Mo(CO)$_4$. In that work, the origin of the greater rate of loss of PPh$_3$ at the cis position was entropic, and has been attributed to steric interference of the two bulky triphenylphosphine ligands. Similarly, it has been observed that cis-[(chlorobenzene)(η^1-NP)Cr(CO)$_4$] has an anomalously high rate of chelate ring closure compared to the corresponding Mo and W compounds. This is the result of a more favorable entropy of activation for the Cr, which has been attributed to steric acceleration of desolvation at the smaller Cr atom.[5b]

Table V also shows the trend in the reactivities of cis-[LW(CO)$_4$(s)] (**6**) with CO as a function of L. The reactivity increases with the increasing bulkiness of L (as measured by Tolman cone angles)[28] in the order CO < P(OEt)$_3$ < P(O-i-Pr)$_3$ < PPh$_3$. This trend parallels that observed for *thermal dissociation* of pip from the parent cis-(pip)LW(CO)$_4$,[29] again suggesting the greater reactivity of the cis-[LW(CO)$_4$(s)] (**6**) to steric acceleration of desolvation.

Thus parallel trends in reactivity are observed for [LW(CO)$_4$(s)] intermediates and related coordinatively saturated complexes. These trends support the view that the intermediates should be viewed not as coordinatively unsaturated species but as highly reactive "quasicoordination complexes", which differ from their less-reactive coordinatively saturated counterparts because one coordination site is occupied not by a Lewis base but by a weakly bound solvent molecule, acting as a Token Ligand.

Formation of *trans*-[LW(CO)$_4$(s)] (5). We have shown that photolysis of cis(pip)LW(CO)$_4$ (**3**) leads to loss of the piperidine group, cis to the ligand L. One of the photoproducts is $trans$-[LW(CO)$_4$(s)] (**5**) with the token ligand trans to L. Our observation that the cis and trans isomers are not stereochemically interconvertible on the time scale of their further reaction[30] suggests that the trans isomer must be produced prior to the coordination of the token ligand. This conclusion is in agreement with investigations on the photoisomerization of [W(CO)$_4$CS][9] and [MeMn(CO)$_4$][31] in inert gas matrices.

Thermodynamic Stability of [LW(CO)$_4$(s)] Intermediates. Our results indicate that cis-[LW(CO)$_4$(s)] (**6**) is kinetically less stable than the trans isomer **5**. The relative kinetic and thermodynamic stabilities of the two isomers **5** and **6** may now be profitably compared. Brown has suggested that the ability of π-accepting ligands to labilize cis carbonyls in [LM(CO)$_5$] complexes is due to the preferential stabilization of an [LM(CO)$_4$] intermediate with L in a basal site of the hypothetical square pyramid.[32]

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(30) Attention is drawn to the distinction between *isomerization*, through which the cis- and $trans$-[LW(CO)$_4$(s)] (**6** and **5**) are interconverted and *fluxionality*, which would permute labeled CO groups in each of these species without isomerization. Fluxional processes have been studied extensively through isotopic labeling experiments; for a general review see: Howell, J. A.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 537.

(31) Horton-Mastin, A.; Poliakoff, M.; Turner, J. J. *Organometallics* **1986**, *5*, 405.

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Similar conclusions have been reached by Veillard and coworkers.[33] Thus, ignoring the token solvent ligand of the sixth coordination site, we would predict **6** to be thermodynamically more stable than **5**.

Both kinetic and thermodynamic factors therefore favor the cis intermediate **6**, as is widely observed for substitution by ligands which do not pose stringent steric demands. A qualitative diagram of potential energy and reaction coordinate is shown in Figure 6.

Conclusions

We have shown how time-resolved IR spectroscopy has provided positive confirmation that both isomers of $[LW(CO)_4(s)]$ (**5** and **6**) are the important intermediates in the photolysis of $LW(CO)_5$ and *cis*-(pip)$LW(CO)_4$ compounds. **5** and **6** react with CO at different rates, indicating that these isomers are not stereochemically interconvertible on the time scale of their reaction with CO even in a solvent as nonpolar as *n*-heptane. The values of the rate constants suggest that the *n*-heptane is acting as a *Token Ligand* filling the vacant coordination site of the $[LW(CO)_4(s)]$ species.

It is reasonable to suppose that the presence of the token ligand inhibits trans $\rightleftarrows$ cis isomerization of the $[LW(CO)_4(s)]$ species examined here. It will therefore be of interest to investigate such isomerization in other metal carbonyl intermediates, particularly as a function of the solvent and of the transition metal. It will also be important to investigate in detail how the token ligand is exchanged and the precise nature of solvent–metal interactions in these intermediates.

Acknowledgment. We are grateful to SERC, the Paul Instrument Fund of the Royal Society, EEC, NATO (Grant No. 591/83), and Applied Photophysics Ltd. for supporting this research. The financial support of the National Science Foundation (Grant CHE 84-15153) and the Robert A. Welch Foundation (Grant No. B-434) is also greatly appreciated. G.R.D. thanks North Texas State University (NTSU) for a faculty development leave and the SERC for a Fellowship. We thank Professor J. K. Burdett, Dr. G. Davidson, A. J. Dixon, J. G. Gamble, Dr. F.-W. Grevels, R. E. Parsons, W. E. Porter, and J. M. Whalley for their help and advice.

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Chemisorption and Reaction of Ethylene on Chemically Modified Ru(001) Surfaces

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Abstract: The adsorption and reaction of ethylene on a Ru(001) surface on which ordered p(2×2) and p(1×2) overlayers of oxygen adatoms are present have been investigated using high-resolution electron energy loss spectroscopy, thermal desorption mass spectrometry, and low-energy electron diffraction. In contrast to the di-σ-bonded ethylene that is observed on clean Ru(001), ethylene chemisorbs molecularly in a π-bonded configuration at temperatures below 200 K on both the Ru(001)–p(2×2)O and Ru(001)–p(1×2)O surfaces. All of the ethylene that is chemisorbed on Ru(001)–p(1×2)O desorbs reversibly at 160 and 240 K, whereas approximately one-third of the ethylene on the Ru(001)–p(2×2)O surface desorbs molecularly at these temperatures. Upon annealing to 250 K, the irreversibly adsorbed ethylene on the Ru(001)–p(2×2)O surface dehydrogenates to ethylidyne (CCH_3), which dehydrogenates further to vinylidene (CCH_2) below 350 K. This represents the first unambiguous identification of a surface vinylidene species, as well as the first isolation of an intermediate in the decomposition of surface ethylidyne that preserves carbon–carbon bonding. The vinylidene decomposes to adsorbed carbon and methylidyne (CH) below 400 K, and the methylidyne decomposes with the evolution of hydrogen between 500 and 700 K.

I. Introduction

Recent spectroscopic investigations of the interaction of ethylene and acetylene with the Ru(001) surface have revealed both the nature of the molecularly chemisorbed species and the decomposition products of these unsaturated hydrocarbons.[1,2] Coadsorption experiments of hydrogen with ethylene, carbon monoxide with ethylene, and hydrogen with acetylene have clarified further the decomposition mechanisms.[3,4] The combined results of these studies[5] have led to the following mechanistic picture:[1-5] (1) both ethylene and acetylene chemisorb molecularly below 150 K on the Ru(001) surface, with rehybridization of the carbon atoms to nearly sp^3 occurring; (2) upon heating to between 150 and 280 K, both ethylene and acetylene form a $HCCH_2$ species, while acetylene also forms acetylide (CCH) at these temperatures; (3) the $HCCH_2$ species reacts rapidly to form acetylide and ethylidyne (CCH_3); (4) the ethylidyne decomposes to carbon adatoms and hydrogen near 350 K, while the acetylide decomposes via carbon–carbon bond cleavage near 380 K, forming methylidyne (CH) and carbon adatoms; and (5) the methylidyne dehydrogenates, evolving hydrogen above approximately 500 K.

We report here the results of a study of the interaction of ethylene with Ru(001) surfaces on which preadsorbed overlayers of dissociatively adsorbed oxygen are present. We have concentrated on the reproducible and well-characterized Ru(001)–p(2×2)O and Ru(001)–p(1×2)O surfaces, although we have also examined the effects of disordered oxygen overlayers, the fractional coverages of which varied from approximately 0.05 to 0.5. The

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[†] AT&T Bell Laboratories Predoctoral Fellow.

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