

Kinetics and mechanism of the reaction of photogenerated (η^1 -(tetrachloromethane)pentacarbonylmetal(0) complexes, (η^1 -(CCl_4) $\text{M}(\text{CO})_5$; $\text{M} = \text{Mo}, \text{W}$) with 1-hexene: the initial steps in the creation of olefin metathesis catalysts

Gerard R. Dobson *, Jaap P. Smit, Walter Purcell, Santino Ladogana

Department of Chemistry, University of North Texas, Denton, TX 76203, USA

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Abstract

The initial steps in the formation of the heterogeneous olefin metathesis catalysts produced by photolysis of $\text{M}(\text{CO})_6/\text{CCl}_4$ solutions ($\text{M} = \text{Mo}, \text{W}$) have been studied by pulsed laser flash photolysis with infrared and visible detection. In both systems, $(\text{Cl}_3\text{CCl})\text{M}(\text{CO})_5$ (datively bonded to M through a single Cl) is produced immediately after the flash. In the presence of the trapping nucleophile, 1-hexene (hex), this species affords $(\eta^2\text{-hex})\text{M}(\text{CO})_5$. For $\text{M} = \text{W}$, there is also a competitive unimolecular decay pathway which affords the solid catalyst. Infrared and rate data for $(\text{Cl}_3\text{CCl})\text{W}(\text{CO})_5$ and related complexes suggest that CCl_4 bonds weakly to W and is a poor net donor of charge to the metal atom, which could promote fast oxidative addition of CCl_4 to $[\text{M}(\text{CO})_5]$. The rate-determining step for the unimolecular pathway is envisioned to involve slow decomposition via CO loss of the possible oxidative addition product to afford the heterogeneous catalyst. © 1997 Elsevier Science S.A.

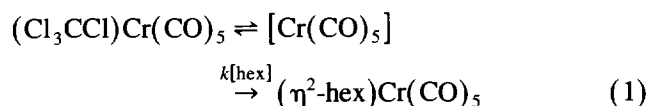
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1. Introduction

Photolysis of $\text{W}(\text{CO})_6/\text{CCl}_4$ solutions affords olefin metathesis [1] and polymerization [2] catalysts. In the case of the former, the active catalyst is a precipitate of approximate stoichiometric composition $[\text{WC}_{0.6}\text{Cl}_{0.9}]_x$ [3]. For polymerization of phenylacetylene, photolysis of $\text{Mo}(\text{CO})_6/\text{CCl}_4$ solutions provides lower catalytic activity [2]. For $\text{W}(\text{CO})_6$, the species produced immediately after the flash has been identified as $(\text{CCl}_4)\text{W}(\text{CO})_5$, and the carbonyl stretching spectrum of this species has been determined both in solid matrices [4] and in solution [5].

In contrast, $\text{Cr}(\text{CO})_6/\text{CCl}_4$ solutions after photolysis are not active catalysts in the polymerization of olefins [2]. Kinetics results for reactions taking place after pulsed laser flash photolysis of $\text{Cr}(\text{CO})_6/\text{CCl}_4$ solutions in the presence of 1-hexene (hex) trap support a single mechanism involving reversible dissociation of

CCl_4 from photogenerated $(\text{Cl}_3\text{CCl})\text{Cr}(\text{CO})_5$ followed by irreversible reaction of $[\text{Cr}(\text{CO})_5]$ with the hex trap [6]:



These results have prompted a further spectroscopic and kinetic study of the initial reactions taking place after pulsed laser flash photolysis of $\text{M}(\text{CO})_6/\text{CCl}_4$ solutions ($\text{M} = \text{Mo}, \text{W}$), to elucidate possible kinetic differences in systems in which catalysis has been observed to take place, from $\text{Cr}(\text{CO})_6/\text{CCl}_4/\text{hex}$ solutions, where catalytic activity is not observed.

2. Experimental details

2.1. Materials

$\text{W}(\text{CO})_6$ (Pressure Chemical) and $\text{Mo}(\text{CO})_6$ (Climax Molybdenum) were vacuum-sublimed before use. Tetra-

* Corresponding author.

chloromethane (CCl_4 , EM Science) was fractionally distilled from P_2O_5 under nitrogen. 1-Hexene (hex, $\text{C}_4\text{H}_9\text{CH}=\text{CH}_2$, Johnson Matthey) was similarly distilled from anhydrous MgSO_4 . *n*-Heptane (hep, Sigma-Aldrich) was fractionally distilled under nitrogen from sodium.

2.2. Identification of photogenerated transients

The identities of the photogenerated $(\text{CCl}_4)_m\text{M}(\text{CO})_5$ intermediates ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and the trapping products, $(\eta^2\text{-C}_4\text{H}_9\text{CH}=\text{CH}_2)\text{M}(\text{CO})_5$, were confirmed by

Table 1
Pseudo-first-order rate constants for reactions of $\text{M}(\text{CO})_6/\text{CCl}_4/1$ -hexene solutions ($\text{M} = \text{Mo}, \text{W}$) after flash photolysis at various temperatures

M	T (°C)	[1-hexene] (M)	$10^{-3}k_{\text{obsd}}$ (s^{-1})	
Mo	15.2	0.1022	1.21(4)	
		0.3086	2.39(5)	
		0.5020	3.14(5)	
		0.7171	4.39(6)	
		1.0101	6.2(1)	
		2.0010	12.2(1)	
		3.0047	17.6(1)	
		4.0128	24.1(4)	
		25.0	0.0889	1.17(1)
			0.2783	3.52(2)
			0.5200	7.05(4)
			0.6939	11.1(1)
	1.0040		15.0(1)	
	2.0087		28.2(2)	
	35.4	3.0047	39.7(3)	
		4.0148	53.3(4)	
		0.1022	3.76(3)	
		0.3086	7.90(6)	
		0.5020	14.0(2)	
		0.7171	20.5(3)	
	W	15.0	1.0101	31.2(7)
			2.0087	59(2)
			0	0.168(4)
			0.4947	0.254(2)
0.7558			0.295(2)	
1.0071			0.350(4)	
1.3940			0.406(3)	
2.0084			0.519(4)	
2.5101			0.621(6)	
25.0			0	0.512(3)
			0.4947	0.686(6)
			0.7558	0.776(8)
		1.0071	0.847(8)	
		1.3940	0.969(7)	
		2.0084	1.22(8)	
35.0		2.5010	1.42(13)	
		0	1.31(5)	
		0.2593	1.480(14)	
		0.4947	1.610(14)	
		0.7558	1.78(2)	
		1.0071	1.98(2)	
35.0		1.3940	2.51(2)	
		2.0084	2.92(3)	
		2.5010	3.33(4)	

employing flash photolysis with IR-detection (FP-IR). The primary components of the FP-IR system are a Tachisto Model 850 XR excimer (photolyzing) laser (N_2 gas fill; 337 nm, 10 mJ, 14 ns FWHI) and a Spectra Physics line-tunable (analyzing) CW IR laser. A CaF_2 infrared cell (1.0 mm pathlength) was employed with $[\text{M}(\text{CO})_6] = 3 \times 10^{-3}$ M. Attempts to observe the very weak, high energy A_1 bands (equatorial 'breathing' modes) for monosubstituted pentacarbonylmetal complexes, expected at ca. 2070–2080 cm^{-1} [7], were not successful. The equipment and the methods employed have been fully described elsewhere [8,9]. Details of the FP-IR studies are given in Section 3.

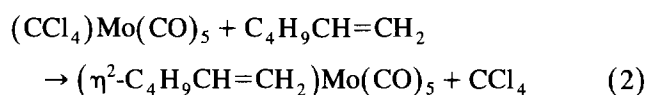
2.3. Laser flash photolysis kinetic studies

Kinetic studies monitored 425 and 415 nm respectively for Mo and W, because of superior signal-to-noise ratios in the visible spectral region. The solvents and traps were weighed (but the total volume of the solutions was determined volumetrically), so that $[\text{solvent}]/[\text{trap}]$ were known with accuracy. Solutions ca. 3.5×10^{-3} M in $\text{M}(\text{CO})_6$ ($\text{M} = \text{Mo}, \text{W}$) also containing large excesses of solvent and trap (to insure pseudo-first-order reaction conditions) were employed. Temperatures were maintained within ± 0.05 °C by employing a VWR 1140 external circulator and a jacketed 1 cm quartz cell. Values for k_{obsd} were obtained from averages of 3–10 traces of plots of $\ln(A_t - A_\infty)$ vs. time (A_t and A_∞ are measured absorbances at time t and at infinite time respectively). The kinetics data were analyzed employing ASYST-based computer programs developed in-house. All plots exhibited correlation coefficients above 0.99. Values of k_{obsd} are given in Table 1; error limits, given in parentheses as the uncertainties of the last digit(s) of the cited value, are 1 standard deviation.

3. Results

3.1. $\text{Mo}(\text{CO})_6/\text{CCl}_4/1$ -hexene solutions

Fig. 1 exhibits plots of k_{obsd} vs. $[\text{hex}]$ for reactions taking place after pulsed laser flash photolysis of $\text{Mo}(\text{CO})_6/\text{CCl}_4$ solutions in the presence of various concentrations of hex trap. Infrared spectral analysis of the solutions within the first millisecond after the flash (not shown) indicate that $(\text{CCl}_4)_m\text{Mo}(\text{CO})_5$ produced immediately after the flash disappears according to



as the two low energy bands for $(\text{CCl}_4)_m\text{Mo}(\text{CO})_5$, ($\nu(\text{CO}) = 1942$ (A_1 , s), 1971 (E, vs) cm^{-1}) are re-

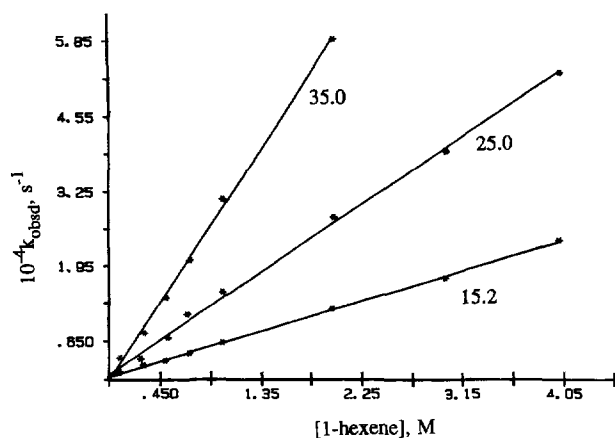


Fig. 1. Plots of k_{obsd} vs. [1-hexene] for reactions taking place after pulsed laser flash photolysis of $\text{Mo}(\text{CO})_6/\text{CCl}_4/1\text{-hexene}$ solutions at various temperatures.

placed by bands of the product, $(\eta^2\text{-C}_4\text{H}_9\text{CH}=\text{CH}_2)\text{Mo}(\text{CO})_5$ ($\nu(\text{CO}) = 1958, 1971 \text{ cm}^{-1}$). The kinetics data are consistent with a second-order rate law

$$-d[\text{Mo}(\text{CO})_6]/dt = k_2[\text{Mo}(\text{CO})_6][\text{hex}] \quad (3)$$

The second-order rate constants k_2 for data taken at three temperatures are given in Table 2. Activation parameters $\Delta H_2^\ddagger = 12.94(5) \text{ kcal mol}^{-1}$ and $\Delta S_2^\ddagger = 4.1(2) \text{ cal K}^{-1} \text{ mol}^{-1}$ are consistent with an interchange or displacement mechanism for the reaction.

3.2. $\text{W}(\text{CO})_6/\text{CCl}_4/1\text{-hexene}$ solutions

Kinetics data taken at three temperatures after pulsed laser flash photolysis of $\text{W}(\text{CO})_6/\text{CCl}_4$ solutions in the absence and presence of hex trap are shown in Table 2. Plots of k_{obsd} vs. [1-hexene] for these data are shown in Fig. 2. They have large intercepts and smaller slopes, and obey the rate law

$$-d[\text{W}(\text{CO})_6]/dt = k_1[\text{W}(\text{CO})_6] + k_2[\text{W}(\text{CO})_6][\text{hex}] \quad (4)$$

suggestive of two competing reaction pathways.

Comparisons of plots of absorbance vs. time monitoring both the IR and visible spectra confirmed that both sets of time-resolved spectral changes correspond to the same decay process. Fig. 3(i) shows time-resolved IR

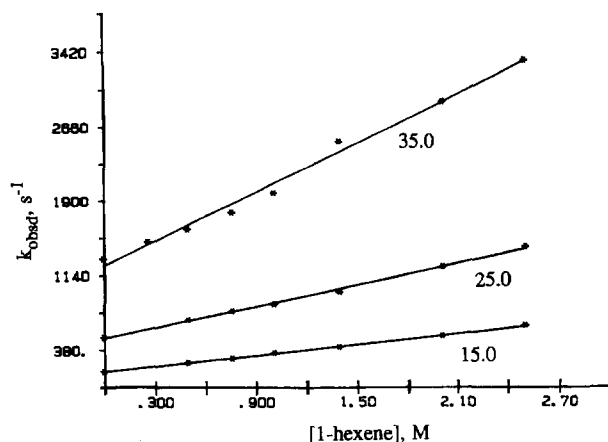


Fig. 2. Plots of k_{obsd} vs. [1-hexene] for reactions taking place after pulsed laser flash photolysis of $\text{W}(\text{CO})_6/\text{CCl}_4/1\text{-hexene}$ solutions at various temperatures.

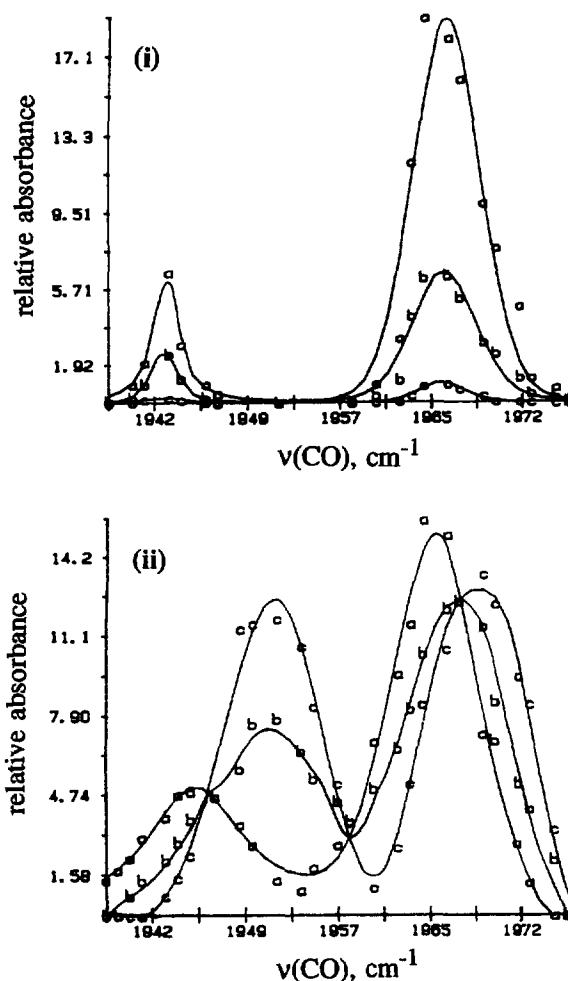


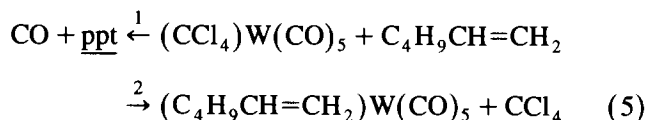
Fig. 3. Time-resolved carbonyl stretching spectra, ambient temperatures, for reactions taking place after pulsed laser flash photolysis of (i) a $\text{W}(\text{CO})_6/\text{CCl}_4/n\text{-heptane}$ solution: a 0.5 ms; b 1.5 ms; c 3.0 ms after the flash and (ii) a $\text{W}(\text{CO})_6/\text{CCl}_4$ (0.500 M)/1-hexene (0.25 M)/ $n\text{-heptane}$ solution: a 0.040 ms; b 0.8 ms; c 2.0 ms after the flash.

Table 2
Rate data for $\text{M}(\text{CO})_6/\text{tetrachloromethane}/1\text{-hexene}$ reactions

M	T (°C)	$10^3 k_1$ (s^{-1})	$10^3 k_2$ (Ms^{-1})
Mo	15.2	0.01(33)	6.21(12)
	25.0	0.2(5)	13.8(2)
	35.4	-0.02(6)	29.6(7)
W	15.0	0.164(4)	0.179(3)
	25.0	0.499(12)	0.360(8)
	35.0	1.24(4)	0.836(3)

spectra (1970–1930 cm^{-1}) taken after pulsed laser flash photolysis of a $\text{W}(\text{CO})_6/\text{CCl}_4$ (= 0.5 M)/*n*-heptane solution. It has been shown that for IR spectra in which concentrations of coordinating (such as CCl_4) and trapping nucleophile (*n*-hexane) are low (< 0.5 M), IR absorption FWHI approach those of a non-coordinating diluting solvent (in this case, *n*-heptane). Thus the IR spectra reported are approximately those one would observe in *n*-heptane solution [9]. In the time-resolved spectra, carbonyl stretching bands at 1964 and 1944 cm^{-1} are produced immediately after the flash. These bands are closely similar to those observed after photolysis of $\text{W}(\text{CO})_6/\text{CCl}_4$ solutions in Ar matrices (at 1973 and 1943 cm^{-1}) [4] and in cyclohexane solution (at 1959 and 1933 cm^{-1}) attributed to $(\text{CCl}_4)\text{W}(\text{CO})_5$ [5]. They correspond to the two lower-energy carbonyl stretching bands to be expected for a square-pyramidal $\text{M}(\text{CO})_5$ moiety of C_{4v} symmetry (E and A_1 stretching modes respectively). Photogenerated $(\text{CCl}_4)\text{W}(\text{CO})_5$ then decays, evidently without generation of a carbonyl-containing product, because no carbonyl stretching absorptions are observed over the range 1933–1970 cm^{-1} , or over the 2063–2103 cm^{-1} region of the infrared where one might hope to find evidence for the formation of an oxidative addition product such as $(\text{CCl}_3)(\text{Cl})\text{W}^{\text{II}}(\text{CO})_5$ [10]. Effervescence, together with formation of a blue precipitate, was observed immediately after the flash. Nujol mulls of this insoluble product reveal the presence of no carbonyl stretching absorptions.

Fig. 3(ii) shows time-resolved spectra taken after pulsed laser flash photolysis of $\text{W}(\text{CO})_6/\text{CCl}_4$ (= 0.5 M)/hex (= 0.25 M)/*n*-heptane solutions. They show the disappearance of the absorptions attributable to $(\text{CCl}_4)\text{W}(\text{CO})_5$ and the growth of two bands of roughly equal intensity at 1952 and 1969 cm^{-1} , characteristic of $(\eta^2\text{-hex})\text{W}(\text{CO})_5$ [the infrared spectrum for $(\eta^2\text{-1-hexene})\text{W}(\text{CO})_5$ observed after pulsed laser flash photolysis closely resembles (band positions and intensities) those for a variety of (mono-olefin) $\text{W}(\text{CO})_5$ complexes first reported in Ref. [11]]. These observations indicate that two competing reaction pathways are accessible after initial formation of $(\text{CCl}_4)\text{W}(\text{CO})_5$. The first, governed by k_1 , involves formation of the precipitate, which had been shown to be the catalytically-active species [3]. The second, governed by k_2 , involves competitive CCl_4 solvent-displacement by hex to afford $(\eta^2\text{-C}_4\text{H}_9\text{CH}=\text{CH}_2)\text{W}(\text{CO})_5$, kinetically stable on these timescales:



Activation parameters from kinetics data taken at three temperatures, $\Delta H_1^\ddagger = 17.2(5) \text{ kcal mol}^{-1}$ and $\Delta S_1^\ddagger =$

$12.2(16) \text{ cal K}^{-1} \text{ mol}^{-1}$, and $\Delta H_2^\ddagger = 13.6 \text{ kcal mol}^{-1}$ and $\Delta S_2^\ddagger = 2.8(23) \text{ cal K}^{-1} \text{ mol}^{-1}$, exhibit reasonable values for decomposition and interchange reactions respectively.

4. Discussion

The data clearly show that $(\text{CCl}_4)\text{M}(\text{CO})_5$ is produced immediately after flash photolysis of $\text{M}(\text{CO})_6/\text{CCl}_4$ solutions (M = Mo, W). In the presence of hex, the kinetics data for $(\text{CCl}_4)\text{Mo}(\text{CO})_5$ are consistent with a single further reaction pathway. In view of the reported weak catalytic activity of photolyzed $\text{Mo}(\text{CO})_6$ solutions [2], it is possible that a small decomposition pathway is also accessible upon prolonged photolysis. The failure to observe a ligand-independent pathway for Mo may be due as much to the 20-fold greater rate of the ligand-dependent pathway for Mo than W as to the inability of Mo to undergo decomposition.

The results for Mo differ from those previously reported for Cr, for which plots of k_{obsd} vs. [hex] are concave upward at high [hex] as the concentrations of CCl_4 decrease, indicative of a role for CCl_4 in the ligand-exchange process [6]. For $\text{Cr}(\text{CO})_6/\text{CCl}_4$ solutions, results overall very strongly support competition between CCl_4 and hex for an intermediate of stoichiometry $[\text{Cr}(\text{CO})_5]$ (Eq. (1)). In terms of k_{obsd} , the applicable rate law is

$$k_{\text{obsd}} = k_1 k_2 [\text{hex}] / (k_{-1} [\text{CCl}_4] + k_2 [\text{hex}]) \quad (6)$$

In the limit, $k_1 [\text{CCl}_4] \gg k_2 [\text{hex}]$, the rate behavior observed for $(\text{CCl}_4)\text{Mo}(\text{CO})_5$ would be consistent with this mechanism. However, it is more likely that a CCl_4 -displacement mechanism is applicable in view of the more positive entropy of activation observed in the Cr system and the tendency toward a displacement mechanism, $\text{Cr} \ll \text{Mo} \approx \text{W}$ [12].

For photogenerated $(\text{CCl}_4)\text{W}(\text{CO})_5$, both ligand-dependent and ligand-independent pathways are observed. It is reasonable to attribute the former to a solvent-displacement mechanism as was the case for $(\text{CCl}_4)\text{Mo}(\text{CO})_5$. For the ligand-independent pathway, the entropy of activation, $12.2(6) \text{ cal K}^{-1} \text{ mol}^{-1}$, is consistent with a dissociative process.

Such a pronounced ligand-independent pathway, for which the bonding properties of CCl_4 are undoubtedly responsible, has not heretofore been observed in flash-photogenerated (solvent) $\text{M}(\text{CO})_5$ systems. Thus it is important to consider the mode of bonding of CCl_4 to the $\text{W}(\text{CO})_5$ moiety. Table 3 presents the carbonyl stretching absorptions ($\text{A}_1 + \text{E}$), together with approximate rates of W–L bond-breaking at ambient temperature for several relevant molecules [6,7,9,13–15]. The complex (aniline) $\text{W}(\text{CO})_5$ is taken as typical of a ‘nor-

Table 3
Carbonyl stretching frequencies and approximate rates of ligand dissociation in LW(CO)₅ complexes^a

L	$\nu(\text{CO})$ (cm ⁻¹) ^a		k_1 (s ⁻¹) ^b	Reference
	E	A ₁		
CCl ₄	1964 ^c	1944 ^c	500	this work
C ₆ H ₅ Cl ^d	1957 ^c	1930 ^c	≈ 150	[6,13]
<i>n</i> -C ₄ H ₉ Cl ^d	1952	1929	≈ 10	[6,9]
C ₆ H ₅ NH ₂	1936	1920	≈ 10 ⁻⁵	[7,14]
(C ₆ H ₅) ₃ Sb	1950	1950	≈ 10 ⁻⁹	[14,15]

^a Alkane solution.

^b At ambient temperature.

^c This work.

^d By analogy to variation in rate from LCr(CO)₅ to LW(CO)₅ for L = benzene [6,13], CCl₄ [6].

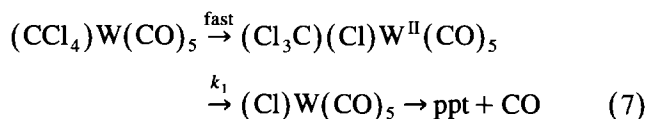
mal' monosubstituted complex in which nitrogen is bonded to the W(CO)₅ moiety via a strong N → W dative bond (with no M-to-aniline π-'back-bonding'), while (triphenylstibine)W(CO)₅ is taken to exemplify a complex in which there is both strong L → W dative σ-bonding and strong W → L π-'back-bonding' [14]. It can be seen that the A₁ (axial carbonyl) stretching mode is largely sensitive to the π-component of the synergistic bonding in the triphenylstibine complex.

It has been established that *n*-C₄H₉Cl and C₆H₅Cl each coordinate in the same manner, through Cl [9,16]. The carbonyl stretching frequencies for the three chlorine-containing complexes increase in order of the electron-withdrawing abilities of substituents bonded to Cl, *n*-C₄H₉Cl < C₆H₅Cl < Cl₃CCl, and their reactivities increase in the same order, as the basicity of Cl in each coordinating solvent decreases. Based on these observed systematics, there is no reason to suppose that CCl₄ bonds to W through two or three chlorines in this complex, as opposed to a Cl → W dative interaction [4]. However, the relative positions of the A₁ and E modes are widely divergent in the complexes bonding through N and As vs. those bonding through Cl. This observation, coupled with data on the approximate rates of W–L bond-breaking in these complexes at ambient temperature, which are 6–12 orders of magnitude slower in the N- and Sb- [14] than in the Cl-bonded complexes, indicate that bonding of Cl to W is qualitatively very different from N–W or As–W bonding.

There has yet to be developed a satisfactory analysis of bonding of main-group atoms to M(CO)₅ metal fragments based on carbonyl stretching frequencies (or force constants) [17]. σ- and π-bonding [7,18,19], together with Fenske direct ligand-to-equatorial CO charge donation [7,20], have all been considered. However, it is evident that Cl-to-W bonding, by whatever bonding mechanism, is relatively weak. In a qualitative sense it is generally accepted that whatever the bonding mechanism(s) in these complexes, higher carbonyl stretching frequencies are indicative of diminished charge-dona-

tion from the ligand to the metal atom. These conclusions, coupled with the observation that carbonyl stretching frequencies in (Cl₃CCl)W(CO)₅ are relatively high, strongly indicate that CCl₄ is weakly bonded and not strongly electron-releasing relative to ligands containing many 'conventional' donor atoms. Both these bonding features could facilitate an oxidative addition reaction pathway: weak bonding of Cl to W could lower the energy of activation for the oxidative addition process by raising the ground-state energy in (Cl₃CCl)W(CO)₅ relative to that in the N- and As-bonding analogues. Relatively poor Cl-to-W charge donation enhances the ability of the W center to undergo oxidation.

The key role of photogenerated (CCl₄)W(CO)₅ in the formation of the solid catalyst is underscored by the observation that catalytic activity decreases with increased olefin concentration, that is with the increased rate of formation of (olefin)W(CO)₅ product and the decrease in [CCl₄] [2]. This observation, together with data presented above, indicates that the ligand-independent reaction pathway leads largely to rapid decomposition of (CCl₄)W(CO)₅ to afford the active solid catalyst. The large positive entropy of activation observed for this pathway further suggests that the rate-determining step for the ligand-independent pathway involves decomposition of a possible oxidative-addition product, and not its formation:



In this regard it is to be noted that oxidative addition reactions for tungsten carbonyl complexes have been widely observed [10,21], and that *cis*-W(CO)₄Cl₂ has been reported to be a by-product of the CW photolysis of W(CO)₆/CCl₄ solutions [3].

Acknowledgements

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