

Figure 1 shows the C 1s photoelectron spectra for a clean Pd{111} sample exposed to a series of different methanol exposures at 105 K and subsequently heated to 300 K. The peaks with BEs of 285.8 and 283.8 eV are assigned to OCH₃ and CH₃, respectively.¹ The formation of CH₃ exhibits a striking dependence on the initial coverage of methanol, forming only between exposures of 1.00 and 1.75 L. This requirement suggests that there is a specific arrangement of methanol molecules occurring near monolayer coverage on the Pd surface which is required to activate the C-O bond, perhaps involving hydrogen bonding between OH units of adjacent methanol molecules.²¹ Although the details of the initial coverage effect is still an open question, the observation would certainly explain the variability of results obtained with this seemingly straightforward model system.

The temperature dependence of CH₃ formed by a 1.25-L exposure of methanol to Pd{111} at 105 K is striking. The methanol itself remains molecularly adsorbed until the temperature is increased to 225 K. At this point, the single C 1s peak at 286.2 eV splits into two peaks at 285.8 and 283.8 eV as noted above. Thereafter, the surface OCH₃ and CH₃ species undergo two independent reaction channels. The high binding energy peak shifts slightly, to 286.0 eV, by 400 K, suggesting decomposition of OCH₃ to CO and H₂. Above 400 K, CO and H₂ desorption is observed, accompanied by a gradual shift of the 283.8-eV peak toward 285.0 eV. This trend suggests that the CH₃ species is undergoing a decomposition reaction, presumably involving dehydrogenation, where the products are characterized by using SIMS as discussed below.

The positive-ion SIMS peak intensities as a function of temperature after exposing Pd{111} 1.25 L of CH₃¹⁸OH at 105 K are shown in Figure 2. The intensities of methanol ions (*m/e* = 35, 33, 31) and CH_x⁺ ions decline concurrently as the temperature is increased from 105 to 275 K. This result indicates that in this temperature range molecularly adsorbed methanol either desorbs or decomposes into other species. When the surface temperature reaches 300 K, however, the CH₃⁺ ion intensity increases and CH₃⁺ is the major carbon-containing secondary ion. This ion correlates with the XPS C 1s peak at 283.8 eV seen in Figure 1 and is associated with CH₃. Note the development of secondary ions with *m/e* 14 and 13 at 400 and 500 K, respectively, which eventually ends up with a mixed phase of CH_x (*x* = 0-3) at 550 K. The appearance of CH_x (*x* < 3) secondary ions is consistent with the XPS C 1s peak shift from 283.8 to 285.0 eV and indicates that a stepwise dehydrogenation of CH₃ occurs at *T* ≥ 400 K. This unusual stability of CH₃ on the Pd{111} is generally not found on clean metal surfaces above 300 K. In our case, however, the CH₃ species is stable to the temperature where CO begins to desorb from the surface. Hence, it is possible that CO chemisorption may block the dehydrogenation or recombination of CH₃. A similar site-blocking mechanism has been observed for C₂ fragments coadsorbed with CO on Ni{001} and Ru{001}.²²

We believe that the results presented here are important for several reasons. (1) The formation of CH₃ from CH₃OH is found to occur over a very limited initial coverage of methanol. This observation implies that the formation of CH₃ is contingent upon a special molecular arrangement of precursors before reaction and that the CH₃ product is stabilized by ancillary reaction products, such as CO. (2) The dramatic dependence of the reaction pathway on initial reaction conditions helps to explain divergent observations from other laboratories. (3) The combination of XPS and SIMS provides a unique approach for examining the fate of these important reaction intermediates.

Acknowledgment. We appreciate many helpful discussions with Dr. Ying Zhou and Dr. Robert J. Levis. Financial support from the National Science Foundation, the Office of Naval Research, and the Department of Energy is gratefully acknowledged.

Registry No. Methanol, 67-56-1; palladium, 7440-05-3.

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New Intermediates Observed in the Flash Photolysis of Cp₂Fe₂(CO)₄

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Received November 18, 1991

Revised Manuscript Received January 27, 1992

The photochemistry of Cp₂Fe₂(CO)₄, **1**, has received a great deal of attention.¹⁻⁷ Both CO loss and metal-metal bond homolysis are established as primary photochemical pathways.^{2,4,5} The CO loss species of symmetrical structure, Cp₂Fe₂(μ-CO)₃, **2**, is the most thoroughly established intermediate.^{1b,5c} Other than that it is formed exclusively from the trans isomer and not seen within 1 ns following 580-nm laser excitation,^{6b} nothing is known of the mechanism or kinetics of its formation. We have investigated the photochemistry of **1** in hydrocarbon solution, using conventional xenon flash and laser flash photolysis, at both room temperature and low temperatures. We report here the existence of three previously unreported intermediates, and observations that indicate the origin and fate of each.

Xenon flash lamp irradiation of a hexane solution of **1** at room temperature under Ar results in the appearance of **2** (λ_{max} = 510 nm), which decays with second-order kinetics. However, the absorbance at 510 nm does not return to the original value within 8 s. The UV-visible spectrum of the solution taken within 20-30 s following the flash (by which time **2** has disappeared) reveals the presence of a longer-lived species (λ_{max} ≈ 380 nm). The difference IR spectrum, taken after **2** has disappeared, reveals negative absorbances due to **1** and three new bands (1839, 1786, 1674 cm⁻¹) which disappear over 2-3 h (Figure 1a). Several isosbestic points are observed, showing that the new species, designated **3**, decays to form **1**. **3** is not observed following photolysis in solutions under CO.

Sunlamp irradiation (predominantly 366 nm) causes rapid loss of **3** to form **1**. The IR spectrum of **3** is consistent with a semi-bridged species, as shown in Scheme I. Making allowance for the presence of an additional terminal CO on each metal in the Mo species, the observed pattern of bands is closely similar to that ascribed to Cp₂Mo₂(CO)₂(μ-CO)₂(μ-η¹,η²-CO) (1978, 1933, 1898, 1855, and 1665 cm⁻¹).^{3b,8}

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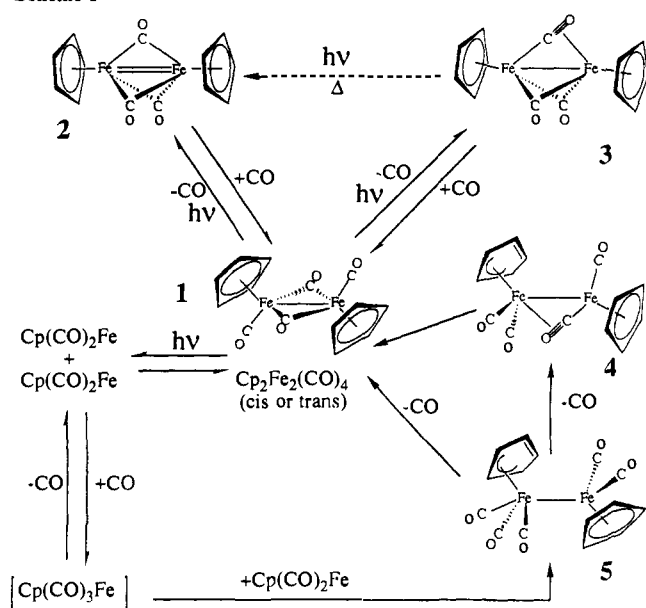
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Scheme I



Despite its being formed in relatively small amounts, **3** is remarkably stable. It is considerably less reactive toward CO than its isomer, **2**, or other semibridging species for which observations of reactivity have been made, e.g., $\text{Mn}_2(\text{CO})_9$.⁹ Visible-light irradiation probably excites the molecule so as to open the semibridge or transform it into a normal bridge, permitting rapid reaction with CO.

Under CO, xenon flash irradiation produces a new decay process in the time regime of 100 ms, slow with respect to the loss of **2** reacting with CO.^{2a,4a} The concentration of the new species, designated **4**, increases with CO partial pressure over the solution. However, the rate of decay is unaffected by [CO]. A time-resolved UV-visible spectrum obtained using xenon flash photolysis or laser flash (nitrogen laser, 337 nm) with photodiode array detection reveals a broad maximum at 490 nm.^{10a}

Using laser flash photolysis of solutions under CO, the rapid formation of still another species is seen. The transient absorbance at 400–430 nm initially increases due to recombination of $\text{CpFe}(\text{CO})_2$ radicals to form **1**. However, it eventually substantially exceeds the initial absorbance, before decaying to the preflash level. This indicates the presence of an additional species, designated **5**, with $\lambda_{\text{max}} \approx 400$ nm. Although the amount of **5** formed increases with [CO], its rate of decay ($k = 5 \times 10^3 \text{ s}^{-1}$ at 22 °C) is independent of [CO].^{10b}

Figure 1b shows IR spectra taken about 1 min following xenon flash irradiations of solutions under 1 atm of Ar or 1 atm of CO at –25 °C. The spectrum under CO shows IR absorptions due to **4**, at 1990, 1956, 1941, and 1684 cm^{-1} . The band at 1684 cm^{-1} is consistent with a semibridging CO; we therefore assign the structure shown in Scheme I. The spectrum for solutions under Ar also shows bands due to **2**^{1b,4,5} and **3**.

At –70 °C under CO, bands are observed at 2040, 1992, 1974, 1967, and 1941 cm^{-1} (Figure 1c). These bands, ascribed to **5**, disappear over a period of 1 h, with an increase in the bands assigned to **4**. **5** apparently has five terminal CO groups. The grouping of IR bands is consistent with the presence of three CO

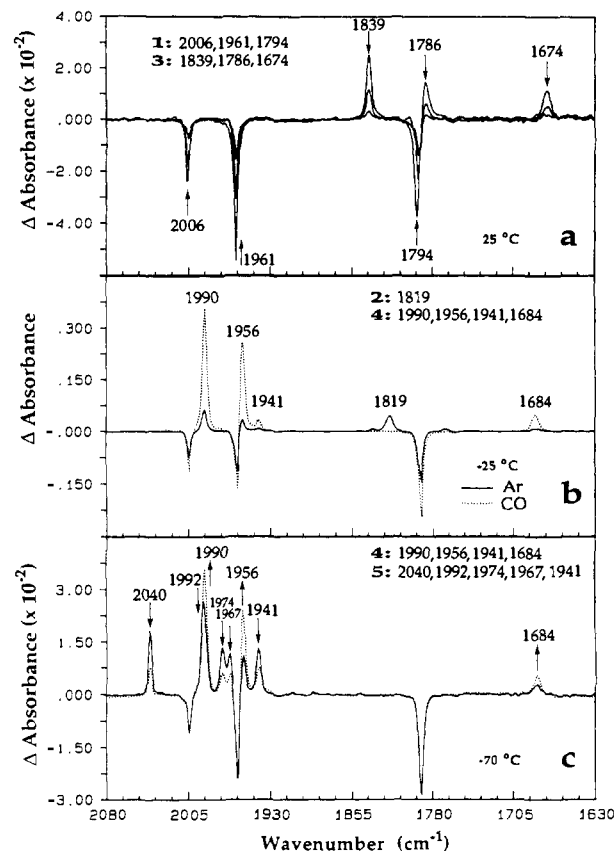


Figure 1. Difference IR spectra of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$. (a) In hexane under Ar before and after seven flashes (1, 60, and 150 min, respectively). (b) In methylcyclohexane (90%) and 3-methylpentane (10%) at –25 °C under 1 atm of Ar or CO, before and 1 min after seven flashes. (c) In methylcyclohexane (90%) and 3-methylpentane (10%) at –70 °C, before and after 1 flash: (---) 1 min after the flash; (—) 36 min after the flash.

groups on one Fe atom (e.g., 2047, 1980, and 1972 cm^{-1} in $(\eta^4\text{-C}_5\text{H}_6)\text{Fe}(\text{CO})_3$)¹¹ and two CO groups on the second Fe (e.g., 1992 and 1941 cm^{-1} in $\text{CpFe}(\text{CO})_2\text{SiEt}_3$).¹² The existence of a band at about 400 nm in the UV-vis spectrum is consistent with a structure involving a nonbridged Fe–Fe bond.¹³

The sequence of decays in IR bands is **5** → **4** → **1**. Clearly, both **4** and **5** are formed more extensively under CO. Their formation is thus inconsistent with their descent from a CO-loss product. Experiments involving use of highly enriched ¹³CO show that essentially *all* the CO groups in **4** and **5** are exchanged, even in the course of a single flash. This strongly suggests that their formation occurs via a radical pathway; the lability of 17-electron carbonyl radicals is well-established.^{4e,14,15} The most plausible explanation for the formation of both **4** and **5** is that a $\text{CpFe}(\text{CO})_2$ radical reacts with CO to form a nominally 19-electron species, which then recombines with a 17-electron radical to form **5**.¹⁶ **5** then decays to form **4** and possibly also decays directly to **1**.

These new observations further illuminate the complex character of the several processes that occur upon photolysis of **1**. The newly identified species might be important reactive intermediates in photochemical reactions of **1** with various substrates. The facile

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(10) (a) The rate constant for the disappearance of **2**, $k = 280 \text{ s}^{-1}$, measured by Caspar and Meyer in cyclohexane under 1 atm of CO^{2a} is lower than both that observed by Turner and co-workers ($k = 550 \text{ s}^{-1}$)^{4a} and that observed in our experiments ($k = 750 \text{ s}^{-1}$ in hexane at 25 °C). This may be due to the existence of the process of **4** → **1**, which could have affected the value estimated for the rate constant in Caspar and Meyer's experiments. (b) Turner and co-workers have also observed an intermediate, designated X (1975 cm^{-1}),^{4a} using time-resolved infrared spectroscopy for a solution of **1** in cyclohexane under 1 atm of CO. X appears 25 μs after the flash and decays with $k = 4.6 \times 10^3 \text{ s}^{-1}$.

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(15) In separate experiments we have demonstrated that exchange of ¹³CO with thermally or photochemically generated $\text{CpFe}(\text{CO})_2$ radicals is rapid with respect to recombination of the radicals under 1 atm of CO.

(16) The low relative concentration of the 19-electron form may preclude its reaction with another 19-electron radical.

addition of CO to the CpFe(CO)₂ radical is remarkable, though consistent with other evidence of ready addition to a 17-electron CpFe center.^{4d,14} Evidence of **5** and **4** formation is seen even in photolysis under Ar. Further characterization of the photochemistry of Cp₂Fe₂(CO)₄ is underway.

Acknowledgment. This research was supported by the National Science Foundation through Grant CHE89-12773.

Enhanced Reactivity from Noninnocent Behavior by an Alkoxide Ligand in Cp^{*}RuP(OR): Toward the Mechanism of Alcohol Elimination

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Received October 25, 1991

We seek to identify the bonding and reactivity patterns of late transition metal alkoxide compounds.¹ In particular, we anticipate that altered π-donation by alkoxide lone pairs might allow facile ligand addition and dissociation. The potentially unsaturated molecules Cp^{*}Ru(P)(OR)_f (Cp^{*} = η⁵-C₅Me₅; P = PCy₃ or PⁱPr₂Ph;² R_f = CH₂CF₃) are accessible from reaction of Cp^{*}Ru(P)Cl³ with TiOR_f in Et₂O. The crystal structure⁴ of one of these (Figure 1) shows a two-legged piano-stool structure with the metal coplanar with O, P, and the Cp^{*}-ring midpoint. A distorted trigonal bipyramid is favored for d⁶ ML₄X systems when X is a π-donor.^{5,6} Since Cp occupies three *fac* coordination sites and since X prefers the equatorial site in such a trigonal bipyramid, the M-Cp axis is predicted to lie in the MLX plane, as observed. The Ru-O-C angle (124.6 (9)°) and especially the Ru-O distance (1.992 (10)°)⁷ indicate that the ground state of the molecule involves O→Ru π-donation and is thus going toward a formal 18-valence-electron ground state.

Nevertheless, in marked contrast to Cp^{*}Ru(PMe₃)₂X species,⁸ the Cp^{*}Ru(PⁱPr₂Ph)(OR)_f representative reacts in time of mixing with 1 equiv of CO to give the adduct Cp^{*}Ru(PⁱPr₂Ph)CO(OR)_f.⁹ The observation of four ¹Pr methyl chemical shifts in C₆D₅CD₃ proves that the ruthenium center is chiral, and thus no ligand is dissociated upon CO addition. The methylene protons of OC-H₂CF₃ also show the diastereotopic inequivalence necessitated by the adduct formula.

Consistent with the bulky environment imposed by Cp^{*} and the large phosphines employed, Cp^{*}Ru(PⁱPr₂Ph)(OR)_f shows selectivity for Lewis base binding. The ³¹P and ¹³C NMR spectra

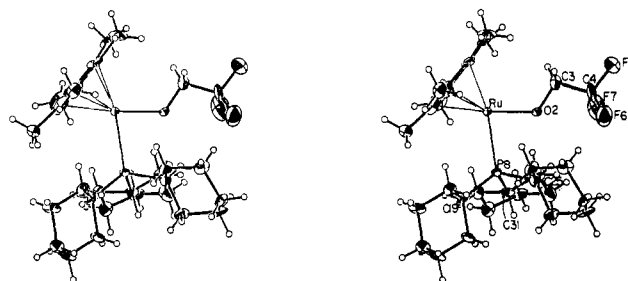
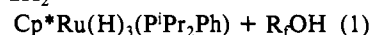


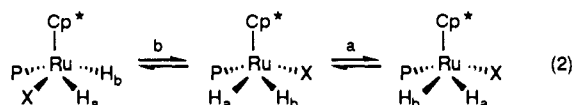
Figure 1. Stereo ORTEP drawing of (η⁵-C₅Me₅)Ru(OCH₂CF₃)(PCy₃), showing selected atom labeling.

show negligible coordination of C₂H₄ at 25 °C,¹⁰ while ethylene binding is complete (>95%) in the presence of an equimolar amount of C₂H₄ at -60 °C. Ethylene rotation is halted at -60 °C.¹¹

Cp^{*}Ru(PⁱPr₂Ph)(OR)_f reacts with H₂ in a multistep reaction under exceptionally mild conditions (1 h at 25 °C and 1 atm of H₂) according to eq 1.¹² The resulting product is a classical Cp^{*}Ru(PⁱPr₂Ph)(OR)_f + 2H₂ →



Ru(IV) trihydride.^{13,14} In order to better understand the mechanism of this *heterolytic* splitting¹⁵ of H₂, Cp^{*}Ru(PⁱPr₂Ph)(OR)_f was reacted with equimolar H₂ at 25 °C. The result is partial consumption of Cp^{*}Ru(PⁱPr₂Ph)(OR)_f as well as partial production of Cp^{*}Ru(H)₃(PⁱPr₂Ph) together with *cis*-Cp^{*}Ru(H)₂(OR)_f(PⁱPr₂Ph).^{16,17} Subjecting a solution of this dihydride to vacuum at 25 °C completely reverses the oxidative addition. Only in the presence of additional H₂ is the *cis* dihydride completely converted to Cp^{*}Ru(H)₃(PⁱPr₂Ph) and R_fOH, thus proving the intermediacy of the dihydride in eq 1. *cis*-Cp^{*}Ru(H)₂(OR)_f(PⁱPr₂Ph) is a fluxional species at 25 °C, showing one hydride doublet, two ¹Pr methyl chemical shifts, and equivalent OCH₂CF₃ methylene hydrogens. At -85 °C, the hydride pattern shows two doublets (*J*_{PH} = 27 and 45 Hz), and the ¹Pr methyl groups show four chemical shifts. Taken together, these data prove that the fluxional process is not simply site exchange of the two hydrides (eq 2a), but instead occurs with concurrent racemization at the metal (eq 2b). The time-average molecular mirror plane



implicit in the process in eq 2b could traverse the species *trans*-Cp^{*}Ru(H)₂(OR)_f(PⁱPr₂Ph), but the 25 °C hydride chemical shift value (the average of the two values at -85 °C) precludes any significant (>10%) presence of the *trans* isomer¹⁸ at 25 °C; it could only be a transition state.

It is noteworthy that elimination of alcohol from Cp^{*}Ru(H)₂(OR)_f(PⁱPr₂Ph) is neither spontaneous nor unimolecular at

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(5) Rachidi, I. E.-I.; Eisenstein, O.; Jean, Y. *New J. Chem.* **1990**, *14*, 671.

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(9) Selected spectroscopic data (25 °C, *d*₈-toluene): ¹H NMR, Cp^{*} 1.31, OCH₂CF₃ 4.22 and 4.25, ¹Pr 0.93, 1.22, 1.23, and 1.49; ³¹P{¹H}, 52.3; ¹³C{¹H}, 210.4 (CO *J*_{PC} = 20 Hz); ν_{CO} = 1906 cm⁻¹.

(10) For comparison, Cp^{*}RuCl(PⁱPr₂Ph) is 80% converted (³¹P NMR) to an adduct under 1 equiv of (¹³C)₂H₄ at 25 °C in toluene. Olefin rotation is facile in this adduct at 25 °C (δ(¹³C) = 43.3 ppm).

(11) δ(¹³C) = 42.0 and 40.5 ppm with *J*(CC') = 44 Hz.

(12) This overall reaction was reported recently for Cp^{*}Ru(PCy₃)(OMe). See: Chaudret, B.; Duteil, A.; He, X. D. *J. Organomet. Chem.* **1990**, *391*, C45.

(13) Arliquie, T.; Border, C.; Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1989**, *8*, 1308. A structure determination of Cp^{*}Ru(H)₃(PPh₃) shows that no coordinated H₂ is involved. See: Suzuki, H.; Lee, D. H.; Oshima, N.; Moro-oka, Y. *Organometallics* **1987**, *6*, 1569.

(14) Selected spectroscopic data (25 °C, *d*₈-toluene): ¹H NMR, Cp^{*} 1.96, ¹Pr 0.99 and 0.78, RuH -10.77 (d, *J*_{PH} = 22 Hz); ³¹P{¹H}, 92.7.

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(16) Selected spectroscopic data: ¹H NMR (-85 °C, *d*₈-toluene), Cp^{*} 1.96, RuH -10.0 (d, *J*_{PH} = 27 Hz) and -10.83 (d, *J*_{PH} = 45 Hz); ³¹P{¹H}, 52.5.

(17) Alternative to the *cis* and *trans* labels are *lateral* and *diagonal*, since the H-Ru-H angle in the "trans" isomer is not 180°. See: King, R. B.; Reimann, R. H.; Darenbourg, D. J. *J. Organomet. Chem.* **1970**, *93*, C23.

(18) Rearrangement 2a would be readily accomplished by a dihydrogen intermediate, but an H₂ species could also be an intermediate in eq 2b.