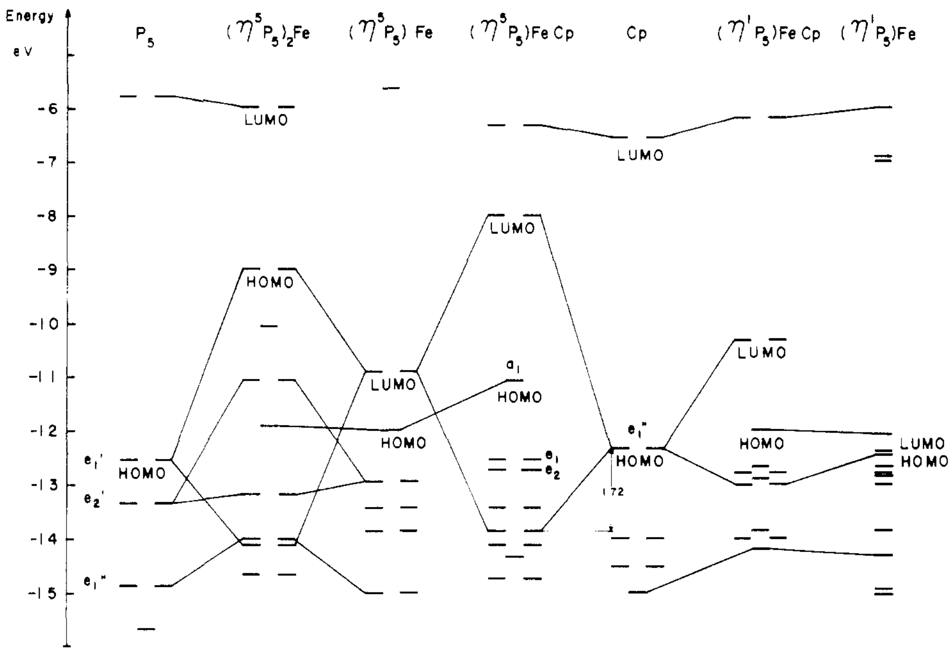


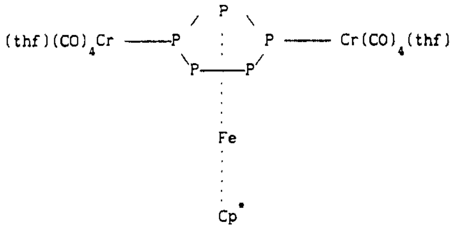
Figure 1. Interaction energy level diagram for the complexes.

Table II. Extended Hückel Parameters

atom	orbital	H_{ii}, eV	ζ_1	ζ_2	$C_1{}^a$	C_2
P	3s	−18.6	1.75			
	3p	−14.0	1.30			
Fe	4s	−9.17	1.90			
	4p	−5.37	1.90			
	3d	−12.70	5.35	1.80	0.5366	0.6678
Cr	4s	−8.66	1.70			
	4p	−5.24	1.70			
	3d	−11.22	4.95	1.80	0.5060	0.6750

[a] Contraction coefficients used in the double-ζ expansion.

It is possible, however, to get a σ bond between the P_5 ring and Fe. In this direction Scherer reported[6] that the P_5 ring in **1** interacts with two molecules of $H[Cr(CO)_5(thf)]$ to give compound **4**. Preliminary results of calculations with **4** indicate an overlap population of 0.4 for each σ Cr–P bond.



4

Hence, $[(\eta^1\text{-}P_5)FeCp]$ (**3**) can be interpreted in a way similar to that for **1** and **2** as the result of a π interaction between the $(\eta^1\text{-}P_5)Fe$ fragment and the e_1'' Cp HOMO. Here the stabilization energy is 1.1 eV, in other words 0.62 eV less than that computed for **1**. An overlap population analysis for **3** showed the formation of an important σ Fe–P bond. This remains if the interaction between Fe and the two P_5 rings is σ, as is shown in Table I for $[(\eta^1\text{-}P_5)_2Fe]$ (**5**). Furthermore, we have considered a mixed species with both σ and π bonds, $[(\eta^1\text{-}P_5)Fe(\eta^5\text{-}P_5)]$ (**6**). It is interesting to note that the overlap population for the σ bond is a little less than in **3** but the π bond is dramatically reduced compared with the other cases. The stabilization energy for this species, as can be seen in Table I, is computed to be higher than that for **2**. Hence, if we compare only the overlap populations, the results of these calculations indicate that the most favorable isomer is **5** followed by **6**, while the phosphorus analogue to ferrocene appears to be improbable.

Acknowledgment. We are most grateful to R. Hoffmann for kindly supplying us with information of related systems prior to publication and Dra. M. Ruiz-Santoyo and Dra. M. J. Rosales-Hoz for helpful discussions and assistance.

Appendix

All calculations were performed by using the extended Hückel method[7] with the weighted H_{ii} formula.[8] The bond lengths reported by Scherer were used for compounds **1**–**3** and **6**. The P–Cr bond length of 2.18 Å was used in compound **4**, and 2.22 Å was used for all the σ P–Fe bonds. The values for the H_{ii} and orbital exponents are listed in Table II. The parameters of C and H are the standard ones.[7]

Registry No. **1**, 124716-07-0; **2**, 124687-20-3.

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Reactions of 4-Acetylpyridine with $[(RH)W(CO)_5]$ Intermediates (RH = Cyclohexane, Methylcyclohexane) Produced via Pulsed Laser Flash Photolysis

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Received May 1, 1989

Pulsed laser flash photolysis studies of $W(CO)_6$ in the presence of 4-acetylpyridine (4-acpy) in methylcyclohexane (MCH) solution (eq 1), reported several years ago,[1] revealed the presence of a

$$W(CO)_6 + \text{4-acpy} \xrightarrow[\text{MCH}]{h\nu} (\text{4-acpy})W(CO)_5 + CO \quad (1)$$

reactive $[(MCH)W(CO)_5]$ intermediate with an absorption

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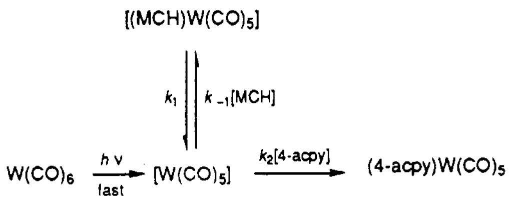
(1) Lees, A. J.; Adamson, A. W. *Inorg. Chem.* **1981**, *20*, 4381.

0020-1669/90/1329-0880$02.50/0

Scheme I



maximum at 425 nm. Kinetics data obtained for the decay of this transient were observed to obey a pseudo-first-order rate law (eq 2). Thus, plots of k_{obsd} vs [4-acpy] were observed to be curved

$$k_{obsd} = k[\text{4-acpy}]/(1 + k'[\text{4-acpy}]) \qquad (2)$$

(concave downward), and plots of $1/k_{obsd}$ vs 1/[4-acpy] were linear, with finite intercepts $[k'/k]$. These results are consistent with a mechanism (Scheme I) in which [(MCH)W(CO)$_5$] is produced as the predominant reaction species after photolysis, [W(CO)$_5$] is a steady-state intermediate, and competitive reaction of 4-acpy and MCH with [W(CO)$_5$] takes place ($k = k_1k_2/k_{-1}$[MCH]; $k' = k_2/k_{-1}$[MCH]).

The "competition ratio" of rate constants for the reaction of 4-acpy and MCH with [W(CO)$_5$], k_2/k_{-1}, was determined to be 270. This result may be contrasted to other studies which have indicated that five-coordinate intermediates derived from group VIB metal carbonyls and derivatives do not discriminate as significantly among incoming nucleophiles.[2-5] It has been shown in this regard, both in solution and in the gas phase, that such reactions are extremely rapid, approaching the diffusion-controlled rate[4,6] or that expected for the gas kinetics reaction cross section.[7] For competition ratios (k') close to 1, and [4-acpy] $\lesssim$ 0.01 M, the conditions of the Lees and Adamson study,[1] eq 2 becomes

$$k_{obsd} = k[\text{4-acpy}] \qquad (3)$$

and second-order reaction kinetics should be observed. These inconsistencies led us to reinvestigate the reaction taking place after flash photolysis of W(CO)$_6$ with 4-acetylpyridine in alkane solvents (=RH). The results reported here support the earlier conclusion that photoexcitation of W(CO)$_6$ leads to rapid production of highly reactive [W(CO)$_5$], which then forms [(RH)W(CO)$_5$] as the predominant reactive intermediate.[1,4,8] However, the present kinetics data differ qualitatively from those of the first study and implicate an alternative mechanistic interpretation. In addition, time-resolved absorption spectra obtained here suggest that while N-bonded (4-acpy)W(CO)$_5$ is the final reaction product, its O-bonded linkage isomer may initially be produced after displacement of RH from [(RH)W(CO)$_5$].

Experimental Part

General Procedures. Infrared spectra were obtained with a Nicolet 20 SXB FTIR spectrophotometer; UV–visible spectra were obtained on a Hewlett Packard 8452A diode-array spectrophotometer.

Materials. 4-Acetylpyridine (Aldrich) was vacuum-distilled (bp 65 °C/1 Torr) before use. Tetrahydrofuran (THF), after having been tested for peroxides, was refluxed over Na/benzophenone for 0.5 h and was then distilled and stored under nitrogen. Cyclohexane (CH; Baker Analyzed) was refluxed and then distilled from Na under nitrogen. Methylcyclohexane (MCH; Aldrich Gold Label) was stored over clean Na. W(CO)$_6$ was vacuum-sublimed before use. (4-acpy)W(CO)$_5$ was prepared and purified by employing the literature method[1,9,10] and was identified through its IR and UV–visible spectra, which were in agreement with the literature values.[10]

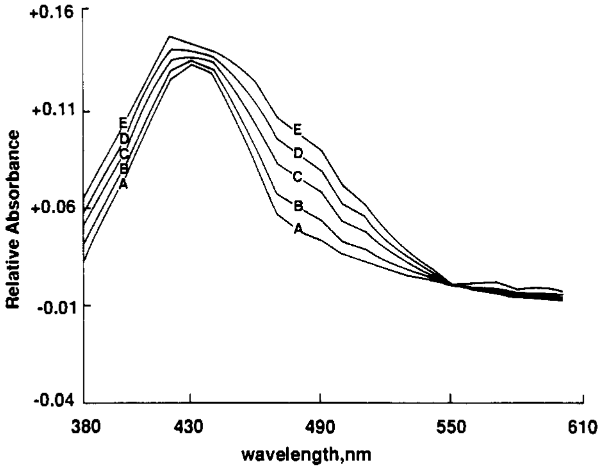


Figure 1. Time-resolved spectra after flash photolysis of W(CO)$_6$ in 4-acetylpyridine/methylcyclohexane solution (0.02194 M) at 24.5 °C. Time after photolysis (μs): A, 0.34; B, 0.64; C, 1.09; D, 1.69; E, 2.69.

Kinetics Studies. Pulsed laser flash-photolysis studies were carried out at the Center for Fast Kinetics Research (CFKR) by employing a Quantel YG481 Nd:YAG laser operating at 355 nm (100 mJ; 11 ns fwhi). The system employs an Oriel 150-W xenon lamp as the analyzing source and a Hammamatsu R928 pmt detector, and the signal is digitized by employing a Biomation 8100 transient digitizer (10 ns/point). System operations and data analysis employed a PDP 11/70 minicomputer. Temperature control (±0.1 °C precision) was effected with a Haake D8 external circulator. The average of 5–10 successive pulses employing the same reaction solution constituted a kinetics run. It was noted that there were no significant differences between rate constants obtained from earlier or later pulses. Values of k_{obsd} at various [4-acpy] and temperatures in CH and MCH solutions are given in Supplementary Table I. Limits of error, given in parentheses as the uncertainties of the last digits of the cited value, are one standard deviation.

Results and Discussion

Figure 1 shows time-resolved spectra obtained after pulsed laser flash photolysis of W(CO)$_6$ in methylcyclohexane solution with 4-acetylpyridine as the "trapping" agent. The spectrum taken immediately after the flash, attributable to [(MCH)W(CO)$_5$], is similar to that reported earlier;[1] however, later spectra (on the microsecond timescale) are *not* consistent with those expected for the final product, N-bonded (4-acpy)W(CO)$_5$, for which two absorptions in the visible region (λ_{max} = 404, 440 nm) are observed.[1,10] However, the UV–visible spectrum of the flash-photolysis solution taken several minutes later clearly indicates the presence of N-bonded (4-acpy)W(CO)$_5$.[1,10] The spectral changes that take place may be attributable to the conversion of O-bonded (4-acpy)W(CO)$_5$ initially produced via displacement of MCH from [(MCH)W(CO)$_5$] to its N-bound linkage isomer. Such a result has precedence in analogous linkage isomerization, which has been observed in (4-CNpy)W(CO)$_5$ (4-CNpy = 4-cyanopyridine) produced via CW photolysis of W(CO)$_6$ in 4-CNpy/THF solutions.[11] The preferential initial formation of the CN-bonded isomer of (4-CNpy)W(CO)$_5$ was attributed to steric hindrance expected at the pyridine nitrogen relative to the CN group.[11] A similar explanation would appear reasonable here. The time-resolved spectra taken in CH solution are very similar to those in MCH illustrated in Figure 1, indicating that the species produced in predominant concentration after flash photolysis, i.e., [(RH)W(CO)$_5$], and those formed upon displacement of RH by 4-acpy are also the same species, O-bonded (4-acpy)W(CO)$_5$.

Figure 2 shows plots of absorbance (A) vs time (t) and ln ($A_\infty - A_t$) vs time (inset) monitored at 460 nm which indicate that the reaction after flash photolysis of W(CO)$_6$ in 4-acpy/MCH

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(2) (a) Hyde, C. L.; Darensbourg, D. J. *Inorg. Chem.* **1973**, *12*, 1286. (b) Covey, W. D.; Brown, T. L. *Inorg. Chem.* **1973**, *12*, 2820. (c) Shultz, L. D.; Dobson, G. R. *J. Organomet. Chem.* **1976**, *124*, 19.

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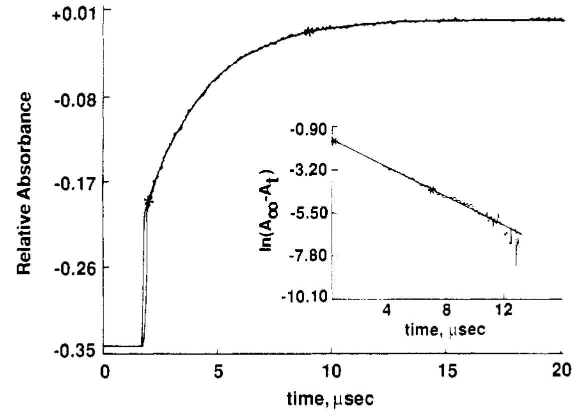


Figure 2. Plot of absorbance vs time after pulsed laser flash photolysis of $W(CO)_6$ in 4-acetylpyridine/methylcyclohexane solution (0.0110 M) at 24.5 °C. The observation wavelength is 460 nm. The inset is a plot of ln $(A_\infty - A_t)$ vs time for this reaction.

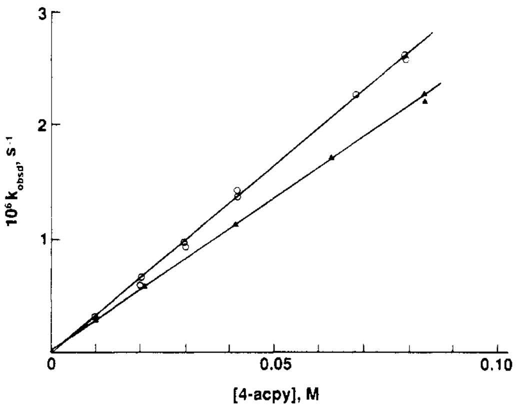


Figure 3. Plots of k_{obsd} vs [4-acetylpyridine] in (○) cyclohexane and (▲) methylcyclohexane at 24.5 °C.

solution (0.0110 M) at 24.5 °C exhibits pseudo-first-order kinetics (as do plots at other concentrations). Plots of k_{obsd} vs [4-acpy] at 24.5 °C in both MCH and CH, shown in Figure 3, exhibit similar rates, again suggestive of similar intermediates produced as predominant reactive species. In contrast to the earlier report that such plots were curved and that plots of $1/k_{obsd}$ vs 1/[4-acpy] were linear with finite intercepts (vide supra),[1] those obtained here are linear over the entire concentration range, a range similar to that employed in the earlier investigation. Values of the second-order rate constants, k $(=k_{obsd}/[\text{4-acpy}])$, at different temperatures and in CH and MCH, together with the corresponding activation parameters, are given in Table I.

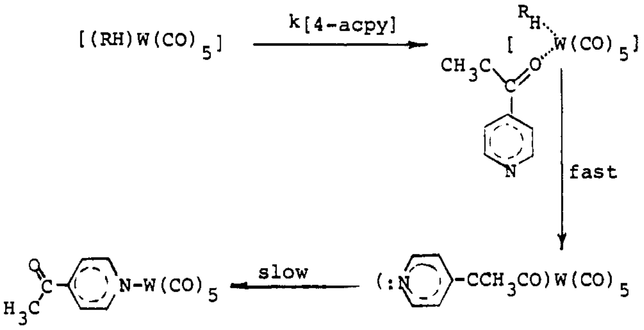
While the observed rate behavior, consistent with eq 3, could be interpreted in terms of the dissociative mechanism proposed by Lees and Adamson,[1] the activation data and other recent studies strongly support an interchange mechanism (Scheme II) in which there is appreciable 4-acpy-W bond making in the transition state. Rate constants taken over a temperature range 7.9–45.6 °C afford $\Delta H^* = 3.4$ (2) kcal/mol. This value may be contrasted to the strength of the W–H–C agostic interaction,[12,13] recently determined from photoacoustical calorimetric data to be 13.4 (28) kcal/mol in $[(n\text{-heptane})W(CO)_5]$.[14] The calculated entropy of activation, −13.0 (6) cal/(deg mol) (Table I), also strongly supports an interchange mechanism. Finally, other recent studies in mixed solvents have indicated such a hydrocarbon displacement pathway to be accessible in $[(n\text{-heptane})W(CO)_5]$ even for 1-hexene,[15] a much weaker nucleophile than 4-acetylpyridine.

Table I. Bimolecular Rate Constants for Reactions Taking Place after Flash Photolysis of $W(CO)_6$ in 4-Acetylpyridine Solutions (Solvent = Methylcyclohexane, Cyclohexene) at Various Temperatures[a]

T, °C	solvent	$10^{-7}k$, M^{-1} s^{-1}
7.9	cyclohexane	2.28 (3)
14.8		2.73 (3)
24.5		3.17 (18)
24.9		3.37 (9)
35.7		4.32 (2)
45.6		5.30 (8)
24.5	methylcyclohexane	2.78 (4)

[a] Activation parameters: $\Delta H^* = 3.4$ (2) kcal/mol; $\Delta S^* = -13.0$ (6) cal/(deg mol).

Scheme II



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Registry No. $W(CO)_5$, 30395-19-8; 4-acpy, 1122-54-9.

Supplementary Material Available: Supplementary Table I, giving pseudo-first-order rate constants for reactions taking place after pulsed laser flash photolysis of $W(CO)_6$ in 4-acetylpyridine/alkane solutions (alkane = cyclohexane, methylcyclohexane) at various temperatures (3 pages). Ordering information is given on any current masthead page.

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(12) It is probable that interaction between CH and MCH with the $W(CO)_5$ moiety is via a linear "agostic" R–C–H interaction, see: (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.

(13) For a dissociative (D) mechanism leading to formation of a $[W(CO)_5]$ intermediate, the enthalpy of activation should be equal to or greater than the solvent–W bond strength.

(14) Morse, J.; Parker, G.; Burkey, T. J. *Organometallics* **1989**, *8*, 2471.

(15) Zhang, S.; Dobson, G. R. *Inorg. Chim. Acta* **1989**, *165*, L11.

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^{99}Ru NMR Spectroscopy of Ruthenium(II) Polypyridyl Complexes

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Received August 1, 1989

The ground- and excited-state properties of ruthenium(II) polypyridyls have been the subject of enormous attention in recent

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