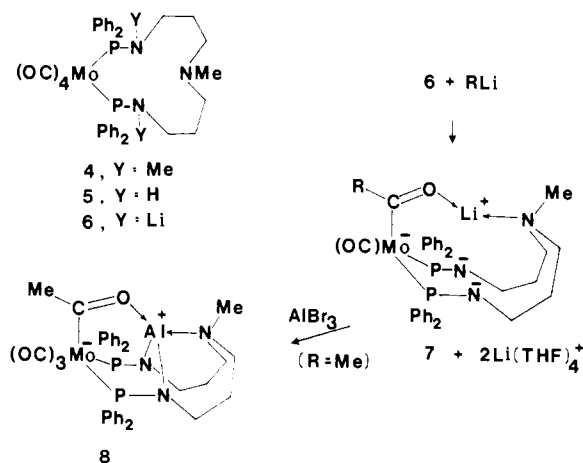
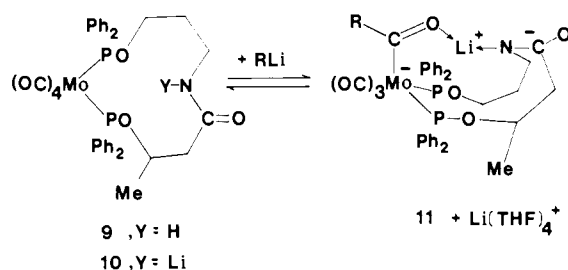


Scheme I



$AlBr_3$  to a solution of **7** ( $R = CH_3$ ) gives **8** as an isolable orange, crystalline solid.<sup>5</sup> Solution IR studies indicate that the molecules *cis*-( $OC$ )<sub>4</sub>Mo[ $Ph_2PNH(CH_2)_4NHPPH_2$ ], *cis*-( $OC$ )<sub>4</sub>Mo-( $Ph_2PNH_2$ )<sub>2</sub>,<sup>6</sup> and *cis*-{(OC)<sub>4</sub>Mo[( $Ph_2PO$ )<sub>2</sub>H]}Et<sub>3</sub>NH<sup>6</sup> likewise react sequentially with 3RLi to give acylate type products similar to **7**.<sup>7</sup>

A third example of strong  $Li^+$  binding favoring acylate-type products involves RLi reactions with complex **9**, containing an



amide function in the pseudo crown ether ring ( $\nu_{NH}$  3375,  $\nu_{CO}$  (amide) 1676  $cm^{-1}$ ). Addition of 1 equiv of RLi to **9** gives the lithium amide **10**, which can be isolated as a highly reactive yellow solid (no  $\nu_{NH}$ ,  $\nu_{CO}$  (amide) 1583  $cm^{-1}$ ). Addition of excess RLi to **10** gives the benzoylate/acylate products **11**.<sup>8</sup>

The above results indicate that the important feature to be considered when varying P-donor crown ether ligand substituents is the effect these changes have on  $Li^+$  binding by the product molecule with strong  $Li^+$  binding favoring nucleophilic addition to a coordinated CO. The effect(s) that these changes may have on the CO electron distribution in the starting tetracarbonyl is of secondary importance.

**Acknowledgment.** This work was supported by a grant from the Natural Science and Engineering Research Council of Canada.

(4) E.g., spectroscopic data for **7** ( $R = Me$ ):  $\nu_{CO}$  1905 (s), 1815 (s), 1725 (s, br)  $cm^{-1}$ ;  $^{31}P$  NMR (THF)  $\delta$  75.8;  $^{13}C$  NMR  $\delta$  342.8 (MeCO, 1:2:1, t,  $J_{31P,13C} = 15$  Hz).

(5) Anal. Calcd for  $C_{36}H_{38}AlMoN_3O_4P_2$  (**8**) C, 56.8; H, 5.0; N, 5.5; Al, 3.5. Found: C, 56.5; H, 5.2; N, 5.3; Al, 3.3. The postulated structure for **8** is similar to the dimethylamide derivative [(OC)<sub>4</sub>Fe(Me<sub>2</sub>NCO)Al(NMe<sub>2</sub>)<sub>2</sub>] derived from the reaction of Fe(CO)<sub>5</sub> with Al<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub>; Petz, W.; Schmid, G. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 934.

(6) Gray, G. M.; Kraihanzel, C. S. *J. Organomet. Chem.* **1978**, *146*, 23. Reference 6 reports that the complex *cis*-(OC)<sub>4</sub>Mo(PPh<sub>2</sub>NH<sub>2</sub>)<sub>2</sub> reacts sequentially with RLi to give the dilithium salt *cis*-(OC)<sub>4</sub>Mo(PPh<sub>2</sub>NHLi)<sub>2</sub> as an insoluble yellow solid. Further reaction with RLi was reported to give an orange-red solution, but the structure of this solution species was not elucidated.

(7) A qualitative order for the stability of the acylate/benzoylate products obtained from reaction of RLi with the following: **5** > *cis*-(OC)<sub>4</sub>Mo[ $Ph_2PNH(CH_2)_4NHPPH_2$ ] ~ *cis*-(OC)<sub>4</sub>Mo(PPh<sub>2</sub>NH<sub>2</sub>)<sub>2</sub> > *cis*-(OC)<sub>4</sub>Mo[( $Ph_2PO$ )<sub>2</sub>H]Et<sub>3</sub>NH. This order reflects a decrease in  $Li^+$  binding by the product molecule.

(8) E.g., **11** ( $R = Ph$ ) may be isolated as a highly reactive orange oil,  $\nu_{CO}$  1933 s, 1855, 1831  $cm^{-1}$ . Reaction of **11** with alcohols or water regenerates the starting tetracarbonyl **9**.

## Low-Temperature Photochemistry of Fe(CO)<sub>4</sub>(ethylene) and Fe(CO)<sub>4</sub>(propylene). Spectroscopic Observation of Catalytically Significant Intermediates

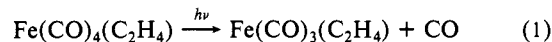
James C. Mitchener and Mark S. Wrighton\*

Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

Received August 20, 1982

We report the low-temperature photochemistry of Fe(CO)<sub>4</sub>(olefin) (olefin = ethylene, propylene, 1-pentene, 3,3-dimethyl-1-pentene, 1,4-pentadiene) and the IR spectroscopic characterization of several intermediates involved in the Fe(CO)<sub>5</sub>-photocatalyzed isomerization of alkenes. There are reports of extraordinary catalytic activity for the light-generated catalyst derived from Fe(CO)<sub>5</sub> in the presence of 1-pentene,<sup>1,2</sup> and many papers document<sup>3</sup> the thermal and photoinduced catalytic reactions in this system. While a HFe(CO)<sub>3</sub>( $\pi$ -allyl) intermediate has been invoked to account for the alkene isomerization,<sup>3g-i</sup> the only Fe species observed under (photo)catalysis conditions is Fe(CO)<sub>4</sub>(alkene).<sup>3a,4</sup> The Fe(CO)<sub>4</sub>(alkene) alone is not sufficiently thermally active to account for the high activity found upon photoactivation of Fe(CO)<sub>5</sub>.

It has been reported<sup>5</sup> that Fe(CO)<sub>4</sub>(C<sub>2</sub>H<sub>4</sub>) undergoes loss of CO upon irradiation in a rigid Ar matrix at low temperature as detected by IR spectroscopy (eq 1). With this result in hand we



undertook a study of the reactivity of such species for alkenes having allylic hydrogens. Figure 1 shows a comparison of the IR spectral changes accompanying irradiation of matrix-isolated Fe(CO)<sub>4</sub>(C<sub>2</sub>H<sub>4</sub>) and Fe(CO)<sub>4</sub>(C<sub>3</sub>H<sub>6</sub>) in alkane at 77 K.<sup>6</sup> The spectral changes for the C<sub>2</sub>H<sub>4</sub> complex are nearly identical with those found in an Ar matrix<sup>5</sup> and show a feature attributable to the photoejected CO (2132  $cm^{-1}$ ) and three bands associated with the 16-electron Fe(CO)<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>) (Table I). In contrast, the spectral changes for Fe(CO)<sub>4</sub>(C<sub>3</sub>H<sub>6</sub>) are consistent with a different product that we suggest is HFe(CO)<sub>3</sub>( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>). The infrared band pattern is similar to that for BrFe(CO)<sub>3</sub>( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>).<sup>7</sup> The light-induced loss of CO from the propylene complex is evident in that there is a free CO band at 2132  $cm^{-1}$ , but the three-band

(1) Mitchener, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 975.  
 (2) (a) Chase, D. B.; Weigert, F. J. *J. Am. Chem. Soc.* **1981**, *103*, 977.  
 (b) Whetten, R. L.; Fu, K.-J.; Cerant, E. R. *Ibid.* **1982**, *104*, 4270.  
 (3) (a) Schroeder, M. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 551; *J. Organomet. Chem.* **1977**, *128*, 345. (b) Asinger, F. Y.; Fell, B.; Schrage, K. *Chem. Ber.* **1965**, *98*, 372, 381. (c) Asinger, F.; Fell, B.; Collin, G. *Ibid.*, **1963**, *96*, 716. (d) Carr, M. D.; Kane, V. V.; Whiting, M. C. *Proc. R. Chem. Soc. London* **1964**, 408. (e) Howard, J. F.; Chalk, A. J. *Org. Synth. Met. Carbonyls* **1977**, *2*, 680-694. (f) Frankel, E. N.; Emken, E. A.; Peters, H. M.; Davison, V. L.; Butterfield, R. O. *J. Org. Chem.* **1964**, *29*, 3292, 3620. (g) Casey, C. P.; Cry, C. R. *J. Am. Chem. Soc.* **1973**, *95*, 2248. (h) Cowherd, F. G.; von Rosenberg, J. L. *Ibid.* **1969**, *91*, 2157. (i) Barborak, J. C.; Dasher, L. W.; McPhail, A. T.; Nichols, J. B.; Oman, K. D. *Inorg. Chem.* **1978**, *17*, 2936.

(4) (a) We note the report of the very labile Fe(CO)<sub>3</sub>( $\eta^2$ -methylacrylate)<sub>2</sub> formed photochemically at low temperature (-30 °C): Grevels, F.-W.; Schulz, D.; Koerner von Gustorf, E. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 534. (b) Further, we note the postulate of HFe(CO)<sub>3</sub>( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>) as an intermediate in the formation of Fe(CO)<sub>3</sub>( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>) upon photolysis of Fe(CO)<sub>5</sub> in the presence of C<sub>3</sub>H<sub>6</sub>: Krusic, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 2131.

(5) Ellerhorst, G.; Gerhartz, W.; Grevels, F.-W. *Inorg. Chem.* **1980**, *19*, 67.

(6) Low-temperature irradiations were carried out with olefin-free methylcyclohexane or 3-methylpentane as the matrix material. Fe(CO)<sub>4</sub>(olefin) can be prepared in situ by irradiation of Fe(CO)<sub>5</sub> in the presence of olefin.<sup>3a</sup> This concentration of Fe(CO)<sub>4</sub>(olefin) was <10<sup>-2</sup> M to avoid complications due to lack of site isolation. For olefin = C<sub>2</sub>H<sub>4</sub> or C<sub>3</sub>H<sub>6</sub> the olefin can be purged from the solution by using an Ar stream to completely remove uncomplexed olefin. For these and other olefins the concentration of olefin was varied to determine the ability to form multiple-substitution products. The irradiation source was a Pyrex-filtered 200W high-pressure Hg lamp. Spectral changes were monitored by using a Nicolet 7199 FT IR employing a variable-temperature cell that serves as the reaction vessel. Full details will be given in the full paper.

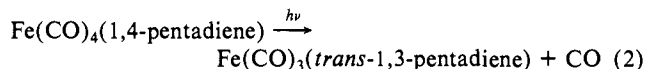
(7) An IR of a sample prepared by the literature method was recorded in alkane solution: Mudoch, H. D.; Weiss, E. *Helv. Chim. Acta* **1963**, *45*, 1927.

Table I. Infrared Data for Relevant Iron Carbonyl Species

species	medium (T, K) <sup>a</sup>	bands (rel Abs), cm <sup>-1</sup>
Fe(CO) <sub>5</sub>	3MP (298)	2023 (1.0), 2001 (1.5)
	3MP (77)	2023 (1.0), 1996 (1.2)
Fe(CO) <sub>4</sub>	MCH (77)	1988 (1.0), 1945 (1.0)
Fe(CO) <sub>4</sub> (C <sub>2</sub> H <sub>4</sub> )	MCH (298)	2087 (1.0), 2022 (0.8), 2007 (8.7), 1984 (5.1)
	MCH (77)	2088 (1.0), 2023 (0.4), 2006 (5.8), 1980 (4.2)
	Ar (10) <sup>b</sup>	2094, 2020, 2009, 1991
Fe(CO) <sub>3</sub> (C <sub>2</sub> H <sub>4</sub> )	MCH (77)	2041 (1.0), 1963 (1.3), 1957 (1.6)
	Ar(10) <sup>b</sup>	2039, 1976, 1950
Fe(CO) <sub>3</sub> (C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	MCH (77)	1929
Fe <sub>2</sub> (CO) <sub>6</sub> (C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	MCH (273)	2059 (1.0), 1982 (16.3)
Fe(CO) <sub>4</sub> (3,3-dimethyl-1-pentene)	3MP (298)	2079 (1.0), 2023 (0.5), 1997 (4.8), 1978 (3.1)
	3MP (77)	2080 (1.0), ~2023 (0.6), 1993 (4.6), 1973 (3.4)
Fe(CO) <sub>3</sub> (3,3-dimethyl-1-pentene)	3MP (77)	2041 (1.0), 1966 (~1.1), 1953 (1.5)
Fe(CO) <sub>3</sub> (3,3-dimethyl-1-pentene) <sub>2</sub>	3MP (77)	1928
Fe <sub>2</sub> (CO) <sub>6</sub> (3,3-dimethyl-1-pentene) <sub>2</sub>	3MP (~195)	2046 (1.0), 1970 (15)
Fe(CO) <sub>4</sub> (C <sub>3</sub> H <sub>6</sub> )	MCH(298)	2081 (1.0), 2022 (0.7), 2000 (8.1), 1979 (4.8)
	MCH (77)	2083 (1.0), 2022 (0.5), 2000 (5.7), 1975 (3.6)
HFe(CO) <sub>3</sub> (η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> ) <sup>c</sup>	MCH (77)	2064 (3.0), 1994 (4.8), 1945 (1.0)
Fe(CO) <sub>3</sub> (C <sub>3</sub> H <sub>6</sub> ) <sub>2</sub>	MCH(77)	1929
Fe <sub>2</sub> (CO) <sub>6</sub> (C <sub>3</sub> H <sub>6</sub> ) <sub>2</sub>	MCH (273)	2050 (1.0), ~1975 (~12)
Fe(CO) <sub>4</sub> (1-pentene)	3MP (298)	2083 (1.0), 2024 (0.8), 2002 (5.4), 1981 (4.2)
	MCH (77)	2082 (1.0), ~2024, 2000 (~4.4), 1975 (3.6)
	MCH (77)	2059 (2.1), 1989 (3.1), 1945 (1.0)
HFe(CO) <sub>3</sub> (η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> ) <sup>c</sup>	1-pentene (77)	1925
Fe(CO) <sub>3</sub> (1-pentene) <sub>2</sub>	1-pentene (195)	2048 (1.0), 1972 (16.6)
Fe <sub>2</sub> (CO) <sub>6</sub> (1-pentene) <sub>2</sub>	MCH (298)	2083 (1.0), ~2024, 2002 (6.1), 1981 (3.7)
Fe(CO) <sub>4</sub> (1,4-pentadiene)	MCH (77)	2084 (1.0), ~2024, 2001 (5.4), 1976 (4.0)
Fe(CO) <sub>3</sub> ( <i>trans</i> -1,3-pentadiene)	MCH (298)	2049 (1.0), 1982 (1.6), 1973 (1.1)
	MCH (77)	2047 (1.0), 1978 (1.8), 1968 (1.1)
BrFe(CO) <sub>3</sub> (η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )	MCH (298)	2089 (1.1), 2043 (1.4), 2010 (1.0)
Fe(CO) <sub>4</sub> (PPh <sub>3</sub> )	MCH (298)	2052 (1.4), 1979 (1.0), 1946 (3.8)
Fe(CO) <sub>3</sub> (PPh <sub>3</sub> ) <sub>2</sub>	MCH (298)	1895
Fe(CO) <sub>3</sub> (C <sub>2</sub> H <sub>4</sub> )(PPh <sub>3</sub> )	MCH (298)	2022 (1.0), 1961 (~1.0), 1931 (1.0)

<sup>a</sup> 3MP ≡ 3-methylpentane, MCH ≡ methylcyclohexane. <sup>b</sup> Band positions obtained from ref 5. <sup>c</sup> May contain a small amount of Fe(CO)<sub>4</sub>.

pattern is quite different from that for the C<sub>2</sub>H<sub>4</sub> complex. The 16-electron Fe(CO)<sub>3</sub>(C<sub>3</sub>H<sub>6</sub>) would be expected to have an IR spectrum in the CO stretching region that is similar to that for the Fe(CO)<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>). Substantiating this argument, irradiated Fe(CO)<sub>4</sub>(3,3-dimethyl-1-pentene) (having no allylic hydrogens) at 77 K in an alkane matrix yields a three-band pattern nearly identical with that for the 16-electron C<sub>2</sub>H<sub>4</sub> species (Table I). Irradiation of Fe(CO)<sub>4</sub>(1-pentene) (having allylic hydrogens) yields IR spectral changes like those for the propylene complex and different from the ethylene and 3,3-dimethyl-1-pentene complexes (Table I). Another compelling result comes from the irradiation of Fe(CO)<sub>4</sub>(1,4-pentadiene): at 77 K in alkane we observe clean spectral changes consistent with the chemistry represented by eq 2 (Table I). It is evident that even at 77 K there



is sufficient activation to effect the rearrangement of the olefin to form the 1,3-diene complex beginning with the 1,4-diene.<sup>8</sup> Thus, it appears that photojection of CO from Fe(CO)<sub>4</sub>(olefin) where the olefin has allylic hydrogens can yield a π-allyl hydride at a temperature as low as 77 K, whereas for olefins such as ethylene or 3,3-dimethyl-1-pentene, having no allylic hydrogens, the 16-electron product can be spectroscopically detected. In all cases CO extrusion, not loss of olefin, is a major excited-state reaction of Fe(CO)<sub>4</sub>(olefin), though there is some evidence for loss of C<sub>2</sub>H<sub>4</sub> from Fe(CO)<sub>4</sub>(C<sub>2</sub>H<sub>4</sub>).<sup>9</sup>

When Fe(CO)<sub>4</sub>(olefin) is irradiated at 77 K in a hydrocarbon matrix containing significant uncomplexed olefin, the IR spectral changes include the formation of a strong feature at ~1930 cm<sup>-1</sup>

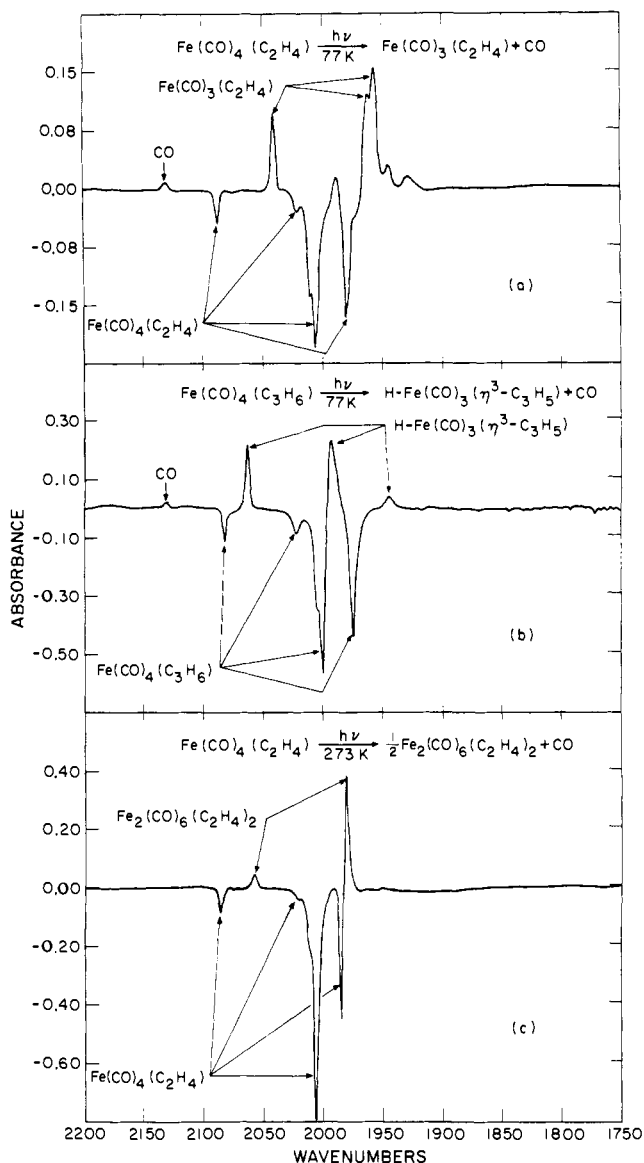
attributable to *trans*-Fe(CO)<sub>3</sub>(olefin)<sub>2</sub> (Table I). The importance of the bis-olefin complex relative to the 16-electron species (for olefin having no allylic hydrogens) or the π-allyl hydrides (for olefins having allylic hydrogens) depends on the concentration of the added olefin in a manner consistent with the primary generation of a 16-electron species upon irradiation. The ~1930-cm<sup>-1</sup> feature becomes the dominant absorption, for example, when Fe(CO)<sub>4</sub>(1-pentene) is irradiated in neat 1-pentene at 77 K. The assignment of the ~1930-cm<sup>-1</sup> band to a *trans*-Fe(CO)<sub>3</sub>L<sub>2</sub> complex is consistent with the spectra of well-characterized complexes of this geometry, e.g., L = P donor.<sup>10</sup>

Generation of the HFe(CO)<sub>3</sub>(π-allyl) or the *trans*-Fe(CO)<sub>3</sub>(olefin)<sub>2</sub> in the presence of 1-pentene at 77 K does not lead to significant isomerization of the uncomplexed 1-pentene, even though the 1,4- to 1,3-diene conversion of a complexed olefin does occur at 77 K. Thus, the catalysis is (not surprisingly) limited by diffusion and/or olefin substitution rates at 77 K. We attempted to raise the temperature to observe dark catalytic isomerization via the photogenerated intermediates. Interestingly, no significant isomerization occurs up to 195 K, but at the softening point (~150 K) of the matrix spectral changes in the metal carbonyl region occur. The ~1930-cm<sup>-1</sup> feature completely disappears, and new features grow in at ~1970 (s) and ~2050 (w) cm<sup>-1</sup>. For example, starting with *trans*-Fe(CO)<sub>3</sub>(1-pentene)<sub>2</sub> in neat 1-pentene at 77 K and warming to 195 K yields a prominent feature at 1972 cm<sup>-1</sup> and a small band at 2048 cm<sup>-1</sup>. At 195 K this species is inert, but further warming of the sample to 298 K does yield extensive 1-pentene → 2-pentene isomerization (~30%) along with regeneration of significant quantities of Fe(CO)<sub>4</sub>(pentene). The species associated with the 1972-cm<sup>-1</sup> absorption can apparently yield isomerization, though it is not the species we have assigned as the HFe(CO)<sub>3</sub>(π-allyl). Similar spectral changes occur upon warming the other photogenerated

(8) Irradiation of Fe(CO)<sub>4</sub>(1,4-pentadiene) at room temperature gives Fe(CO)<sub>3</sub>(1,3-pentadiene), also. Authentic Fe(CO)<sub>3</sub>(1,3-pentadiene) was formed by irradiation of Fe(CO)<sub>5</sub> in the presence of *trans*-1,3-pentadiene.

(9) For comparison, Fe(CO)<sub>4</sub> (Table I) was photogenerated from Fe(CO)<sub>5</sub> in an alkane matrix at 77 K; cf.: (a) Poliakoff, M. *J. Chem. Soc., Dalton Trans.* 1974, 210. (b) Poliakoff, M.; Turner, J. *J. Chem. Soc., Faraday Trans.* 1974, 70, 93.

(10) Calderazzo, F.; Ercoli, R.; Natta, G. In "Organic Synthesis via Metal Carbonyls", Wender, I., Pino, P., Eds; Interscience: New York, 1968; Vol. 1, pp 120-123.



**Figure 1.** Difference IR spectra associated with near-UV-induced reactions of  $\text{Fe}(\text{CO})_4(\text{olefin})$  at  $<10^{-2}$  M in methylcyclohexane solvent. Changes shown are for  $\sim 50\%$  conversion; difference spectra at  $<5\%$  conversion show the same features.

*trans*- $\text{Fe}(\text{CO})_3(\text{olefin})_2$  complexes, including the ethylene and 3,3-dimethyl-1-pentene species, from 77 K to the softening point of the matrix. This shows that allylic hydrogens are not essential to formation of the species characterized by the  $\sim 1970$ - and  $\sim 2050\text{-cm}^{-1}$  absorptions.

We propose that the  $\sim 1970$ - and  $\sim 2050\text{-cm}^{-1}$  features are attributable to  $\text{Fe}_2(\text{CO})_6(\text{olefin})_2$ , a derivative of the known  $\text{Fe}_2(\text{CO})_8$ .<sup>11</sup> The most compelling evidence for the  $\text{Fe}_2(\text{CO})_6(\text{olefin})_2$  formulation comes from experiments with the  $\text{C}_2\text{H}_4$  complex, the most thermally inert of the complexes studied. Irradiation of  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  in a  $\text{C}_2\text{H}_4$ -purged or an Ar-purged alkane solution below 25 °C yields the same IR-detectable product (Figure 1c) as obtained upon warming a 77 K matrix containing

(11) Poliakoff, M.; Turner, J. J. *J. Chem. Soc. Dalton Trans.* **1974**, 2276. It is noteworthy that coordinatively unsaturated species such as  $\text{Re}_2(\text{CO})_8\text{X}_2$  can be formed from photogenerated  $\text{Re}(\text{CO})_4\text{X}$  fragments: Wrighton, M. S.; Morse, D. L.; Gray, H. B.; Ottesen, D. K. *J. Am. Chem. Soc.* **1976**, *98*, 1111. Byers, B. H.; Brown, T. L. *Ibid.* **1977**, *99*, 2527. Cf. also: Fischer, I.; Hildebrand, K.; Koerner von Gustorf, E. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 54 for speculations concerning the dimerization of coordinatively unsaturated Fe-carbonyls. We note the related complex  $\text{Fe}_2(\text{NO})_6^{2+}$  that has an IR pattern in the NO stretching region and a reactivity pattern, that parallels our  $\text{Fe}_2(\text{CO})_6(\text{olefin})_2$ : Herberhold, M.; Klein, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 454.

$\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)$  or *trans*- $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ . <sup>1</sup>H NMR shows the formation of a single product retaining a 1:1 Fe: $\text{C}_2\text{H}_4$  ratio.<sup>12</sup>

Reactions of  $\text{Fe}_2(\text{CO})_6(\text{C}_2\text{H}_4)_2$  are consistent with its formulation as a labile, dinuclear, Fe-Fe double-bonded species: (i) purging with CO and warming to 25 °C yields rapid formation of  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ ; (ii) addition of  $\text{PPh}_3$  followed by warming to 25 °C yields  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)(\text{PPh}_3)$ ; (iii) addition of *trans*-1,3-pentadiene or 1,4-pentadiene and warmup to 25 °C yields  $\text{Fe}(\text{CO})_3(\text{trans-1,3-pentadiene})$ . Finally, the  $\text{Fe}_2(\text{CO})_6(\text{C}_2\text{H}_4)_2$  is very catalytically active: addition of 1.0 mL of 1-pentene at 25 °C to 1.0 mL of  $10^{-2}$  M  $\text{Fe}_2(\text{CO})_6(\text{C}_2\text{H}_4)_2$  in methylcyclohexane yielded  $\sim 60\%$  isomerization to 2-pentene in  $<10$  s giving 600 turnovers per  $\text{Fe}_2(\text{CO})_6(\text{C}_2\text{H}_4)_2$  unit and a turnover rate of at least 3600 per minute!

In summary, we have observed the photogenerated 16-electron species  $\text{Fe}(\text{CO})_3(\text{olefin})$  for olefin = ethylene or 3,3-dimethyl-1-pentene in rigid media at 77 K, whereas the data are consistent with a  $\text{HFe}(\text{CO})_3(\pi\text{-allyl})$  species when the olefin has allylic hydrogens such as in propylene or 1-pentene. In the presence of excess olefin in the matrix the dominant Fe species becomes *trans*- $\text{Fe}(\text{CO})_3(\text{olefin})_2$ , which is surprisingly labile with respect to formation of a dimer. At 195 K the dominant species becomes  $\text{Fe}_2(\text{CO})_6(\text{olefin})_2$ , which leads to very rapid alkene catalysis upon further warmup, presumably via the  $\pi$ -allyl hydride. Further characterization of these species will be included in the full paper.

**Acknowledgment.** We thank the Office of Naval Research and the National Science Foundation for partial support of this research. J.C.M. acknowledges support as a Halcon Research Fellow, 1980-1981. We thank Cynthia G. Brinkley for some confirmatory experiments with  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ .

(12) Clusters of higher nuclearity than two are seemingly ruled out by the fact that solutions of  $\text{Fe}_2(\text{CO})_6(\text{olefin})_2$  are yellow, not highly colored as is  $\text{Fe}_3(\text{CO})_{12}$ , for example: Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979. We note also that the species we formulate as  $\text{Fe}_2(\text{CO})_6(\text{C}_3\text{H}_5)_2$  is yellow in solution and therefore cannot be the known dimer  $\text{Fe}_2(\text{CO})_6(\eta^2\text{-C}_3\text{H}_5)_2$ , which is red: Putnik, C. F.; Wetter, J. J.; Stucky, G. D.; D'Aniello, M. J., Jr.; Sosinsky, B. A.; Kirner, J. F.; Muetteries, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 4107. We have synthesized this dimer, and it is spectroscopically distinct from the species claimed here.

(13) Analysis was by gas chromatography as described in ref 1.

### Raman Spectroscopy of Electronic Excited Organometallic Complexes: A Comparison of the Metal to 2,2'-Bipyridine Charge-Transfer State of *fac*-(2,2'-Bipyridine)tricarbonylhalorhenium and Tris(2,2'-bipyridine)ruthenium(II)

William K. Smothers and Mark S. Wrighton\*

Department of Chemistry and  
George Russel Harrison Spectroscopy Laboratory  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

Received November 8, 1982

The Raman spectrum of the lowest electronic excited state of  $\text{Ru}(\text{bpy})_3^{2+}$  (bpy = 2,2'-bipyridine) shows features that have been attributed to the reduced character of 2,2'-bipyridine in the excited species.<sup>1,2</sup> Significantly, near coincidence in the frequency of Raman bands for the excited complex and the ground state 2,2'-bipyridine radical anion is observed,<sup>1,2</sup> suggesting that the excited state, which is associated with a metal-to-ligand charge-transfer transition in absorption,<sup>3</sup> can be viewed as having the

(1) (a) Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 4391. (b) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *Ibid.* **1981**, *103*, 7441 and references cited therein.

(2) Forster, M.; Hester, R. E. *Chem. Phys. Lett.* **1981**, *81*, 42.