

In summary, the key feature of these studies is that the $\text{Ru}_3(\text{CO})_{11}(\text{CO}_2\text{CH}_3)^-$ anion is dramatically activated toward reduction by H_2 relative to the neutral parent $\text{Ru}_3(\text{CO})_{12}$. Although kinetics studies have not been reported for the H_2 reduction of the latter cluster, this reaction is generally accomplished under conditions such as refluxing octane (bp 125 °C),²⁴ the ruthenium product being the tetranuclear tetrahydride $\text{H}_4\text{Ru}_4(\text{CO})_{12}$. The

likely reason for this activation toward H_2 is the markedly greater lability of the anionic cluster toward ligand substitution reactions in comparison to that of the relatively inert parent cluster. The similarity of these results to those for the mononuclear cobalt complexes suggests some generality to this aspect of nucleophilic activation of metal carbonyl complexes.

Acknowledgment. This research was supported by a grant from the U.S. Department of Energy, Office of Basic Energy Sciences. Ruthenium used in these studies was provided on loan by Johnson Matthey, Inc.

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Photochemical Formation of Mononuclear Bis- and Tris(ethylene) Complexes from Irradiation of Iron Pentacarbonyl or Triruthenium Dodecacarbonyl: Species Involved in Catalytic Alkene Isomerization

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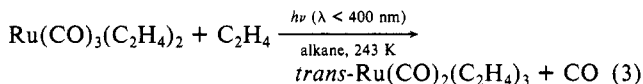
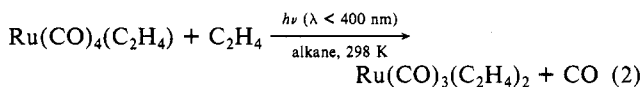
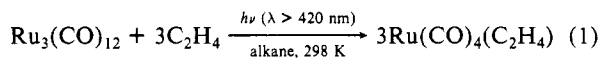
Received September 2, 1986

In alkane or $\text{CF}_3\text{C}_6\text{F}_{11}$ solutions that contain excess C_2H_4 , near-UV irradiation of $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$, formed quantitatively in situ from visible light ($\lambda > 420$ nm) irradiation of $\text{Ru}_3(\text{CO})_{12}$, yields $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ at 298 K. At temperatures below 253 K further substitution can be effected photochemically to give *trans*- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$. Near-UV irradiation of $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ in rigid, C_2H_4 -saturated, 3-methylpentane glasses at 90 K yields $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$, but further CO loss to give *cis*- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ is observed after only ~5% consumption of $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$. Isomerization of photogenerated *cis*- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ to *trans*- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ is only observed on warming the glass above 210 K. Prolonged irradiation of photogenerated *cis*- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ at 90 K yields loss of additional CO to give a monocarbonyl complex, formulated as $\text{Ru}(\text{CO})(\text{C}_2\text{H}_4)_4$, which reacts on warming with photoreleased CO to initially regenerate *cis*- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$. The photochemistry of $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ is the same as that of the $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ except that *trans*- $\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ could only be detected by IR spectroscopy at temperatures below 210 K. The new results show that species previously formulated as $\text{Fe}_2(\text{CO})_6(\text{alkene})_2$ are in fact $\text{Fe}(\text{CO})_3(\text{alkene})_2$. In solution, $\text{M}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ ($\text{M} = \text{Fe}, \text{Ru}$) and $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ are substitutionally labile and may serve as versatile reagents in preparative chemistry. Addition of deoxygenated 1-pentene to solutions of the bis- and tris(ethylene) complexes results in rapid catalytic isomerization at 293 K to a mixture of 2-pentenes, thus establishing the viability of both $\text{M}(\text{CO})_3$ and $\text{M}(\text{CO})_2$ species as repeating units in the catalytic alkene isomerization. Deactivation of $\text{M}(\text{CO})_3(\text{alkene})_2$ as a 1-pentene isomerization catalyst, in the absence of excess CO, proceeds, at least in part, by dehydrogenation of 1-pentene to form the stable, catalytically inactive (at 298 K) $\text{M}(\text{CO})_3(\eta^4\text{-1,3-pentadiene})$ complexes.

Research in this group and elsewhere has established that an extraordinarily active alkene isomerization catalyst results from photolysis of $\text{Fe}(\text{CO})_5$ in the presence of alkenes.¹⁻³ A carbonyl-bridged diiron complex⁴ and, alternatively, a mononuclear tricarbonyl iron unit^{1b,3} have been proposed to carry the catalytic cycle. A report from this group⁵ establishes that iron carbonyl intermediates in the photocatalytic systems could be observed spectroscopically at subambient temperatures, including $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ from photolysis of $\text{Fe}(\text{CO})_4(\text{C}_3\text{H}_6)$ in a rigid alkane glass at 77 K. In neat 1-pentene, warmup of photogenerated $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ (from $\text{Fe}(\text{CO})_5/1\text{-pentene}$ at 77 K) result in significant catalytic isomerization of 1-pentene above 243 K in the dark. Eventual regeneration of $\text{Fe}(\text{CO})_4(\text{alkene})$ is accompanied by decline of catalytic activity. $\text{Fe}(\text{CO})_3(\eta^3\text{-allyl})$ radical species, also detected at 143 K in 1-3% yield as photoproducts of $\text{Fe}(\text{CO})_5$ and olefins, have been implicated in catalytic reactions of olefins.⁶

New findings reported here reveal the nature of the dominant species resulting from near-UV irradiation of $\text{Fe}(\text{CO})_5/\text{alkene}$ solutions. Species previously formulated as $\text{Fe}_2(\text{CO})_6(\text{alkene})_2$ ⁵ are in fact mononuclear $\text{Fe}(\text{CO})_3(\text{alkene})_2$ complexes, consistent with a report by Fleckner, Grevels, and Hess.⁷ Other important mononuclear Fe species are reported herein including *di*- and monocarbonyl complexes. We have also extended the low-temperature photochemistry to $\text{Ru}(\text{CO})_4(\text{alkene})$ systems and find

that mononuclear bis- and tris(ethylene) complexes can be generated photochemically via sequential photochemical reactions represented by eq 1-3 for the case of alkene = C_2H_4 . Photo-



chemistry according to eq 1 is known⁸⁻¹⁰ and provides an excellent

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route to $\text{Ru}(\text{CO})_4(\text{alkene})$ complexes. $\text{Ru}_3(\text{CO})_{12}$ is a known photocatalyst for alkene reactions such as isomerization^{11,12} and hydrosilation;¹³ catalytically active mononuclear species have been proposed. Our key finding is that the mononuclear species $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ and $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ can both isomerize 1-pentene in the dark, in accord with the activity found upon photoactivation of $\text{Ru}_3(\text{CO})_{12}$. $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ shows very little activity. The results for both the $\text{Fe}(\text{CO})_5/\text{alkene}$ and $\text{Ru}_3(\text{CO})_{12}/\text{alkene}$ system are consistent with photocatalysis via mononuclear species with no obvious role for cluster complexes. A contributor to deactivation of the catalysts is dehydrogenation of the alkene substrate, leading to the formation of inert $\text{M}(\text{CO})_3(\eta^4\text{-1,3-diene})$ complexes.

Experimental Section

Materials. $\text{Fe}(\text{CO})_5$ and $\text{Ru}_3(\text{CO})_{12}$ were obtained from Strem Chemicals. $\text{Fe}(\text{CO})_5$ was passed through Al_2O_3 prior to use, and $\text{Ru}_3(\text{CO})_{12}$ was used as received. The photochemistry at low temperature was carried out by using 3-methylpentane (Aldrich) or methylcyclohexane (J. T. Baker) as the glassing materials. Quantitative ^1H NMR data were obtained by using $\text{CF}_3\text{C}_6\text{F}_{11}$ solvent from Fluka AG. 1-Pentene (99% pure) was obtained from Aldrich and passed through Al_2O_3 prior to use. Research grade CO , C_2H_4 , and C_3H_6 were obtained from Matheson. ^{13}CO (99% ^{13}C) was obtained from Cambridge Isotope Laboratories. PPh_3 was recrystallized prior to use.

Instrumentation. IR spectra were recorded on a Perkin-Elmer 180 grating instrument or a Nicolet 7199 or 60SX Fourier transform IR spectrometer. ^1H NMR spectra were recorded on either a Bruker 270- or 250-MHz Fourier transform instrument with cycloheptane (in the $\text{CF}_3\text{C}_6\text{F}_{11}$ solvent) used as an internal standard, 1.54 ppm vs. SiMe_4 . The 1-pentene to *cis*- and *trans*-2-pentene isomerization was analyzed by gas chromatography using a 30 ft. $\times$ $1/8$ in. 20% propylene carbonate on Chromasorb P column operated at 20 $^\circ\text{C}$.

High-pressure liquid chromatography (HPLC) was accomplished with a Hewlett-Packard 1084 B chromatograph with a Hewlett-Packard 1040 rapid-scan UV-vis detector. Detection was made at 254 nm, and separations were accomplished by using a LiChrosorb Alox T 5- μm column (250 mm $\times$ 4.6 mm i.d.) with hexane solvent. Identities of molecules associated with the peaks were established by comparison of rapid-scan UV-vis spectra and retention times with those of an authentic sample. Gas chromatograph mass spectra (GC-MS) were recorded on a Hewlett-Packard Model 5992 mass spectrometer. All mass spectra were recorded at 70 eV. Separations were performed on a 10 ft. $\times$ $1/8$ in. SE-30 on Chromasorb W column.

Procedures. Generally, all manipulations were carried out under N_2 in a Vacuum Atmospheres drybox or under Ar using conventional Schlenk line techniques. Low-temperature irradiations involved the use of a Bausch and Lomb SP200 200-W high-pressure Hg lamp filtered with a 10-cm Pyrex water filter. Low-temperature IR spectra were recorded by using a Precision Cell, Inc. Model P/N 21.000 variable-temperature cell or CTI-Cryogenics Model 21 cryocooler equipped with CaF_2 windows. Sample temperatures are estimated to be ± 2 K at a fixed temperature.

Clean solutions of $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ were prepared by near-UV photolysis of 4×10^{-3} M $\text{Fe}(\text{CO})_5$ at 273 K in a C_2H_4 -saturated alkane solution until no $\text{Fe}(\text{CO})_5$ remained as determined by spectroscopy IR. At this point, both $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ and $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ were present. The mixture was then purged with CO and warmed to 298 K to yield $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ as the only detectable metal carbonyl. Clean solutions of $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ were obtained by continuing to photolyze the C_2H_4 -saturated solution at ≤ 273 K until no $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ remained, as established by IR spectroscopy. The $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ was prepared quantitatively via visible light ($\lambda > 420$ nm) irradiation of $\sim 1 \times 10^{-3}$

Table I. UV-Visible Data for Relevant Compounds^a

species	medium (T, K)	λ , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)
$\text{Ru}_3(\text{CO})_{12}$	MCH (298)	237 (30 200), 278 (sh), 325 (sh), 391 (7700)
$\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$	MCH (298)	240 (3400), 266 (1700)
$\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$	MCH (298)	220 (11 700), 262 (4900)
$\text{Ru}(\text{CO})_3(1,3\text{-pentad})$	MCH (298)	245 (10 000), 280 (7600)
$\text{Fe}(\text{CO})_5$	3MP (90)	242 (21 000), 290 (5200)
$\text{Fe}(\text{CO})_4$	3MP (90)	390
$\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$	MCH (298)	255 (sh, ~ 10 000)
$\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$	MCH (90)	234, 447
$\text{Fe}(\text{CO})_4(\text{C}_3\text{H}_6)$	MCH (298)	255 (sh, ~ 10 000)

^a MCH = methylcyclohexane; 3MP = 3-methylpentane; 1,3-pentad = 1,3-pentadiene.

M $\text{Ru}_3(\text{CO})_{12}$ in a continuously C_2H_4 -purged alkane solution using a filtered Hanovia 450-W medium-pressure Hg lamp. The $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ solutions were prepared by subsequent near-UV irradiation of a $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ solution at 298 K in the presence of C_2H_4 . Only $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ and $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ were spectroscopically detected in these solutions. After $\sim 90\%$ conversion of $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$, the photolysis was stopped and the solution was purged with C_2H_4 to remove photogenerated CO . The *trans*- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ solutions were prepared by irradiation at 232 K (liquid $\text{N}_2/\text{CH}_3\text{CN}$ bath) of an alkane solution containing $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ and $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ under a slow purge of C_2H_4 necessary to remove photogenerated CO . Only $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ and *trans*- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ were detectable by IR in these solutions. In order to avoid secondary photodecomposition, the irradiations were discontinued after approximately 70% conversion to *trans*- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$.

Photolysis of $\text{M}(\text{CO})_4(\text{C}_2\text{H}_4)$ ($\text{M} = \text{Fe}, \text{Ru}$), in a C_2H_4 -saturated $\text{CF}_3\text{C}_6\text{F}_{11}$ solution, was monitored by ^1H NMR spectroscopy by first generating the $\text{M}(\text{CO})_4(\text{C}_2\text{H}_4)$ in situ in a septum-sealed NMR tube containing the cycloheptane internal standard. The NMR of the sample was then recorded at the temperature of the subsequent irradiation. Irradiations were carried out in a clear Dewar flask at the temperature necessary to observe the $\text{M}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ (Fe , 273 K; Ru , 298 K) or *trans*- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ (243 K). IR spectral changes for the $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ to $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ conversion showed the same extent conversion as determined by ^1H NMR for the same solution, thereby establishing correlation of IR absorptions and the ^1H NMR attributed to $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$.

The 1-pentene isomerization kinetics were determined by generating a methylcyclohexane solution of the appropriate catalyst precursor and removing excess C_2H_4 , which inhibits the isomerization, by a vigorous Ar purge at 195 K, a temperature at which $\text{M}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ ($\text{M} = \text{Fe}, \text{Ru}$) and $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ are stable in the absence of C_2H_4 . The appropriate amount of precooled 1-pentene, passed through Al_2O_3 and deoxygenated by three freeze-pump-thaw cycles, was added at 195 K, a temperature where no catalytic isomerization occurs. Rapid warming to 273 K initiated catalysis. A syringe was used to withdraw samples from the solution for analysis. Instantaneous deactivation of the catalyst was achieved by mixing the drawn aliquot with a saturated solution of PPh_3 in methylcyclohexane. The volatiles were stripped off under vacuum and condensed in liquid- N_2 -cooled traps. The condensate, containing a mixture of the linear pentenes, was subsequently analyzed by gas chromatography.

$\text{Fe}(\text{CO})_2(^{13}\text{CO})(\text{C}_2\text{H}_4)_2$ was prepared in situ by reacting $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ with 1 atm of ^{13}CO in methylcyclohexane or 3-methylpentane at 298 K to form $\text{Fe}(\text{CO})_3(^{13}\text{CO})(\text{C}_2\text{H}_4)_2$. Excess ^{13}CO was purged from the solution with C_2H_4 at 298 K, and the resulting C_2H_4 -saturated solution was irradiated at 273 K to convert $\text{Fe}(\text{CO})_3(^{13}\text{CO})(\text{C}_2\text{H}_4)_2$ to $\text{Fe}(\text{CO})_{3-n}(^{13}\text{CO})_n(\text{C}_2\text{H}_4)_2$ ($n = 0, 1$). $\text{Fe}(\text{CO})_{3-n}(^{13}\text{CO})_n$ was prepared by $\lambda > 540$ nm irradiation of $\text{Fe}_3(\text{CO})_{12}$ in a ^{13}CO -saturated 3-methylpentane solution at 298 K.

Results and Discussion

(a) Mononuclear Ruthenium Carbonyl-Ethylene Complexes. UV-vis, IR, and ^1H NMR spectral data for relevant complexes are reported in Tables I-III, respectively. Irradiation of $\text{Ru}_3(\text{CO})_{12}$ in C_2H_4 -saturated alkane (3-methylpentane or methylcyclohexane) or $\text{CF}_3\text{C}_6\text{F}_{11}$ solutions yields $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ (eq 1), as expected. Indeed, for excitation using wavelengths of light longer than ~ 420 nm, where $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ does not absorb significantly, the generation of $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ is quantitative. Thus, visible irradiation of $\text{Ru}_3(\text{CO})_{12}$ in the presence of C_2H_4 provides an excellent route to $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$. If C_2H_4 is purged from solution with Ar at 298 K, $\text{Ru}_3(\text{CO})_{12}$ is regenerated quantitatively.

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Table II. IR Data for Relevant Complexes

species	medium (T, K) ^a	ν , cm ⁻¹ (ϵ , M ⁻¹ cm ⁻¹ or rel abs)
Ru ₃ (CO) ₁₂	3MP (298)	2061 (24 500), 2031 (14 600), 2012 (9000)
Ru(CO) ₅	3MP (298)	2037 (1.0), 2002 (1.4)
Ru(CO) ₄ (C ₂ H ₄)	3MP (298)	2104 (470), 2023 (8100), 1996 (4000)
	3MP (90)	2106 (980), 2023 (9900), 1994 (8000)
Ru(CO) ₃ (C ₂ H ₄)	3MP (55)	2055 (1.0), 1978 (1.2), 1972 (1.3)
Ru(CO) ₃ (C ₂ H ₄) ₂	3MP (298)	2081 (320), 2005 (2100), 1995 (6500)
	3MP (90)	2082 (350), 2004 (1300), 1993 (7200)
<i>trans</i> -Ru(CO) ₂ (C ₂ H ₄) ₃	3MP (233)	1956
	3MP (90)	1953
<i>cis</i> -Ru(CO) ₂ (C ₂ H ₄) ₃	MCH (90)	2019 (1.4), 1975 (1.0)
Ru(CO) ₂ (C ₂ H ₄) ₂	MCH (90)	2020 (1.0), 1948 (1.3)
Ru(CO)(C ₂ H ₄) ₄	MCH (90)	1964
Ru(CO)(C ₂ H ₄) ₃ ^b	MCH (90)	1923
Ru(CO) ₄ (C ₃ H ₆)	3MP (298)	2100 (1.0), 2018 (10.6), 1991 (6.4)
	MCH (90)	2101 (1.0), 2018 (11.5), 1987 (6.4)
HRu(CO) ₃ (η^3 -C ₃ H ₅) isomer a	MCH (90)	2082 (1.0), 2008 (1.2)
<i>endo</i> -BrRu(CO) ₃ (η^3 -C ₃ H ₅)	3MP (298)	2109 (1.0), 2060 (1.4), 2019 (1.3)
<i>exo</i> -BrRu(CO) ₃ (η^3 -C ₃ H ₅)	3MP (298)	2107 (1.0), 2055 (1.1), 2025 (1.2)
Ru(CO) ₃ (C ₃ H ₆) ₂	3MP (298)	2075 (1.0), 2005 (3.3), 1988 (14)
<i>trans</i> -Ru(CO) ₂ (C ₃ H ₆) ₃	3MP (233)	1949
Ru(CO) ₄ (1-pentene)	3MP (298)	2100 (1.9), 2018 (9.3), 1989 (5.8)
	3MP (90)	2102 (1.0), 2019 (8.9), 1988 (6.0)
	3MP (55)	2102 (1.0), 2019 (8.5), 1987 (5.5)
	1-pentene (90)	2102 (1.0), 2020 (10.1), 1983 (7.0)
HRu(CO) ₃ (η^3 -C ₅ H ₉)	MCH (90)	2078 (1.0), 2004 (1.2)
	3MP (55)	2078 (1.0), 2003 (1.2)
Ru(CO) ₃ (1-pentene) ₂	3MP (298)	2072 (1.0), 2000 (2.6), 1987 (9.4)
	3MP (90)	2073 (1.0), 2000 (1.6), 1987 (8.4)
	1-pentene (90)	2076 (1.0), 2000 (1.8), 1984 (8.9)
<i>trans</i> -Ru(CO) ₂ (1-pentene) ₃	3MP (233)	1946
Ru(CO) ₄ (3,3-Me ₂ -1-pentene)	(CH ₃) ₂ C ₅ H ₈ (298)	2099 (1.0), 2017 (5.6), 1990 (3.6)
Ru(CO) ₃ (3,3-Me ₂ -1-pentene) ₂	(CH ₃) ₂ C ₅ H ₈ (233)	2077 (1.0), 1995 (2.3), 1986 (10.0)
Ru(CO) ₃ (<i>trans</i> -1,3-pentadiene)	3MP (298)	2062 (3600), 1997 (6500), 1986 (5400)
Ru(CO) ₄ (PPh ₃)	3MP (298)	2061 (5400), 1987 (3400), 1954 (8000)
Ru(CO) ₃ (PPh ₃) ₂	3MP (298)	1907 (8000)
Fe(CO) ₅	3MP (298)	2023 (9600), 2001 (14 000)
	3MP (90)	2023 (15 000), 1996 (19 000)
Fe(CO) ₄	MCH (90)	2083 (1.0), 1988 (12), 1979 (4.5)
		1946 (14)
Fe(CO) ₄ (C ₂ H ₄)	MCH (298)	2087 (~1700), 2013 (sh), 2007 (~13 000), 1984 (~8400)
	MCH (90)	2088 (~2900), 2011 (sh), 2006 (~16 000), 1980 (13 000)
Fe(CO) ₃ (C ₂ H ₄)	MCH (90)	2041 (1.0), 1963 (1.3), 1957 (1.6)
	Ar (10) ^c	2039, 1976, 1950
Fe(CO) ₃ (C ₂ H ₄) ₂	MCH (273)	2060 (940), 1988 (sh, ~5100), 1981 (12 600)
	MCH (90)	2060 (1.0), 1988 (4.8), 1981 (12)
	CF ₃ C ₆ F ₁₁ (273)	2064 (1.0), 1997 (5.0), 1988 (13.6)
<i>trans</i> -Fe(CO) ₂ (C ₂ H ₄) ₃	MCH (90)	1942
<i>cis</i> -Fe(CO) ₂ (C ₂ H ₄) ₃	MCH (90)	1998 (1.5), 1955 (1.0)
Fe(CO) ₂ (C ₂ H ₄) ₂	MCH (90)	2003 (1.0), 1938 (1.3)
Fe(CO)(C ₂ H ₄) ₄	MCH (90)	1952
Fe(¹³ CO)(C ₂ H ₄) ₄	MCH (90)	1908
Fe(CO) ₄ (C ₃ H ₆)	MCH (298)	2082 (1800), 2006 (sh), 2001 (12 000), 1980 (7500)
	MCH (90)	2083 (2900), 2006 (sh), 2001 (15 000), 1976 (12 000)
HFe(CO) ₃ (η^3 -C ₃ H ₅)		
isomer a	MCH (90)	2064 (1.0), 1994 (1.5)
isomer b	MCH (173)	2066 (1.0), 2003 (1.5), 1994 (1.2)
Fe(CO) ₃ (η^3 -C ₃ H ₅) ^d	pet. ether (298)	2046, 1968, 1960
Fe(CO) ₃ (C ₃ H ₆) ₂	MCH (90)	2051 (1.0), 1971 (11)
HFe(CO)(C ₃ H ₆) ₂ (η^3 -C ₃ H ₅) ^b	MCH (90)	1929
Fe(CO) ₄ (3,3-Me ₂ -1-pentene)	3MP (298)	2079 (1.0), 2003 (sh), 1997 (4.0), 1978 (3.1)
	3MP (90)	2080 (1.0), 2003 (1.6), 1996 (3.3), 1973 (2.9)
Fe(CO) ₃ (3,3-Me ₂ -1-pentene)	3MP (90)	2041 (1.0), 1966 (1.1), 1953 (1.2)
Fe(CO) ₃ (3,3-Me ₂ -1-pentene) ₂	3MP (195)	2046 (1.0), 1970 (15)
<i>cis</i> -Fe(CO) ₂ (3,3-Me ₂ -1-pentene) ₃	3MP (90)	1989 (~1.2), 1929 (1.0)
Fe(CO) ₄ (1-pentene) ^e	3MP (298)	2083 (1.0), 2002 (5.4), 1981 (4.2)
Fe(CO)(η^4 -1,3-butadiene) ^f	hexane (298)	1984.5
HFe(CO) ₃ (η^3 -C ₅ H ₉)	MCH (90)	2059 (1.0), 1989 (1.5)
Fe(CO) ₃ (1-pentene) ₂	1-pentene (195)	2048 (1.0), 1972 (16.6)
HFe(CO)(C ₅ H ₁₀) ₂ (η^3 -C ₅ H ₉) ^b	1-pentene (90)	1925
Fe(CO) ₃ (<i>trans</i> -1,3-pentadiene)	MCH (298)	2049 (1.0), 1982 (1.6), 1973 (1.1)
BrFe(CO) ₃ (η^3 -C ₃ H ₅)	MCH (298)	2089 (1.1), 2043 (1.4), 2010 (1.0)
Fe(CO) ₃ (η^4 -C ₅ H ₈) ^g		2053, 1994, 1989
Fe(CO) ₄ PPh ₃	MCH (298)	2052 (6000), 1979 (3700), 1946 (15 000)
Fe(CO) ₃ (PPh ₃) ₂	MCH (298)	1895 (10 500)
Fe(CO) ₃ (C ₂ H ₄)(PPh ₃)	MCH (298)	2022 (1.0), 1961 (~1.0), 1931 (1.0)

^a 3MP = 3-methylpentane, MCH = methylcyclohexane. ^b Tentative assignment; see text. ^c Band positions obtained from ref 23. ^d Band positions obtained from ref 29. ^e Contaminated with Fe(CO)₅. ^f Band position obtained from ref 20. ^g Band positions for 1,3,4,5-*n*-pent-4-en-3,1-yliron tricarbonyl obtained from ref 25.

Table III. ^1H NMR Data for C_2H_4 Complexes^a

species	temp, K	chem shift, ppm vs. SiMe_4
$\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$	243	2.10
$\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$	243	2.50
$\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$	243	3.02
$\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$	273	2.37
$\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$	273	2.68
C_2H_4	243	5.28
C_7H_{14}	243	1.54

^a All data are for $\text{CF}_3\text{C}_6\text{F}_{11}$ solutions.**Table IV.** ^1H NMR Peak Integration vs. Irradiation Time for $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ in C_2H_4 -Saturated $\text{CF}_3\text{C}_6\text{F}_{11}$ Solution at 298 K

irradiation time, min	integration of ^1H NMR singlet			[Ru] ^b
	$\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ (2.10 ppm)	$\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ (2.50 ppm)	C_7H_{14} ^a (1.54 ppm)	
0.0	0.64	0	1.00	1.00
0.5	0.50	0.36 (0.28) ^c	1.00	1.06 (1.00) ^d
1.0	0.37	0.63 (0.62) ^c	1.00	1.07 (1.01) ^d

^a Used as an internal standard. ^b Total (relative) Ru concentration assuming the only species present are $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ and $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$. ^c "Predicted" integral for $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ based on consumption of $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ from preceding irradiation time. ^d Calculated by using only $t = 0.5$ and 1 min data.

Near-UV irradiation of $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ in the presence of C_2H_4 leads to additional spectral (IR and NMR) changes that are consistent with the photosubstitution represented by eq 2 (Figure 1 and Table IV). In particular, in the ^1H NMR spectra (Table IV), we observe that the singlet at 2.10 ppm due to $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ declines and a new singlet at 2.50 ppm grows. Quantitative analysis from several NMR-monitored photoreactions (Table IV) indicates that the photoproduct has a 1:2 ratio of $\text{Ru}:\text{C}_2\text{H}_4$. The IR spectral changes that occur at 298 K are essentially duplicated when the $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ is irradiated in a rigid C_2H_4 -saturated 3-methylpentane glass at 90 K. The initial ($\sim 5\%$ conversion) IR spectral changes for the 90 K photolysis reveal the generation of free CO (2132 cm^{-1})¹⁴ in the glass and growth of the characteristic 2082-cm^{-1} feature (2081 cm^{-1} in solution at 298 K) of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$. The rigid glass precludes the rapid diffusion of a presumed $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)$ intermediate, thus ruling out polynuclear species, and in particular $\text{Ru}_2(\text{CO})_6(\text{C}_2\text{H}_4)_2$, as photoproducts. However, the low molecular weight of C_2H_4 and its high concentration, $\sim 0.05\text{ M}$,¹⁵ allow reaction of the photogenerated $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)$ (not observed at 90 K) with C_2H_4 to form $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$. The $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ is very photosensitive, and after $\sim 5\%$ conversion of $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ at 90 K, there is evidence for secondary product formation (vide infra) by further loss of CO from the $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$. Such is not the case at 298 K in fluid solutions, where extensive accumulation of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ is achieved. Accumulation of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ is probably a result of rapid back reaction of secondary photoproducts, such as $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ (vide infra), with liberated CO.

At 90 K, in either 3-methylpentane or the more rigid methylcyclohexane, irradiation of $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ is only observed to give $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$, presumably because excess C_2H_4 present in the glass reacts with the 16-electron $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)$ fragment. When $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ is irradiated in a 3-methylpentane glass at 55 K, a new species assigned as the $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)$ fragment can be detected. The IR spectral band pattern for $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)$ ($2055, 1978, 1972\text{ cm}^{-1}$; 3-methylpentane, 55 K) is similar to that for $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)$ ⁵ (Table II). The ability to detect the $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)$ at the lower temperature reflects slower C_2H_4 diffusion and/or a slower rate of C_2H_4 binding to the unsaturated

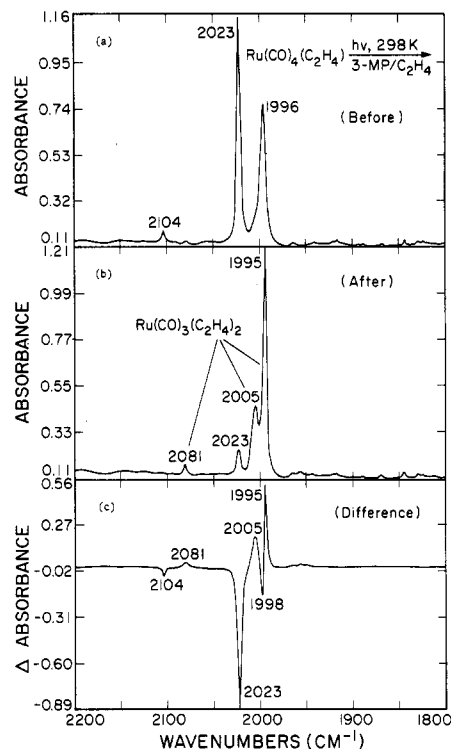


Figure 1. IR spectral changes accompanying near-UV irradiation of $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ in C_2H_4 -saturated 3-methylpentane solution at 298 K: (a) spectrum before irradiation; (b) spectrum after 1 min irradiation; (c) difference spectrum (of spectra a and b).

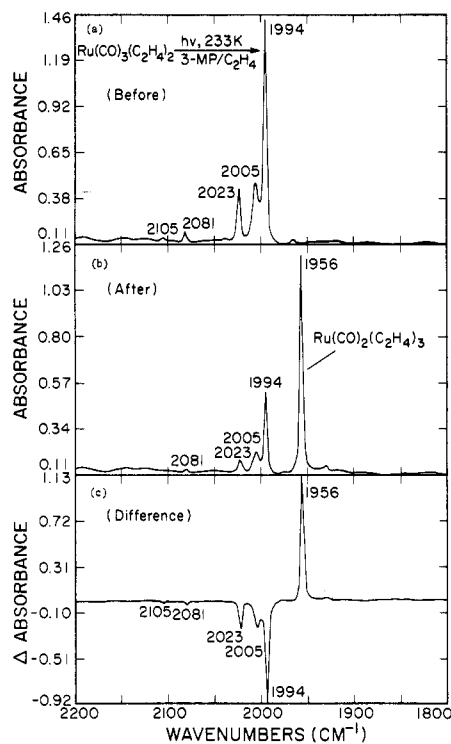


Figure 2. IR spectral changes accompanying near-UV irradiation of predominantly $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ [$\nu(\text{cm}^{-1}) = 2081, 2005, 1994$] and some $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ [$\nu(\text{cm}^{-1}) = 2105, 2023, 1995$] in C_2H_4 -saturated 3-methylpentane solution at 233 K: (a) spectrum before irradiation; (b) spectrum after 1 min irradiation; (c) difference spectrum (of spectra a and b).

Ru center. Warmup to 90 K of the irradiated 55 K glass results in rapid conversion of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ to $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$.

For $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$, the IR spectrum in the CO stretching region is consistent with a C_{2v} local symmetry of the $\text{Ru}(\text{CO})_3$ fragment [$\nu(\text{CO}) = 2081$ (w, A_1), 2005 (m, A_1), and 1995 cm^{-1}

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Table V. ^1H NMR Peak Integration vs. Irradiation Time for $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ in C_2H_4 -Saturated $\text{CF}_3\text{C}_6\text{F}_{11}$ Solution at 243 K

irradiation time, min	integration of ^1H NMR singlet				[Ru] ^b
	$\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ (2.10 ppm)	$\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ (2.50 ppm)	$\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ (3.02 ppm)	$\text{C}_7\text{H}_{14}^a$ (1.54 ppm)	
0	1.46	0.09	0	1.00	1.00
0.33	1.35	0.28	0	1.00	0.99
1	1.09	0.74	0.07	1.00	0.99
2	0.91	1.06	0.15	1.00	0.99
4	0.66	1.33	0.45	1.00	0.99

^a Used as an internal standard. ^b Total (relative) Ru concentration assuming only Ru species present are $\text{Ru}(\text{CO})_n(\text{C}_2\text{H}_4)_{5-n}$ ($n = 4, 3, 2$).

(s, B₁); 3-methylpentane, 298 K] possible when the alkene ligands lie in the equatorial plane of a trigonal-bipyramidal structure, as predicted by theory for Fe^{16} complexes and established for the spectroscopically similar and structurally characterized $\text{Ru}(\text{CO})_3(\eta^2\text{-methyl acrylate})_2$,⁹ $\text{Fe}(\text{CO})_3(\eta^2, \eta^2\text{-1,5-dimethylene-2,6-dimethylcyclooctane})$ ¹⁷ and $\text{Fe}(\text{CO})_3(\eta^2\text{-trans-cyclooctene})_2$ ⁷ complexes. The singlet in the ^1H NMR spectrum for $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ is consistent with such a coordination geometry or with a dynamic geometry at temperatures as low as 243 K.

Near-UV irradiation of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ in low-temperature-fluid $\text{CF}_3\text{C}_6\text{F}_{11}$ (243 K) or alkane (233 K) solutions saturated with C_2H_4 leads to additional spectral changes (NMR and IR) that are consistent with the photosubstitution represented in eq 3 (Figure 2 and Table V). The ^1H NMR spectrum (Table V) shows that a singlet at 3.02 ppm grows at the expense of singlets attributed to $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ and its precursor $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$. Quantitative analysis of the ^1H NMR spectral changes for several experiments (Table V) shows the $\text{Ru}:\text{C}_2\text{H}_4$ ratio to be 1:3 for the 3.02 ppm feature. A corresponding single product absorption at 1956 cm^{-1} in the CO stretching region of the IR spectrum (Figure 2) is consistent with a cylindrical local symmetry of a $\text{Ru}(\text{CO})_2$ fragment and, consequently, formulation of the product as *trans*- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ having three equatorially disposed C_2H_4 ligands in a trigonal-bipyramidal structure. To our knowledge, this represents the first reported preparation of an $\text{M}(\text{CO})_2(\text{alkene})_3$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) complex.

Surprisingly, *trans*- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$, observed as a photoproduct in low-temperature-fluid solutions, is *not* observed as a product in the near-UV photolysis of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ in a C_2H_4 -saturated 3-methylpentane glass at 90 K. However, CO loss from $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ does occur in low-temperature organic glasses. We have exploited the properties of methylcyclohexane to establish the photochemical properties of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$. It must be pointed out that the investigation of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ involves solutions that invariably contain excess C_2H_4 in order to preserve purity of the $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ while the samples are manipulated prior to cooling them to the low temperature of the rigid glasses. Unlike 3-methylpentane, a methylcyclohexane glass at 90 K inhibits the reaction of excess C_2H_4 , N_2 , or CO with a number of well-established 16-electron photoproduct species. However, warming of such a glass to $\sim 110\text{ K}$ retains its integrity while greatly accelerating bimolecular reactions of stationary 16-electron intermediates with diffusing small ligands to form characterized 18-electron substitution complexes.¹⁸ Near-UV irradiation of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ in a methylcyclohexane glass containing excess C_2H_4 at 90 K results in the IR spectral changes shown in Figure 3. A feature attributed to photoejected CO (2132 cm^{-1}) and two bands attributed to the 16-electron $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_2$ species at 2020 and 1948 cm^{-1} grow while features attributed to $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ decline. Warming the matrix to 110 K results in complete loss of $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_2$ absorptions, but there is growth of carbonyl absorptions at 2018 and 1975 cm^{-1} , which remain upon recooling to 90 K . Importantly, the amount of photoejected CO (2132 cm^{-1}) in the glass remains constant

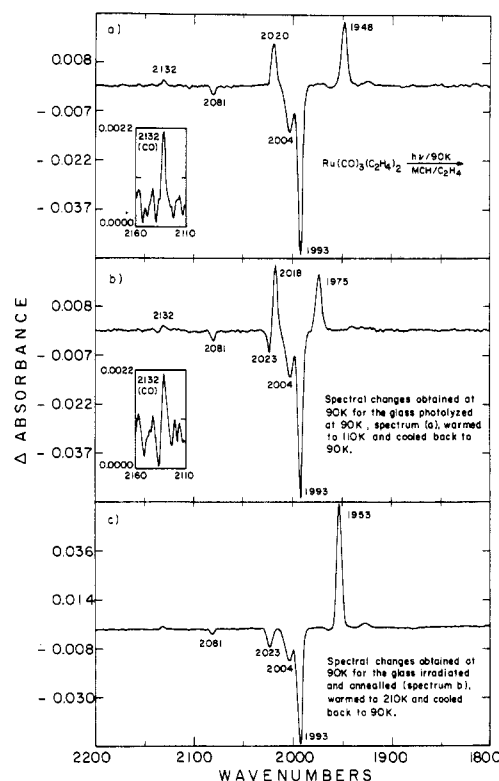


Figure 3. IR difference spectral changes accompanying near-UV irradiation of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ in a C_2H_4 -containing methylcyclohexane glass at 90 K : (a) spectrum after 5 min irradiation; (b) spectrum after subsequent warming to 110 K and recooling to 90 K ; (c) spectrum after subsequent warming to 210 K and recooling to 90 K . All difference spectra are obtained by digital subtraction of the IR spectrum for the glass prior to irradiation from spectra obtained in the subsequent designated treatments; declining spectral features in spectra a–c are associated with loss of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ in the initial 90 K irradiation. Insets display the feature at 2132 cm^{-1} associated with growth of free CO in the glass. The amount of CO in the glass after irradiation is unaffected by annealing to 110 K . The 2020 - and 1948-cm^{-1} features are due to $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_2$, the 2018 - and 1975-cm^{-1} features are due to *cis*- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$, and the 1953-cm^{-1} feature is due to *trans*- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$.

during annealing to 110 K (see insets, Figure 3a,b), ruling out formation of another isomer of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ by reaction of CO with $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_2$. The IR spectrum shows that *trans*- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ ($\nu(\text{CO}) = 1953\text{ cm}^{-1}$) is not formed in detectable amounts. The spectral features obtained are those observed for the 90 K photolysis of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ in C_2H_4 -saturated 3-methylpentane. These results imply the formation of an 18-electron $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ species, which we formulate as *cis*- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$, containing one equatorial and one axial CO ligand in a trigonal-bipyramidal structure. In support of this formulation, an OC-Ru-CO bond angle of 81° is calculated for the $\text{Ru}(\text{CO})_2$ fragment by evaluation¹⁹ of the ratio of the relative intensities of the symmetric and antisymmetric carbonyl absor-

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bances. Furthermore, warmup of $cis\text{-Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ to 210 K leads to net IR spectral changes which are retained on recooling to 90 K, consistent with quantitative conversion to the $trans\text{-Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ complex (1953 cm^{-1}) mentioned above. In C_2H_4 -saturated 3-methylpentane glasses at 90 K, photochemical isomerization of matrix-isolated $trans\text{-Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ to the cis form is accompanied by loss of CO to form a monocarbonyl species (1964 cm^{-1}), presumably a $\text{Ru}(\text{CO})(\text{C}_2\text{H}_4)_4$ complex, related to well-characterized $\text{Fe}(\text{CO})(\text{diene})_2$ complexes.²⁰ $\text{Ru}(\text{CO})(\text{C}_2\text{H}_4)_4$ can also be obtained directly by photolysis of $cis\text{-Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ at 90 K in C_2H_4 -saturated 3-methylpentane. Warmup of 90 K glasses containing the $\text{Ru}(\text{CO})(\text{C}_2\text{H}_4)_4$ and the photogenerated CO results, initially, in formation of $cis\text{-Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$, and, eventually, $trans\text{-Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ at higher temperatures. In methylcyclohexane the photoconversion of $cis\text{-Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ to $\text{Ru}(\text{CO})(\text{C}_2\text{H}_4)_4$ (1964 cm^{-1}) proceeds via transient formation of a second monocarbonyl species (1923 cm^{-1}) tentatively formulated as the coordinatively unsaturated $\text{Ru}(\text{CO})(\text{C}_2\text{H}_4)_3$. At high C_2H_4 concentrations in the dark at 90 K, the 1964-cm^{-1} feature grows in at the expense of the photogenerated 1923-cm^{-1} feature without change in the amount of free CO (2132 cm^{-1}) detected in the glass.

The thermally labile $\text{Ru}(\text{CO})_n(\text{C}_2\text{H}_4)_{5-n}$ ($n = 4, 3$) complexes are stabilized by excess C_2H_4 toward decomposition in fluid solutions at 298 K, but are quite stable in Ar-purged alkane solutions at sufficiently low temperatures (195 K). $trans\text{-Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ is more labile than the bis(ethylene) complex and back-reacts with photoreleased CO at $\sim 253\text{ K}$ to regenerate $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$. Purging a C_2H_4 -saturated alkane solution of $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ with Ar at 298 K rapidly generates $\text{Ru}_3(\text{CO})_{12}$, purging with CO at 298 K yields $\text{Ru}(\text{CO})_5$, and reaction with 0.05 M PPh_3 at 298 K yields $\text{Ru}(\text{CO})_4\text{PPh}_3$. The $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ reacts with CO to yield first $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ and then $\text{Ru}(\text{CO})_5$, reaction with 0.05 M PPh_3 yields $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$, and reaction with $trans\text{-1,3-pentadiene}$ rapidly yields $\text{Ru}(\text{CO})_3(trans\text{-1,3-pentadiene})$.

(b) Mononuclear Iron Carbonyl-Ethylene Complexes. The formation of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ from $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ and work published by Fleckner, Grevels, and Hess⁷ prompted us to reinvestigate the alkene products derived from the low-temperature photolysis of $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$. Irradiation of $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ at 273 K in the presence of C_2H_4 results in the formation of $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$, not $\text{Fe}_2(\text{CO})_6(\text{C}_2\text{H}_4)_2$ as previously concluded.⁵ The ^1H NMR spectral changes (Table III) are consistent with the product $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$, and quantitative integrations confirm the stoichiometry. The ^1H NMR integrations show that the product associated with the singlet at 2.68 ppm has two C_2H_4 ligands per Fe, not one C_2H_4 as concluded previously, consistent with conversion of one $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ and one C_2H_4 to one $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$. In the earlier work,⁵ ^1H NMR integration data were unreliable, presumably owing to sample decomposition. IR spectral changes accompanying photolysis of $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ in C_2H_4 -saturated $\text{CF}_3\text{C}_6\text{F}_{11}$ solution are shown in Figure 4. In the present work IR spectral changes for the same solution show the same extent conversion as determined by ^1H NMR spectroscopy, thereby establishing correlation of IR absorptions and the ^1H NMR singlet attributed to $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$. The remarkable spectroscopic similarity to $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ suggests the same C_{2v} structure for both the Fe and Ru species.

Irradiation of $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ in a C_2H_4 -saturated 3-methylpentane glass at low temperature results in the ultimate formation of a monocarbonyl Fe complex, possibly $\text{Fe}(\text{CO})(\text{C}_2\text{H}_4)_4$, not $trans\text{-Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ as previously concluded.⁵ As with $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$, loss of CO (2132 cm^{-1}) from $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ initially yields $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ (Figure 4b); here, competitive loss of C_2H_4 leads to formation of some $\text{Fe}(\text{CO})_4$ (1946 cm^{-1}). [The $\text{Fe}(\text{CO})_4$ can be photogenerated independently by irradiation of $\text{Fe}(\text{CO})_5$ under the same conditions.] However, just beyond the initial stages of reaction we find that further photo-

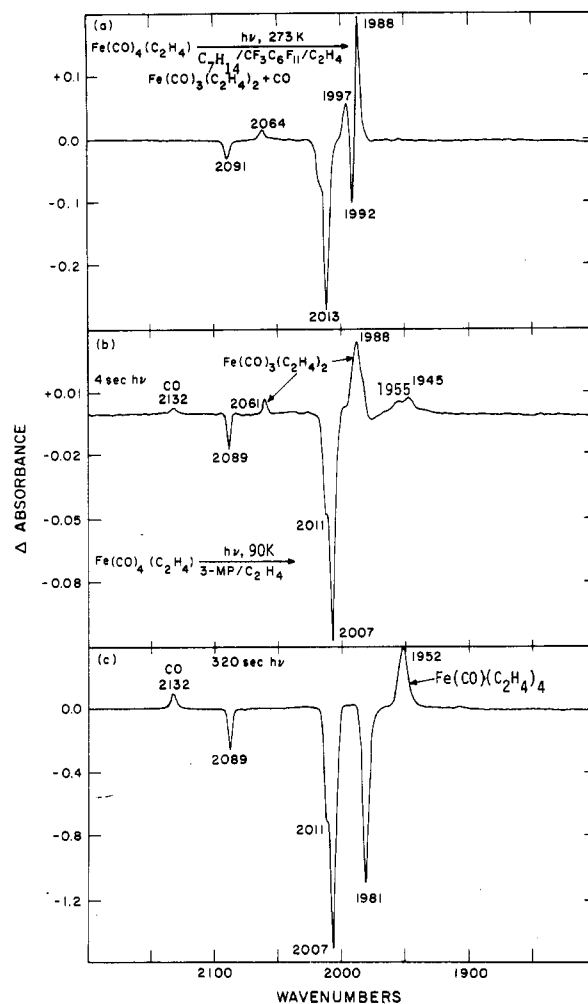


Figure 4. (a) IR difference spectrum accompanying the same near-UV irradiation of $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ in C_2H_4 -saturated $\text{CF}_3\text{C}_6\text{F}_{11}$ solution at 273 K for which ^1H NMR spectral changes were acquired. (b and c) IR difference spectral changes accompanying the near-UV irradiation of $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ in a C_2H_4 -saturated 3-methylpentane glass at 90 K for (b) 4 s and (c) 320 s.

reaction of $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ occurs to yield new carbonyl features at 1955 and 1998 cm^{-1} , which are only detected by spectral subtraction of masking absorptions of unreacted $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$. The 1955- and 1998-cm^{-1} features are associated with $cis\text{-Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ (vide infra). This secondary photoproduct is also photosensitive and continued irradiation (Figure 4c; 320-s $h\nu$), yields only a single carbonyl product band at 1952 cm^{-1} . The total yield of liberated CO (2132 cm^{-1}) per $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ molecule consumed is three times that observed in the initial photoconversion (4-s $h\nu$) to $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$. The $cis\text{-Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ escaped detection in previous work,³ presumably as a result of spectral masking by unreacted $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ and the 1952-cm^{-1} product band.

As for $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$, photolysis at 100 K of a C_2H_4 -saturated 3-methylpentane glass containing only $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ proceeds cleanly at low extent conversion to give well-resolved spectral features associated with $cis\text{-Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_3$, 1955 and 1998 cm^{-1} with a calculated OC-M-CO angle of 82° (Figure 5). Our new data show that $trans\text{-Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ is not observed in C_2H_4 -saturated alkane glasses as a product of 100 K photolysis of $\text{Fe}(\text{CO})_n(\text{C}_2\text{H}_4)_{5-n}$ ($n = 5, 4, 3$). However, warmup of photogenerated $cis\text{-Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ to 200 K (Figure 5b) results in decline of its spectral features, significant regeneration of $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$, and growth of a single band at 1942 cm^{-1} , which remains upon recooling to 100 K. We attribute this band to $trans\text{-Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_3$, in analogy with the ^1H NMR characterized $trans\text{-Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$. $trans\text{-Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ back-reacts with free CO upon warming above 210 K. $trans\text{-Fe}$ -

(20) (a) Koerner von Gustorf, E.; Buchkremer, J.; Pfajfer, Z.; Grevels, F.-W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 260. (b) Kruger, C.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 261.

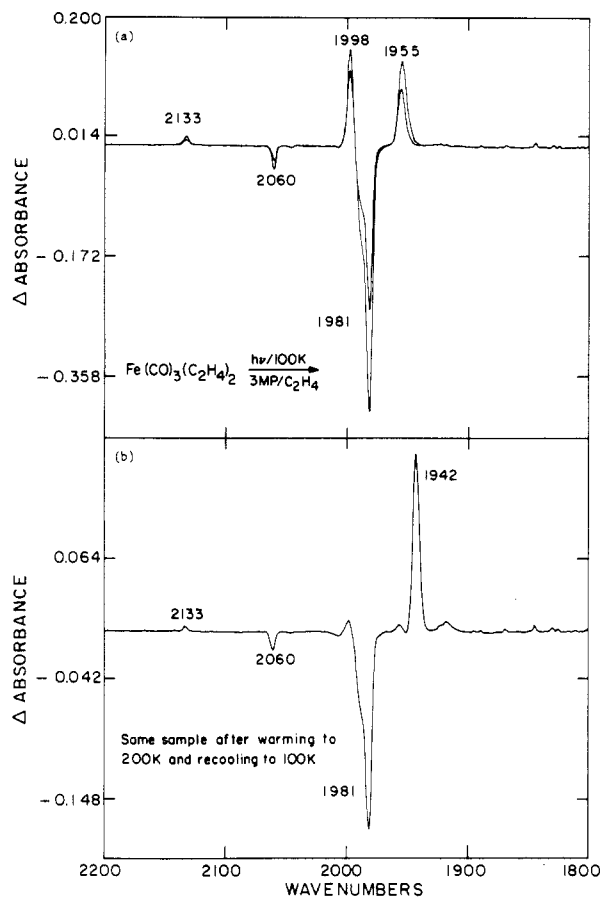


Figure 5. (a) IR difference spectrum accompanying the near-UV irradiation of $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ in a C_2H_4 -containing 3-methylpentane glass at 100 K. The 2133-cm^{-1} feature is associated with the growth of free CO in the glass. (b) IR difference spectrum for the irradiated sample (spectrum a) after warming to 200 K and recooling to 100 K. $\text{cis-Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ [$\nu(\text{cm}^{-1}) = 1998, 1955$ (a)] has isomerized to the *trans* isomer [$\nu(\text{cm}^{-1}) = 1942$ (b)], and some $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ [$\nu(\text{cm}^{-1}) = 2060, 1981$] has been regenerated (based on change in negative absorbances).

$(\text{CO})_2(\text{C}_2\text{H}_4)_3$ cannot be detected by ^1H NMR spectroscopy upon photolysis of $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ in C_2H_4 -saturated $\text{CF}_3\text{C}_6\text{F}_{11}$ solutions at temperatures as low as 243 K, presumably because back-reaction of the tris(ethylene) complex with CO occurs rapidly. Photolysis of photogenerated *cis-Fe*($\text{CO})_2(\text{C}_2\text{H}_4)_3$ at 90 K in the presence of C_2H_4 generates only the 1952-cm^{-1} feature and free CO (2132 cm^{-1}). Here, the final yield of liberated CO per $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ molecule consumed is two times that observed in the initial conversion to *cis-Fe*($\text{CO})_2(\text{C}_2\text{H}_4)_3$. Warmup to 150 K of alkane glasses exhibiting only the 1952-cm^{-1} band and liberated CO results in regeneration of only *cis-Fe*($\text{CO})_2(\text{C}_2\text{H}_4)_3$ in high yield with respect to the known concentration of starting material, be it $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ or $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$. The *cis-Fe*($\text{CO})_2(\text{C}_2\text{H}_4)_3$ spectral features are retained upon recooling to 90 K, and subsequent near-UV irradiation results in liberation of free CO and regeneration of the 1952-cm^{-1} feature at the expense of *cis-Fe*($\text{CO})_2(\text{C}_2\text{H}_4)_3$ features. The new data show that both $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ and *cis-Fe*($\text{CO})_2(\text{C}_2\text{H}_4)_3$ are extremely photosensitive and simply do not accumulate during irradiation of $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ in C_2H_4 -saturated alkane glasses. The 1952-cm^{-1} feature was previously attributed^{5,21} to *trans-Fe*($\text{CO})_3(\text{C}_2\text{H}_4)_2$. However, this new set of experiments suggests that the 1952-cm^{-1} band is associated with a metal-alkene complex retaining only one CO, namely $\text{Fe}(\text{CO})(\text{C}_2\text{H}_4)_4$. $\text{Fe}(\text{CO})(\text{C}_2\text{H}_4)_4$ is relatively photoinert and is unchanged after 1 h of irradiation

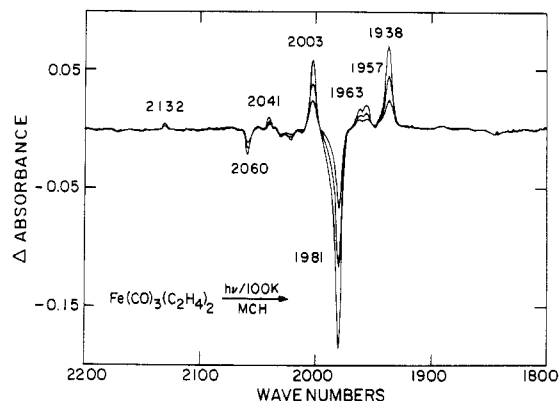


Figure 6. IR difference spectral changes accompanying near-UV irradiation of $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ in a methylcyclohexane glass at 100 K. The 2132-cm^{-1} feature is associated with growth of free CO, the 2041- , 1963- , and 1957-cm^{-1} features are attributed to $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$, and the 2003- and 1938-cm^{-1} features are attributed to $\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_2$ (see text).

at 100 K where ~ 15 min is required to convert $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ to $\text{Fe}(\text{CO})(\text{C}_2\text{H}_4)_4$.

Isotopic labeling experiments further support the IR spectral assignments for $\text{Fe}(\text{CO})_{5-n}(\text{C}_2\text{H}_4)_n$ complexes. $\text{Fe}(\text{CO})_3(^{13}\text{CO})(\text{C}_2\text{H}_4)$ is prepared by reacting $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ with ^{13}CO in 3-methylpentane at 298 K. Subsequent near-UV irradiation in a C_2H_4 -saturated solution at 273 K yields $\text{Fe}(\text{CO})_{3-n}(^{13}\text{CO})_n(\text{C}_2\text{H}_4)_2$ ($n = 0, 1$; vide infra). After the solution of $\text{Fe}(\text{CO})_{3-n}(^{13}\text{CO})_n(\text{C}_2\text{H}_4)_2$ is cooled to 90 K, extended near-UV irradiation yields species formulated as $\text{Fe}(\text{CO})(\text{C}_2\text{H}_4)_4$ (1952 cm^{-1}) and $\text{Fe}(^{13}\text{CO})(\text{C}_2\text{H}_4)_4$ (1908 cm^{-1}) in a 3:1 ratio, assuming the absorptivities of the ^{12}CO and ^{13}CO species to be the same. The absence of observable vibrational coupling is consistent with a monocarbonyl formulation. Warmup to 150 K yields *cis-Fe*($\text{CO})_2(\text{C}_2\text{H}_4)_3$ ($1998, 1955\text{ cm}^{-1}$; 3-methylpentane, 90 K) and *cis-Fe*($\text{CO})(^{13}\text{CO})(\text{C}_2\text{H}_4)_3$ ($1984, 1924\text{ cm}^{-1}$; 3-methylpentane, 90 K) as the only products, which persist on recooling to 90 K. The CO stretching (K) and interaction (K_i) force constants have been calculated for the C_{2v} $\text{Fe}(\text{CO})_2$ fragment of *cis-Fe*($\text{CO})_2(\text{C}_2\text{H}_4)_3$ by normal coordinate analysis²² ($K = 1578.3$, $K_i = 34.3\text{ N m}^{-1}$) and used to correctly predict ($1985.0, 1923.8\text{ cm}^{-1}$) the observed frequencies for *cis-Fe*($\text{CO})(^{13}\text{CO})(\text{C}_2\text{H}_4)_3$. Warmup of the *cis*-tris(ethylene) complex to 200 K yields *trans-Fe*($\text{CO})_2(\text{C}_2\text{H}_4)_3$ (1945 cm^{-1}) and *trans-Fe*($\text{CO})(^{13}\text{CO})(\text{C}_2\text{H}_4)_3$ (1918 cm^{-1}). The small wavenumber shift between these two features ($\Delta\nu = 27\text{ cm}^{-1}$) rules out formulation as a monocarbonyl species and suggests a strong interaction force constant for the cylindrical $\text{Fe}(\text{CO})_2$ fragment of *trans-Fe*($\text{CO})_2(\text{C}_2\text{H}_4)_3$ ($K = 1570.4$, $K_i = 39.8\text{ N m}^{-1}$). At low temperature, the monocarbonyl photoproduct distribution and the absence of *cis*- or *trans-Fe*($^{13}\text{CO})_2(\text{C}_2\text{H}_4)_3$ during subsequent warmup (1) rules out rapid disproportionation of $\text{Fe}(\text{CO})_2(^{13}\text{CO})(\text{C}_2\text{H}_4)_2$ or $\text{Fe}(\text{CO})_3(^{13}\text{CO})(\text{C}_2\text{H}_4)$ at ≤ 273 or $\leq 298\text{ K}$, respectively, or thermal substitution of ^{12}CO by excess ^{13}CO on $\text{Fe}(\text{CO})_3(^{13}\text{CO})(\text{C}_2\text{H}_4)$ at $\leq 298\text{ K}$ and (2) suggests predominant recombination of the matrix-isolated monocarbonyl with CO initially photoejected from the same metal center to form *cis*- and then *trans-Fe*($\text{CO})_{2-n}(^{13}\text{CO})_n(\text{C}_2\text{H}_4)_3$ ($n = 0, 1$) during warmup from 90 to 200 K.

The conspicuous absence of *trans-M*($\text{CO})_2(\text{C}_2\text{H}_4)_3$ species ($M = \text{Fe, Ru}$) as initial photoproducts from $\text{M}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ in alkane glasses has been investigated further. In a methylcyclohexane glass, FTIR spectral features attributed to the 16-electron $\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_2$ ($2003, 1938\text{ cm}^{-1}$; methylcyclohexane, 100 K) and free CO are generated upon photolysis of matrix-isolated $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ (Figure 6) in analogy with data for the Ru analogue. However, the growth of additional features at 2041 (m), 1963 (m), and 1957 (s) cm^{-1} in constant ratio with these is attributed to the concomitant generation of $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ (Table II), which has been characterized previously in alkane⁵ and Ar²³

(21) The feature attributed to *trans-Fe*($\text{CO})_2(\text{C}_2\text{H}_4)_3$ appears in the original spectral data at 1952 cm^{-1} and was incorrectly reported at 1929 cm^{-1} in ref 5.

(22) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.

matrices as the product obtained upon light-induced loss of CO from $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$. Competitive loss of CO and olefin has previously been observed for $\text{Fe}(\text{CO})_3(\eta^4\text{-1,3-diene})$ species.²³ We cannot rule out a similar competition for $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$, since we are unable to remove excess C_2H_4 , which might scavenge $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)$, if it formed. $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)$ exhibits a weak electronic absorption at 447 nm, consistent with a coordinatively unsaturated product (Table I). In the presence of excess C_2H_4 , warmup of a 90 K glass containing $\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_2$ and $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)$ to 110 K yields net FTIR spectral changes that persist on recooling to 90 K. These spectral changes are consistent with conversion of $\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_2$ to *cis*- $\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ (as observed for Ru) and also regeneration of the C_{2v} symmetry isomer of $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ as a result of thermal back-reaction of $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)$ with C_2H_4 . These results are consistent with the net conversion of $\text{M}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ to *cis*- $\text{M}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ via the 16-electron $\text{M}(\text{CO})_2(\text{C}_2\text{H}_4)_2$ intermediate and the net conversion of $\text{M}(\text{CO})_4(\text{C}_2\text{H}_4)$ to C_{2v} isomer of $\text{M}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ via the 16-electron $\text{M}(\text{CO})_3(\text{C}_2\text{H}_4)$ intermediate in C_2H_4 -saturated 3-methylpentane. The metal carbonyl features for the 16-electron $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)$ show similarities in relative energy and intensity to those of the C_{2v} $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ (Table II), thereby suggesting little rearrangement of the $\text{Fe}(\text{CO})_3$ unit of $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)$ on reaction with C_2H_4 . Also, OC-M-CO^{19} bond angles of 97° ($\text{M} = \text{Ru}$) and 94° ($\text{M} = \text{Fe}$) are calculated for 16-electron $\text{M}(\text{CO})_2(\text{C}_2\text{H}_4)_2$ complexes. A *cis* geometry for the $\text{M}(\text{CO})_2$ fragment of the coordinatively unsaturated $\text{M}(\text{CO})_2(\text{C}_2\text{H}_4)_2$ intermediate is apparently retained upon reaction with C_2H_4 , explaining the conspicuous absence of the thermodynamically favored *trans*- $\text{M}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ complexes in the low-temperature photolysis of matrix-isolated $\text{M}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ ($\text{M} = \text{Ru}, \text{Fe}$) to yield *cis*- $\text{M}(\text{CO})_2(\text{C}_2\text{H}_4)_3$.

Like $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$, $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ is very labile at 298 K. However, $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ is less labile than $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$. For example, purging an alkane solution of $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ with CO yields a pure solution of $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$, a substance that is difficult to obtain in a pure state by conventional procedures. As noted above, CO reacts with $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ to yield $\text{Ru}(\text{CO})_5$ under conditions where $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ is inert. Further, the reaction of $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ with 0.05 M PPh_3 at room temperature yields $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)(\text{PPh}_3)$, with only minor amounts of $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$, whereas $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ gives exclusively $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$. Reaction of $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ with *trans*-1,3- or *trans*-1,4-pentadiene yields $\text{Fe}(\text{CO})_3(\text{trans-1,3-pentadiene})$ in analogy to the Ru species. The simple generation of pure alkane solutions of $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ allows this complex to serve as an excellent, versatile $\text{Fe}(\text{CO})_3$ transfer reagent promising a wide range of applications, including its use in mechanistic studies of the $\text{Fe}(\text{CO})_5$ photocatalyzed reactions of alkenes.

(c) Catalytic Isomerization of 1-Pentene. $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ readily undergoes alkene exchange as detected by IR spectroscopy. Addition of precooled 1-pentene (pent) to an Ar-purged methylcyclohexane (no excess C_2H_4 present) solution containing ~ 1 mM $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ at 195 K, followed by warming to 260 K, results in the decline of spectral features for $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ and growth of new features attributed to $\text{Ru}(\text{CO})_3(\text{pent})_2$ (Table II). This assignment is based on the spectral similarity to the bis(ethylene) complex, and the shift to lower frequencies is consistent with the substitution of C_2H_4 by 1-pentene [cf. the IR data of the corresponding $\text{Fe}(\text{CO})_4(\eta^2\text{-alkene})$ complexes]. Continued warming leaves the IR spectral features initially unchanged at 293 K. However, gas chromatographic analysis of the solution shows that 1-pentene undergoes catalytic isomerization above 260 K, yielding *cis*- and *trans*-2-pentene. Turnover numbers (number of product molecules per catalyst precursor molecule initially present) exceeding 250 have been obtained in the dark. *trans*- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ is more labile than $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ and undergoes substitution by added 1-pentene at 240 K to form *trans*- $\text{Ru}(\text{CO})_2(\text{pent})_3$ (Table II). Interestingly, catalytic activity is displayed by *trans*- $\text{Ru}(\text{CO})_2(\text{alkene})_3$ above 240 K with turnover

numbers near 50. Some representative data for catalytic 1-pentene isomerization are given in Table VI. Turnover rates (number of product molecules per minute per catalyst precursor molecule initially present), Table VI, decrease systematically with reaction time at 293 K in correlation with declining $\text{Ru}(\text{CO})_3(\text{pent})_2$ or $\text{Ru}(\text{CO})_2(\text{pent})_3$ spectral features. The range of catalyst concentrations used is limited to < 6 mM by solubility of the $\text{Ru}_3(\text{CO})_{12}$ precursor and to > 1 mM by low turnover numbers. With these restrictions we note that for two different catalyst concentrations within this range the average turnover rates after similar reaction times are in close agreement, suggesting kinetics first order in metal concentration for both the $\text{Ru}(\text{CO})_3(\text{alkene})_2$ and *trans*- $\text{Ru}(\text{CO})_2(\text{alkene})_3$ complexes, in accord with the more detailed report⁷ for $\text{Fe}(\text{CO})_3(\text{pent})_2$. Importantly, the initial (1 min) average turnover rate achieved with *trans*- $\text{Ru}(\text{CO})_2(\text{pent})_3$ ($\geq 9 \text{ min}^{-1}$) at 293 K represents a lower limit due to rapid catalyst deactivation, and it clearly exceeds the rate achieved with $\text{Ru}(\text{CO})_3(\text{pent})_2$ ($\sim 4 \text{ min}^{-1}$) under the same conditions ([catalyst] = 2.78 mM, [pentene] = 1.83 M, 293 K, methylcyclohexane). Under photocatalytic conditions, efficient photochemical conversion of $\text{Ru}(\text{CO})_3(\text{pent})_2$ to *trans*- $\text{Ru}(\text{CO})_2(\text{pent})_3$ is offset by facile thermal back-reaction unless liberated CO is deliberately removed. The importance of $\text{M}(\text{CO})_2(\text{pent})_3$ species ($\text{M} = \text{Fe}, \text{Ru}$) under photocatalysis conditions is therefore ambiguous. Our results suggest that substitutionally labile $\text{Ru}(\text{CO})_3(\text{alkene})_2$ and $\text{Ru}(\text{CO})_2(\text{alkene})_3$ complexes play key roles in the $\text{Ru}_3(\text{CO})_{12}$ -photocatalyzed alkene isomerization, since we have demonstrated that their photogeneration from $\text{Ru}_3(\text{CO})_{12}$ provides an entrance to the catalytic cycle (Table VI).¹¹ With $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ we have been able to achieve turnover numbers in the dark approaching 2000 and turnover rates of $\sim 600 \text{ min}^{-1}$ at 293 K. These results are in qualitative agreement with the report by Grevels and co-workers⁷ in which $\text{Fe}(\text{CO})_3(\eta^2\text{-cis-cyclooctene})_2$ was used as a catalyst precursor. Although solutions of $\text{Fe}(\text{CO})_3(\text{alkene})_2$ containing 1-pentene approach the equilibrium of the three pentene isomers rapidly and in constant thermodynamic ratio²⁴ (*trans*/*cis*-2-pentene = 3.8), the same cannot be said for the Ru catalysts. An initial ratio of ~ 6 for *trans*/*cis*-2-pentene is achieved photochemically by using $\text{Ru}_3(\text{CO})_{12}$ or thermally by using $\text{Ru}(\text{CO})_n(\text{C}_2\text{H}_4)_{5-n}$ ($n = 3, 2$).

The turnover rate of catalysis for both Ru and Fe catalysts decreases with reaction time at 293 K. This decrease in rate is accompanied by loss of IR spectral features attributed to $\text{M}(\text{CO})_3(\text{pent})_2$ and the corresponding growth of spectral features attributed to $\text{M}(\text{CO})_3(1,3\text{-pentad})$ ($\sim 75\%$) and $\text{M}(\text{CO})_4(\text{pent})$ ($\sim 25\%$) (Table II), identified by comparison of IR spectra with those of authentic samples. These complexes, especially $\text{M}(\text{CO})_3(1,3\text{-pentad})$, once formed are relatively inert and show no catalytic activity. Formation of $\text{M}(\text{CO})_4(\text{pent})$ is reasonable, considering that catalyst decomposition would release CO which can react with $\text{M}(\text{CO})_3(\text{pent})_2$ to give $\text{M}(\text{CO})_4(\text{pent})$. The dehydrogenation of 1-pentene to yield inert 1,3-pentadiene complexes is a new finding. The mechanism of 1-pentene dehydrogenation deserves further study; previous work²⁵ rules out the intermediacy of 1,3,4,5-*n*-pent-4-en-3,1-yliron tricarbonyl as an intermediate leading to $\text{Fe}(\text{CO})_3(1,3\text{-pentad})$. Evidence for the formation of $\text{Ru}(\text{CO})(1,3\text{-pentad})$ comes from GC-mass spectra and HPLC analysis of the metal-containing product from the catalytic mixture. The GC-mass spectra show a molecular ion peak ($M^+ = 254$) and fragmentation pattern consistent with $M^+ - \text{CO}$, $M^+ - 2\text{CO}$, and $M^+ - 3\text{CO}$. This pattern is indistinguishable from that obtained from an authentic sample of $\text{Ru}(\text{CO})_3(1,3\text{-pentad})$. In addition, both GC and HPLC show the same retention time for the organometallic species recovered from the catalytic samples and an authentic sample.

(d) Photochemical Formation of $\text{HM}(\text{CO})_3(\eta^3\text{-allyl})$. We expect the catalytic cycle for Ru to be similar to that for $\text{Fe}(\text{CO})_5$ -photocatalyzed alkene isomerization. Beyond the involvement of the $\text{M}(\text{CO})_3(\text{alkene})_2$, we prefer not to speculate extensively here

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Table VI. Turnover Rates for 1-Pentene Isomerization by $M(\text{CO})_3(\text{C}_2\text{H}_4)_2$ ($M = \text{Fe}, \text{Ru}$), $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$, and Irradiated $\text{Ru}_3(\text{CO})_{12}$ at 293 K

catalyst precursor		[1-pentene], M	t , min	% pentene			turnover rate ^a
formula	concn, mM			1-	<i>trans</i> -2-	<i>cis</i> -2-	
$\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$	5.0	4.12	0.33	76.99	16.82	6.19	568
	2.0	6.60	0.33	93.78	4.28	1.94	615
	5.32	1.83	1	98.56	1.31	0.13	4.95
$\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$	5.32	1.83	5	96.22	3.54	0.24	2.60
			30	91.28	8.31	0.41	1.00
			120	85.07	15.16	0.77	0.43
			1440	60.37	36.17	3.46	0.09
			1	98.13	1.20	0.07	4.37
			5	96.40	3.39	0.21	2.47
	2.78	1.83	30	90.83	8.72	0.45	1.05
			120	85.35	13.91	0.74	0.41
			1440	61.07	35.18	3.75	0.09
			4	97.93	1.92	0.15	3.41
			20	96.62	3.21	0.17	1.11
			120	89.79	9.72	0.49	0.56
	2.78	1.83	1	98.71	1.09	0.20	8.53
			5	97.44	2.24	0.32	3.37
			30	95.55	3.95	0.50	0.98
			60	93.98	5.43	0.59	0.66
			120	91.44	7.80	0.76	0.47
			1	98.58	1.20	0.22	9.34
$\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$	2.78	1.83	5	97.40	2.29	0.31	3.42
			30	95.25	4.23	0.52	1.04
			60	93.65	5.74	0.61	0.70
			120	91.11	8.07	0.82	0.49
			1	98.81	1.11	0.08	3.11
			30	97.78	2.10	0.12	0.97
	1.40	1.83	5	99.09	0.86	0.05	2.38
			30	98.08	1.82	0.10	0.84
			10	97.51	2.26	0.23	>5 ^c
			20	96.10	3.46	0.31	>4 ^c
			60	88.07	10.78	1.15	>4 ^c
			10	97.17	2.56	0.24	>6 ^c
$\text{Ru}_3(\text{CO})_{12}$ ^b	0.85	1.83	20	96.33	3.36	0.38	>4 ^c
			60	87.91	10.92	1.17	>4 ^c

^a Turnover rate is the number of product molecules produced per minute per molecule of catalyst precursor initially present. ^b Conversion of $\text{Ru}_3(\text{CO})_{12}$ to mononuclear species is complete within the first 7 min of continuous near-UV irradiation with a 550-W medium-pressure Hg lamp. ^c Turnover rate is not defined in these cases, because higher excitation rate will increase the rate of observed product formation. Thus, the numbers are lower limits, at the light intensity used, 10^{-6} einstein/min. The quantum yield was observed to be ~ 5 , similar to that in ref 11.

about the particular steps of the catalytic cycle, except to note the previous observation⁵ of $\text{HFe}(\text{CO})_3(\eta^3\text{-allyl})$, potentially the essential intermediate in the catalytic cycle. We find that the major product of irradiation of $\text{Fe}(\text{CO})_4(\text{C}_3\text{H}_6)$ in a 90 K methylcyclohexane glass exhibits two features, one sharp feature at 2064 cm^{-1} and a broader absorbance with a maximum at about 1994 cm^{-1} . These features are unrelated to those for $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)$; $\text{Fe}(\text{CO})_4$ is also a minor product that accounts completely for the remaining 1946-cm^{-1} product feature previously attributed to one of three characteristic carbonyl features for $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$. Warmup of the irradiated 90 K glass to 173 K yields conversion to a three-band pattern attributable to $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ (2066, 2003, and 1994 cm^{-1}) on the basis of spectral similarity to $\text{BrFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ ²⁶ and the structurally related 1,3,4,5-*n*-pent-4-en-3,1-yliron tricarbonyl²⁵ (Table II).

Chemical evidence for $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ has been obtained by producing $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ in a methylcyclohexane/1-bromo-2-methylpropane matrix ($\sim 50/50$ by volume) at 90 K. Warming above $\sim 200\text{ K}$ yields IR spectral changes consistent with regeneration of $\text{Fe}(\text{CO})_4(\text{C}_3\text{H}_6)$ ($\sim 80\%$) and formation of the known $\text{BrFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ ($\sim 20\%$).²⁶ Similarly, irradiation of $\text{Fe}(\text{CO})_4(\text{C}_3\text{H}_6)$ in a 90 K methylcyclohexane glass followed by addition of CCl_4 and warmup to 298 K yields CHCl_3 and the known²⁶ $\text{ClFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$. Metal hydrides are known to react with alkyl halides,²⁷ providing evidence for the existence of $\text{HFe}(\text{CO})_3(\eta^3\text{-allyl})$. It should also be pointed out that metal-centered radicals can also react with alkyl halides to produce the

metal halide,²⁸ and radicals, e.g. $\text{Fe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$, are known to be produced upon irradiation of $\text{Fe}(\text{CO})_5$ in the presence of C_3H_6 .⁶ We have irradiated $\text{Fe}(\text{CO})_4(\text{C}_3\text{H}_6)$ through Pyrex ($\lambda > 280\text{ nm}$) and find no IR evidence for the known²⁹ $\text{Fe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ species. Thus, we conclude $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ to be the dominant, essential species in the catalyzed isomerization of alkenes upon irradiation of $\text{Fe}(\text{CO})_5$ through Pyrex.

The three-IR-band pattern (2066, 2003, 1994 cm^{-1}) attributed to $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ at 173 K is retained on cooling to 90 K, but photochemical reaction occurs at 90 K to give the initial two-band pattern ($2064, 1994\text{ cm}^{-1}$), without additional CO loss, consistent with the existence of two isomers of $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$. Two isomers of $\text{XFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are known,³⁰ and we believe these to be related to the two isomers of $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$. Preliminary results show that the thermodynamically stable isomer of $\text{XM}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ ($\text{X} = \text{Cl}, \text{Br}; \text{M} = \text{Fe}, \text{Ru}$) can be photochemically converted to the less stable isomer.³¹

Irradiation of the two-band isomer of $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ at 90 K in a C_3H_6 -containing alkane glass yields loss of additional CO and growth of a single CO-stretching feature at 1929 cm^{-1} , too low in energy to be attributable to an $\text{Fe}(\text{CO})(\text{alkene})_4$ species analogous to $\text{Fe}(\text{CO})(\text{C}_2\text{H}_4)_4$. The product responsible for the 1929-cm^{-1} feature was previously misidentified as *trans*- $\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_6)_2$. Our data clearly indicate that there are between two and three photoejected CO's (2132 cm^{-1}) for each Fe-

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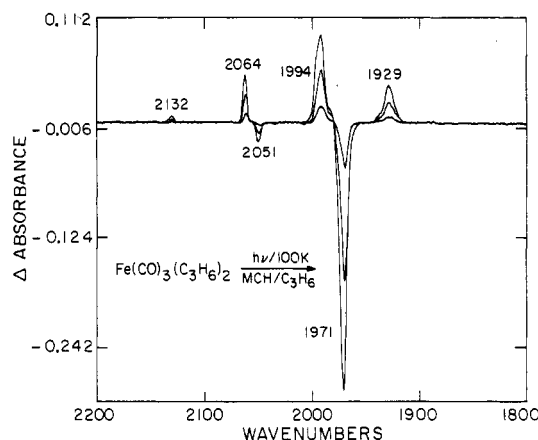
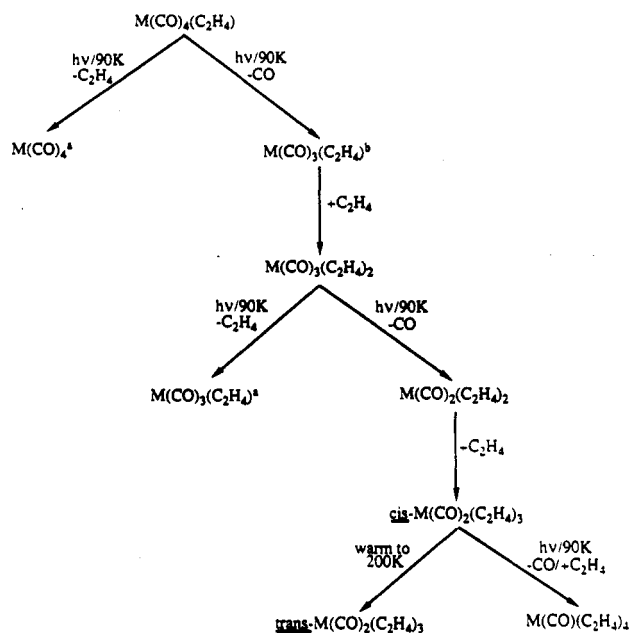


Figure 7. Infrared difference spectral changes accompanying near-UV irradiation of $\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_6)_2$ in a C_3H_6 -containing methylcyclohexane glass at 100 K. The 2132-cm^{-1} feature is associated with growth of free CO. The features at 2064 and 1994 cm^{-1} are due to $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$, and the 1929-cm^{-1} feature is tentatively assigned as $\text{HFe}(\text{CO})(\text{C}_3\text{H}_6)_2(\eta^3\text{-C}_3\text{H}_5)$.

$(\text{CO})_4(\text{C}_3\text{H}_6)$ molecule consumed.³² Near-UV irradiation of $\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_6)_2$ (formed in situ via photolysis of $\text{Fe}(\text{CO})_4(\text{C}_3\text{H}_6)$ plus C_3H_6 at 210 K) at 100 K in the presence of a large excess of C_3H_6 (Figure 7) yields free CO (2132 cm^{-1}), the two-band isomer of $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$, and a strong feature at 1929 cm^{-1} . The amount of photogenerated CO³² is consistent with loss of two CO's per molecule of $\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_6)_2$ converted to the 1929-cm^{-1} product based on quantitation of consumed $\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_6)_2$ [ν , cm^{-1} (ϵ , $\text{M}^{-1}\text{ cm}^{-1}$): 2052 (1200 ± 100); 3-methylpentane, 90 K] and photogenerated $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ [ν , cm^{-1} (ϵ , $\text{M}^{-1}\text{ cm}^{-1}$): 2065 (7200 ± 700); 3-methylpentane, 90 K] by FTIR spectroscopy. The *cis*- $\text{Fe}(\text{CO})_2(\text{C}_3\text{H}_6)_3$ complex is never observed as a photoproduct from irradiation of $\text{Fe}(\text{CO})_4(\text{C}_3\text{H}_6)$ or $\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_6)_2$ in the presence of excess C_3H_6 . In the presence of only small amounts of C_3H_6 , the 1929-cm^{-1} feature grows in only very weakly, suggesting that consumption of C_3H_6 by the (unobserved) product of CO loss from $\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_6)_2$ leads to formation of the 1929-cm^{-1} product. When samples containing the 1929-cm^{-1} absorber are warmed to $\sim 150\text{ K}$, the 1929-cm^{-1} feature disappears and $\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_6)_2$ is formed with associated consumption of free CO. Interestingly, spectral changes similar to those accompanying irradiation of $\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_6)$ characterize the low-temperature photochemistry of $\text{Fe}(\text{CO})_4(1\text{-pent})$ in a neat 1-pentene glass, while *cis*- $\text{Fe}(\text{CO})_2(3,3\text{-Me}_2\text{-1-pent})_3$ is the final product of near-UV irradiation of $\text{Fe}(\text{CO})_4(3,3\text{-Me}_2\text{-1-pent})$ in a 3-methylpentane glass containing 2 M 3,3-dimethyl-1-pentene at 90 K. These results suggest that the low-energy feature at $\sim 1929\text{ cm}^{-1}$ obtains only for alkenes containing allylic hydrogens, for which *cis*- $\text{Fe}(\text{CO})_2(\text{alkene})_3$ complexes are not accumulated as photoproducts. The 90 K irradiation of $\text{Fe}(\text{CO})_4(3,3\text{-Me}_2\text{-1-pent})$ in a ^{13}C in a C_3H_6 -saturated 3-methylpentane glass yields final product features at 1929 and 1885 cm^{-1} consistent with formulation of the 1929-cm^{-1} absorber as a monocarbonyl or a *trans*-dicarbonyl species exhibiting an interaction force constant $K_i = 0$. The two dicarbonyl complexes *cis*- and *trans*- $\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ exhibit significant interaction force constants, and it is therefore unlikely that an $\text{Fe}(\text{CO})_2(\text{C}_3\text{H}_6)_n$ complex would have $K_i = 0$. On the basis of the evidence available, we tentatively formulate the 1929-cm^{-1} absorber as $\text{HFe}(\text{CO})(\text{C}_3\text{H}_6)_2(\eta^3\text{-C}_3\text{H}_5)$. We do not find evidence for formation of $(\eta^3\text{-C}_3\text{H}_5)_2\text{Fe}(\text{CO})_2$.³³

Complete conversion of $\text{Ru}_3(\text{CO})_{12}$ to $\text{Ru}(\text{CO})_4(1\text{-pent})$ can only be done in the presence of a large excess of 1-pentene ($>1\text{ M}$). Photolysis of $\text{Ru}(\text{CO})_4(1\text{-pent})$ in either methylcyclohexane

Scheme I. Summary of the Photochemistry of $\text{M}(\text{CO})_n(\text{C}_2\text{H}_4)_{5-n}$ ($\text{M} = \text{Fe}, \text{Ru}; n = 4, 3, 2$)



^a Not detected for $\text{M} = \text{Ru}$. ^b Detection requires $T < 90\text{ K}$ for $\text{M} = \text{Ru}$.

or 3-methylpentane glasses containing 1.0 M 1-pentene at 90 K results in photoejection of CO (2132 cm^{-1}) and formation of mostly $\text{Ru}(\text{CO})_3(1\text{-pent})_2$. The generation of $\text{Ru}(\text{CO})_3(1\text{-pent})_2$ is probably due to reaction of 1-pentene present in the glass with the 16-electron $\text{Ru}(\text{CO})_3(1\text{-pent})$ fragment (not observed). When a 3-methylpentane matrix containing $\text{Ru}(\text{CO})_4(1\text{-pent})$ is photolyzed at 55 K, IR spectral changes for the photolysis reveal the generation of free CO (2132 cm^{-1}) and growth of new spectral features that are different from those observed with alkene = C_2H_4 . These new features are attributed to $\text{HRu}(\text{CO})_3(\eta^3\text{-C}_5\text{H}_9)$ on the basis of spectral similarity to the IR bands of $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_5\text{H}_9)$. The ability to detect the $\text{HRu}(\text{CO})_3(\eta^3\text{-C}_5\text{H}_9)$ at the lower temperature likely reflects slower 1-pentene diffusion and/or a slower rate of 1-pentene binding to the unsaturated Ru center. Due to the experimental difficulty, the trapping of $\text{HRu}(\text{CO})_3(\eta^3\text{-C}_5\text{H}_9)$ with alkyl halides has not yet been successful.

Conversion of $\text{Ru}_3(\text{CO})_{12}$ to $\text{Ru}(\text{CO})_4(\text{C}_3\text{H}_6)$ at 298 K is not complete, even after prolonged irradiation in solution saturated with C_3H_6 . Presumably, a photostationary state is reached, and upon switching off the light source, we observe reformation of $\text{Ru}_3(\text{CO})_{12}$. However, $\text{HRu}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ can still be generated as a minor product ($<10\%$) at 90 K by photolysis of $\text{Ru}(\text{CO})_4(\text{C}_3\text{H}_6)$ in the presence of $\text{Ru}_3(\text{CO})_{12}$ in a C_3H_6 -containing methylcyclohexane glass. The other products are $\text{Ru}_3(\text{CO})_{11}(\text{C}_3\text{H}_6)$ and $\text{Ru}(\text{CO})_3(\text{C}_3\text{H}_6)_2$.

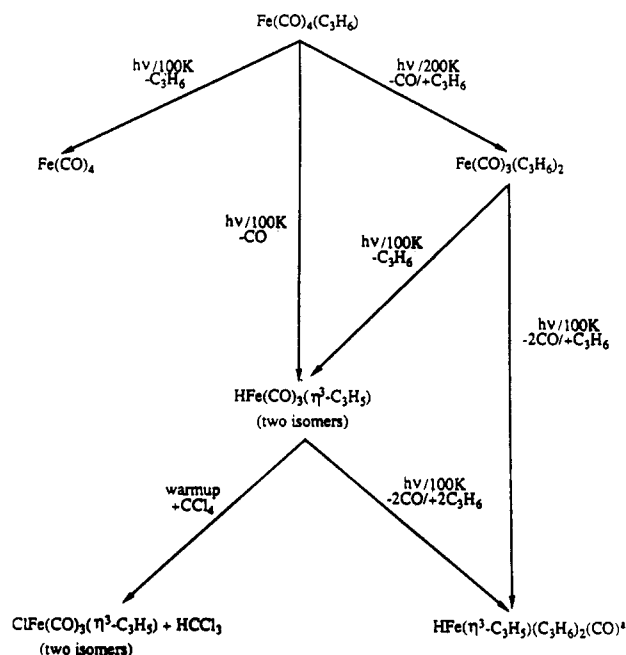
Conclusions

Scheme I summarizes the photochemistry of $\text{M}(\text{CO})_n(\text{C}_2\text{H}_4)_{5-n}$ ($\text{M} = \text{Fe}, \text{Ru}; n = 4, 3, 2$). Interestingly, warmup of glasses containing photogenerated $\text{M}(\text{CO})(\text{C}_2\text{H}_4)_4$ leads to nearly quantitative regeneration at 298 K of $\text{M}(\text{CO})_4(\text{C}_2\text{H}_4)$ ($\text{M} = \text{Ru}$) or a mixture of $\text{M}(\text{CO})_4(\text{C}_2\text{H}_4)$ and $\text{M}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ ($\text{M} = \text{Fe}$). Thus, the photochemical substitution of CO by C_2H_4 is reversible. The $\text{M}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ and $\text{M}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ complexes serve as catalyst precursors for the isomerization of 1-pentene, consistent with the conclusion that π -allyl hydride species are essential in the catalytic cycle. The photochemistry of the $\text{Fe}(\text{CO})_n(\text{C}_3\text{H}_6)_{5-n}$ complexes (Scheme II) shows that π -allyl hydride species can actually be detected. The π -allyl hydride reacts thermally with alkyl halides, providing additional chemical evidence for its formulation.

The data for the $\text{M}(\text{CO})_3(\text{alkene})_2$ complexes support the conclusion that, in general, the loss of CO or alkene can be ex-

(32) The molar extinction coefficient for free CO in an alkane glass has been determined to be $400\text{ M}^{-1}\text{ cm}^{-1}$, $\pm 20\%$: Pope, K. R.; Wrighton, M. S. *Inorg. Chem.* **1985**, *24*, 2792.

(33) Nesmeyanov, A. N.; Kristskaya, I. I.; Vstynuk, Y. A.; Fedin, E. I. *Dokl. Akad. Nauk SSSR* **1967**, *176*, 341.

Scheme II. Summary of the Photochemistry of $\text{Fe}(\text{CO})_n(\text{C}_3\text{H}_6)_{5-n}$ ($n = 4, 3$)

^a Identification of this compound is tentative.

pected from complexes containing both CO and alkene. This finding is consistent with the fact that CO and alkene are both π -acceptor ligands. The relative importance of CO vs. alkene loss has not been determined, but since we now know the various product identities, we are in a position to make a systematic investigation for the Fe and Ru complexes as has been done with $\text{W}(\text{CO})_5(\text{alkene})$.³² Our finding that alkene can be dissociated photochemically is consistent with work on $\text{Fe}(\text{CO})_3(\eta^4\text{-1,3-butadiene})$ which forms $\text{Fe}(\text{CO})_2(\eta^4\text{-1,3-butadiene})$ and $\text{Fe}(\text{CO})_3(\eta^2\text{-1,3-butadiene})$ upon photoexcitation in rigid media at low temperature.²³

The photogenerated $\text{M}(\text{CO})_3(\text{alkene})_2$ and $\text{M}(\text{CO})_2(\text{alkene})_3$ complexes provide useful entries to derivatives of $\text{M}(\text{CO})_5$ because the alkenes are so labile. Such reactive complexes may be useful in preparing substitution derivatives that are thermally or photochemically sensitive. In terms of understanding photocatalyzed reactions of alkenes, the characterization of the photoreactions of $\text{M}(\text{CO})_n(\text{alkene})_{5-n}$ is an important step in providing a step-by-step rationale of the catalytic chemistry. Further, the eventual finding of $\text{M}(\text{CO})_3(1,3\text{-pentadiene})$ in $\sim 75\%$ yield ($\sim 25\%$ $\text{M}(\text{CO})_4(\text{pent})$) from thermal reaction of $\text{M}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ with 1-pentene provides a rationale for finite turnover number from a system that appears to be so reversible when considering only the C_2H_4 complexes. Further work is needed to establish the mechanism of the dehydrogenation of 1-pentene, but the consequence is clear: the 1,3 pentadiene effectively suppresses catalytic action by leading to formation of $\text{M}(\text{CO})_3(1,3\text{-pentadiene})$.

One final point should be made concerning intermediates formed from $\text{M}(\text{CO})_n(\text{alkene})_{5-n}$ ($n = 4, 3, 2$). We find no evidence for high concentrations of radical species, consistent with the levels of such species previously suggested.⁶ However, it is well-appreciated that very active species, though present in small concentration, can be catalytically significant. While it is known that $\text{Fe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ radicals are very active catalysts for alkene isomerization,³⁴ it appears that $\text{M}(\text{CO})_3(\text{alkene})_2$ and $\text{M}(\text{CO})_2(\text{alkene})_3$ can account for the photocatalytic activity of $\text{Fe}(\text{CO})_5$ or $\text{M}_3(\text{CO})_{12}$.

Acknowledgment. We thank the National Science Foundation and the Office of Naval Research for partial support of this work. We thank Dr. J. A. Crayston for use of the computer program used in the normal-coordinate analyses of ^{13}C -enriched iron carbonyl olefin complexes by *F* and *G* matrix techniques.

Supplementary Material Available: Three figures showing ^1H NMR spectral changes for $\text{M}(\text{CO})_4(\text{C}_2\text{H}_4)$ ($\text{M} = \text{Ru}, \text{Fe}$) photolysis in the presence of C_2H_4 forming $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$, $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$, and $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ (3 pages). Ordering information is given on any current masthead page.

(34) Putnik, C. F.; Welter, J. J.; Stucky, G. D.; D'Aniello, M. J. D., Jr.; Sosinsky, B. A.; Kirner, J. F.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 4107.