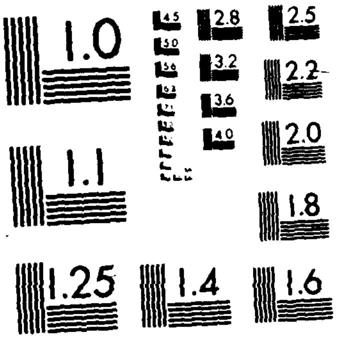
AD-A171 941 PHOTOCHEMICAL FORMATION OF MONONUCLEAR BIS AND TRIS 1/1
ETHYLENE COMPLEXES FR..(U) MASSACHUSETTS INST OF TECH
CAMBRIDGE DEPT OF CHEMISTRY Y WUU ET AL. 09 SEP 86
UNCLASSIFIED TR-12 N00014-85-K-0553 F/G 7/5 NL


1.0
4.5
5.0
5.6
2.8
3.2
3.6
4.0
2.5
2.2
2.0
1.1
1.8
1.25
1.4
1.6

12

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER ONR TR 12	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Photochemical Formation of Mononuclear Bis and Tris Ethylene Complexes From Irradiation of Iron Pentacarbonyl or Triruthenium Dodecarcarbonyl....		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Y.M.-Wuu, J.G. Bentsen, C.G. Brinkley and M.S. Wrighton		8. CONTRACT OR GRANT NUMBER(s) N00014-85-K-0553
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Massachusetts Institute of Technology Cambridge, MA 02139		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-051-579
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy, Arlington, VA 22217		12. REPORT DATE September 9, 1986 13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; reproduction is permitted for any purpose of the United STates Government; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Distribution of this document is unlimited

SEP 16 1986

A

18. SUPPLEMENTARY NOTES

Prepared for publication in Inorganic Chemistry

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

photocatalysis, iron carbonyl, cluster photochemistry, alkene complexes

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Attached

86 9 15 203

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

OFFICE OF NAVAL RESEARCH
Contract N00014-85-K-0553
Task No. NR-051-579
TECHNICAL REPORT NO. 12

Photochemical Formation of Mononuclear Bis and Tris Ethylene Complexes From Irradiation of Iron Pentacarbonyl or Triruthenium Dodecarcarbonyl: Species Involved in Catalytic Alkene Isomerization

by

Yee-Min Wuu, James G. Bentsen, Cynthia G. Brinkley and Mark S. Wrighton

Prepared for Publication

in

Inorganic Chemistry

Department of Chemistry
Massachusetts Instittue of Technology
Cambridge, MA 02139

Abstract

In alkane or $CF_3C_6F_{11}$ solutions which contain excess C_2H_4, near-UV irradiation of $Ru(CO)_4(C_2H_4)$, formed quantitatively in situ from visible light (λ >420nm) irradiation of $Ru_3(CO)_{12}$, yields $Ru(CO)_3(C_2H_4)_2$ at 298K. At temperatures below 253K further substitution can be effected photochemically to give trans-$Ru(CO)_2(C_2H_4)_3$. Near-UV irradiation of $Ru(CO)_4(C_2H_4)$ in rigid, C_2H_4-saturated, 3-methylpentane glasses at 90K yields $Ru(CO)_3(C_2H_4)_2$, but further CO loss to give cis-$Ru(CO)_2(C_2H_4)_3$ is observed after only $\sim 5\%$ comsumption of $Ru(CO)_4(C_2H_4)$. Isomerization of photogenerated cis-$Ru(CO)_2(C_2H_4)_3$ to trans-$Ru(CO)_2(C_2H_4)_3$ is only observed on warming the glass above 210K. Prolonged irradiation of photogenerated cis-$Ru(CO)_2(C_2H_4)_3$ at 90K yields loss of additional CO to give a monocarbonyl complex, formulated as $Ru(CO)(C_2H_4)_4$, which reacts on warming with photoreleased CO to initially regenerate cis-$Ru(CO)_2(C_2H_4)_3$. The photochemistry of $Fe(CO)_4(C_2H_4)$ is the same as that of the $Ru(CO)_4(C_2H_4)$ except that trans-$Fe(CO)_2(C_2H_4)_3$ could only be detected by IR spectroscopy at temperatures below 210K. The new results show that species previously formulated as $Fe_2(CO)_6(alkene)_2$ are in fact $Fe(CO)_3(alkene)_2$. In solution, the $M(CO)_3(C_2H_4)_2$ (M = Fe, Ru) and $Ru(CO)_2(C_2H_4)_3$ are substitutionally labile and may serve as versatile reagents in preparative chemistry. Addition of deoxygenated 1-pentene to solutions of the bis and tris C_2H_4 complexes results in rapid catalytic isomerization at 293K to a mixture of 2-pentenes, thus establishing the viability of both $M(CO)_3$ and $M(CO)_2$ species as repeating units in the catalytic alkene isomerization. Deactivation of $M(CO)_3(alkene)_2$ 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 298K) $M(CO)_3(\eta^4\text{-}1,3\text{-pentadiene})$ complexes.

Photochemical Formation of Mononuclear Bis and Tris Ethylene Complexes From Irradiation of Iron Pentacarbonyl or Triruthenium Dodecarcarbonyl: Species Involved in Catalytic Alkene Isomerization

Yee-Min Wuu, James G. Bentsen, Cynthia G. Brinkley and Mark S. Wrighton*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

---

*Address correspondence to this author

Abstract

In alkane or $CF_3C_6F_{11}$ solutions which contain excess C_2H_4, near-UV irradiation of $Ru(CO)_4(C_2H_4)$, formed quantitatively in situ from visible light (λ >420nm) irradiation of $Ru_3(CO)_{12}$, yields $Ru(CO)_3(C_2H_4)_2$ at 298K. At temperatures below 253K further substitution can be effected photochemically to give trans-$Ru(CO)_2(C_2H_4)_3$. Near-UV irradiation of $Ru(CO)_4(C_2H_4)$ in rigid, C_2H_4-saturated, 3-methylpentane glasses at 90K yields $Ru(CO)_3(C_2H_4)_2$, but further CO loss to give cis-$Ru(CO)_2(C_2H_4)_3$ is observed after only ~5% comsumption of $Ru(CO)_4(C_2H_4)$. Isomerization of photogenerated cis-$Ru(CO)_2(C_2H_4)_3$ to trans-$Ru(CO)_2(C_2H_4)_3$ is only observed on warming the glass above 210K. Prolonged irradiation of photogenerated cis-$Ru(CO)_2(C_2H_4)_3$ at 90K yields loss of additional CO to give a monocarbonyl complex, formulated as $Ru(CO)(C_2H_4)_4$, which reacts on warming with photoreleased CO to initially regenerate cis-$Ru(CO)_2(C_2H_4)_3$. The photochemistry of $Fe(CO)_4(C_2H_4)$ is the same as that of the $Ru(CO)_4(C_2H_4)$ except that trans-$Fe(CO)_2(C_2H_4)_3$ could only be detected by IR spectroscopy at temperatures below 210K. The new results show that species previously formulated as $Fe_2(CO)_6(alkene)_2$ are in fact $Fe(CO)_3(alkene)_2$. In solution, the $M(CO)_3(C_2H_4)_2$ (M = Fe, Ru) and $Ru(CO)_2(C_2H_4)_3$ are substitutionally labile and may serve as versatile reagents in preparative chemistry. Addition of deoxygenated 1-pentene to solutions of the bis and tris C_2H_4 complexes results in rapid catalytic isomerization at 293K to a mixture of 2-pentenes, thus establishing the viability of both $M(CO)_3$ and $M(CO)_2$ species as repeating units in the catalytic alkene isomerization. Deactivation of $M(CO)_3(alkene)_2$ 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 298K) $M(CO)_3(\eta^4$-1,3-pentadiene) complexes.

Research in this group and elsewhere has established that an extraordinarily active alkene isomerization catalyst results from photolysis of $Fe(CO)_5$ in the presence of alkenes.[1-3] A carbonyl-bridged diiron complex[4] and, alternatively, a mononuclear tricarbonyl iron unit[1b,3] have been proposed to carry the catalytic cycle. A report from this group[5] establishes that iron carbonyl intermediates in the photocatalytic systems could be observed spectroscopically at sub-ambient temperatures, including $HFe(CO)_3(\eta^3\text{-}C_3H_5)$ from photolysis of $Fe(CO)_4(C_3H_6)$ in a rigid alkane glass at 77K. In neat 1-pentene, warmup of photogenerated $HFe(CO)_3(\eta^3\text{-}C_5H_9)$ (from $Fe(CO)_5$/1-pentene at 77K) results in significant catalytic isomerization of 1-pentene above 243K in the dark. Eventual regeneration of $Fe(CO)_4$(alkene) is accompanied by decline of catalytic activity. $Fe(CO)_3(\eta^3\text{-allyl})$ radical species, also detected at 143K in 1-3% yield as photoproducts of $Fe(CO)_5$ 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 $Fe(CO)_5$/alkene solutions. Species previously formulated as $Fe_2(CO)_6(\text{alkene})_2$[5] are in fact mononuclear $Fe(CO)_3(\text{alkene})_2$ complexes, consistent with a report by Fleckner, Grevels, and Hess.[7] Other important mononuclear Fe species are reported herein including bis and monocarbonyl complexes. We have also extended the low temperature photochemistry to $Ru(CO)_4$(alkene) systems and find that mononuclear bis and tris C_2H_4 complexes can be generated photochemically via sequential photochemical reactions represented by equations (1)-(3) for the case of

$$Ru_3(CO)_{12} + 3C_2H_4 \xrightarrow[\text{alkane, 298K}]{h\nu\ (\lambda\ >420\text{nm})} 3Ru(CO)_4(C_2H_4) \qquad (1)$$

$$Ru(CO)_4(C_2H_4) + C_2H_4 \xrightarrow[\text{alkane, 298K}]{h\nu,\ (\lambda < 400\text{nm})} Ru(CO)_3(C_2H_4)_2 + CO \qquad (2)$$

$$Ru(CO)_3(C_2H_4)_2 + C_2H_4 \xrightarrow[\text{alkane, 243K}]{h\nu,\ (\lambda < 400\text{nm})} \underline{\text{trans}}\text{-}Ru(CO)_2(C_2H_4)_3 + CO \qquad (3)$$

alkene = C_2H_4. Photochemistry according to equation (1) is known[8-10] and provides an excellent route to $Ru(CO)_4$(alkene) complexes. $Ru_3(CO)_{12}$ 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 $Ru(CO)_3(C_2H_4)_2$ and $Ru(CO)_2(C_2H_4)_3$ can both isomerize 1-pentene in the dark, in accord with the activity found upon photoactivation of $Ru_3(CO)_{12}$. $Ru(CO)_4(C_2H_4)$ shows very little activity. The results for both the $Fe(CO)_5$/alkene and $Ru_3(CO)_{12}$/alkene systems 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 $M(CO)_3(\eta^4\text{-}1,3\text{-diene})$ complexes.

Experimental

Materials. The $Fe(CO)_5$ and $Ru_3(CO)_{12}$ were obtained from Strem Chemicals. The $Fe(CO)_5$ was passed through Al_2O_3 prior to use and the $Ru_3(CO)_{12}$ was used as received. The photochemistry at low temperature was carried out using 3-methylpentane (Aldrich) or methylcyclohexane (J.T. Baker) as the glassing materials. Quantitative ^1H-NMR data were obtained using $CF_3C_6F_{11}$ solvent from Fluka AG. The 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. The ^{13}CO (99% ^{13}C) was obtained from Cambridge Isotope Laboratories. The PPh_3 was recrystallized prior to use.

Instrumentation. IR spectra were recorded using 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 using cycloheptane (in the $CF_3C_6F_{11}$ solvent) 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. x 1/8 in. 20% propylene carbonate on chromasorb P column operated at 20°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 using a LiChrosorb Alox T 5 micron column (250mm x 4.6mm 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 done using a 10 ft. x 1/8 in. SE-30 on chromasorb W column.

Procedures. Generally, all manipulations were carried out under N_2 in a Vacuum Atmospheres dry box or under Ar using conventional Schlenk line techniques. Low temperature irradiations involved the use of a Bausch and Lomb SP200 200W high pressure Hg lamp filtered with a 10 cm Pyrex water filter. Low temperature IR spectra were recorded 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 ± 2K at a fixed temperature.

Clean solutions of $Fe(CO)_4(C_2H_4)$ were prepared by near-UV photolysis of 4 x 10^{-3} M $Fe(CO)_5$ at 273K in C_2H_4-saturated alkane solution until no $Fe(CO)_5$ remained by IR. At this point, both $Fe(CO)_4(C_2H_4)$ and $Fe(CO)_3(C_2H_4)_2$ were present. The mixture was then purged with CO and warmed to 298K to yield $Fe(CO)_4(C_2H_4)$ as the only detectable metal carbonyl. Clean solutions of $Fe(CO)_3(C_2H_4)_2$ were obtained by continuing to photolyze the C_2H_4-saturated solution at <273K until no $Fe(CO)_4(C_2H_4)$ remained, as established by IR. The $Ru(CO)_4(C_2H_4)$ was prepared quantitatively via visible light (λ >420 nm) irradiation of ~1 x 10^{-3} M $Ru_3(CO)_{12}$ in a continuously C_2H_4-purged alkane solution using a filtered Hanovia 450W medium pressure Hg lamp. The $Ru(CO)_3(C_2H_4)_2$ solutions were prepared by subsequent near-UV irradiation of a $Ru(CO)_4(C_2H_4)$ solution at 298K in the presence of C_2H_4. Only $Ru(CO)_4(C_2H_4)$ and $Ru(CO)_3(C_2H_4)_2$ were spectroscopically detected in these solutions. After ~90% conversion of $Ru(CO)_4(C_2H_4)$, the photolysis was stopped and the solution was purged with C_2H_4 to remove photogenerated CO. The trans-$Ru(CO)_2(C_2H_4)_3$ solutions were prepared by irradiation at 232K (liquid N_2/CH_3CN bath) of an alkane solution containing $Ru(CO)_3(C_2H_4)_2$ and $Ru(CO)_4(C_2H_4)$ under a slow purge of C_2H_4 necessary to remove photogenerated CO. Only $Ru(CO)_3(C_2H_4)_2$ and trans-$Ru(CO)_2(C_2H_4)_3$ were detectable by IR in these solutions. In order to avoid secondary photodecomposition the irradiations were discontinued after approximately 70% conversion to trans-$Ru(CO)_2(C_2H_4)_3$.

Photolysis of $M(CO)_4(C_2H_4)$ (M = Fe, Ru), in a C_2H_4-saturated $CF_3C_6F_{11}$ solution, was monitored by ^1H-NMR by first generating the $M(CO)_4(C_2H_4)$ 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 $M(CO)_3(C_2H_4)_2$ (Fe, 273K; Ru, 298K) or trans-$Ru(CO)_2(C_2H_4)_3$ (243K). IR spectral changes for the $Fe(CO)_4(C_2H_4$ to $Fe(CO)_3(C_2H_4)_2$ 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 singlet attributed to $Fe(CO)_3(C_2H_4)_2$.

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 195K, a temperature at which the $M(CO)_3(C_2H_4)_2$ (M = Fe, Ru) and $Ru(CO)_2(C_2H_4)_3$ are stable in the absence of C_2H_4. The appropriate amount of pre-cooled 1-pentene, passed through Al_2O_3 and deoxygenated by three freeze-pump-thaw cycles, was added at 195K, a temperature where no catalytic isomerization occurs. Rapid warming to 273K 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.

$Fe(CO)_2(^{13}CO)(C_2H_4)_2$ was prepared in situ by reacting $Fe(CO)_3(C_2H_4)_2$ with 1 atm of ^{13}CO in methylcyclohexane or 3-methylpentane at 298K to form

$Fe(CO)_3(^{13}CO)(C_2H_4)$. Excess ^{13}CO was purged from the solution by C_2H_4 at 298K and the resulting C_2H_4-saturated solution was irradiated at 273K to convert $Fe(CO)_3(^{13}CO)(C_2H_4)$ to $Fe(CO)_{3-n}(^{13}CO)_n(C_2H_4)_2$ (n = 0, 1). The $Fe(CO)_{5-n}(^{13}CO)_n$ was prepared by λ >540 nm irradiation of $Fe_3(CO)_{12}$ in a ^{13}CO-saturated 3-methylpentane solution at 298K.

Results and Discussion

a. Mononuclear Ru Carbonyl-Ethylene Complexes. UV-VIS, IR and ^{1}H-NMR spectral data for relevant complexes are reported in Tables I, II, and III respectively. Irradiation of $Ru_3(CO)_{12}$ in C_2H_4-saturated alkane (3-methylpentane or methylcyclohexane) or $CF_3C_6F_{11}$ solutions yields $Ru(CO)_4(C_2H_4)$, equation (1), as expected. Indeed, for excitation using wavelengths of light longer than ~420 nm, where $Ru(CO)_4(C_2H_4)$ does not absorb significantly, the generation of $Ru(CO)_4(C_2H_4)$ is quantitative. Thus, visible irradiation of $Ru_3(CO)_{12}$ in the presense of C_2H_4 provides an excellent route to $Ru(CO)_4(C_2H_4)$. If C_2H_4 is purged from solution by Ar at 298K, $Ru_3(CO)_{12}$ is regenerated quantitatively.

Near-UV irradiation of $Ru(CO)_4(C_2H_4)$ in the presence of C_2H_4 leads to additional spectral (IR and NMR) changes that are consistent with the photosubstitution represented by equation (2), Figures 1 and 2 and Table IV. In particular, in the ^{1}H-NMR, Figure 1, we observe that the singlet at 2.10 ppm due to $Ru(CO)_4(C_2H_4)$ 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 Ru:C_2H_4. The IR spectral changes that occur at 298K are essentially duplicated when the $Ru(CO)_4(C_2H_4)$ is irradiated in a rigid C_2H_4-saturated 3-methylpentane glass at 90K. The initial (~5% conversion) IR spectral changes for the 90K 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 298K) of $Ru(CO)_3(C_2H_4)_2$. The rigid glass precludes the rapid diffusion of a presumed $Ru(CO)_3(C_2H_4)$ intermediate, thus ruling out polynuclear species, and in particular $Ru_2(CO)_6(C_2H_4)_2$, as photoproducts. However, the low molecular weight of C_2H_4 and its high concentration, ~0.05 M,[15] allows reaction of the photogenerated $Ru(CO)_3(C_2H_4)$ (not observed at 90K) with C_2H_4 to form $Ru(CO)_3(C_2H_4)_2$. The $Ru(CO)_3(C_2H_4)_2$ is very photosensitive and, after ~5% conversion of $Ru(CO)_4(C_2H_4)$ at 90K, there is evidence for secondary product formation (vide infra) by further loss of CO from the $Ru(CO)_3(C_2H_4)_2$. Such is not the case at 298K in fluid solutions, where extensive accumulation of $Ru(CO)_3(C_2H_4)_2$ is achieved. Accumulation of $Ru(CO)_3(C_2H_4)_2$ is probably a result of rapid back reaction of secondary photoproducts, such as $Ru(CO)_2(C_2H_4)_3$ (vide infra), with liberated CO.

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

For $Ru(CO)_3(C_2H_4)_2$, the IR spectrum in the CO stretching region is consistent with a C_{2v} local symmetry of the $Ru(CO)_3$ fragment [ν(CO) = 2081 (w, A_1), 2005 (m, A_1) and 1995 cm^{-1} (s, B_1); 3-methylpentane, 298K] 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 $Ru(CO)_3(\eta^2$-methylacrylate$)_2$,[9] $Fe(CO)_3(\eta^2,\eta^2$-1,5-dimethylene-2,6-dimethylcyclooctane$)$[17] and $Fe(CO)_3(\eta^2$-trans-cyclooctene$)_2$[7] complexes. The singlet in the ^{1}H-NMR for $Ru(CO)_3(C_2H_4)_2$ is consistent with such a coordination geometry or with a dynamic geometry at temperatures as low as 243K.

Near-UV irradiation of $Ru(CO)_3(C_2H_4)_2$ in low temperature fluid $CF_3C_6F_{11}$ (243K) or alkane (233K) solutions saturated with C_2H_4 leads to additional spectral changes (NMR and IR) that are consistent with the photosubstitution represented in equation (3), Figures 3 and 4 and Table V. The ^{1}H-NMR, Figure 3, shows that a singlet at 3.02 ppm grows at the expense of singlets attributed to $Ru(CO)_3(C_2H_4)_2$ and its precursor $Ru(CO)_4(C_2H_4)$. Quantitative analysis of the ^{1}H-NMR spectral changes for several experiments, Table V, shows the Ru:C_2H_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, Figure 4, is consistent with a cylindrical local symmetry of a $Ru(CO)_2$ fragment and, consequently, formulation of the product as trans-$Ru(CO)_2(C_2H_4)_3$ having three equatorially disposed C_2H_4 ligands in a trigonal bipyramidal structure. To our knowledge, this represents the first reported preparation of an $M(CO)_2(alkene)_3$ (M = Fe, Ru, Os) complex.

Surprisingly, trans-$Ru(CO)_2(C_2H_4)_3$, observed as a photoproduct in low temperature fluid solutions, is not observed as a product in the near-UV photolysis of $Ru(CO)_3(C_2H_4)_2$ in a C_2H_4-saturated 3-methylpentane glass at 90K. However, CO loss from $Ru(CO)_3(C_2H_4)_2$ does occur in low temperature organic glasses. We have exploited the properties of methylcyclohexane to establish the photochemical properties of $Ru(CO)_3(C_2H_4)_2$. It must be pointed out that the investigation of $Ru(CO)_3(C_2H_4)_2$ involves solutions which invariably contain excess C_2H_4 in order to preserve purity of the $Ru(CO)_3(C_2H_4)_2$ while manipulating the samples prior to cooling them to the low temperature of the rigid glasses. Unlike 3-methylpentane, a methylcyclohexane glass at 90K 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 ~110K 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 $Ru(CO)_3(C_2H_4)_2$ in a methylcyclohexane glass containing excess C_2H_4 at 90K results in the IR spectral changes shown in Figure 5. A feature attributed to photoejected CO (2132 cm^{-1}) and two bands attributed to the 16-electron $Ru(CO)_2(C_2H_4)_2$ species at 2020 and 1948 cm^{-1} grow while features attributed to $Ru(CO)_3(C_2H_4)_2$ decline. Warming the matrix to 110K results in complete loss of $Ru(CO)_2(C_2H_4)_2$ absorptions, but there is growth of carbonyl absorptions at 2019 and 1975 cm^{-1} which remain upon recooling to 90K. Importantly, the amount of photoejected CO (2132 cm^{-1}) in the glass remains constant during annealing to 110K (see insets; Figure 5a and b), ruling out formation of another isomer of $Ru(CO)_3(C_2H_4)_2$ by reaction of CO with $Ru(CO)_2(C_2H_4)_2$. The IR shows that trans-$Ru(CO)_2(C_2H_4)_3$ ($\nu(CO) = 1953$ cm^{-1}) is not formed in detectable amounts. The spectral features obtained are those observed for the 90K photolysis of $Ru(CO)_3(C_2H_4)_2$ in C_2H_4-saturated 3-methylpentane. These results imply the formation of an 18-electron $Ru(CO)_2(C_2H_4)_3$ species which we formulate as cis-$Ru(CO)_2(C_2H_4)_3$, containing one equatorial and one axial CO ligand in a trigonal bipyramidal structure. In support of this formulation, a OC-Ru-CO bond angle of 81° is calculated for the $Ru(CO)_2$ fragment by evaluation[19] of the ratio of the relative intensities of the symmetric and antisymmetric carbonyl absorbances. Furthermore, warmup of cis-$Ru(CO)_2(C_2H_4)_3$ to 210K leads to net IR spectral changes which are retained on recooling to 90K, consistent with quantitative conversion to the trans-$Ru(CO)_2(C_2H_4)_3$ complex (1953 cm^{-1}) mentioned above. In C_2H_4-saturated 3-methylpentane glasses at 90K, photochemical isomerization of matrix isolated trans-$Ru(CO)_2(C_2H_4)_3$ to the cis-form is accompanied by loss of CO to form a monocarbonyl species (1964 cm^{-1}), presumably a $Ru(CO)(C_2H_4)_4$ complex, related to well-characterized $Fe(CO)(diene)_2$ complexes.[20]

$Ru(CO)(C_2H_4)_4$ can also be obtained directly by photolysis of cis-$Ru(CO)_2(C_2H_4)_3$ at 90K in C_2H_4-saturated 3-methylpentane. Warmup of 90K glasses containing the $Ru(CO)(C_2H_4)_4$ and the photogenerated CO results, initially, in formation of cis-$Ru(CO)_2(C_2H_4)_3$, and, eventually, trans-$Ru(CO)_2(C_2H_4)_3$ at higher temperatures. In methylcyclohexane the photoconversion of cis-$Ru(CO)_2(C_2H_4)_3$ to $Ru(CO)(C_2H_4)_4$ (1964 cm^{-1}) proceeds via transient formation of a second monocarbonyl species (1923 cm^{-1}) tentatively formulated as the coordinatively unsaturated $Ru(CO)(C_2H_4)_3$. At high C_2H_4 concentrations in the dark at 90K, 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 $Ru(CO)_n(C_2H_4)_{5-n}$ ($n = 4, 3$) complexes are stabilized by excess C_2H_4 toward decomposition in fluid solutions at 298K, but are quite stable in Ar-purged alkane solutions at sufficiently low temperatures (195K). The trans-$Ru(CO)_2(C_2H_4)_3$ is more labile than the bis-C_2H_4 complex and back reacts with photoreleased CO at ~253K to regenerate $Ru(CO)_3(C_2H_4)_2$. Purging a C_2H_4-saturated alkane solution of $Ru(CO)_4(C_2H_4)$ with Ar at 298K rapidly generates $Ru_3(CO)_{12}$; purging with CO at 298K yields $Ru(CO)_5$; and reaction with 0.05 M PPh_3 at 298K yields $Ru(CO)_4PPh_3$. The $Ru(CO)_3(C_2H_4)_2$ reacts with CO to yield first $Ru(CO)_4(C_2H_4)$, then $Ru(CO)_5$; reaction with 0.05 M PPh_3 yields $Ru(CO)_3(PPh_3)_2$; and reaction with trans-1,3-pentadiene rapidly yields $Ru(CO)_3$(trans-1,3-pentadiene).

b. Mononuclear Fe Carbonyl-Ethylene Complexes. The formation of $Ru(CO)_3(C_2H_4)_2$ from $Ru(CO)_4(C_2H_4)$, and work published by Fleckner, Grevels, and Hess[7] prompted us to reinvestigate the alkene products derived from the low temperature photolysis of $Fe(CO)_4(C_2H_4)$. Irradiation of $Fe(CO)_4(C_2H_4)$ at 273K in the presence of C_2H_4 results in the formation of $Fe(CO)_3(C_2H_4)_2$, not $Fe_2(CO)_6(C_2H_4)_2$ as previously concluded.[5] The ^1H-NMR and IR spectral changes accompanying photolysis of $Fe(CO)_4(C_2H_4)$ in C_2H_4-saturated $CF_3C_6F_{11}$ solution are shown in Figures 6 and 7, respectively. 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 1.05 $Fe(CO)_4(C_2H_4)$ and 1.00 C_2H_4 to 0.98 $Fe(CO)_3(C_2H_4)_2$. In the earlier work,[5] ^1H-NMR integration data were unreliable, presumably owing to sample decomposition. In the present work IR spectral changes for the same solution show the same extent conversion as determined by ^1H-NMR, thereby establishing correlation of IR absorptions and the ^1H-NMR singlet attributed to $Fe(CO)_3(C_2H_4)_2$. The remarkable spectroscopic similarity to $Ru(CO)_3(C_2H_4)_2$ suggests the same C_{2v} structure for both the Fe and Ru species.

Irradiation of $Fe(CO)_4(C_2H_4)$ in a C_2H_4-saturated 3-methylpentane glass at low temperature results in the ultimate formation of a monocarbonyl Fe complex, possibly $Fe(CO)(C_2H_4)_4$, not trans-$Fe(CO)_3(C_2H_4)_2$ as previously concluded.[5] As with $Ru(CO)_4(C_2H_4)$, loss of CO (2132 cm^{-1}) from $Fe(CO)_4(C_2H_4)$ initially yields $Fe(CO)_3(C_2H_4)_2$ (Figure 7b); here competitive loss of C_2H_4 leads to formation of some $Fe(CO)_4$ (1946 cm^{-1}). [The $Fe(CO)_4$ can be photogenerated independently by irradiation of $Fe(CO)_5$ under the same conditions.] However, just beyond the initial stages of reaction we find that further photoreaction of $Fe(CO)_3(C_2H_4)_2$ occurs to yield new carbonyl features at 1955 and 1998 cm^{-1} which are only detected by spectral subtraction of masking absorptions of unreacted $Fe(CO)_4(C_2H_4)$. The 1955 and 1998 cm^{-1} features are associated with cis-$Fe(CO)_2(C_2H_4)_3$ (vide infra). This secondary photoproduct is also photosensitive and continued irradiation, Figure 7c (320 sec hν), yields only a single carbonyl product band at 1952 cm^{-1}. The total yield of liberated CO (2132 cm^{-1}) per $Fe(CO)_4(C_2H_4)$ molecule consumed is three times that observed in the initial photoconversion (4 sec hν) to $Fe(CO)_3(C_2H_4)_2$. The *cis*-$Fe(CO)_2(C_2H_4)_3$ escaped detection in previous work,[5] presumably as a result of spectral masking by unreacted $Fe(CO)_4(C_2H_4)$ and the 1952 cm^{-1} product band.

As for $Ru(CO)_3(C_2H_4)_2$, photolysis at 100K of a C_2H_4-saturated 3-methylpentane glass containing only $Fe(CO)_3(C_2H_4)_2$ proceeds cleanly at low extent conversion to give well resolved spectral features associated with *cis*-$Fe(CO)_2(C_2H_4)_3$, 1955 and 1998 cm^{-1} with a calculated OC-M-CO angle of 82°, Figure 8. Our new data show that *trans*-$Fe(CO)_2(C_2H_4)_3$ is not observed in C_2H_4-saturated alkane glasses as a product of 100K photolysis of $Fe(CO)_n(C_2H_4)_{5-n}$ (n = 5, 4, 3). However, warmup of photogenerated *cis*-$Fe(CO)_2(C_2H_4)_3$ to 200K, Figure 8b, results in decline of its spectral features, significant regeneration of $Fe(CO)_3(C_2H_4)_2$, and growth of a single band at 1942 cm^{-1} which remains upon recooling to 100K. We attribute this band to *trans*-$Fe(CO)_2(C_2H_4)_3$, in analogy with the ^1H-NMR characterized *trans*-$Ru(CO)_2(C_2H_4)_3$. The *trans*-$Fe(CO)_2(C_2H_4)_3$ back reacts with the free CO upon warming above 210K. The *trans*-$Fe(CO)_2(C_2H_4)_3$ cannot be detected by ^1H-NMR upon photolysis of $Fe(CO)_3(C_2H_4)_2$ in C_2H_4-saturated $CF_3C_6F_{11}$ solutions at temperatures as low as 243K, presumably because back reaction of the *tris*-C_2H_4 complex with CO occurs rapidly. Photolysis of photogenerated *cis*-$Fe(CO)_2(C_2H_4)_3$ at 90K 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 $Fe(CO)_3(C_2H_4)_2$ molecule consumed is two times that observed in the initial conversion to *cis*-$Fe(CO)_2(C_2H_4)_3$. Warmup to 150K of alkane glasses exhibiting only the 1952 cm^{-1} band and liberated CO results in regeneration of only *cis*-$Fe(CO)_2(C_2H_4)_3$ in high yield with respect to the known concentration of starting material, be it $Fe(CO)_4(C_2H_4)$ or $Fe(CO)_3(C_2H_4)_2$. The *cis*-$Fe(CO)_2(C_2H_4)_3$ spectral features are retained upon recooling to 90K, and subsequent near-UV irradiation results in liberation of free CO and regeneration of the 1952 cm^{-1} feature at the expense of *cis*-$Fe(CO)_2(C_2H_4)_3$ features. The new data show that both $Fe(CO)_3(C_2H_4)_2$ and *cis*-$Fe(CO)_2(C_2H_4)_3$ are extremely photosensitive and simply do not accumulate during irradiation of $Fe(CO)_4(C_2H_4)$ in C_2H_4-saturated alkane glasses. The 1952 cm^{-1} feature was previously attributed[5,21] to trans-$Fe(CO)_3(C_2H_4)_2$. 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 $Fe(CO)(C_2H_4)_4$. $Fe(CO)(C_2H_4)_4$ is relatively photoinert and is unchanged after 1 h of irradiation at 100K where ~15 min is required to convert $Fe(CO)_4(C_2H_4)$ to the $Fe(CO)(C_2H_4)_4$.

Isotopic labelling experiments further support the IR spectral assignments for $Fe(CO)_{5-n}(C_2H_4)_n$ complexes. $Fe(CO)_3(^{13}CO)(C_2H_4)$ is prepared by reacting $Fe(CO)_3(C_2H_4)_2$ with ^{13}CO in 3-methylpentane at 298K. Subsequent near-UV irradiation in a C_2H_4-saturated solution at 273K yields $Fe(CO)_{3-n}(^{13}CO)_n(C_2H_4)_2$ (n = 0, 1, vide infra). After cooling the solution of $Fe(CO)_{3-n}(^{13}CO)_n(C_2H_4)_2$ to 90K, extended near-UV irradiation yields species formulated as $Fe(CO)(C_2H_4)_4$ (1952 cm^{-1}) and $Fe(^{13}CO)(C_2H_4)_4$ (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 150K yields cis-$Fe(CO)_2(C_2H_4)_3$ (1998, 1955 cm^{-1}; 3-methylpentane, 90K) and cis-$Fe(CO)(^{13}CO)(C_2H_4)_3$ (1984, 1924 cm^{-1}; 3-methylpentane, 90K) as the only products, which persist on recooling to 90K. The CO stretching (K) and interaction (K_i) force constants have been calculated for the C_{2v} $Fe(CO)_2$ fragment of cis-$Fe(CO)_2(C_2H_4)_3$ by normal coordinate analysis[22] (K = 1578.3, K_i = 34.3 Nm^{-1}) and used to correctly predict (1985.0, 1923.8 cm^{-1}) the observed frequencies for cis-$Fe(CO)(^{13}CO)(C_2H_4)_3$. Warmup of cis-tris-$C_2H_4$ complex to 200K yields trans-$Fe(CO)_2(C_2H_4)_3$ (1945 cm^{-1}) and trans-$Fe(CO)(^{13}CO)(C_2H_4)_3$ (1918 cm^{-1}). The small wavenumber shift between these two features ($\Delta\nu$ = 27 cm^{-1}) rules out formulation as a monocarbonyl species and suggests a strong interaction force constant for the cylindrical $Fe(CO)_2$ fragment of trans-$Fe(CO)_2(C_2H_4)_3$ (K = 1570.4,

K_1 = 39.8 Nm^{-1}). At low temperature, the monocarbonyl photoproduct distribution and the absence of cis- or trans-Fe(^{13}CO)$_2$(C$_2$H$_4$)$_3$ during subsequent warmup (1) rules out rapid disproportionation of Fe(CO)$_2$(^{13}CO)(C$_2$H$_4$)$_2$ or Fe(CO)$_3$(^{13}CO)(C$_2$H$_4$) at < 273K or < 298K, respectively, or thermal substitution of ^{12}CO by excess ^{13}CO on Fe(CO)$_3$(^{13}CO)(C$_2$H$_4$) at < 298K and (2) suggests predominant recombination of the matrix isolated monocarbonyl with CO initially photoejected from the same metal center to form cis-, then trans-Fe(CO)$_{2-n}$(^{13}CO)$_n$(C$_2$H$_4$)$_3$ (n = 0, 1) during warmup from 90K to 200K.

The conspicuous absence of trans-M(CO)$_2$(C$_2$H$_4$)$_3$ species (M = Fe, Ru) as initial photoproducts from M(CO)$_3$(C$_2$H$_4$)$_2$ in alkane glasses has been investigated further. In a methylcyclohexane glass, FTIR spectral features attributed to the 16-electron Fe(CO)$_2$(C$_2$H$_4$)$_2$, (2003 1938 cm^{-1}; methylcyclohexane, 100K) and free CO are generated upon photolysis of matrix isolated Fe(CO)$_3$(C$_2$H$_4$)$_2$, Figure 9, in analogy with data for the Ru analog. 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 Fe(CO)$_3$(C$_2$H$_4$), Table II, which has been characterized previously in alkane[5] and Ar[23] matrices as the product obtained upon light-induced loss of CO from Fe(CO)$_4$(C$_2$H$_4$). Competitive loss of CO and olefin has previously been observed for Fe(CO)$_3$(η^4-1,3-diene) species.[23] We cannot rule out a similar competition for Ru(CO)$_3$(C$_2$H$_4$)$_2$, since we are unable to remove excess C$_2$H$_4$ which might scavange Ru(CO)$_3$(C$_2$H$_4$), if it formed. Fe(CO)$_3$(C$_2$H$_4$) exhibits a weak electronic absorption at 447 nm, consistent with a coordinatively unsaturated product, Table I. In the presence of excess C$_2$H$_4$, warmup of a 90K glass containing Fe(CO)$_2$(C$_2$H$_4$)$_2$ and Fe(CO)$_3$(C$_2$H$_4$) to 110K yields net FTIR spectral changes which persist on recooling to 90K. These spectral changes are consistent with conversion of Fe(CO)$_2$(C$_2$H$_4$)$_2$ to cis-Fe(CO)$_2$(C$_2$H$_4$)$_3$ (as observed for Ru), and also regeneration of the C_{2v} symmetry isomer of Fe(CO)$_3$(C$_2$H$_4$)$_2$ as a result of thermal back reaction of $Fe(CO)_3(C_2H_4)$ with C_2H_4. These results are consistent with the net conversion of $M(CO)_3(C_2H_4)_2$ to cis-$M(CO)_2(C_2H_4)_3$ via the 16-electron $M(CO)_2(C_2H_4)_2$ intermediate and the net conversion of $M(CO)_4(C_2H_4)$ to the C_{2v} isomer of $M(CO)_3(C_2H_4)_2$ via the 16-electron $M(CO)_3(C_2H_4)$ intermediate in C_2H_4-saturated 3-methylpentane. The metal carbonyl features for the 16-electron $Fe(CO)_3(C_2H_4)$ show similarities in relative energy and intensity to those of the C_{2v} $Fe(CO)_3(C_2H_4)_2$, Table II, thereby suggesting little rearrangement of the $Fe(CO)_3$ unit of $Fe(CO)_3(C_2H_4)$ on reaction with C_2H_4. Also, OC-M-CO[19] bond angles of 97° (M = Ru) and 94° (M = Fe) are calculated for 16-electron $M(CO)_2(C_2H_4)_2$ complexes. A cis- geometry for the $M(CO)_2$ fragment of the coordinatively unsaturated $M(CO)_2(C_2H_4)_2$ intermediate is apparently retained upon reaction with C_2H_4, explaining the conspicuous absence of the thermodynamically favored trans-$M(CO)_2(C_2H_4)_3$ complexes in the low temperature photolysis of matrix isolated $M(CO)_3(C_2H_4)_2$ (M = Ru, Fe) to yield cis-$M(CO)_2(C_2H_4)_3$.

Like $Ru(CO)_3(C_2H_4)_2$, $Fe(CO)_3(C_2H_4)_2$ is very labile at 298K. However, $Fe(CO)_4(C_2H_4)$ is less labile than $Ru(CO)_4(C_2H_4)$. For example, purging an alkane solution of $Fe(CO)_3(C_2H_4)_2$ with CO yields a pure solution of $Fe(CO)_4(C_2H_4)$, a substance that is difficult to obtain in a pure state by conventional procedures. As noted above, CO reacts rapidly with $Ru(CO)_4(C_2H_4)$ to yield $Ru(CO)_5$ under conditions where $Fe(CO)_4(C_2H_4)$ is inert. Further, the reaction of $Fe(CO)_3(C_2H_4)_2$ with 0.05 M PPh_3 at room temperature yields $Fe(CO)_3(C_2H_4)(PPh_3)$, with only minor amounts of $Fe(CO)_3(PPh_3)_2$, whereas $Ru(CO)_3(C_2H_4)_2$ gives exclusively $Ru(CO)_3(PPh_3)_2$. Reaction of $Fe(CO)_3(C_2H_4)_2$ with trans-1,3- or 1,4-pentadiene yields $Fe(CO)_3$(trans-1,3-pentadiene) in analogy to the Ru species. The simple generation of pure alkane solutions of $Fe(CO)_3(C_2H_4)_2$ allows this complex to serve as an excellent, versatile $Fe(CO)_3$ transfer reagent promising a wide range of applications including its use in mechanistic studies of the $Fe(CO)_5$ photocatalyzed reactions of alkenes.

c. Catalytic Isomerization of 1-Pentene. $Ru(CO)_3(C_2H_4)_2$ readily undergoes alkene exchange as detected by IR spectroscopy. Addition of precooled 1-pentene to an Ar-purged methylcyclohexane (no excess C_2H_4 present) solution containing ~1 mM $Ru(CO)_3(C_2H_4)_2$ at 195K, followed by warming to 260K, results in the decline of spectral features for $Ru(CO)_3(C_2H_4)_2$ and growth of new features attributed to $Ru(CO)_3(pentene)_2$, Table II. This assignment is based on the spectral similarity to the bis-C_2H_4 complex and the shift to lower frequencies consistent with the substitution of C_2H_4 by 1-pentene [cf. the IR data of the corresponding $Fe(CO)_4(\eta^2\text{-alkene})$ complexes]. Continued warming leaves the IR spectral features initially unchanged at 293K. However, gas chromatographic analysis of the solution shows that 1-pentene undergoes catalytic isomerization above 260K, yielding cis- and trans-2-pentene. Turnover numbers exceeding 250 have been obtained in the dark. The trans-$Ru(CO)_2(C_2H_4)_3$ is more labile than $Ru(CO)_3(C_2H_4)_2$ and undergoes substitution by added 1-pentene at 240K to form trans-$Ru(CO)_2(pentene)_3$, Table II. Interestingly, catalytic activity is displayed by trans-$Ru(CO)_2(alkene)_3$ above 240K with turnover numbers near 50. Some representative data for catalytic 1-pentene isomerization are given in Table VI. Turnover rates, Table VI, decrease systematically with reaction time at 293K in correlation with declining $Ru(CO)_3(pentene)_2$ or $Ru(CO)_2(pentene)_3$ spectral features. The range of catalyst concentrations used is limited to <6 mM by solubility of the $Ru_3(CO)_{12}$ 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 $Ru(CO)_3(alkene)_2$ and trans-$Ru(CO)_2(alkene)_3$ complexes, in accord with the more detailed report[7] for $Fe(CO)_3(pentene)_2$. Importantly, the initial (1 minute) average turnover rate achieved with trans-$Ru(CO)_2(pentene)_3$ (>9 min^{-1}) at 293K represents a lower limit due to rapid catalyst deactivation, and it clearly exceeds the rate achieved with

$Ru(CO)_3(pentene)_2$ (~4 min^{-1}) under the same conditions ([catalyst] = 2.78 *mM*, [pentene] = 1.83 *M* , 293K, methylcyclohexane). Under photocatalytic conditions, efficient photochemical conversion of $Ru(CO)_3(pentene)_2$ to *trans*-$Ru(CO)_2(pentene)_3$ is offset by facile thermal back reaction unless liberated CO is diliberately removed. The importance of $M(CO)_2(pentene)_3$ species (M = Fe, Ru) under photocatalysis conditions is therefore ambiguous. Our results suggest that substitutionally labile $Ru(CO)_3(alkene)_2$ and $Ru(CO)_2(alkene)_3$ complexes play key roles in the $Ru_3(CO)_{12}$ photocatalyzed alkene isomerization, since we have demonstrated that their photogeneration from $Ru_3(CO)_{12}$ provides an entrance to the catalytic cycle, Table VI.[11] With $Fe(CO)_3(C_2H_4)_2$ we have been able to achieve turnover numbers in the dark approaching 2000, and turnover rates of ~600 min^{-1} at 293K. These results are in qualitative agreement with the report by Grevels and coworkers[7] in which $Fe(CO)_3(\eta^2$-*cis*-cyclooctene$)_2$ was used as a catalyst precursor. Although solutions of $Fe(CO)_3(alkene)_2$ containing 1-pentene approach the equilibrium of the three pentene isomers rapidly and in constant thermodynamic ratio[24] (*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 using $Ru_3(CO)_{12}$ or thermally using $Ru(CO)_n(C_2H_4)_{5-n}$ (n = 3, 2).

The turnover rate of catalysis for both Ru and Fe catalysts decreases with reaction time at 293K. This decrease in rate is accompanied by loss of IR spectral features attributed to $M(CO)_3(pentene)_2$ and the corresponding growth of spectral features attributed to $M(CO)_3$(1,3-pentadiene) (~75%) and $M(CO)_4$(pentene) (~25%) Table II, identified by comparison of IR spectra with those of authentic samples. These complexes, especially $M(CO)_3$(1,3-pentadiene), once formed are relatively inert and show no catalytic activity. Formation of $M(CO)_4$(pentene) is reasonable, considering that catalyst decomposition would release CO which can react with $M(CO)_3(pentene)_2$ to give $M(CO)_4$(pentene). 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 work[25] rules out the intermediacy of 1,3,4,5-η-pent-4-ene-3,1-yliron tricarbonyl as an intermediate leading to $Fe(CO)_3$(1,3-pentadiene). Evidence for the formation of $Ru(CO)_3$(1,3-pentadiene) 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^+-CO, M^+-2CO, M^+-3CO. This pattern is indistinguishable from that obtained from an authentic sample of $Ru(CO)_3$(1,3-pentadiene). 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 $HM(CO)_3(\eta^3$-allyl). We expect the catalytic cycle for Ru to be similar to that for $Fe(CO)_5$-photocatalyzed alkene isomerization. Beyond the involvement of the $M(CO)_3(alkene)_2$ we prefer not to speculate extensively here about the particular steps of the catalytic cycle, except to note the previous observation[5] of $HFe(CO)_3(\eta^3$-allyl), potentially the essential intermediate in the catalytic cycle. We find that the major product of irradiation of $Fe(CO)_4(C_3H_6)$ in a 90K 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 $Fe(CO)_3(C_2H_4)$; $Fe(CO)_4$ is also a minor product which accounts completely for the remaining 1946 cm^{-1} product feature previously attributed to one of three characteristic carbonyl features for $HFe(CO)_3(\eta^3-C_3H_5)$. Warmup of the irradiated 90K glass to 173K yields conversion to a three band pattern attributable to $HFe(CO)_3(\eta^3-C_3H_5)$[5] (2066, 2003 and 1994 cm^{-1}) on the basis of spectral similarity to $BrFe(CO)_3(\eta^3-C_3H_5)$[26] and the structurally related 1,3,4,5,-η-pent-4-ene-3,1-yliron tricarbonyl,[25] Table II.

Chemical evidence for the $HFe(CO)_3(\eta^3-C_3H_5)$ has been obtained by producing $HFe(CO)_3(\eta^3-C_3H_5)$ in a methylcyclohexane/1-bromo-2-methylpropane matrix (~50/50 by volume) at 90K. Warming above ~200K yields IR spectral changes consistent with regeneration of $Fe(CO)_4(C_3H_6)$ (~80%) and formation of the known $BrFe(CO)_3(\eta^3-C_3H_5)$ (~20%).[26] Similarly, irradiation of $Fe(CO)_4(C_3H_6)$ in a 90K methylcyclohexane glass followed by addition of CCl_4 and warmup to 298K yields $CHCl_3$ and the known[26] $ClFe(CO)_3(\eta^3-C_3H_5)$. Metal hydrides are known to react with alkyl halides[27] providing evidence for the existence of $HFe(CO)_3(\eta^3$-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. $Fe(CO)_3(\eta^3-C_3H_5)$, are known to be produced upon irradiation of $Fe(CO)_5$ in the presence of C_3H_6.[6] We have irradiated $Fe(CO)_4(C_3H_6)$ through Pyrex (λ >280 nm) and find no IR evidence for the known[29] $Fe(CO)_3(\eta^3-C_3H_5)$ species. Thus, we conclude the $HFe(CO)_3(\eta^3-C_3H_5)$ to be the dominant, essential species in the catalyzed isomerization of alkenes upon irradiation of $Fe(CO)_5$ through Pyrex.

The three IR band pattern (2066, 2003, 1994 cm^{-1}) attributed to $HFe(CO)_3(\eta^3-C_3H_5)$ at 173K is retained on cooling to 90K, but photochemical reaction occurs at 90K to give the initial two band pattern, (2064, 1994 cm^{-1}), without additional CO loss, consistent with the existence of two isomers of $HFe(CO)_3(\eta^3-C_3H_5)$. Two isomers of $XFe(CO)_3(\eta^3-C_3H_5)$ (X = Cl, Br, I) are known[30] and we believe these to be related to the two isomers of $HFe(CO)_3(\eta^3-C_3H_5)$. Preliminary results show that the thermodynamically stable isomer of $XM(CO)_3(\eta^3-C_3H_5)$ (X = Cl, Br; M = Fe, Ru) can photochemically converted to the less stable isomer.[31]

Irradiation of the two band isomer of $HFe(CO)_3(\eta^3-C_3H_5)$ at 90K 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 $Fe(CO)(alkene)_4$ species analogous to $Fe(CO)(C_2H_4)_4$. The product responsible for the 1929 cm^{-1} feature was previously misidentified as trans-$Fe(CO)_3(C_3H_6)_2$. Our data clearly indicate that there are between two and three photoejected CO's (2132 cm^{-1}) for each $Fe(CO)_4(C_3H_6)$ molecule consumed.[32] Near-UV irradiation of $Fe(CO)_3(C_3H_6)_2$ (formed *in situ* via photolysis of $Fe(CO)_4(C_3H_6)$ plus C_3H_6 at 210K) at 100K in the presence of a large excess of C_3H_6, Figure 10, yields free CO (2132 cm^{-1}), the two band isomer of $HFe(CO)_3(\eta^3\text{-}C_3H_5)$, and a strong feature at 1929 cm^{-1}. The amount of photogenerated CO[32] is consistent with loss of two CO's per molecule of $Fe(CO)_3(C_3H_6)_2$ converted to the 1929 cm^{-1} product based on quantitation of consumed $Fe(CO)_3(C_3H_6)_2$ [ν, cm^{-1}(ε, *M*$^{-1}cm^{-1}$) = 2052 (1,200 ± 100); 3-methylpentane, 90K] and photogenerated $HFe(CO)_3(\eta^3\text{-}C_3H_5)$ [ν, cm^{-1}(ε, *M*$^{-1}cm^{-1}$)= 2065 (7,200 ± 700); 3-methylpentane, 90K] by FTIR. The *cis*-$Fe(CO)_2(C_3H_6)_3$ complex is never observed as a photoproduct from irradiation of $Fe(CO)_4(C_3H_6)$ or $Fe(CO)_3(C_3H_6)_2$ in the presense 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 comsumption of C_3H_6 by the (unobserved) product of CO loss from $Fe(CO)_3(C_3H_6)_2$ leads to formation of the 1929 cm^{-1} product. When samples containing the 1929 cm^{-1} absorber are warmed to ~150K, the 1929 cm^{-1} feature disappears and $Fe(CO)_3(C_3H_6)_2$ is formed with associated consumption of free CO. Interestingly, spectral changes similar to those accompanying irradiation of $Fe(CO)_4(C_3H_6)$ characterize the low temperature photochemistry of $Fe(CO)_4$(1-pentene) in a neat 1-pentene glass, while *cis*-$Fe(CO)_2$(3,3-dimethyl-1-pentene)$_3$ is the final product of near-UV irradiation of $Fe(CO)_4$(3,3-dimethyl-1-pentene) in a 3-methylpentane glass containing 2 *M* 3,3-dimethyl-1-pentene at 90K. These results suggest that the low energy feature at ~1929 cm^{-1} obtains only for alkenes containing allylic hydrogens, for which *cis*-$Fe(CO)_2$(alkene)$_3$ complexes are not accumulated as photoproducts. The 90K irradiation of $Fe(CO)_{5-n}(^{13}CO)_n$ (~20% ^{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 monocarbonyl or a *trans*-dicarbonyl species exhibiting an interaction force constant $K_i = 0$. The two dicarbonyl complexes *cis*-

and trans-$Fe(CO)_2(C_2H_4)_3$ exhibit significant interaction force constants and it is therefore unlikely that an $Fe(CO)_2(C_3H_6)_n$ complex would have $K_i = 0$. On the basis of the evidence available, we tentatively formulate the 1929 cm^{-1} absorber as $HFe(CO)(C_3H_6)_2(\eta^3-C_3H_5)$. We do not find evidence for formation of $(\eta^3-C_3H_5)_2Fe(CO)_2$.[33]

Complete conversion of $Ru_3(CO)_{12}$ to $Ru(CO)_4$(1-pentene) can only be done in the presence of a large excess of 1-pentene (>1 M). Photolysis of $Ru(CO)_4$(1-pentene) in either methylcyclohexane or 3-methylpentane glasses containing 1.0 M 1-pentene at 90K results in photoejection of CO (2132 cm^{-1}) and formation of mostly $Ru(CO)_3$(1-pentene)$_2$. The generation of $Ru(CO)_3$(1-pentene)$_2$ is probably due to reaction of 1-pentene present in the glass with the 16-electron $Ru(CO)_3$(1-pentene) fragment (not observed). When a 3-methylpentane matrix containing $Ru(CO)_4$(1-pentene) is photolyzed at 55K, IR spectral changes for the photolysis reveal the generation of free CO (2132 cm^{-1}) and growth of new spectral features which are different from those observed with alkene = C_2H_4. These new features are attributed to $HRu(CO)_3(\eta^3-C_5H_9)$ on the basis of spectral similarity to the IR bands of $HFe(CO)_3(\eta^3-C_5H_9)$. The ability to detect the $HRu(CO)_3(\eta^3-C_5H_9)$ at the lower temperature 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 reaction of $HRu(CO)_3(\eta^3-C_5H_9)$ with alkyl halides has not yet been successful.

Conversion of $Ru_3(CO)_{12}$ to $Ru(CO)_4(C_3H_6)$ 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 $Ru_3(CO)_{12}$. However, $HRu(CO)_3(\eta^3-C_3H_5)$ can still be generated as a minor product (<10%) at 90K by photolysis of $Ru(CO)_4(C_3H_6)$ in the presence of $Ru_3(CO)_{12}$ in a C_3H_6-containing methylcyclohexane glass. The other products are $Ru_3(CO)_{11}(C_3H_6)$ and $Ru(CO)_3(C_3H_6)_2$.

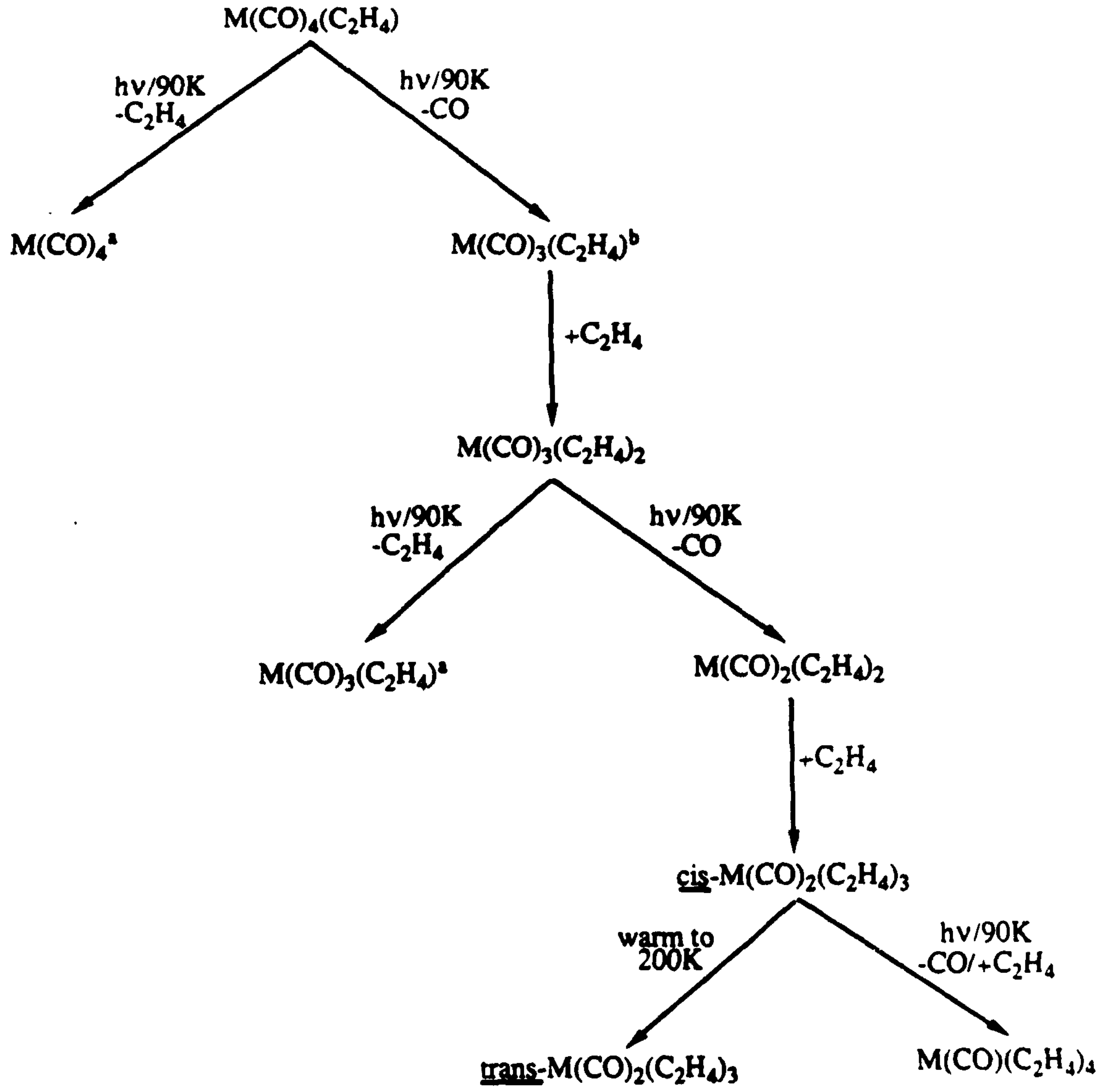
Conclusions

Scheme I summarizes the photochemistry of $M(CO)_n(C_2H_4)_{5-n}$ (M = Fe, Ru; n = 4,3,2) Interestingly, warmup of glasses containing $M(CO)(C_2H_4)_4$ leads to nearly quantitative regeneration at 298 K of $M(CO)_4(C_2H_4)$ (M = Ru) or a mixture of $M(CO)_4(C_2H_4)$ and $M(CO)_3(C_2H_4)_2$ (M = Fe). Thus, the photochemical substitution of CO by C_2H_4 is reversible. The $M(CO)_2(C_2H_4)_3$ and $M(CO)_3(C_2H_4)_2$ complexes serve as catalyst presursors 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 $Fe(CO)_n(C_3H_6)_{5-n}$ 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 $M(CO)_3(alkene)_2$ complexes support the conclusion that, in general, the loss of CO or alkene can be expected 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 $W(CO)_5(alkene)$.[32] Our finding that alkene can be dissociated photochemically is consistent with work on $Fe(CO)_3(\eta^4$-1,3-butadiene) which forms $Fe(CO)_2(\eta^4$-1,3-butadiene) and $Fe(CO)_3(\eta^2$-1,3-butadiene) upon photoexcitation in rigid media at low temperature.[23]

The photogenerated $M(CO)_3(alkene)_2$ and $M(CO)_2(alkene)_3$ complexes provide useful entries to derivatives of $M(CO)_5$ because the alkenes are so labile. Such reactive complexes may be useful in preparing substitution derivatives which are thermally or photochemically sensitive. In terms of understanding photocatalyzed reactions of alkenes, the characterization of the photoreactions of $M(CO)_n(alkene)_{5-n}$ is an important step in providing a step-by-step rationale of the

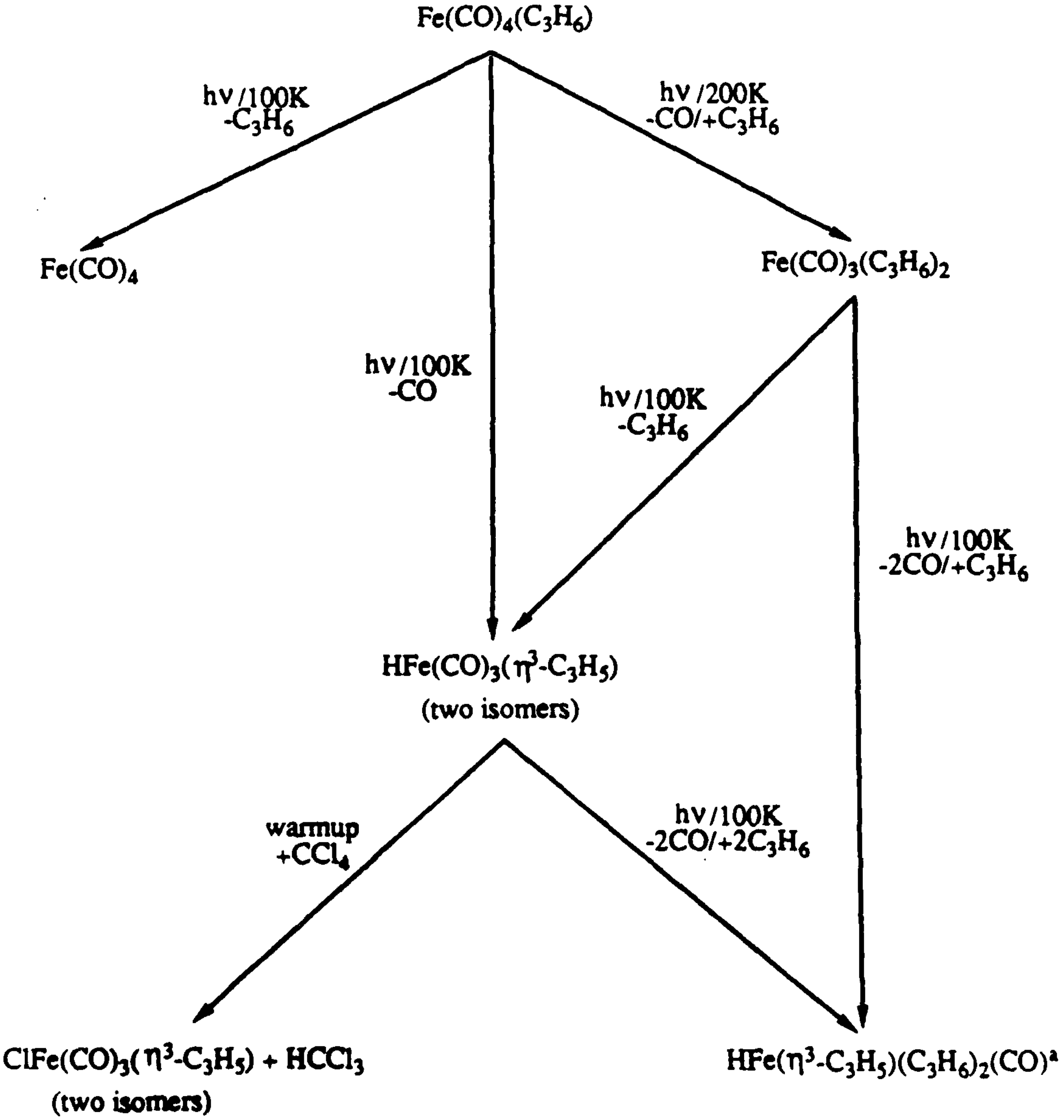
Scheme I. Summary of the photochemistry of $M(CO)_n(C_2H_4)_{5-n}$ ($M = Fe, Ru$; $n = 4, 3, 2$).



[a] Not detected for $M = Ru$

[b] Detection requires $T < 90K$ for $M = Ru$

Scheme II. Summary of the photochemistry of $Fe(CO)_n(C_3H_6)_{5-n}$ (n = 4, 3).



[a] Identification of this compound is tentative.

catalytic chemistry. Further, the eventual finding of $M(CO)_3$(1,3-pentadiene) in ~75% yield (~25% $M(CO)_4$(pentene)) from thermal reaction of $M(CO)_3(C_2H_4)_2$ 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 $M(CO)_3$(1,3-pentadiene).

One final point should be made concerning intermediates formed from $M(CO)_n(alkene)_{5-n}$ (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 $Fe(CO)_3(\eta^3\text{-}C_3H_5)$ radicals are very active catalysts for alkene isomerization,[34] it appears that the $M(CO)_3(alkene)_2$ and $M(CO)_2(alkene)_3$ can account for the photocatalytic activity of $Fe(CO)_5$ or $M_3(CO)_{12}$.

Acknowledgements. 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.

References

1. (a) Mitchener, J.C.; Wrighton, M.S. J. Am. Chem. Soc., 1981, 103, 975.
(b) Schroeder, M.A.; Wrighton, M.S. ibid, 1976, 98, 551; J. Organomet. Chem. 1977, 128, 345.
2. Chase, D.B.; Weigert, F.J. J. Am. Chem. Soc., 1981, 103, 977.
3. Whetten, R.L.; Fu, K.-J.; Grant, E.R. J. Am. Chem. Soc., 1982, 104, 4270.
4. Swartz, G. L.; Clark, R.J. Inorg. Chem. 1980, 19, 3191 and Swartz, G. L., Ph. D. Dissertation, Florida State University, 1977.
5. Mitchener, J.C.; Wrighton, M.S. J. Am. Chem. Soc., 1983, 105, 1065.
6. (a) Krusic, P.J.; Briere, R.; Rey, P. Organometallics, 1985, 4, 801.
(b) Krusic, P.J.; Filippo, J.S. Jr.; Hutchinson, B.; Hance, R.L.; Daniels, L.M. J. Am. Chem. Soc., 1981, 103, 2129.
7. Fleckner, H.; Grevels, F.-W.; Hess, D. J. Am. Chem. Soc., 1984, 106, 2027.
8. Johnson, B.F.G.; Lewis, J.; Twigg, M.V. J. Organomet. Chem., 1974, 67, C75.
9. The actual isolation and characterization of several $Ru(CO)_4(\eta^2$-olefin) complexes have been reported and mechanistic aspects relating to equation (1) have been discussed. Grevels, F.-W.; Reuvers, J.G.A.; Takats, J. J. Am. Chem. Soc., 1981, 103, 4069.
10. We note the report of the surprisingly stable $Ru(CO)_3(\eta^2$-methylacrylate$)_2$ formed photochemically by methods related to equations (1) and (2). Grevels, F.-W.; Reuvers, J.G.A.; Takats, J. Agnew. Chem., Int. Ed. Engl. 1981, 20, 452.
11. Graff, J.L.; Sanner, R.D.; Wrighton, M.S. J. Am. Chem. Soc., 1979, 101, 273; Organometallics, 1982, 1, 837.
12. Castiglioni, M.; Milone, L.; Ostella, D.; Vaglio, G.A.; Valle, M. Inorg. Chem., 1976, 15, 394.

13. Austin, R.G.; Paonessa, R.S.; Giordano, P.J.; Wrighton M.S. Adv. Chem. Ser., 1978, 68, 189.

14. Ewing, G.E.; Pimentel, G.C. J. Chem. Phys., 1961, 35, 925.

15. Stephen, H.; Stephen, T. "Solubility of Inorganic and Organic Compounds", Macmillan, New York, 1963.

16. Stockis, A.; Hoffmann, R. J. Am. Chem. Soc., 102, 1980, 2952.

17. Grevels, F.-W.; Schneider, K.; Kruger, C; Goddard, R. Z. Naturforsch. B. 1980, 35, 360.

18. Bentsen, J.G.; Wrighton, M.S. to be submitted.

19. Cotton, F.A.; Wilkinson, G.F.R.S. "Advanced Inorganic Chemistry", 4th ed., Wiley, New York, 1980, p. 1074.

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

21. The feature attributed to trans-$Fe(CO)_2(C_2H_4)_3$ 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.

23. Ellerhorst, G. ; Gerhartz, W.; Grevels, F.-W. Inorg. Chem. 1980, 19, 67.

24. Bond, G.C.; Hellier, M. J. Catal. 1965, 4, 1.

25. Aumann, R. J. Am. Chem. Soc., 1974, 96, 2631.

26. Simon, F.G.; Lauher, J.W. Inorg. Chem., 1980, 19, 2338.

27. Collman, J.P.; Hegedus, L.S. "Principles and Applications of Organotransition Metal Chemistry", University Science Books, Mill Valley, California, 1980, p. 70.

28. Meyer, T.J.; Caspar, J.V. Chem. Rev., 1985, 85, 187, and references therein.

29. Murdoch, J. D. Lucken, G.A.C. Helv. Chim. Acta., 1964, 47, 1517.

30. Faller, J.W.; Adams, M.A. J. Organomet. Chem., 1979, 170, 71.

31. Wuu, Y.M.; Wrighton, M.S., unpublished results.

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

33. Nesmeyanov, A. N.; Kristskaya, I.I.; Vstynyuk, Y.A.; Fedin, E.I. Dokladay Akademii Nauk. SSSR, 1967, 176, 341.

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.

Table I. UV-Visible Data for Relevant Compounds.

Species	Medium (T,K)	λ, nm (ε)
$Ru_3(CO)_{12}$	MCH(298)	237(30,200),278(sh),325(sh)391(7200)
$Ru(CO)_4(C_2H_4)$	MCH(298)	240(3400),266(1700)
$Ru(CO)_3(C_2H_4)_2$	MCH(298)	220(11,700),262(4900)
$Ru(CO)_3$(1,3-pentadiene)	MCH(298)	245 (10,000),280(7600)
$Fe(CO)_5$	3MP(90)	242(21,000),290(5200)
$Fe(CO)_4$	3MP(90)	390
$Fe(CO)_4(C_2H_4)$	MCH(298)	255(sh, ~10,000)
$Fe(CO)_3(C_2H_4)$	MCH(298)	234,447
$Fe(CO)_4(C_3H_6)$	MCH(298)	255(sh, ~10,000)

---

[a] MCH ≡ methylcyclohexane; 3MP ≡ 3-methylpentane.

Table II. IR Data for Relevant Complexes.

Species	Medium (T, K)[a]	ν, cm^{-1} (ε 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)
$Ru(CO)_4(C_2H_4)$	3MP (298)	2104(470);2023(8100);1996(4000)
	3MP (90)	2106(980);2023(9900);1994(8000)
$Ru(CO)_3(C_2H_4)$	3MP (55)	2055(1.0);1978(1.2);1972(1.3)
$Ru(CO)_3(C_2H_4)_2$	3MP (298)	2081(320);2005(2100);1995(6500)
	3MP (90)	2082(350);2004(1300);1993(7200)
trans-$Ru(CO)_2(C_2H_4)_3$	3MP (233)	1956
	3MP (90)	1953
cis-$Ru(CO)_2(C_2H_4)_3$	MCH (90)	2019(1.4); 1975(1.0)
$Ru(CO)_2(C_2H_4)_2$	MCH (90)	2020(1.0); 1948(1.3)
$Ru(CO)(C_2H_4)_4$	MCH (90)	1964
$Ru(CO)(C_2H_4)_3$[b]	MCH (90)	1923
$Ru(CO)_4(C_3H_6)$	3MP (298)	2100(1.0); 2018(10.6); 1991(6.4)
	MCH (90)	2101(1.0); 2018(11.5); 1987(6.4)
$HRu(CO)_3(\eta^3\text{-}C_3H_5)$ isomer(a)	MCH (90)	2082(1.0); 2008(1.2)
endo-$BrRu(CO)_3(\eta^3\text{-}C_3H_5)$	3MP (298)	2109(1.0);2060(1.4);2019(1.3)
exo-$BrRu(CO)_3(\eta^3\text{-}C_3H_5)$	3MP (298)	2107(1.0);2055(1.1);2025(1.2)
$Ru(CO)_3(C_3H_6)_2$	3MP (298)	2075(1.0); 2005(3.3); 1988(14)
trans-$Ru(CO)_2(C_3H_6)_3$	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)
$HRu(CO)_3(\eta^3\text{-}C_5H_9)$	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)
trans-$Ru(CO)_2$(1-pentene)$_3$	3MP (233)	1946

Table II. (continued)

$Ru(CO)_4$(3,3-dimethyl-1-pentene)	$(CH_3)_2C_5H_8$ (298)	2099(1.0); 2017(5.6); 1990(3.6)
$Ru(CO)_3$(3,3-dimethyl-1-pentene)$_2$	$(CH_3)_2C_5H_8$ (233)	2077(1.0); 1995(2.3); 1986(10.0)
$Ru(CO)_3$(trans-1,3-pentadiene)	3MP (298)	2062(3600); 1997(6500); 1986(5400)
$Ru(CO)_4(PPh_3)$	3MP (298)	2061(2600); 1987(1000); 1954(4300)
$Ru(CO)_3(PPh_3)_2$	3MP (298)	1907(3300)
$Fe(CO)_5$	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)
$Fe(CO)_4(C_2H_4)$	MCH (298)	2087(1300);2013(sh);2007(10,000);1984(6700)
	MCH (90)	2088(2200);2011(sh);2006(12,000);1980(10,000
$Fe(CO)_3(C_2H_4)$	MCH (90)	2041(1.0); 1963(1.3); 1957(1.6)
	Ar (10)^c	2039, 1976, 1950
$Fe(CO)_3(C_2H_4)_2$	MCH (273)	2060(940);1988(sh,~5100);1981(12,600)
	MCH (90)	2060(1.0); 1988(4.8); 1981(12)
	$CF_3C_6F_{11}$ (273)	2064(1.0); 1997(5.0); 1988(13.6)
trans-$Fe(CO)_2(C_2H_4)_3$	MCH (90)	1942
cis-$Fe(CO)_2(C_2H_4)_3$	MCH (90)	1998(1.5); 1955(1.0)
$Fe(CO)_2(C_2H_4)_2$	MCH (90)	2003(1.0); 1938(1.3)
$Fe(CO)(C_2H_4)_4$	MCH (90)	1952
$Fe(^{13}CO)(C_2H_4)_4$	MCH (90)	1908
$Fe(CO)_4(C_3H_6)$	MCH (298)	2082(1800);2006(sh);2001(12,000); 1980(7500)
	MCH (90)	2083(2900);2006(sh);2001(15,000); 1976(12,000)
$HFe(CO)_3(\eta^3-C_3H_5)$ isomer(a)	MCH (90)	2064(1.0); 1994(1.5)
isomer(b)	MCH (173)	2066(1.0); 2003(1.5); 1994(1.2)
$Fe(CO)_3(\eta^3-C_3H_5)^d$	Pet. Ether (298)	2046,1968,1960
$Fe(CO)_3(C_3H_6)_2$	MCH (90)	2051(1.0); 1971(11)

Table II. (continued)

$HFe(CO)(C_3H_6)_2(\eta^3\text{-}C_3H_5)^b$	MCH (90)	1929
$Fe(CO)_4$(3,3-dimethyl-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-dimethyl-1-pentene)	3MP (90)	2041(1.0); 1966(1.1); 1953(1.2)
$Fe(CO)_3$(3,3-dimethyl-1-pentene)$_2$	3MP (195)	2046(1.0); 1970(15)
cis-$Fe(CO)_2$(3,3-dimethyl-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)
$Fe(CO)(\eta^4\text{-}1,3\text{-butadiene})_2{}^f$	hexane (298)	1984.5
$HFe(CO)_3(\eta^3\text{-}C_5H_9)$	MCH (90)	2059(1.0); 1989(1.5)
$Fe(CO)_3$(1-pentene)$_2$	1-pentene (195)	2048(1.0); 1972(16.6)
$HFe(CO)(C_5H_{10})_2(\eta^3\text{-}C_5H_9)^b$	1-pentene (90)	1925
$Fe(CO)_3$(*trans*-1,3-pentadiene)	MCH (298)	2049(1.0); 1982(1.6); 1973(1.1)
$BrFe(CO)_3(\eta^3\text{-}C_3H_5)$	MCH (298)	2089(1.1); 2043(1.4); 2010(1.0)
$Fe(CO)_3(\eta^4\text{-}C_5H_8)^g$		2053, 1994, 1989
$Fe(CO)_4PPh_3$	MCH (298)	2052(4200);1979(3000);1946(11,000)
$Fe(CO)_3(PPh_3)_2$	MCH (298)	1895(10,500)
$Fe(CO)_3(C_2H_4)(PPh_3)$	MCH (298)	2022(1.0); 1961(~1.0); 1931(1.0)

[a] 3MP = 3-methylpentane, MCH = methycyclohexane.

[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-ene-3,1-ylirontricarbonyl obtained from Ref. 25.

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

Species	Temp, K	PPM vs. $SiMe_4$
$Ru(CO)_4(C_2H_4)$	243	2.10
$Ru(CO)_3(C_2H_4)_2$	243	2.50
$Ru(CO)_2(C_2H_4)_3$	243	3.02
$Fe(CO)_4(C_2H_4)$	273	2.37
$Fe(CO)_3(C_2H_4)_2$	273	2.68
C_2H_4	243	5.28
C_7H_{14}	243	1.54

[a] All data are for $CF_3C_6F_{11}$ solutions.

Table IV. ^{1}H-NMR Peak Integration vs. Irradiation Time for $Ru(CO)_4(C_2H_4)$ in C_2H_4-saturated $CF_3C_6F_{11}$ solution at 298K.[a]

	Integration of ^{1}H-NMR Singlet			
Irradiation time (min)	$Ru(CO)_4(C_2H_4)$ (2.10ppm)	$Ru(CO)_3(C_2H_4)_2$ (2.50ppm)	C_7H_{14}[b] (1.54ppm)	[Ru][d]
0.0	0.64	0	1.00	1.00
0.5	0.50	0.36 (0.28)[c]	1.00	1.06 (1.00)[e]
1.0	0.37	0.63 (0.62)[c]	1.00	1.07 (1.01)[e]

[a] Cf. Figure 1 for actual spectra at t = 0 and t = 1 min.

[b] Used as an internal standard.

[c] "Predicted" integral for $Ru(CO)_3(C_2H_4)_2$ based on consumption of $Ru(CO)_4(C_2H_4)$ from preceding irradiation time.

[d] Total (relative) Ru concentration assuming the only species present are $Ru(CO)_4(C_2H_4)$ and $Ru(CO)_3(C_2H_4)_2$.

[e] Calculated using only t = 0.5 and 1 min data.

Table V. ^{1}H-NMR Peak Integration vs. Irradiation Time for $Ru(CO)_4(C_2H_4)$ in C_2H_4-saturated $CF_3C_6F_{11}$ Solution at 243K.[a]

	Integration of ^{1}H-NMR Singlet				
Irradiation time (min)	$Ru(CO)_4(C_2H_4)$ (2.10ppm)	$Ru(CO)_3(C_2H_4)_2$ (2.50ppm)	$Ru(CO)_2(C_2H_4)_3$ (3.02ppm)	C_7H_{14}[b] (1.54ppm)	[Ru][c]
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] Cf. Figure 3 for actual spectra at t = 0, 0.33, and 4 min.

[b] Used as an internal standard.

[c] Total (relative) Ru concentration assuming only Ru species present are $Ru(CO)_n(C_2H_4)_{5-n}$ (n = 4, 3, 2).

Table VI. Turnover Rates for 1-Pentene Isomerization by $M(CO)_3(C_2H_4)_2$ (M = Fe, Ru), $Ru(CO)_2(C_2H_4)_3$ and Irradiated $Ru_3(CO)_{12}$ at 293K.

Catalyst Precursor, mM		1-pentene, M	t, min.	% pentene			turnover rate
				1-	*trans*-2-	*cis*-2-	1-pentene/catalyst min.
$Fe(CO)_3(C_2H_4)_2$	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
$Ru(CO)_3(C_2H_4)_2$	5.32	1.83	1	98.56	1.31	0.13	4.95
			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
	5.32	1.83	1	98.13	1.20	0.07	4.37
			5	96.40	3.39	0.21	2.47
			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
	2.78	1.83	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
$Ru(CO)_2(C_2H_4)_3$	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
	2.78	1.83	1	98.58	1.20	0.22	9.34
			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
	1.40	1.83	5	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

Table VI. (continued)

$Ru_3(CO)_{12}$[a]	0.85	1.83	10	97.51	2.26	0.23	>5[b]
			20	96.10	3.46	0.31	>4[b]
			60	88.07	10.78	1.15	>4[b]
	0.85	1.83	10	97.17	2.56	0.24	>6[b]
			20	96.33	3.36	0.38	>4[b]
			60	87.91	10.92	1.17	>4[b]

[a] Conversion of $Ru_3(CO)_{12}$ to mononuclear species is complete within the first 7 minutes of continuous near-UV irradiation with a 550 W medium pressure Hg lamp.

[b] 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} ein/min. The quantum yield was observed to be ~5, similar to that in ref. 11.

Figure Captions

Figure 1. ^{1}H-NMR spectral changes accompanying near-UV irradiation of $Ru(CO)_4(C_2H_4)$ in C_2H_4-saturated $CF_3C_6F_{11}$ solution at 298K (a) before irradiation and (b) after 1 min irradiation. Cf. Table IV for summary of integration data.

Figure 2. IR spectral changes accompanying near-UV irradiation of $Ru(CO)_4(C_2H_4)$ in C_2H_4-saturated 3-methylpentane solution at 298K (a) before irradation, (b) after 1 min irradiation, (c) difference spectrum of (a) and (b).

Figure 3. ^{1}H-NMR spectral changes accompanying near-UV irradiation of $Ru(CO)_4(C_2H_4)$ in C_2H_4-saturated $CF_3C_6F_{11}$ solution at 243K (a) before irradiation, (b) after 20 s irradiation, (c) after 4 min irradiation.

Figure 4. IR spectral changes accompanying near-UV irradiation of predominantly $Ru(CO)_3(C_2H_4)_2$ [$\nu(cm^{-1})$ = 2081, 2005, 1994] and some $Ru(CO)_4(C_2H_4)$ [$\nu(cm^{-1})$ = 2105, 2023, 1995] in C_2H_4-saturated 3-methylpentane solution at 233K (a) before irradiation, (b) after 1 min irradiation, (c) difference spectrum of (a) and (b).

Figure 5. IR difference spectral changes accompanying near-UV irradiation of $Ru(CO)_3(C_2H_4)_2$ in a C_2H_4-containing methylcyclohexane glass at 90K (a) after 5 min. irradiation, (b) after subsequent warming to 110K and recooling to 90K, (c) after subsequent warming to 210K and recooling to 90K. 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 $Ru(CO)_3(C_2H_4)_2$ in the initial 90K 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 110K. The 2020 and 1948 cm^{-1} features are due to $Ru(CO)_2(C_2H_4)_2$; the 2018 and 1975 cm^{-1} features are due to *cis*-$Ru(CO)_2(C_2H_4)_3$, and the 1953 cm^{-1} feature is due to *trans*-$Ru(CO)_2(C_2H_4)_3$.

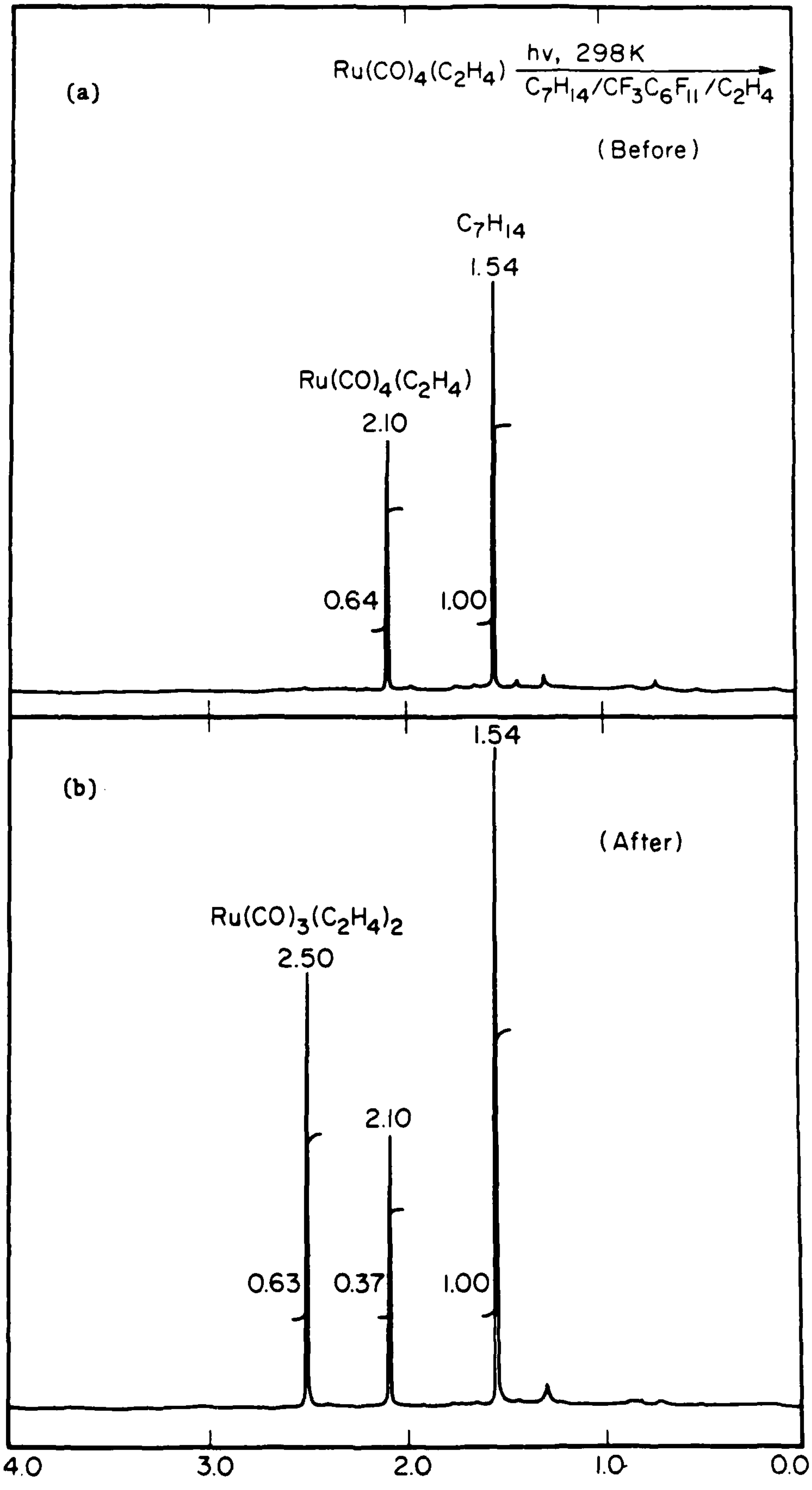
Figure 6. ^{1}H-NMR spectral changes accompanying near-UV irradiation of $Fe(CO)_4(C_2H_4)$ in a C_2H_4-saturated $CF_3C_6F_{11}$ solution at 273K, (a) before irradiation, (b) after 30 seconds irradiation. The integrals are consistent with the photochemical conversion of $Fe(CO)_4(C_2H_4)$ to $Fe(CO)_3(C_2H_4)_2$.

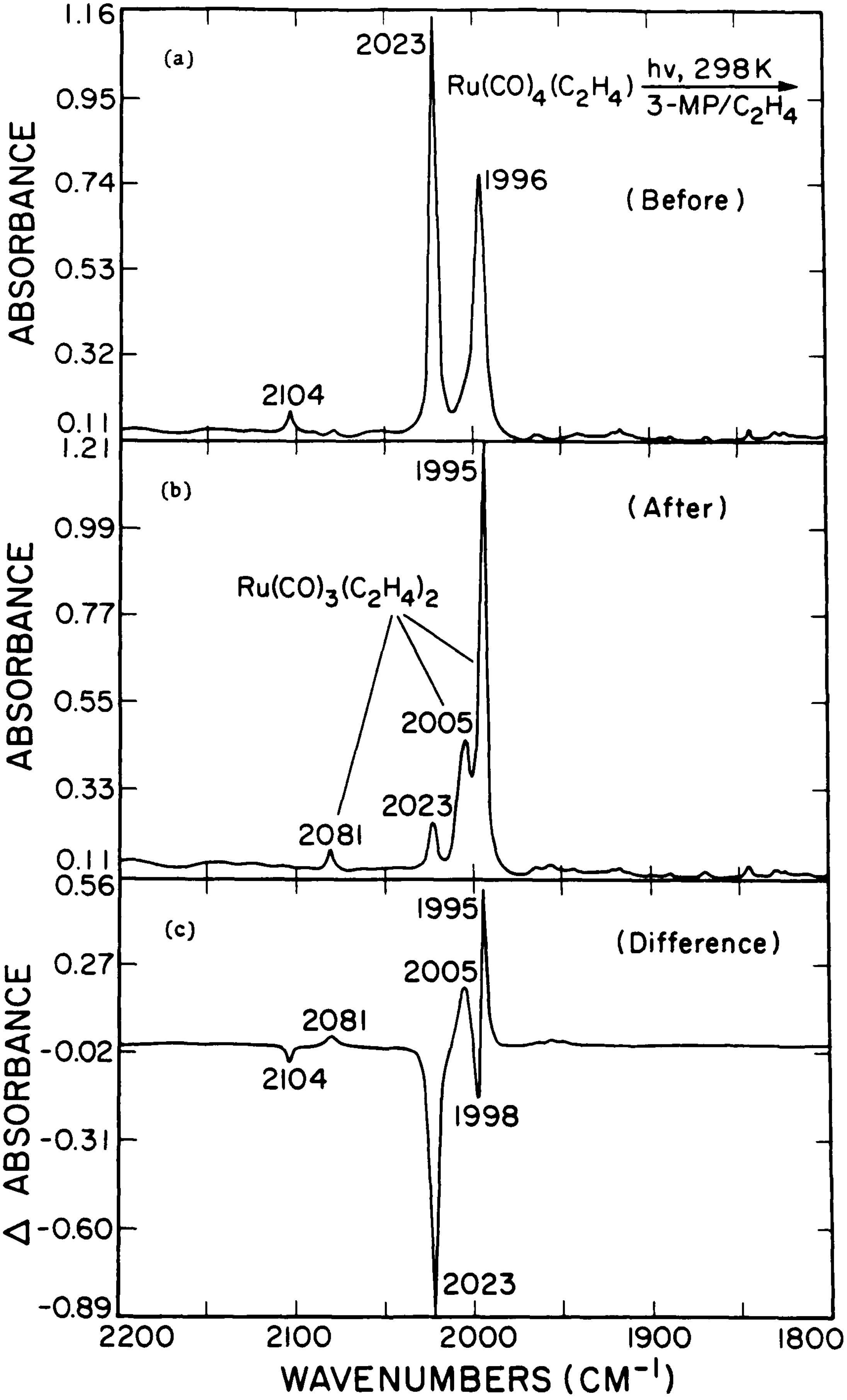
Figure 7. (a) IR difference spectrum accompanying the same near-UV irradiation of $Fe(CO)_4(C_2H_4)$ in C_2H_4-saturated $CF_3C_6F_{11}$ solution at 273K for which ^{1}H-NMR spectral changes were acquired, Figure 6; (b) IR difference spectral changes accompanying the near-UV irradiation of $Fe(CO)_4(C_2H_4)$ in a C_2H_4 saturated 3-methylpentane glass at 90K for 4 s and (c) 320 s.

Figure 8. (a) IR difference spectrum accompanying the near-UV irradiation of $Fe(CO)_3(C_2H_4)_2$ in a C_2H_4-containing 3-methylpentane glass at 100K, 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 200K and recooling to 100K. The cis-$Fe(CO)_2(C_2H_4)_3$ [$\nu(cm^{-1})$ = 1998, 1955, (a)] has isomerized to the trans-isomer [$\nu(cm^{-1})$ = 1942 (b)], and some $Fe(CO)_3(C_2H_4)_2$ [$\nu(cm^{-1})$ = 2060, 1981] has been regenerated (based on change in negative absorbances).

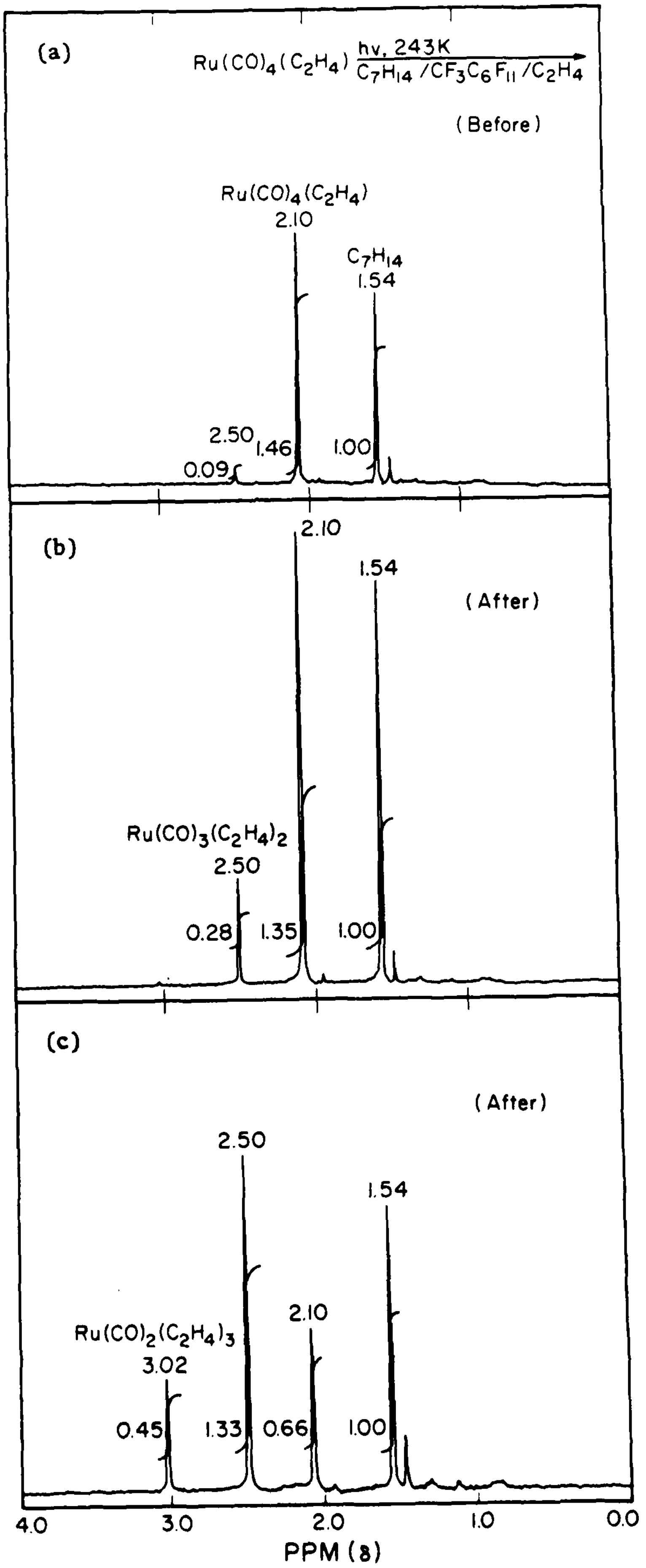
Figure 9. IR difference spectral changes accompanying near-UV irradiation of $Fe(CO)_3(C_2H_4)_2$ in a methylcyclohexane glass at 100K. The 2132 cm^{-1} feature is associated with growth of free CO; the 2041, 1963 and 1957 cm^{-1} features are attributed to $Fe(CO)_3(C_2H_4)$; the 2003 and 1938 cm^{-1} features are attributed to $Fe(CO)_2(C_2H_4)_2$ (see text).

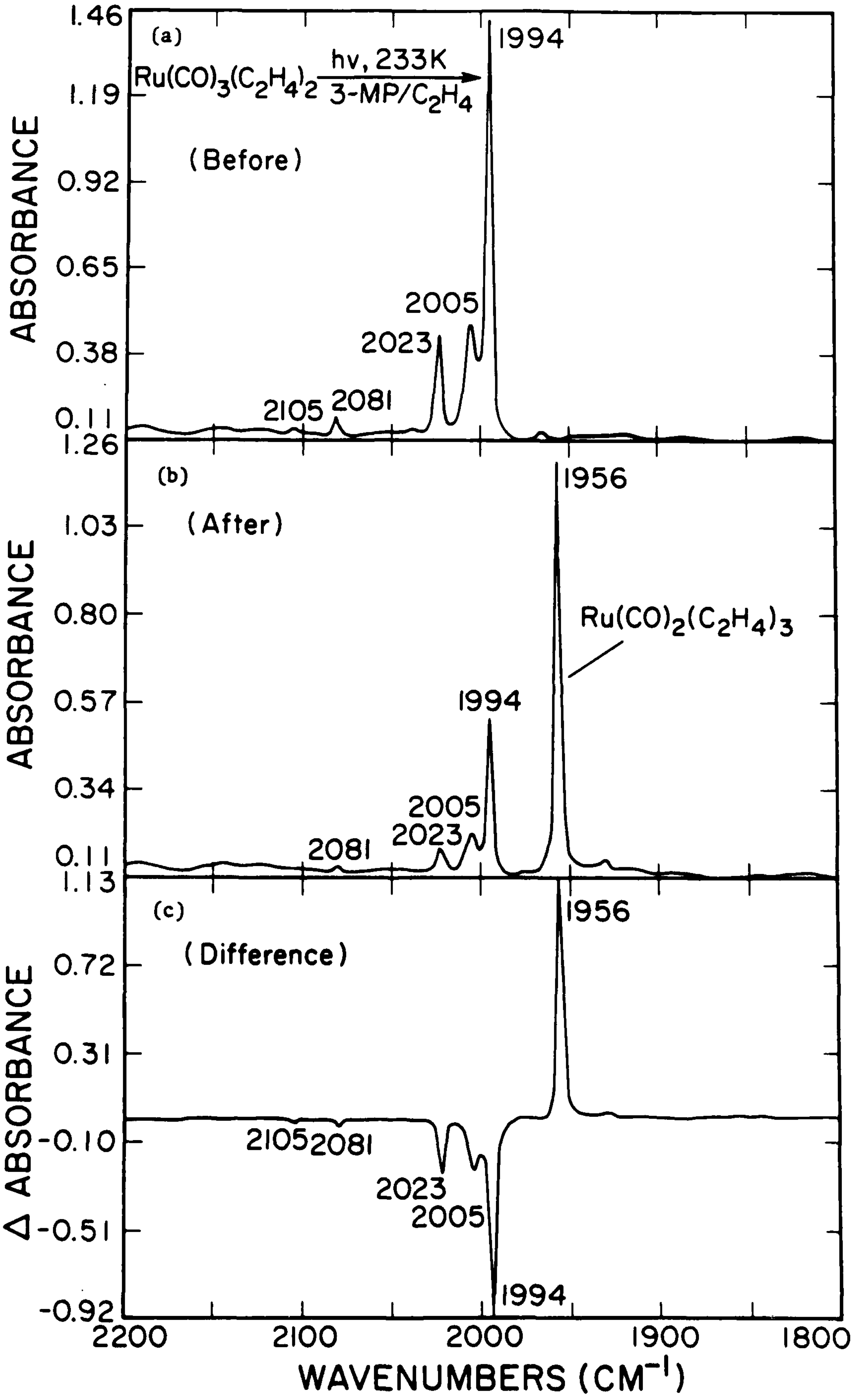
Figure 10. Infrared difference spectral changes accompanying near-UV irradiation of $Fe(CO)_3(C_3H_6)_2$ in a C_3H_6-containing methylcyclohexane glass at 100K. The 2132 cm^{-1} feature is associated with growth of free CO. The features at 2064, 1994 cm^{-1} are due to $HFe(CO)_3(\eta^3\text{-}C_3H_5)$, and the 1929 cm^{-1} feature is tentatively assigned as $HFe(CO)(C_3H_6)_2(\eta^3\text{-}C_3H_5)$.


(a)
$Ru(CO)_4(C_2H_4) \xrightarrow[C_7H_{14}/CF_3C_6F_{11}/C_2H_4]{h\nu,\ 298K}$
(Before)
C_7H_{14}
1.54
$Ru(CO)_4(C_2H_4)$
2.10
0.64
1.00
(b)
1.54
(After)
$Ru(CO)_3(C_2H_4)_2$
2.50
2.10
0.63
0.37
1.00
4.0
3.0
2.0
1.0
0.0
PPM (δ)

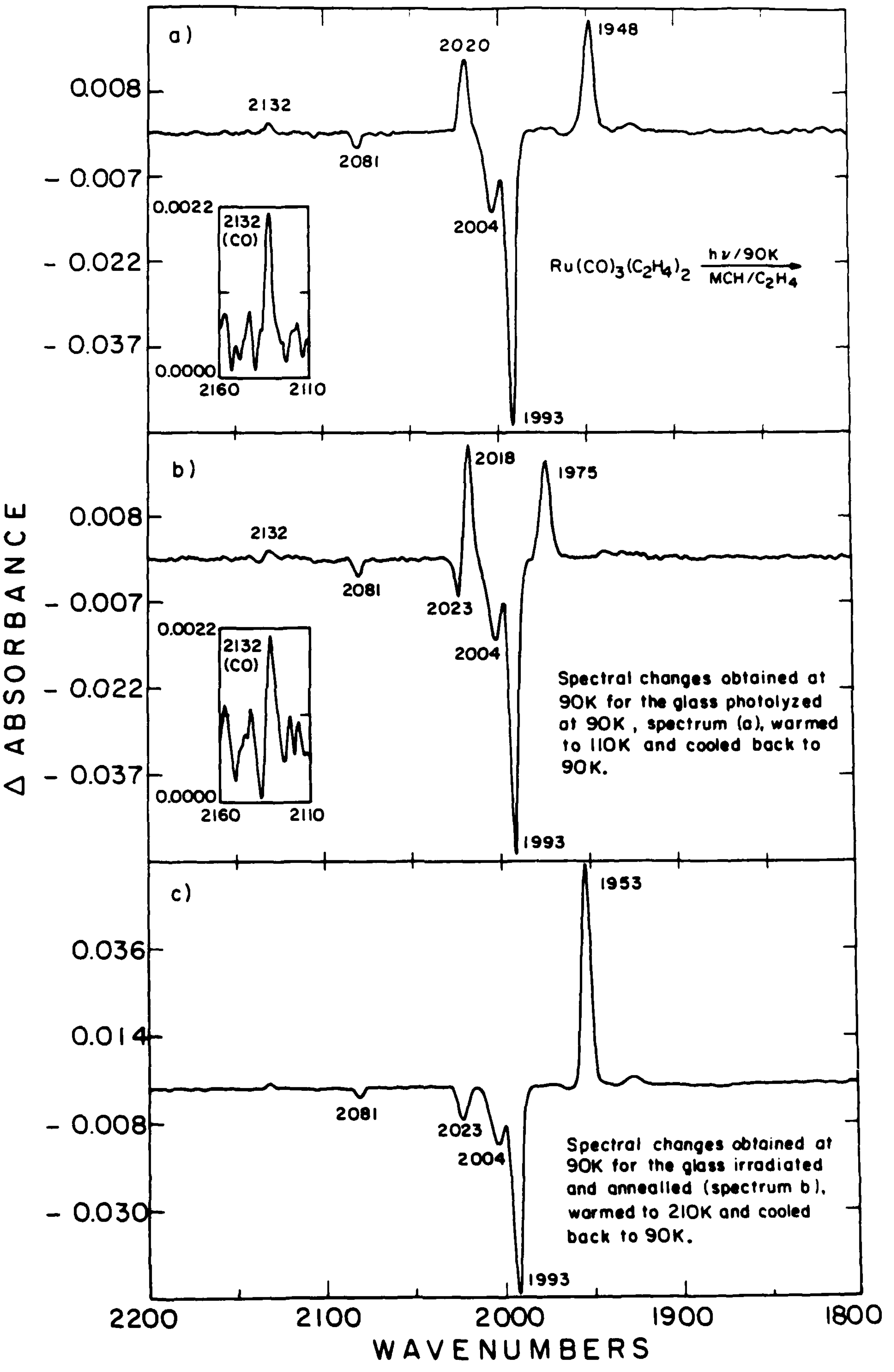


(a)
2023
1996
2104
$Ru(CO)_4(C_2H_4) \xrightarrow[3\text{-}MP/C_2H_4]{h\nu,\ 298K}$
(Before)
ABSORBANCE
1.16
0.95
0.74
0.53
0.32
0.11
(b)
(After)
1995
2005
2023
2081
$Ru(CO)_3(C_2H_4)_2$
ABSORBANCE
1.21
0.99
0.77
0.55
0.33
0.11
(c)
(Difference)
1995
2005
2081
2104
1998
2023
Δ ABSORBANCE
0.56
0.27
-0.02
-0.31
-0.60
-0.89
2200
2100
2000
1900
1800
WAVENUMBERS (CM^{-1})


(a)
Ru(CO)4(C2H4) hv, 243K / C7H14 /CF3C6F11 /C2H4
(Before)
Ru(CO)4(C2H4)
2.10
C7H14
1.54
2.50
1.46
0.09
1.00
(b)
2.10
1.54
(After)
Ru(CO)3(C2H4)2
2.50
0.28
1.35
1.00
(c)
(After)
2.50
1.54
2.10
Ru(CO)2(C2H4)3
3.02
0.45
1.33
0.66
1.00
4.0
3.0
2.0
1.0
0.0
PPM (δ)



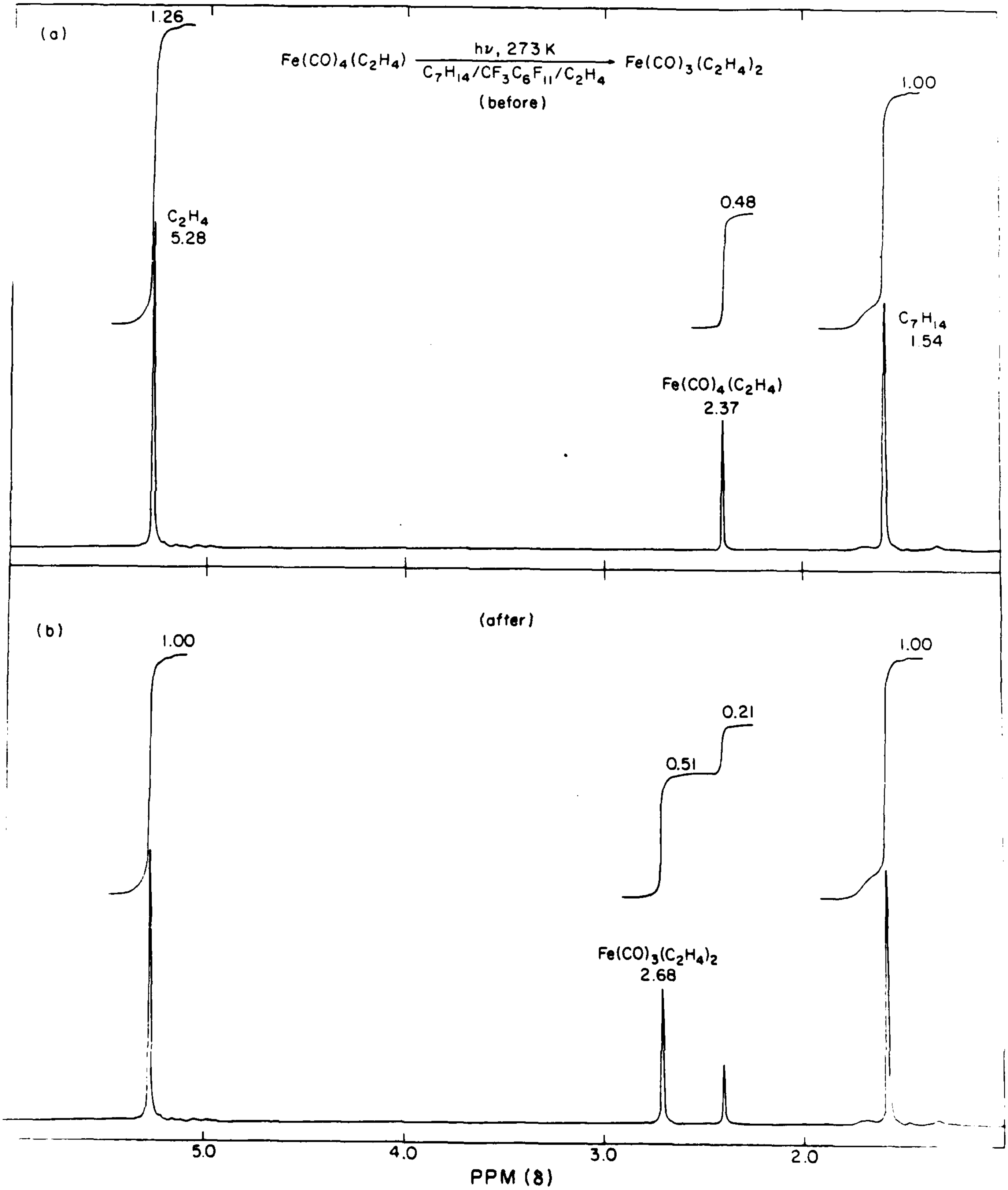
(a)
$Ru(CO)_3(C_2H_4)_2 \xrightarrow[3\text{-}MP/C_2H_4]{hv,\ 233K}$
(Before)
1994
2005
2023
2105
2081
(b)
(After)
1956
$Ru(CO)_2(C_2H_4)_3$
1994
2005
2023
2081
(c)
(Difference)
1956
2105
2081
2023
2005
1994
ABSORBANCE
1.46
1.19
0.92
0.65
0.38
0.11
ABSORBANCE
1.26
1.03
0.80
0.57
0.34
0.11
Δ ABSORBANCE
1.13
0.72
0.31
-0.10
-0.51
-0.92
2200
2100
2000
1900
1800
WAVENUMBERS (CM^{-1})

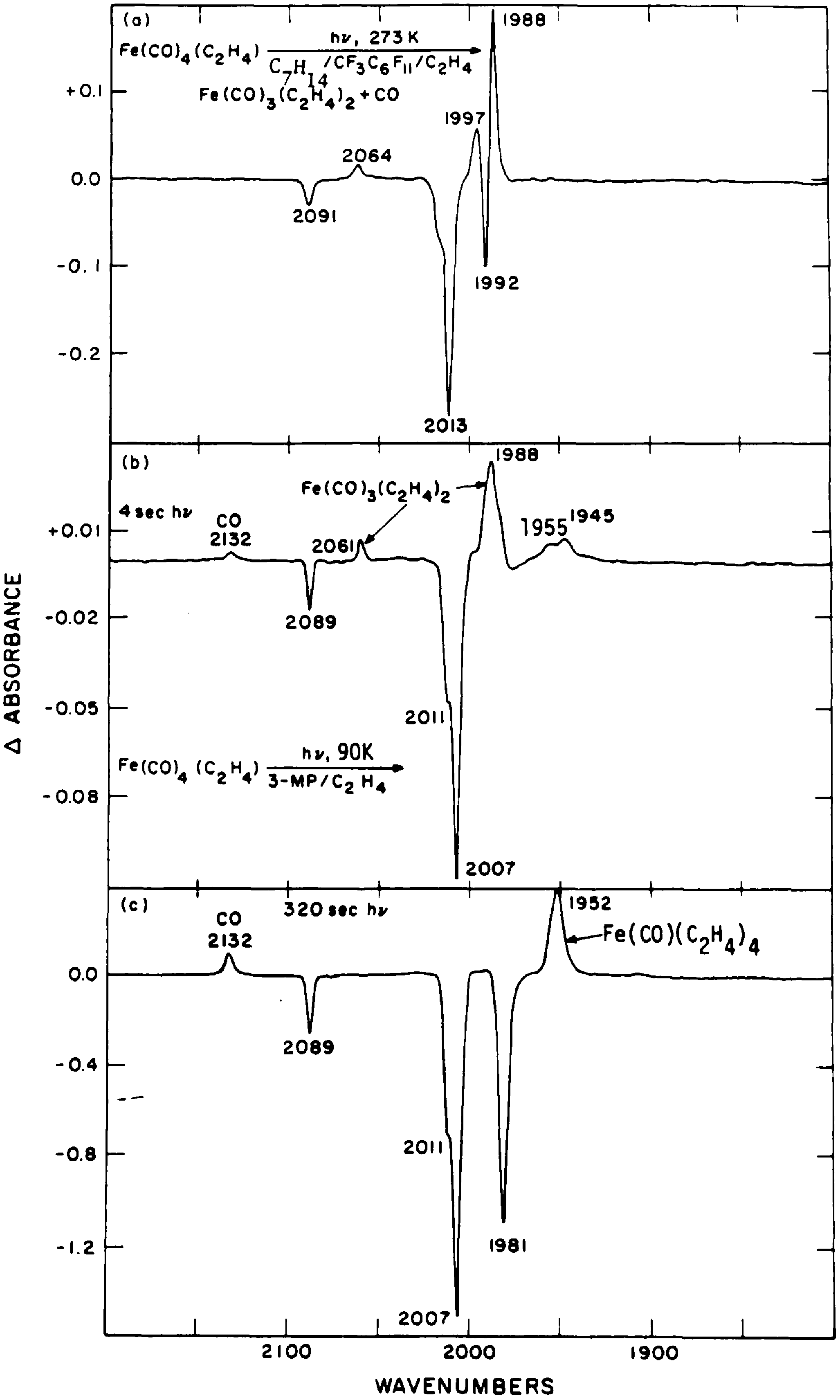


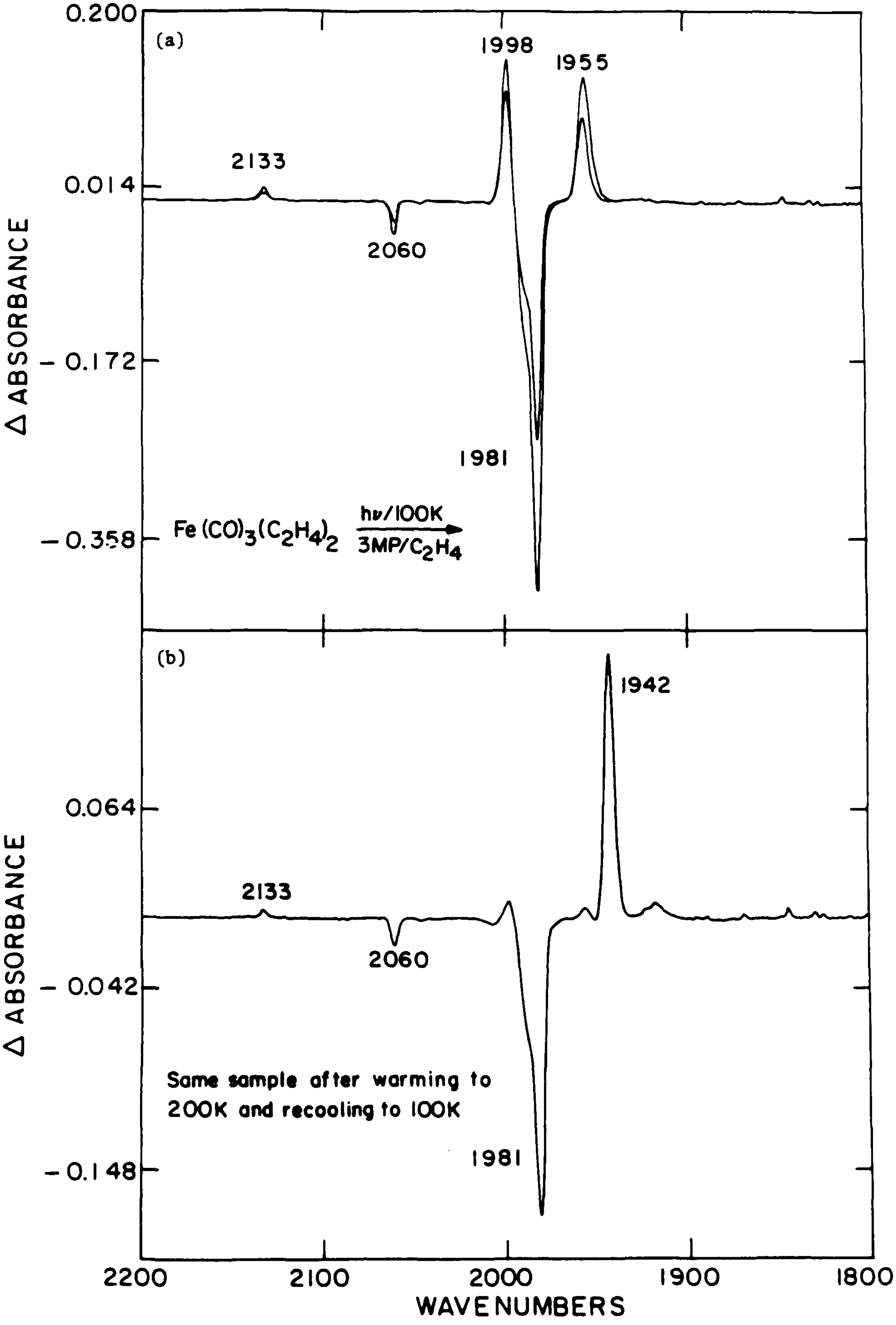
$Ru(CO)_3(C_2H_4)_2 \xrightarrow[MCH/C_2H_4]{h\nu/90K}$

Spectral changes obtained at 90K for the glass photolyzed at 90K, spectrum (a), warmed to 110K and cooled back to 90K.

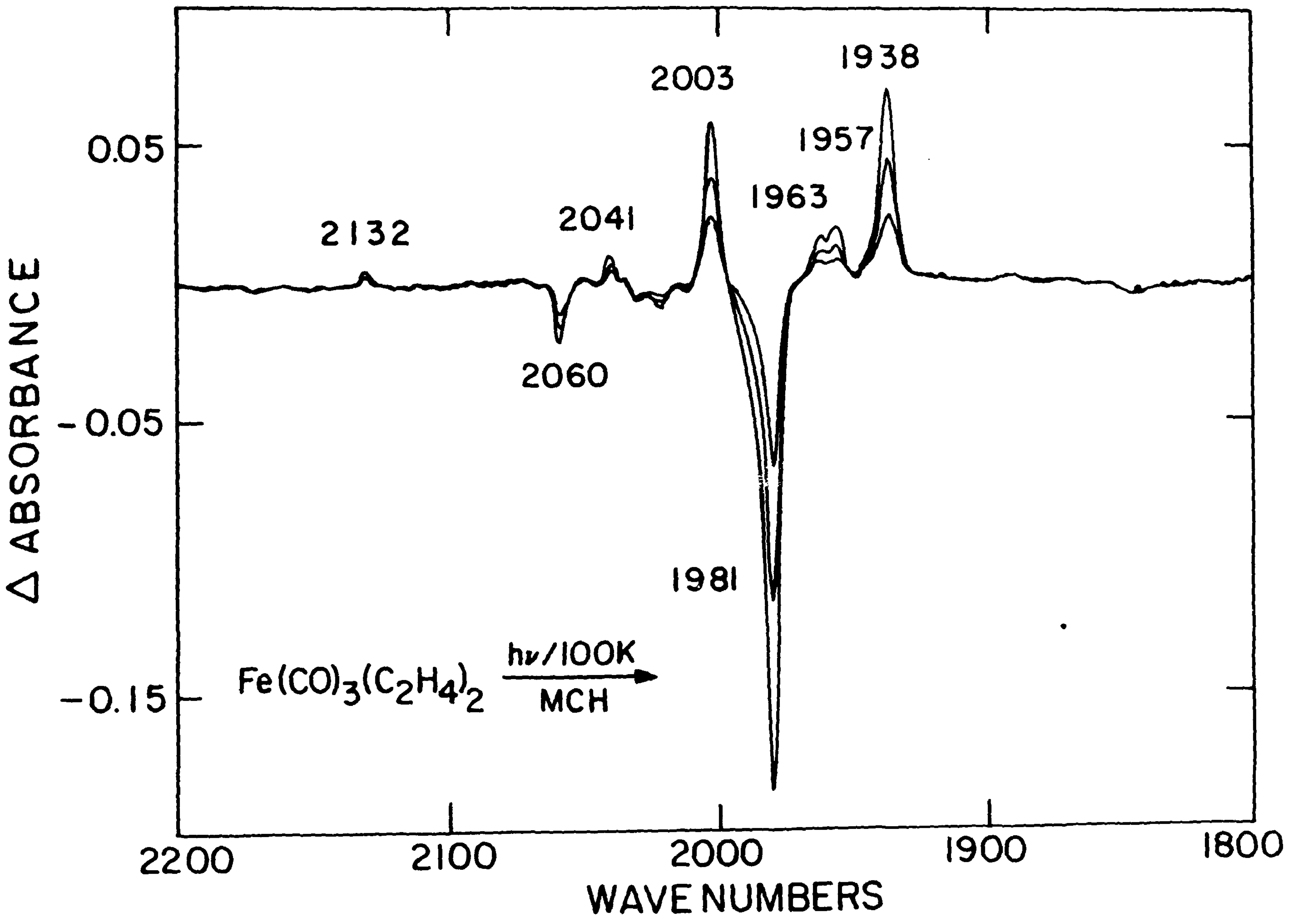
Spectral changes obtained at 90K for the glass irradiated and annealled (spectrum b), warmed to 210K and cooled back to 90K.

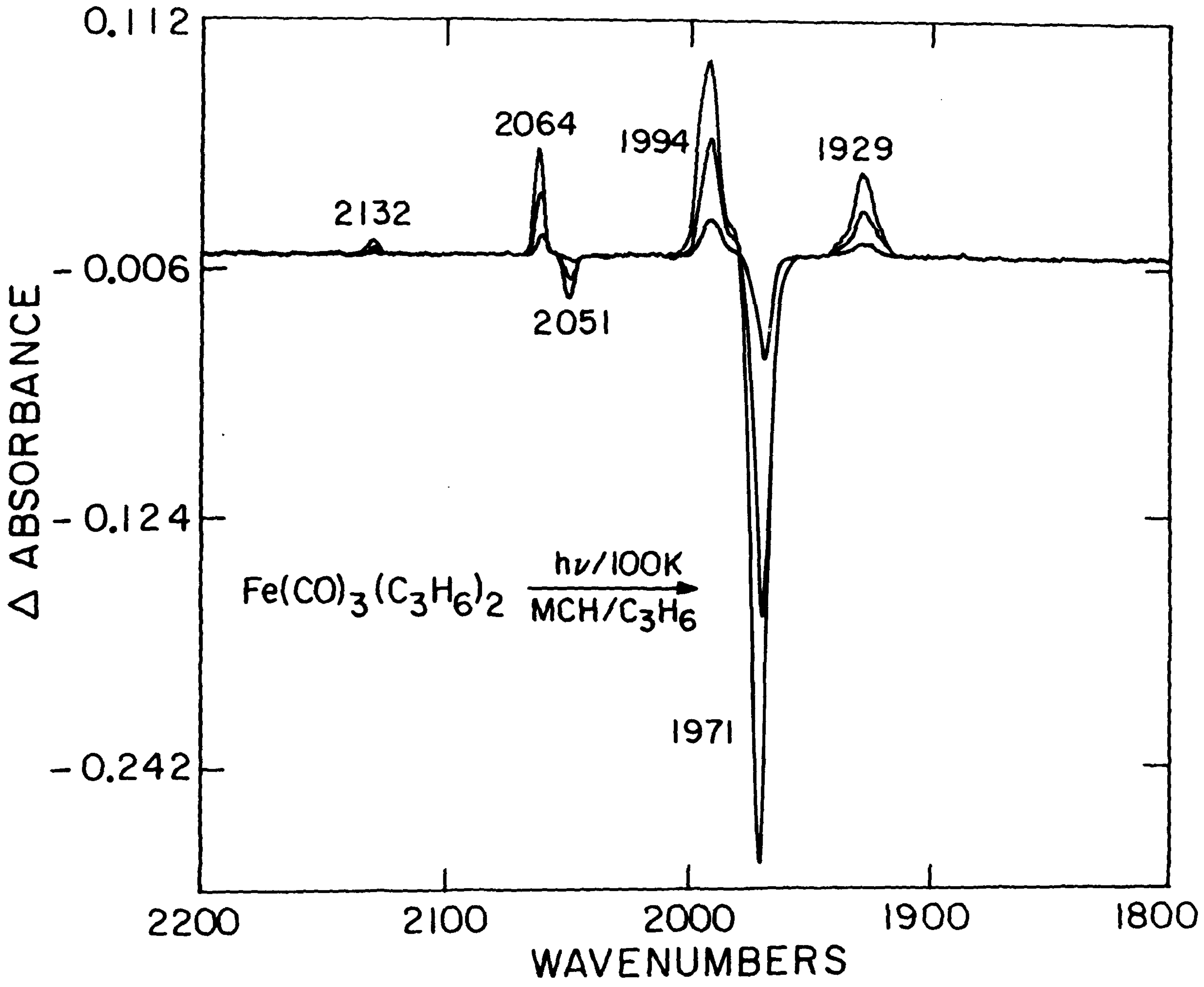

(a)
1.26
Fe(CO)4(C2H4) —hν, 273 K / C7H14/CF3C6F11/C2H4→ Fe(CO)3(C2H4)2
(before)
1.00
0.48
C2H4
5.28
C7H14
1.54
Fe(CO)4(C2H4)
2.37
(b)
(after)
1.00
1.00
0.21
0.51
Fe(CO)3(C2H4)2
2.68
5.0
4.0
3.0
2.0
PPM (δ)


(a)
Fe(CO)4(C2H4) → hν, 273 K / C7H14/CF3C6F11/C2H4
Fe(CO)3(C2H4)2 + CO
+0.1
0.0
-0.1
-0.2
1988
1997
2064
2091
1992
2013
(b)
4 sec hν
Fe(CO)3(C2H4)2
CO
2132
2061
1988
1955
1945
2089
2011
2007
+0.01
-0.02
-0.05
-0.08
Fe(CO)4 (C2H4) → hν, 90K / 3-MP/C2H4
(c)
320 sec hν
CO
2132
1952
Fe(CO)(C2H4)4
2089
2011
1981
2007
0.0
-0.4
-0.8
-1.2
Δ ABSORBANCE
2100
2000
1900
WAVENUMBERS



(a)
0.200
0.014
− 0.172
− 0.358
Δ ABSORBANCE
2133
2060
1998
1955
1981
Fe(CO)$_3$(C$_2$H$_4$)$_2$ $\xrightarrow[3MP/C_2H_4]{h\nu/100K}$
(b)
0.064
− 0.042
− 0.148
Δ ABSORBANCE
2133
2060
1942
1981
Same sample after warming to 200K and recooling to 100K
2200
2100
2000
1900
1800
WAVENUMBERS


2132
2060
2041
2003
1981
1963
1957
1938
0.05
-0.05
-0.15
Δ ABSORBANCE
2200
2100
2000
1900
1800
WAVE NUMBERS
$Fe(CO)_3(C_2H_4)_2 \xrightarrow[MCH]{h\nu/100K}$


0.112
-0.006
-0.124
-0.242
Δ ABSORBANCE
2200
2100
2000
1900
1800
WAVENUMBERS
2132
2064
2051
1994
1971
1929
$\mathrm{Fe(CO)_3(C_3H_6)_2} \xrightarrow[\mathrm{MCH/C_3H_6}]{h\nu/100\mathrm{K}}$

DL/413/83/01
GEN/413-2

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 413 800 N. Quincy Street Arlington, Virginia 22217	2
Dr. Bernard Douda Naval Weapons Support Center Code 5042 Crane, Indiana 47522	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Washington, D.C. 20360	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12
DTNSRDC Attn: Dr. G. Bosmajian Applied Chemistry Division Annapolis, Maryland 21401	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1
Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1

END

10-86

DTIC